Chemistry of novel fluorinated alkenes

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entitled

CHEMISTRY OF NOVEL FLUORINATED ALKENES

submitted by

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To Patrique

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Last, but not least, I would like to thank Patrique for her help and understanding throughout this period of work and my family for their continuing support.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1983 and October 1986. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

Part of this work has been the subject of the following papers:

A. E. Bayliff, M. R. Bryce, R. D. Chambers, J. R. Kirk, and G. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1191.

A. E. Bayliff, M. R. Bryce, R. D. Chambers, and R. S. Mathews, *J. Chem. Soc., Chem. Commun.*, 1985, 1018.

A. E. Bayliff, M. R. Bryce, and R. D. Chambers, *J. Chem. Soc., Perkin Trans. 1*, accepted for publication.

and has been presented by the author at the following meetings:

General Poster Meeting, Newcastle-upon-Tyne, December, 1986.

Graduate Symposium, Durham, July, 1986.

Postgraduate Heterocyclic Symposium, Aston, July, 1986.

Centenary of the Discovery of Fluorine, Paris, August, 1986.

THE CHEMISTRY OF SOME NOVEL FLUORINATED ALKENES

by

ANDREW E. BAYLIFF

ABSTRACT

The work described in this thesis is concerned with three areas relating to nucleophilic reactions of novel polyfluorinated alkenes.

a) Very highly strained fluorinated epoxides have been synthesised from bicyclic internal alkenes using $Ca(OCl)_2$. These molecules display an almost unprecedented thermal and chemical stability.

b) Aromatic bifunctional nucleophiles have been reacted with a variety of perfluorinated alkenes and cycloalkenes to give high yielding heterocyclic compounds. These are discussed within a mechanistic framework which may rationalise the product structures.

c) Additions of fluoride ion from CsF and TAS-F to fluorinated alkenes in a suitable solvent are shown to yield long-lived fluorocarbanions. N.m.r. observations indicate the systems are wholly in the form of the respective anions and are essentially static on the n.m.r. timescale. Competition experiments for a deficiency of CsF are available and can render useful information on F^- affinities. The ^{13}C and ^{19}F n.m.r. spectra of the anions display unusual chemical shift and coupling constant phenomena. The n.m.r. spectra are unchanged over a wide temperature range but at a distinct threshold temperature line broadening occurs. This is indicative of the onset of F^- exchange on the n.m.r. timescale, is specific to the M^+C^- system and, therefore, is a guide to the carbanion stabilities. High yielding trapping reactions with simple electrophiles are described but, in some cases F^- donation from the carbanion is preferred. This competing reaction is found for particular electrophiles and above the threshold exchange temperature as determined by n.m.r.

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CHAPTER FOUR

CHAPTER ONE

INTRODUCTION

CHAPTER ONE

GENERAL INTRODUCTION

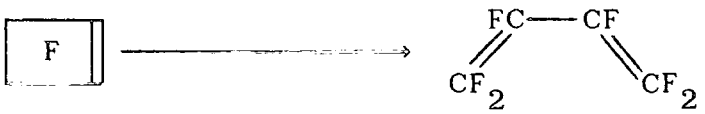
Before the last World War there were relatively few organic compounds containing fluorine available and correspondingly little was known about their chemistry. The greatest stimulus to fluorine chemistry occurred during the war, in the atomic bomb project,[1] because compounds containing a significant degree of fluorine were found to be indispensable as thermally and chemically stable lubricants *etc.* in the uranium isotope enrichment process. In the following years, fluorinated materials have realised an increasingly diverse application in polymer technology, medicine, and as agricultural chemicals. Academics also found the study of organofluorine chemistry a stimulating occupation because there emerged a whole new novel area of organic chemistry built around the fluorine atom rather than the hydrogen atom. It has also been possible[2] to define a so called "mirror image" relationship between the reactions of unsaturated fluorocarbons and hydrocarbons and between the role of the fluoride ion versus the proton. In addition, as a result of the unusual electronic and structural requirements of polyfluorinated organic compounds, it has often been possible to confer stability on normally transient intermediates eg. radicals, carbocations, carbanions, aromatic valence isomers *etc.*,and clearly an understanding of these species is of great importance.

This thesis is concerned with a study of a variety of nucleophilic reactions of fluorinated alkenes and the

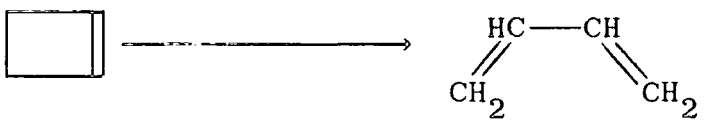
utility of these processes in the synthesis of new fluorinated heterocyclic molecules. The reactions are thought to occur via the intermediacy of carbanionic species and a substantial part of this work has been devoted to the study and characterisation of some particularly long lived members of this class. A basic introduction to a number of relevant areas of fluorine chemistry will be made but justifiable emphasis will be placed on the formation of heterocyclic compounds from fluorinated alkenes using bifunctional nucleophiles and the generation, study and subsequent reactions of fluorinated carbanions.

1.A FLUORINATED ALKENES

If hydrogen bonded to an unsaturated site is replaced by fluorine several processes resulting in loss of the double bond, eg. polymerisation[3] and dimerisation[4], become energetically more favourable. Most sriking are thermochemical data relating to ring opening reactions of substituted cyclobutenes, in which the preference for the butadiene structure in the parent compound is reversed on total substitution by fluorine.[5]



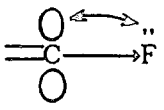
ΔH=11.7 kcal/mol



ΔH=-8 kcal/mol

It appears, therefore, that relative to perfluoroalkyl, fluorine substitution in some way significantly destabilises a π-system.

At first sight this may appear unusual, in that fluorine withdraws charge inductively along the σ-framework it is bonded to. A competing effect, however, is return of electron density to the π-sytem through the fluorine lone pairs. This would be expected[6] to be a significant effect for substituents such as fluorine with filled non-bonding orbitals of a similar size to the carbon p-orbital.



$-I\sigma$ $+I\pi$

With perfluoroalkyl substituents the situation is not complicated by I_{π} effects and only inductive withdrawal is in operation.

$$\text{>C}\cdots\!\!\rightarrow R_f \qquad\qquad \cdots I\sigma$$

Clearly, the replacement of fluorine by a perfluoroalkyl group in a multiple bonded system would be expected to reduce the overall energy. With acetylenes, where the effects are most pronounced, fluorine directly attached to the unsaturated carbon confers remarkable instability whereas similar perfluoroalkyl substituted compounds are highly stable.

eg.[7]

F-C≡C-F	NEVER ISOLATED
F-C≡C-H	DANGEROUSLY EXPLOSIVE
CF_3-C≡C-CF_3	STABLE

1.B NUCLEOPHILIC ATTACK ON FLUORINATED ALKENES

1.B.a Reactivity and orientation of attack

For an unsymmetrically substituted polyfluorinated alkene there are two orientations in which the nucleophile can form a bond with the substrate, to produce one of the two available negatively charged intermediates.

eg. $Nuc^- + \underset{(1)}{CF_3CF{=}CF_2} \longrightarrow \underset{(2)}{Nuc\text{-}CF_2\text{-}\bar{C}FCF_3} + \underset{(3)}{Nuc\text{-}CF(CF_3)\text{-}\bar{C}F_2}$

One approach to explaining the observed orientation is to consider the relative stabilities of the intermediates involved.[8] It will be shown later that, in general, fluorine substitution directly on a centre of negative charge may even be destabilising, relative to hydrogen, whereas fluorine substitution adjacent to a carbanion centre is always strongly stabilising.

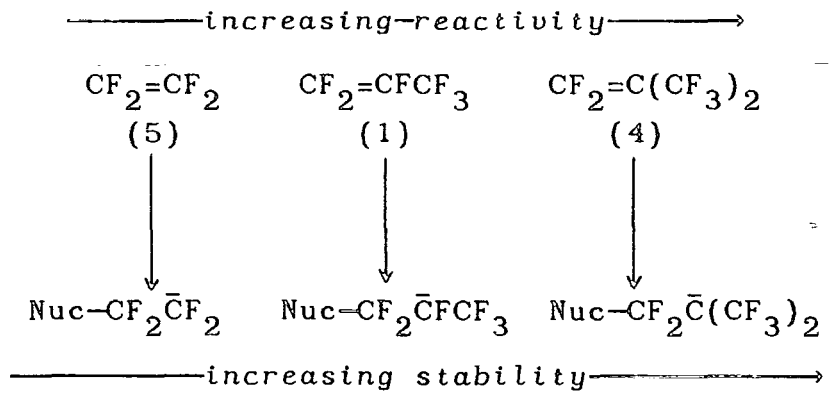
$\bar{C}\text{—}C\text{—}F$ *strongly stabilising*

$\bar{C}\text{—}\ddot{F}$ *potentially destabilising*

From these effects it may be directly deduced that nucleophilic attack on a polyfluorinated alkene will take place at the least substituted end of the molecule, to generate carbanions with the minimum number of α-fluorine substituents. *ie.* (2) is favoured over (3) in the above example.

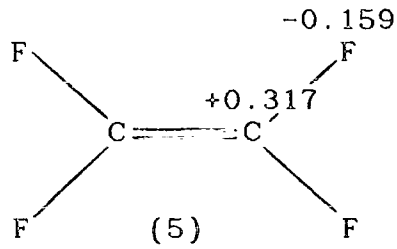
Similarly, a reactivity order may also be deduced for nucleophilic attack in which increasing perfluoroalkyl

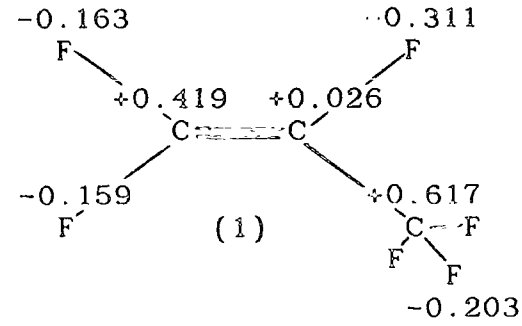
substitution at one of the sp^2 carbons leads to greater ability to support a negative charge. *ie.* reactivity increases with increasing stability of the intermediate anion.

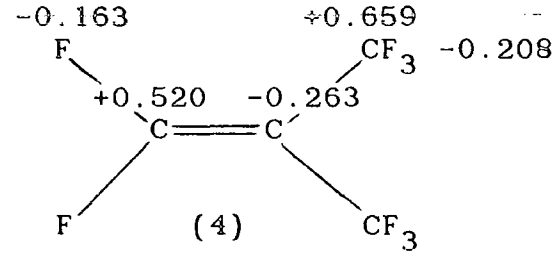


This order is well established experimentally,[9] in that perfluoroisobutene (4) is readily attacked by neutral methanol,[10] hexafluoropropene (1) requires the presence of a base[11] and tetrafluoroethylene (5) only reacts in the presence of a strong base[9] or at elevated pressures.[12] It is worthwhile to add a note of caution here, in that, although the reactivity data given above is probably an accurate representation, all too frequently the effects of solubility *etc.* are not taken into account.

CNDO calculations[13] have been performed on alkenes (1), (4) and (5) and the resulting initial state electron distributions, shown below, may also be used to rationalise the reactivity order and regioselectivity.







For example, the most reactive alkene, (4), contains a vinyl carbon with the greatest ground state positive charge and, therefore, provides the greatest attraction to the incoming nucleophile.

However, the former approach, based on carbanion stability becomes less convincing in rationalising relative reactivities of, for example, (1) and (6) where the relative stabilising influences of similar units are considered.

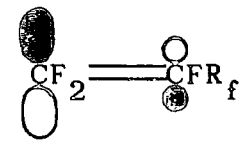
$$\underset{(1)}{CF_2{=}CFCF_3} + Nuc^- \longrightarrow Nuc{-}CF_2{-}\bar{C}FCF_3 \longrightarrow etc.$$
$$\underset{(7)}{\phantom{Nuc{-}CF_2{-}\bar{C}FCF_3}}$$

$$\underset{(6)}{CF_3CF{=}CFCF_3} + Nuc \longrightarrow Nuc{-}CF(CF_3){-}\bar{C}FCF_3 \longrightarrow etc.$$
$$\underset{(8)}{\phantom{Nuc{-}CF(CF_3){-}\bar{C}FCF_3}}$$

Fluorine and perfluoroalkyl substituents have been clearly shown[14] to exert similar influences when adjacent to a negative centre, and so the groups $Nuc{-}CF(CF_3){-}$ and $Nuc{-}CF_2{-}$ in intermediates (7) and (8) should confer similar stability. Nevertheless, alkenes with the configuration $CF_2{=}CFR_f$, such as (1), have been clearly demonstrated[15] to

be more reactive than those with the $R_fCF{=}CFR_f$ structure, such as (6).

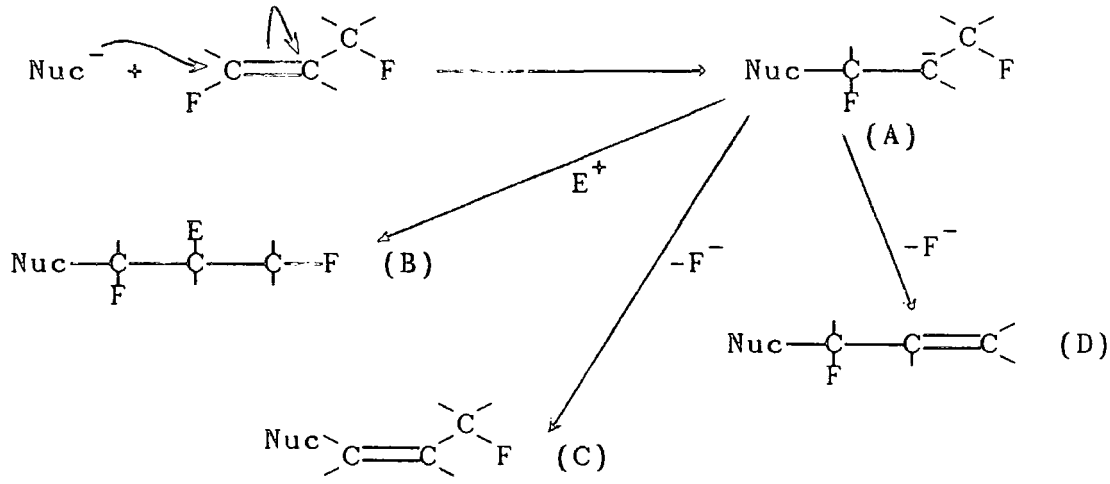
An alternative frontier orbital approach, with more general applicability, has been advanced recently by workers in these laboratories.[16] In this initial state rationalisation the LUMO of the alkene interacts with a filled orbital on the nucleophile to form a new bond. Electronegative substituents lower orbital energies[17] and, consequently, perfluoroalkyl groups will have the overall effect of lowering the alkene LUMO energy. As we have shown earlier, the electronic nature of a fluorine atom bonded to an unsaturated site is ambiguous and so the LUMO energy is likely to be dominated by the number of perfluoroalkyl groups. However, $CF_2{=}C(CF_3)_2$ is a much more reactive olefin than $CF_3CF{=}CFCF_3$ even though both possess two CF_3 substituents and it is necessary, therefore, to assume the disposition of the perfluoroalkyl groups is important. Perfluoroalkyl groups on the same side of the double bond reinforce each other, and on opposite sides of the unsaturation oppose each other. This is manifested in the relative coefficients of the frontier orbitals and, for the LUMO, these are enhanced for the least substituted terminus of an unsymmetrically substituted alkene.

eg. $CF_3CF{=}CFCF_3$ (6) LUMO 

It is now easy to rationalise why less symmetrical and more polarised olefins are more reactive to nucleophiles than symmetrically substituted derivatives.

1.B.b Possible products from nucleophilic attack on a polyfluoroalkene

The intermediate carbanion (A) derived from nucleophilic attack on a fluorinated alkene may react further in three main ways, as shown below:-



1) combination with an electrophile, such as a proton, to yield the overall addition product (B),

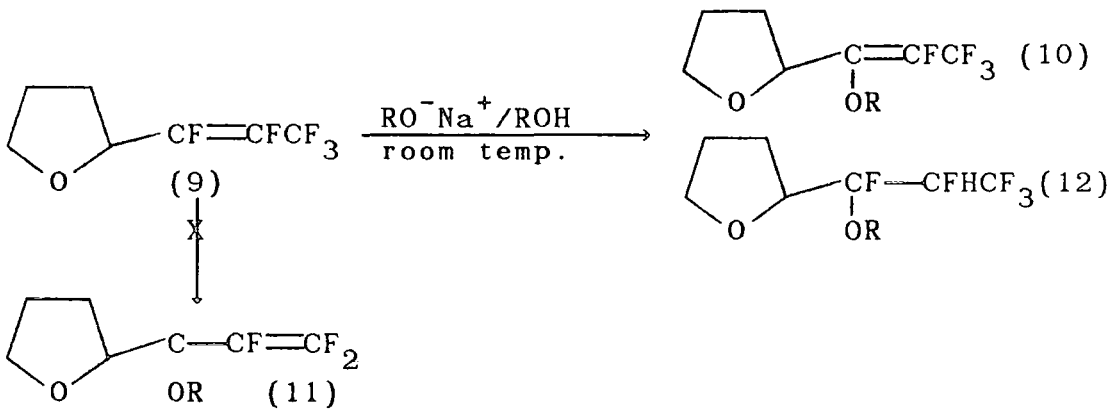
2) elimination of fluoride ion from an initially vinylic site to give the overall substitution product (C) or 3) elimination of fluoride ion from an initially allylic site to produce the alternative substitution product (D); a sequence sometimes known as substitution with rearrangement or "S_N2'".

Preference for any one of the three schemes above will depend on numerous factors, including the lifetime of the anionic intermediate (A), the potency and availability of any electophile, on steric requirements and solvent effects *etc.*

There is difficulty in assigning mechanistic

preference as a result of the huge variety of reaction conditions documented in the literature[9]. However, addition of H-Nuc (sequence 1, E=H) appears to be favoured for the simpler, less electron deficient fluorinated alkenes where the derived carbanions are more basic. By the same token, olefin precursors to more stable and correspondingly less basic anions exhibit a greater propensity for substitution processes.

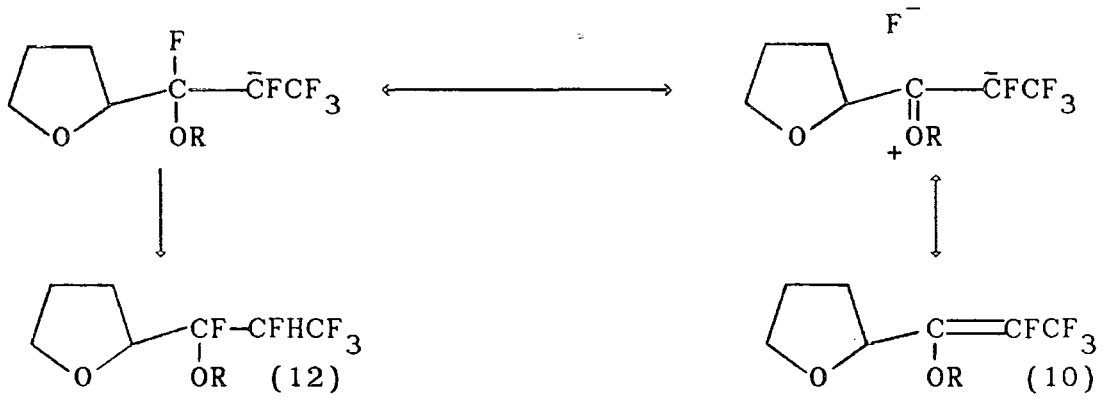
In the reaction between 1-(2-tetrahydrofuryl)-pentafluoropropene (9) with ethoxides in the relevant alcohol as solvent[18] the dominant product (10) was unsaturated, a feature of the strongly basic conditions employed.



Absence of the alternative unsaturated material (11) *via* elimination of an allylic fluorine is a common observation[9] for trifluoromethyl groups when the products are highly reactive terminal difluoromethylene compounds.

R	Et	^{n}Pr	*cyclo*-C_5H_9	$Et_2NCH_2CH_2$
%(10)	70	29	13	98
%(12)	12	7	1	0

The proportion of addition product (12) increases with decreasing ability of the group R to donate electrons, and is consistent with reduced availability of the alcoholic proton. An alternative explanation is that the more electronegative -OR substituents in the intermediate carbanion do not efficiently assist fluoride ejection.



Similar observations have been made for reactions with hexafluoropropene (1) and perfluoroisobutene (4).[19]

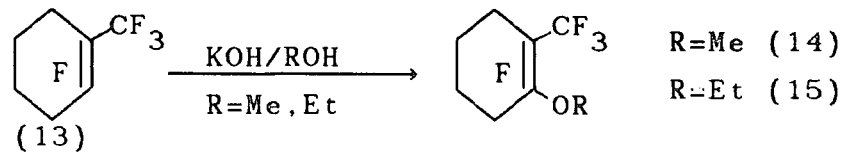
Para-substituted-phenylpentafluoropropenes[20] undergo more substitution reactions with ethanolic ethoxide when the phenyl residue contains a more electron donating *para*-substituent, again indicating internal promotion of fluoride ion elimination.

Nucleophilic substitution of vinyl fluorine (process (2)) is often[9] preferred to the alternative allylic displacement (process (3)), where generation of the product with the maximum stabilising perfluoroalkyl substituents results.

1.B.c Some illustrative recent nucleophilic reactions of fluorinated alkenes

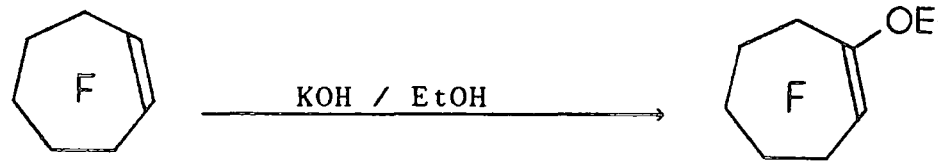
The literature relating to nucleophilic processes in fluoro-olefin reactions has, in the past, been exhaustively studied and excellent books[2,21,22] and review articles[23-28] are available. The purpose of this section is to provide some simple examples of this reaction type while, at the same time, concentrating on very recent (mostly after 1982) publications.

i) Oxygen Nucleophiles Cyclic alkene (13) reacted with methanol and ethanol in the presence of potassium hydroxide to yield the unsaturated ethers (14) and (15)[29] *via* displacement of vinylic fluorine.



(13)

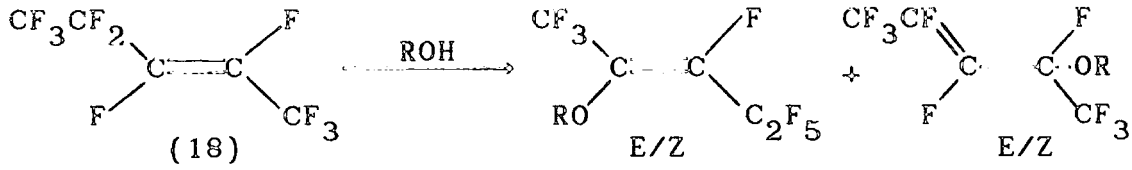
Similarly, dodecafluorocycloheptene (16) afforded the corresponding vinyl ether (17) by treatment with ethanolic potassium hydroxide.[30]



(16) (17)

An analogous acyclic alkene, *z*-perfluoro-2-pentene (18) however, gave a mixture of products derived from attack solely at the 2-position, but with both allylic and vinylic

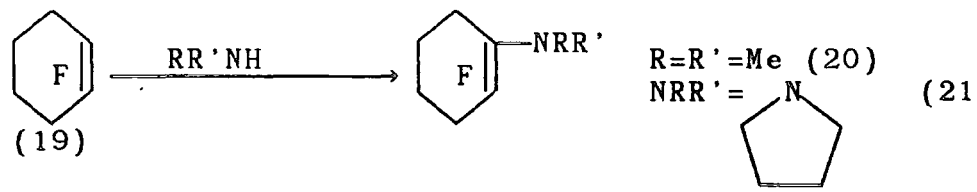
fluorine substitution and partial loss of the stereochemical integrity of the double bond.[31]



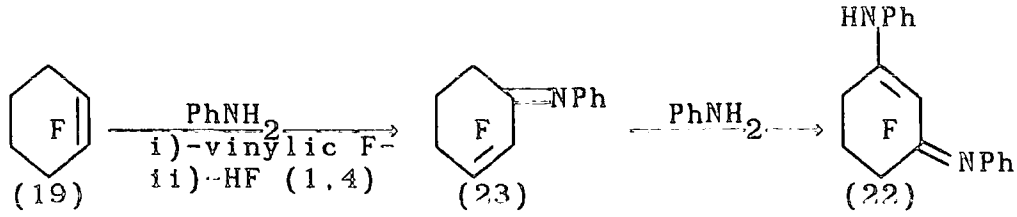
The observed regioselectivity is puzzling in view of the fact that the electronic environments of the unsaturated carbons and of the derived carbanions are strikingly alike.

ii) Nitrogen nucleophiles Although less studied than alkoxide reactions there is a growing literature on the reactions of amines with fluorinated alkenes. The possibility of dehydrofluorination of the adducts and of further reaction of more activated molecules frequently enables the formation of relatively complex products and product mixtures.

Decafluorocyclohexene (19) reacted[32] with dimethylamine and pyrrolidine in the absence of added base to yield the enamine products (20) and (21) respectively.

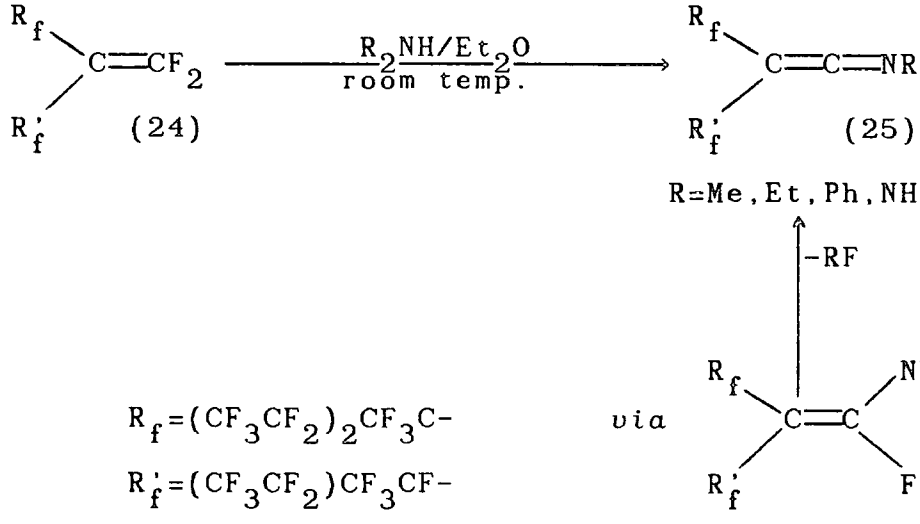


The greater nucleophilicity of nitrogen compared with oxygen in this context often renders the presence of an additional base unnecessary. Aniline reacted slowly with (19) to produce a disubstituted compound (22) formed *via* initial vinylic displacement and 1,4-dehydrofluorination.

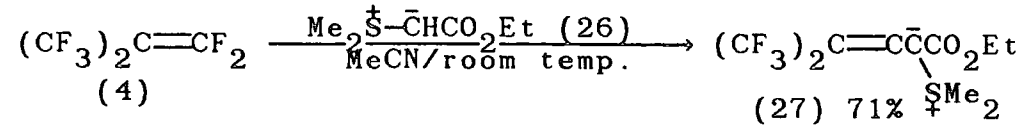


(19) (23) (22)

The resulting azadiene (23) is particularly susceptible to further attack and gives the di-adduct (22) by a second substitution for vinyl fluorine. The highly branched hexamer of tetrafluoroethylene (24) reacts[33] with a variety of amines to give good yields of ketenimines (25) *via* initial attack at the reactive terminal $=CF_2$ group followed by an unusual elimination of an alkyl fluoride residue.



iii) <u>Carbon nucleophiles</u> Perfluoroisobutene (4) has been reported to react with sulphur ylid (26) by displacement of one of the labile vinylic fluorines to leave a new perfluoroalkyl-substitutued ylid (27).[34]



A similar process has also been observed for

hexafluoropropene (1) with the diphenylacetonitrile carbanion (28).[35]

$$CF_3CF{=}CF_2 \quad \underset{10\text{-}15\,^{\circ}C/DMF}{\xrightarrow{Ph_2\bar{C}\text{-}CN\ (28)/NaOH}} \quad CF_3CF{=}CFCPh_2CN$$

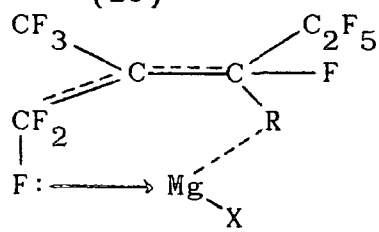
(1) 79%

An excellent paper by Ishikawa and co-workers[36] concerns the reactions of perfluoro-2-methyl-2-pentene (29) with organomagnesium reagents, in which products (30,31) derived from both substitution processes are observed. Formation of the unstable terminal $=CF_2$ derivative (31) is rationalised in terms of the assisted fluoride ion removal by a well positioned metal residue in the transition state.

$$(CF_3)_2C{=}CFC_2F_5 \quad \underset{Et_2O}{\xrightarrow{RMgX/-45\ to\ +23\,^{\circ}C}} \quad (CF_3)_2C{=}CRC_2F_5$$

(29) (30)

via



+ $CF_3C(=CF_2)-CFR(C_2F_5)$ (31)

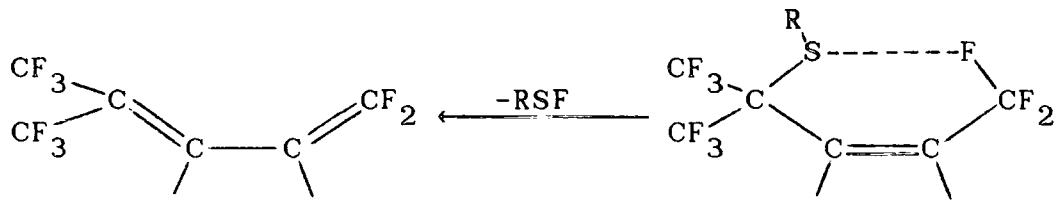
Support for this process is available from studies on the product ratios (30):(31) for different alkyl groups (R), in which greater electron release from the group localises more electron density on the $-C(CF_3)_2$ position and makes the metal more "metallic". This then favours formation of the isomer (31) formed by the above elimination pathway.

iv) Other nucleophiles Sulphur substitution at a double bond favours attack at the opposite olefin terminus as the resulting anionic intermediate is mesomerically

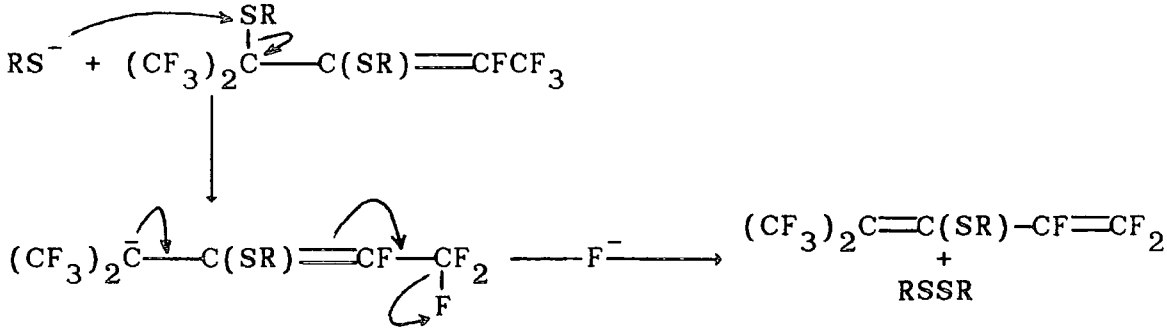
stabilised.

Such activation, coupled with the high nucleophilicity of thiols, often leads to the formation of polysubstituted products in the reactions of sulphur nucleophiles with fluorinated alkenes.

Ishikawa and Maruta[37] reported the action of aromatic thiols with hexafluoropropene dimer (29) and observed a multitude of products, some of which appeared to have arisen from the diene skeleton shown below.

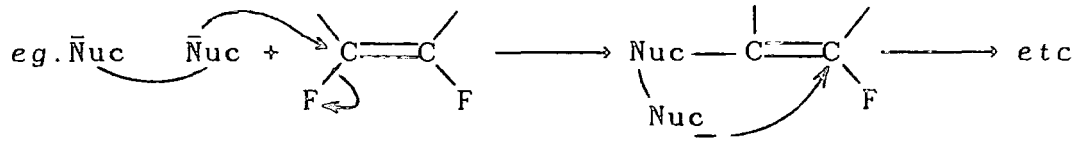


The authors postulate an unprecedented 1,4-elimination of a sulphenyl fluoride to account for the occurence of these species. This mechanism has been contested, however, in the recent literature[38] and a more likely alternative suggested.



1.C BIFUNCTIONAL NUCLEOPHILES

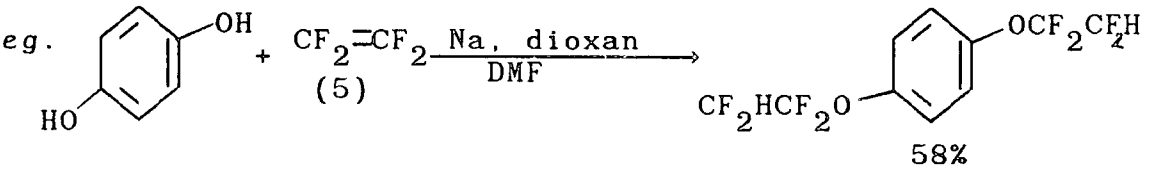
When a nucleophile containing two reactive sites is employed with a fluorinated alkene and undergoes an initial substitution process, the possibility arises that the remaining terminus may attack the new unsaturation thus effecting cyclisation.



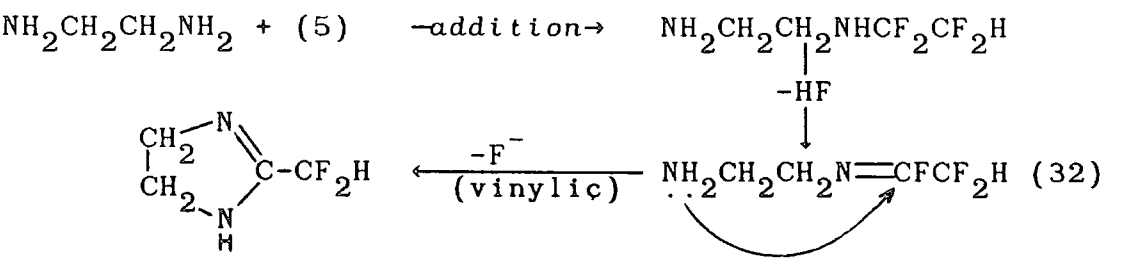
The initial step may involve both vinylic or allylic fluorine substitution to generate the intermediate unsaturation, and the cyclisation step may occur at this functionality by any of the substitution or addition mechanisms described in section 1.B.a. Clearly, for heteronucleophiles this methodology offers a simple route to relatively complex fluorinated heterocyclic skeletons. These are frequently very desirable molecules because they are known to exhibit extremely high biocidal activity[39,40] and indeed, in the past few years there has been an explosion in the patent literature relating to the use of fluorinated heterocyclic compounds as agrochemicals.[39-46] When compared with the wealth of literature now available on simple nucleophile induced reactions of fluorinated alkenes there are relatively few reports on the use of bifunctional nucleophiles. The purpose of the remaining part of this section is to review progress in this area to date.

1.C.a Fluorinated alkenes with simple diheteronucleophiles

i) Tetrafluoroethylene(5) A large paper by England and co-workers[12] concerning the reactions of a wide number of polyhydric alcohols and phenols, amines and amides with tetrafluoroethylene was published in 1960. The reactions of alcohols and thiols were conducted under a pressure of about 2.5 atm. and a temperature of 60-100°C in the presence of a small amount of metallic sodium. Almost exclusively, products derived from addition of H-XR (X=O,S *etc.*) to (5) at all available sites on the nucleophile.



Similar reactions with bifunctional amines lead to cyclic amidines *via* intermediate imidoyl fluorides, *eg.*(32), as shown below for ethylenediamine,



ii) Hexafluoropropene (1) We have previously shown that higher fluorinated alkenes undergo initial substitution processes rather than addition which destroys the unsaturation. Thus, simple monohydric difunctional nucleophiles such as diols *etc.* are more disposed to undergo

cyclisation. In a similar manner to (5), (1) reacts with difunctional aromatic amines in the absence of added base to produce imidoyl fluorides,[47] *eg.*(33), and heterocyclisation *via* this reactive intermediate may occur easily with the second nucleophile. (Table 1 gives some other reactions of difunctional aromatic amines with (1).)

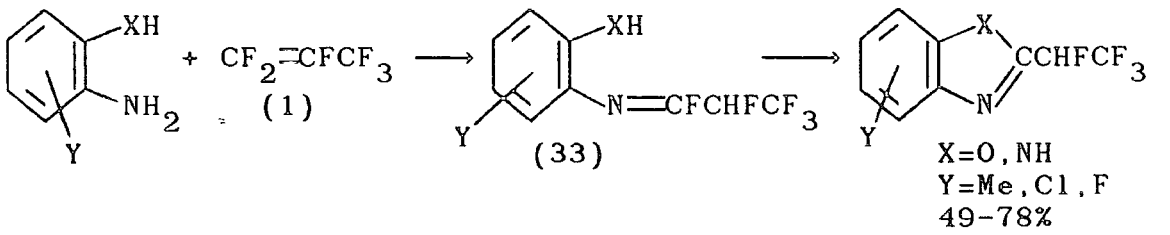
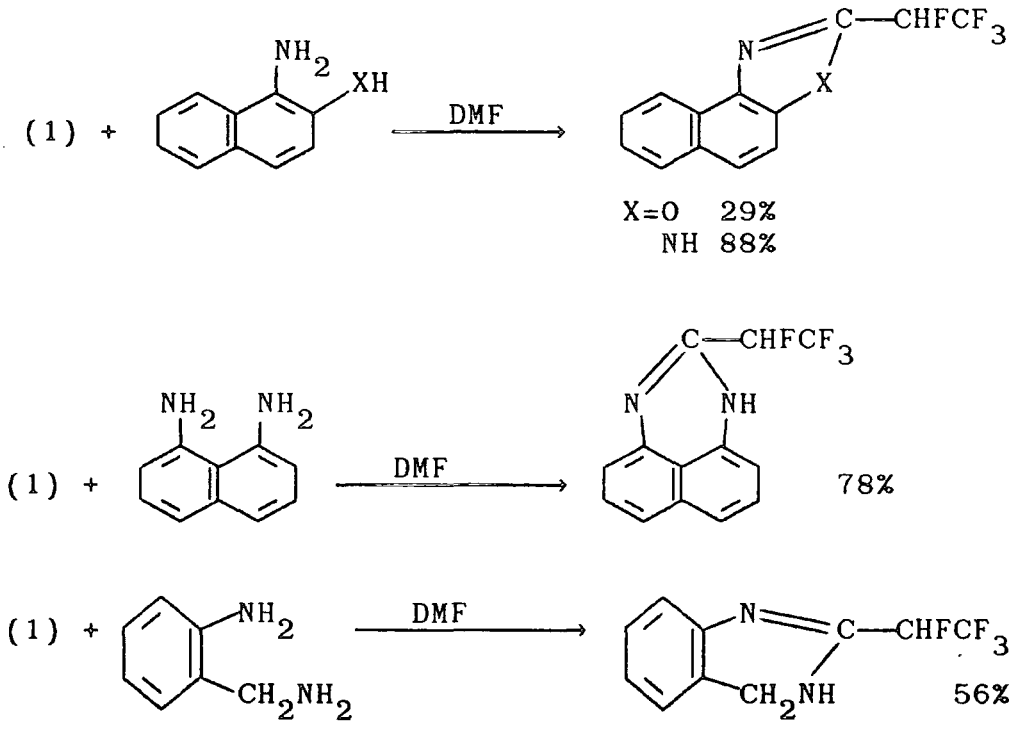


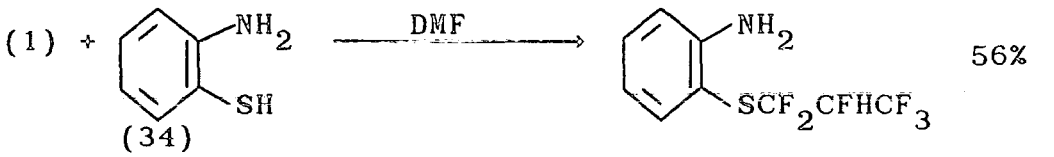
TABLE 1

Difunctional aromatic amines with hexafluoropropene (1)[47]



This type of process has also been reported[48] for ethanolamine which gave the expected oxazoline in good yield. Reactions with polyols, such as glycerin,[49] in the absence of base, afforded products occuring *via* addition

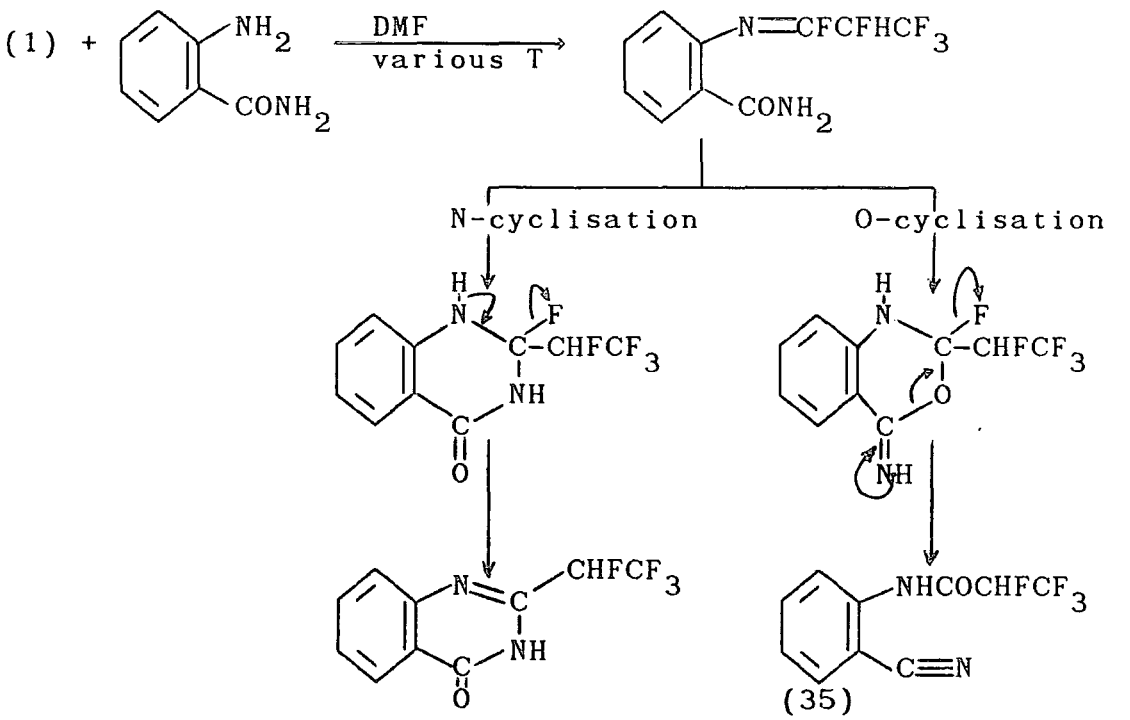
processes. When an amino-thiol, *eg.* (34), is employed, however, the high nucleophilicity of thiols favours simple addition of an S-H unit across the double bond over the precedented imidoyl fluoride mechanism[47]



In a reaction between (1) and *para*-aminophenol where a competition between $-NH_2$ and -OH for (1) exists, with no possibility for cyclisation, the product derives from attack exclusively by the amino group and this allows us to define a reactivity order for heteronucleophiles with (1).

$ArSH > ArNH_2 > ArOH$ (for (1), with no base)

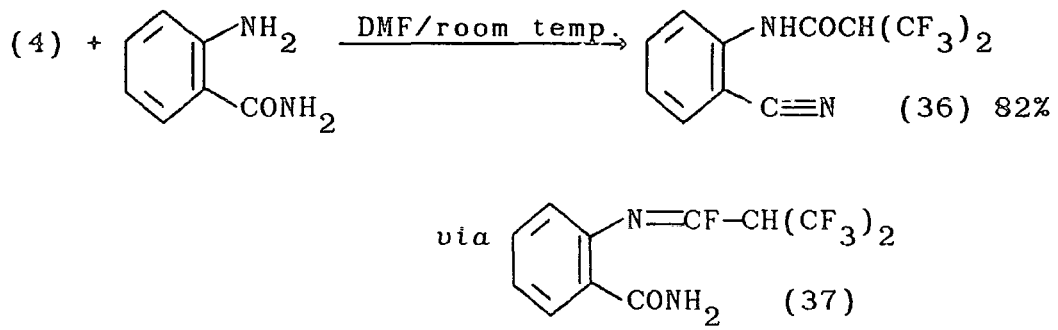
decreasing reactivity →



The above scheme shows that the reaction between 2-

aminobenzamide and (1)[50] gives two products occuring *via* nitrogen and oxygen induced cyclisation through imidoyl fluoride intermediates. The O-6 ring closure is followed by a novel rearrangement, as shown, to yield the cyanide (35).

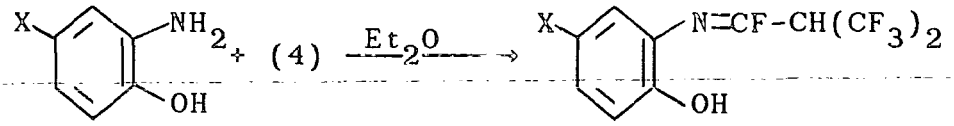
iii) Perfluoroisobutene (4) In a similar reaction, perfluoroisobutene (4) undergoes exclusive O-6 cyclisation, followed by C-O bond cleavage, to give the relevant nitrile[50] (36) in high yield.



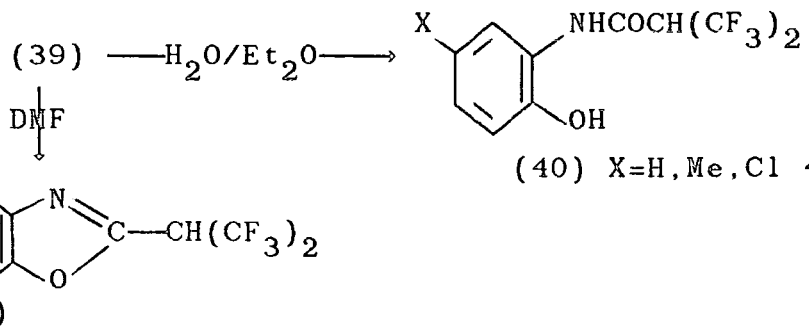
This has been interpreted [50] as an indication that the unsaturated carbon in the relevant imidoyl fluoride (37) is more electrophilic and the associated increase in reactivity then causes reaction only with the more highly donating carbamoyl oxygen. This is not very convincing, however, as we would expect the imidoyl fluorides from both (1) and (4) to be very similar in reactivity when the configurations $Ar-N{=}CF-CH(CF_3)_2$ and $Ar-N{=}CF-CHCFCF_3$ are compared. In any event, enhanced reactivity is commonly associated with reduced selectivity, not the opposite as claimed.

The reaction of perfluoroisobutene (4) with a variety of other *ortho*-substituted aniline derivatives has been reported.[51] With *ortho*-aminophenols in the presence of a high dielectric medium, such as DMF, the benzoxazole

derivatives (38) , analogous to the hexafluoropropene adducts, are formed in good yield. The reactions are not mirrored in ether as solvent, but terminate on formation of the imidoyl fluorides (39).



(39) X=H,Me,Cl



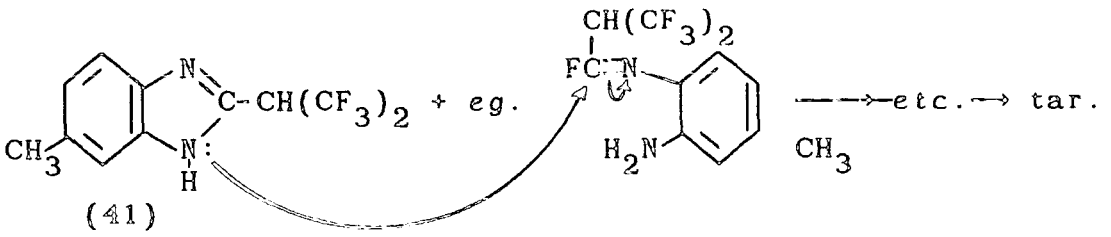
(40) X=H,Me,Cl 47%

(38)

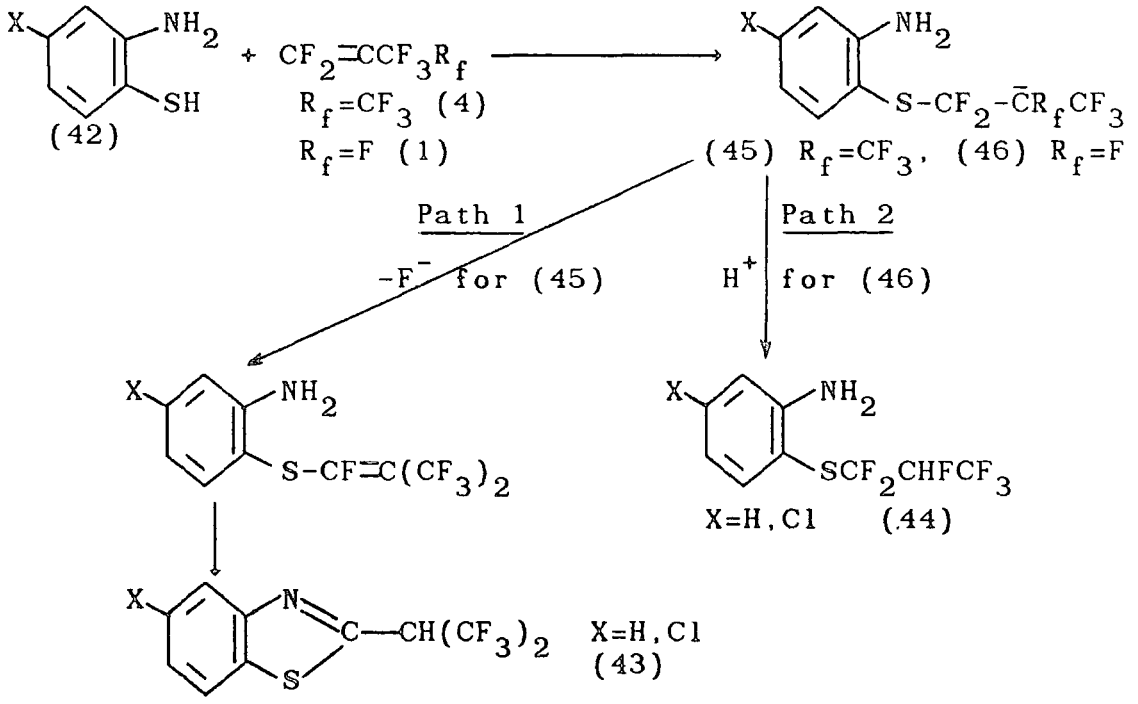
Y=O X=H,Me,Cl 79-95%

Aqueous hydrolysis afforded the readily characterised 2-hydroxyanilides (40).

Ortho-phenylenediamine derivatives behaved similarly in DMF and benzimidazole derivatives were isolated.[51] Unusually however, the 4-methyl derivative gave only tarry matter even at a low reaction temperature. The benzimidazole products *eg.* (41) differ from most of the other cyclised adducts in that they retain an acidic proton, bonded to a ring nitrogen and thus may participate in intermolecular processes with free electrophiles. The 4-methyl derivative (41) will be more nucleophilic through nitrogen than the parent and side reactions with this compound are more likely.



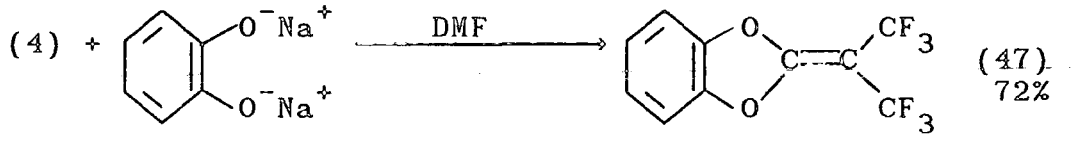
2-Thiol derivatives of aniline (42) also reacted with perfluoroisobutene (4) to yield the relevant cyclised adducts (43). This is in contrast to the analogous reactions of hexafluoropropene (1) which afforded the thioether product (44). In view of the known reactivity order, which places SH>NH_2, it is likely that alkene (4) underwent vinylic fluorine displacement followed by ring closure and dehydrofluorination (Path 1, below) rather than the more common pathway *via* imidoyl fluorides.



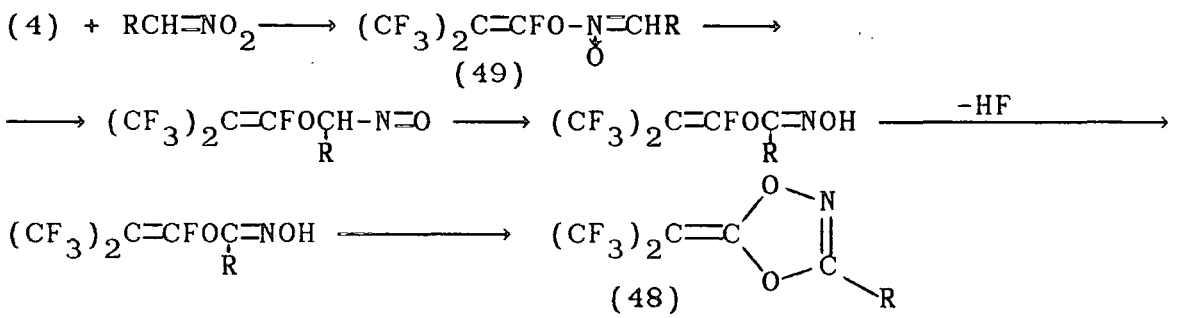
Preference for the initial substitution process with (4) is not surprising given the high stability of anion (45) which would tend to reduce its basicity and thus disfavour the

addition mechanism observed for (1).

Under highly basic conditions, achieved by using a disodium salt in an aprotic solvent, catechol displaced the two vinylic fluorines in (4) to give cyclic ketenacetal (47)

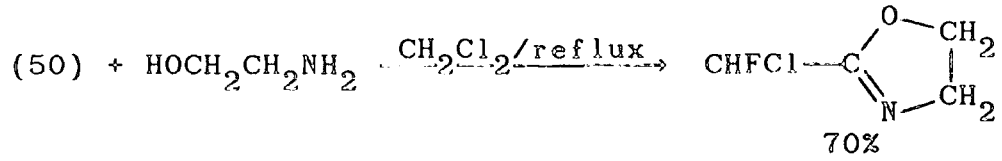


An unusual reaction between (4) and nitroalkanes has been reported,[52,53] leading to the synthesis of dioxazoles (48). The key stage of the reaction is apparently the highly novel migration of the perfluoroisobutenoxide anion from the nitrogen atom to the carbon atom in the intermediate O-perfluoroisobutenylnitrone ether (49).



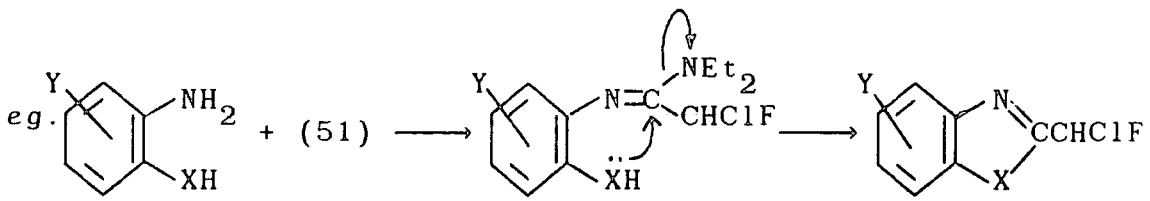
iv) Chlorotrifluoroethylene (50)

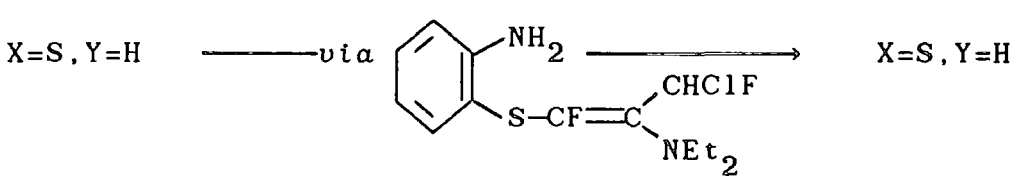
Chlorotrifluoroethylene is rather less electron deficient than some other fluorinated alkenes and therefore is much more sluggish in its reactions with nucleophiles. Nevertheless, workers from Hoechst[48] reported an oxazoline synthesis from this compound with ethanolamine in a similar manner to that described for hexafluoropropene.



Ishikawa and co-workers[54] found the unassisted reactions of (50) with nucleophiles slow and poor yielding, but the presence of diethylamine was found to dramatically improve the situation. The adduct of (50) and diethylamine, 2-chloro-1,1,2-trifluoromethyldiethylamine (51), has been used as a fluorinating agent for alcohols,[55] and is known as the "Yarovenko reagent".

Reaction of (51) with a variety of *ortho*-difunctional benzenes containing an $-NH_2$ group occurs readily *via* the intermediacy of (52) to produce heterocycles containing the chlorofluoromethyl group.

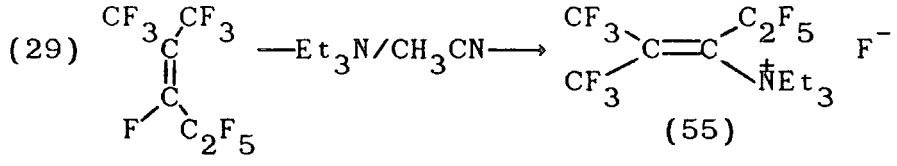




A similar investigation into the mode of reaction of 2-aminobenzamide lead to the observation of only a quinazolone product ((53),X=CONH–). Unusually therefore, cyclisation exclusively through the carbamoyl nitrogen ((52),X=CONH–) has occured. As with perfluoroisobutene, nucleophilic attack

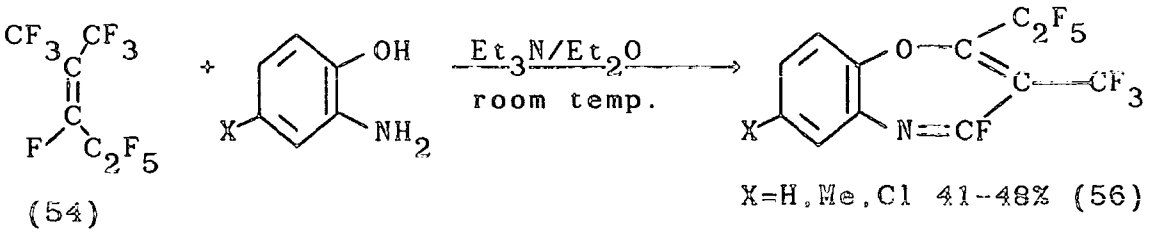
appears to be initiated by addition of the thiol group of 2-aminothiophenol derivatives ((54),X=S) and dehydrofluorination leaves an unsaturation which the residual amino-group utilises to effect cyclisation. Interestingly, (51) appears to behave more like perfluoroisobutene than hexafluoropropene and this may be indicative of its high electrophilicity.

v) Perfluoro-2-methylpent-2-ene (a hexafluoropropene dimer)(29) The highly electrophilic alkene (29) is readily available from hexafluoropropene (1) and its reactions with bifunctional nucleophiles have been well studied. Ishikawa and co-workers have reported, in a series of publications,[56-58] the use of *ortho*-bifunctional benzenes with triethylamine as base and acetonitrile as solvent. Remarkably, it was not until 1981[58] that the significance of this system was reported. The normally insoluble alkene (29) dissolves in acetonitrile in the presence of triethylamine to produce a straw coloured solution with an entirely different ^{19}F n.m.r. which is consistent with the perfluoroalkenyl ammonium structure (55).



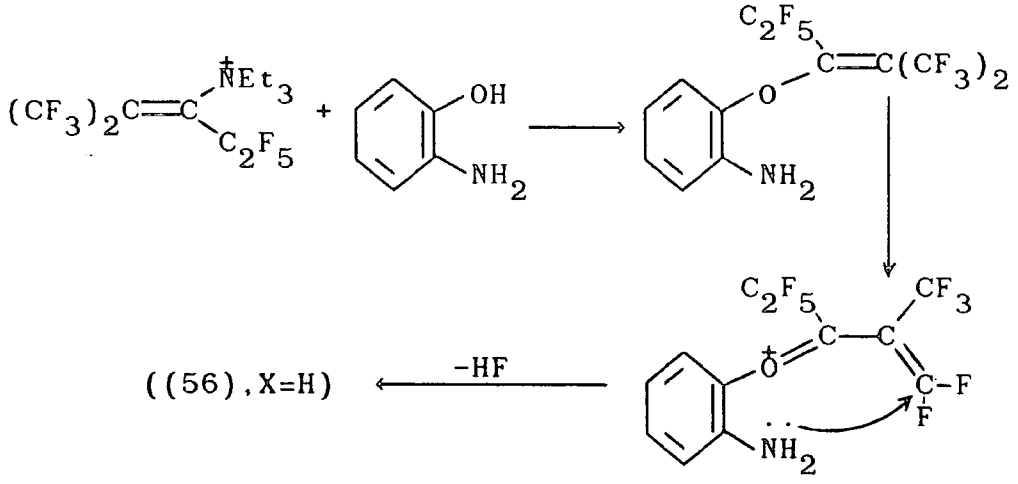
(55) Behaves exactly like an activated form of the precursor alkene (29), with Et_3N making an excellent leaving group.

In the reactions of *ortho*-aminophenols with (29) in the presence of triethylamine seven membered heterocycles (56) were isolated in moderate yield.



(54)

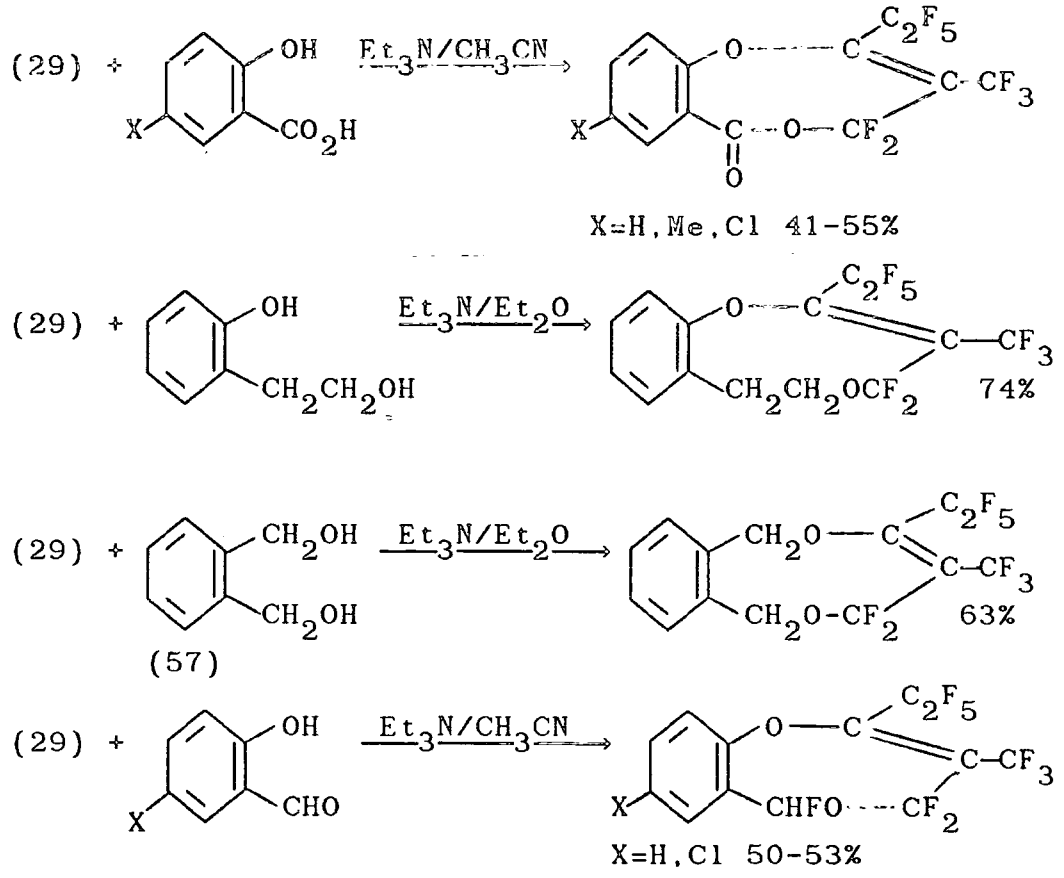
Clearly, oxygen has been involved in the initial attack, in contradiction of the previously described reactivity order. Under basic conditions it is easy to rationalise the enhanced activity of the oxygen residue as the O-H proton is more acidic than the NH_2 proton. A possible mechanism involves substitution for the very labile Et_3N group in the known complex (55), followed by an F^- elimination from a trifluoromethyl group aided by conjugative assistance from the vinyl ether linkage.



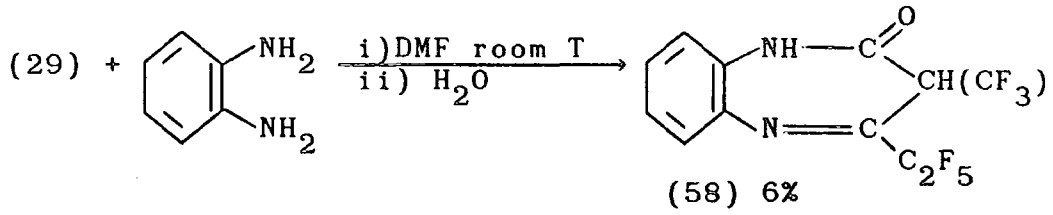
This and related processes have been proposed by the same workers[58] to account for the products from reactions of (29)/triethylamine with salicylic acid , salicylaldehyde , phthalyl alcohol (57) and *ortho*-hydroxyphenethyl alcohol, all of which give 8- and 9-membered benzoheterocycles containing the $X\text{-}CF_2\text{-}C(CF_3)=C(C_2F_5)\text{-}Y$ configuration.

TABLE 2

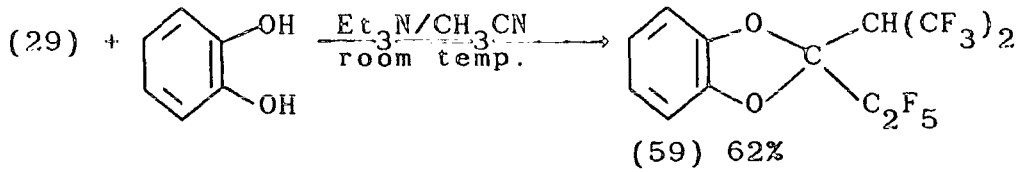
Perfluoro-2-methylpent-2-ene (29) with oxygen nucleophiles[58]



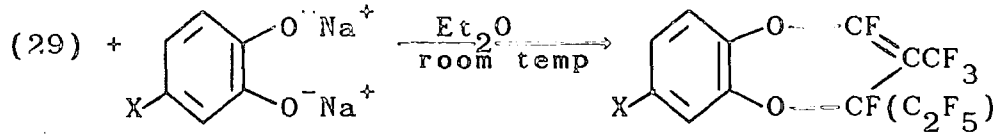
The poor yielding reaction between (29)/triethylamine and *ortho*-phenylenediamine[57] follows a similar course to give, after hydrolysis, the benzodiazepinone (58).



Catechol reacted[57] under similar conditions with (29) to produce the cyclic ketal (59) in good yield, whereas under more basic conditions disodium catecholate afforded a mixture of (60) and a product derived from initial allylic fluorine substitution (61).

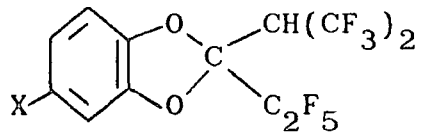


(59) 62%



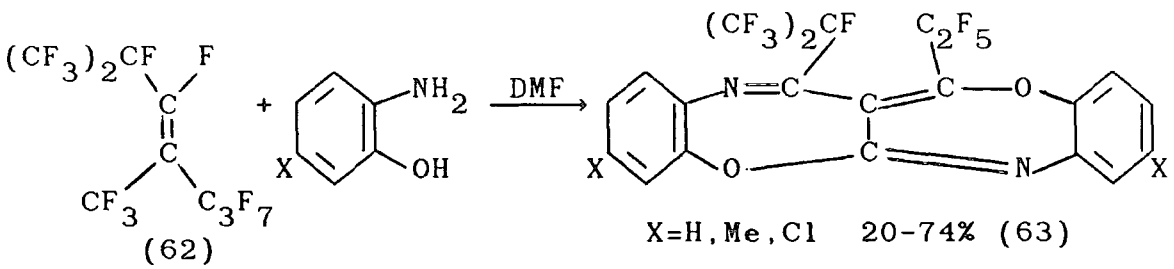
(60) X=H,Me 35-44%

+

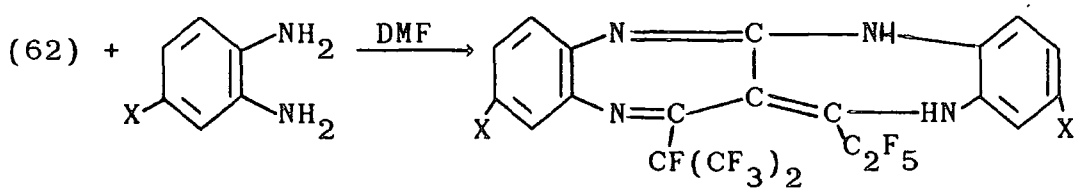


(61) X=H,Me 20%

vi) Miscellaneous acyclic alkenes One of the hexafluoropropene trimers (62) was reacted with *ortho*-aminophenol and *ortho*-phenylenediamine derivatives in the absence of base and found[57] to generate interesting tetracyclic derivatives (63) and (64) containing two units of the nucleophile.



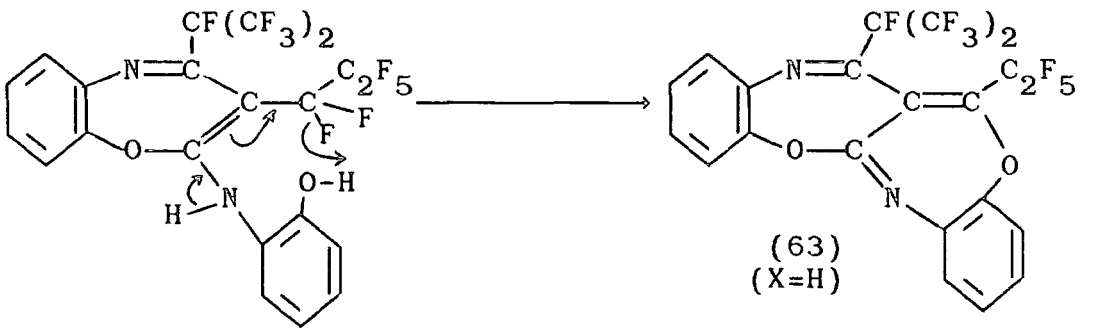
X=H,Me,Cl 20-74% (63)



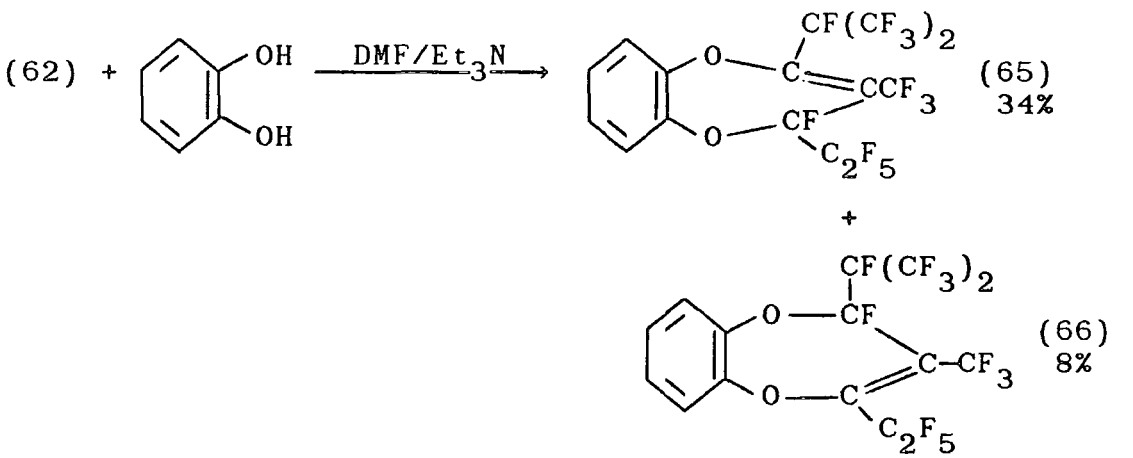
X=H,Me,Cl 17-54% (64)

For *ortho*-aminophenol in the absence of added base the amine functionality is more reactive and this reacts first by

displacement of vinylic fluorine. The final steps in the proposed mechanism are 1,4-elimination of HF to yield an azadiene which the remaining O-H then uses to effect cyclisation. Most interestingly, since (63) is the sole product formed in high yield , the elimination is specific to the diene configuration shown and this is probably due to hydrogen bonded assistance to the process provided by the free O-H.

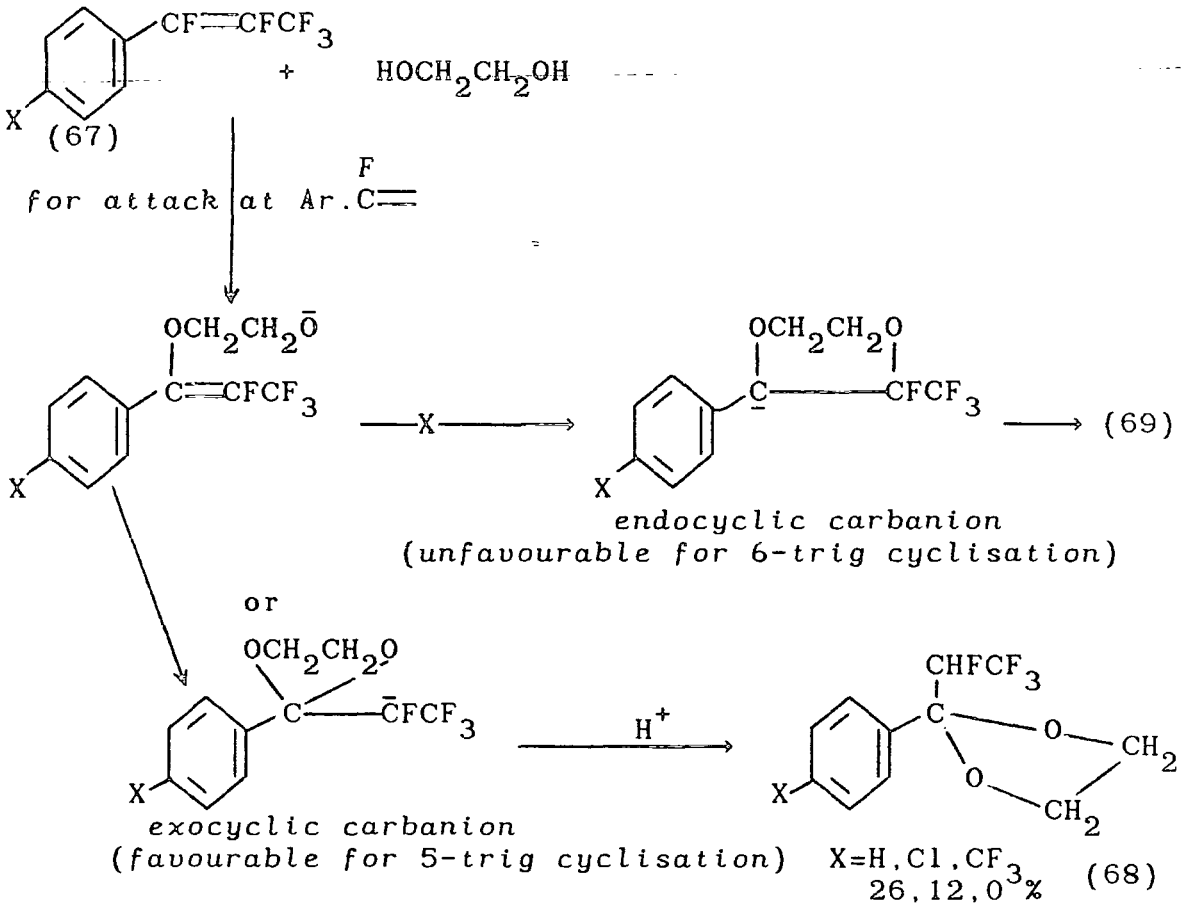


When catechol is employed with alkene (62) two similar 7-membered heterocyclic compounds (65) and (66) are formed *via* conventional allylic and vinylic fluorine substitutions



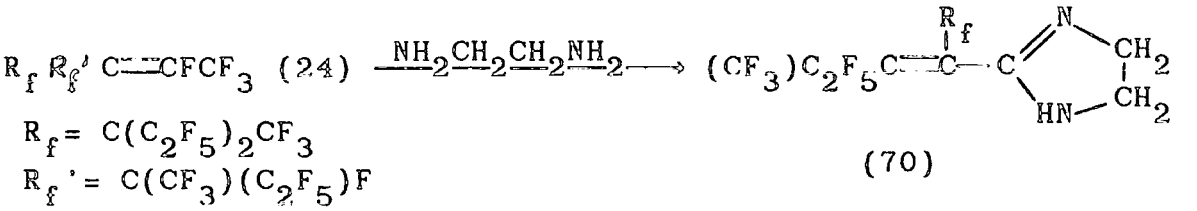
Dmowski and co-workers[59] investigated the reaction of 1-phenylpentafluoropropenes (67) with the sodium salts of ethyleneglycol and 1,3-propanediol, and observed the formation of dioxolanes, *eg.* (68), as the only cyclic

products. They ascribe the absence of any 6-membered ring products (69) to unfavourable stereochemical requirements in the transition state for the relevant ring closure, consistent with the Baldwin rules.[60,61]



Analogous reactions with ethoxide nucleophiles[20] lead exclusively to 1,2-diethoxy derivatives thus lending credence to the suggestion of a stereochemical requirement in the bifunctional systems.

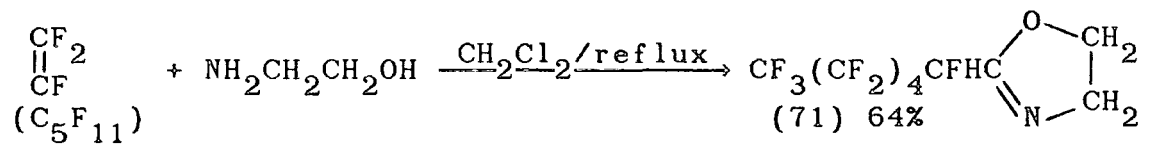
The highly branched tetrafluoroethylene hexamer (24) was reported[33] to react with ethylene diamine *via* two successive vinyl fluorine displacements and a dehydrofluorination to generate the heterocycle (70) in 38% yield.



$R_f = C(C_2F_5)_2CF_3$
$R_f' = C(CF_3)(C_2F_5)F$

(70)

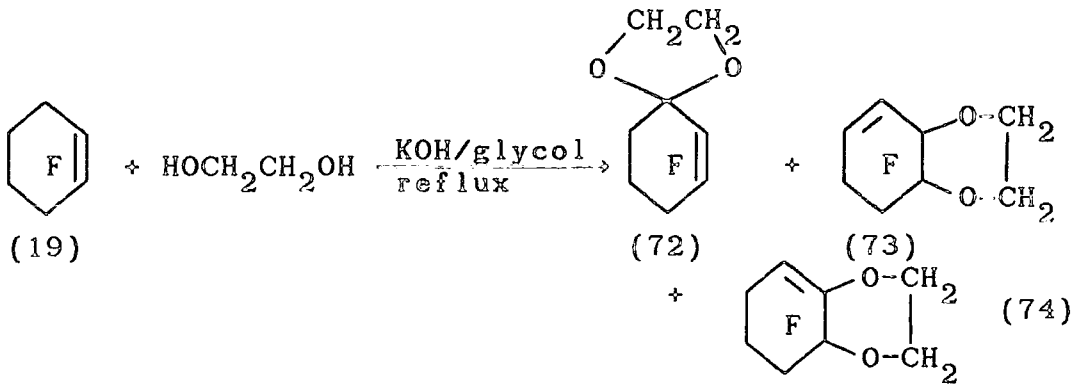
In a similar manner, perfluoro-1-heptene gave oxazoline (71) with ethanolamine, thus confirming the patents claim[48] to a general oxazoline synthesis from terminal difluoromethylene compounds.



(71) 64%

vii) Cyclic alkenes A review[8] on the reactions of fluorinated cycloalkenes with nucleophiles contained only scant reference to any work with bifunctional nucleophiles. Subsequently, there have been but a few reports concerning the reactions of perfluorocyclo-hexene and -pentene with oxygen containing bifunctional nucleophiles by workers from Birmingham.

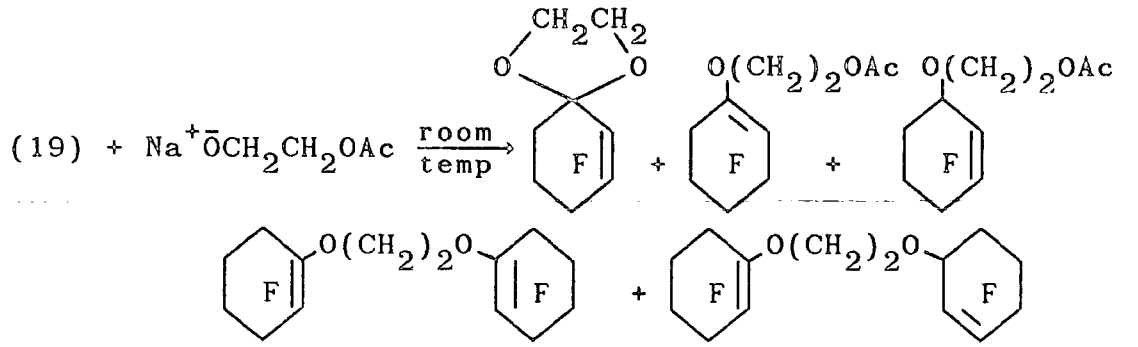
Perfluorocyclohexene (19) was reacted with ethyleneglycol[62] in the presence of potassium hydroxide and three isomeric cyclic products (72-74) derived from combinations of allylic and vinylic fluorine substitutions were isolated in roughly equal proportions. The lack of selectivity observed in such processes serves to define the potential limitations which exist in some heterocyclisation syntheses.

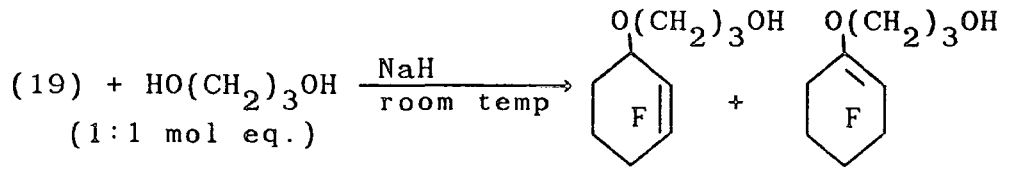


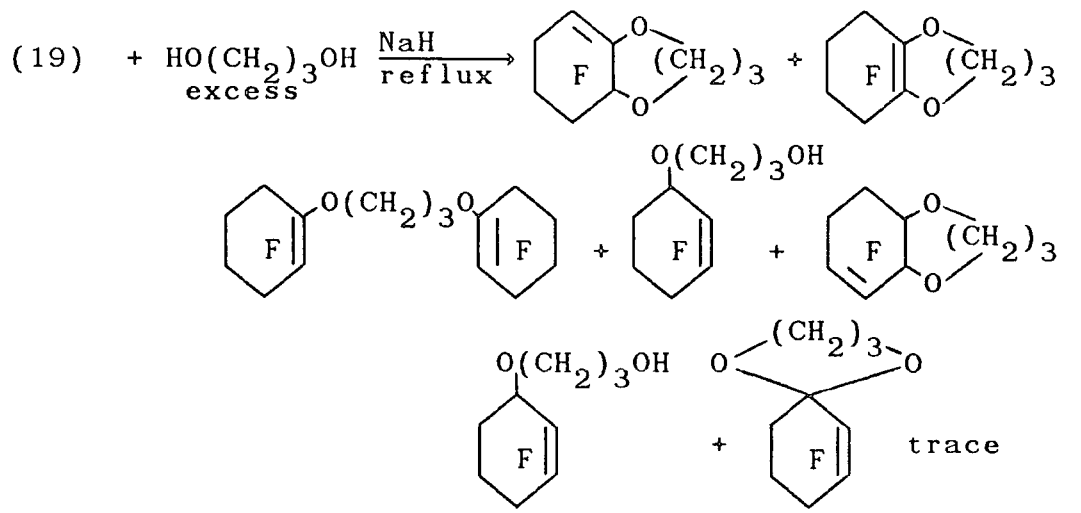
A later publication[63] considers similar reactions of (19) with 2-acetoxyethanol, propane-1,3-diol and butane-1,4-diol. The stoichiometry of the diol could be chosen to maximise adducts with either one or two nucleophile units incorporated (see Table 3). In most cases the reactions were dogged with multitudes of products, from most combinations of fluoride displacements, intramolecular and intermolecular processes and with very low recoveries. Clearly, these should not be regarded as efficient routes to fluorinated heterocycles. However, the isolation of such small amounts of material from multicomponent mixtures is, in itself, praiseworthy.

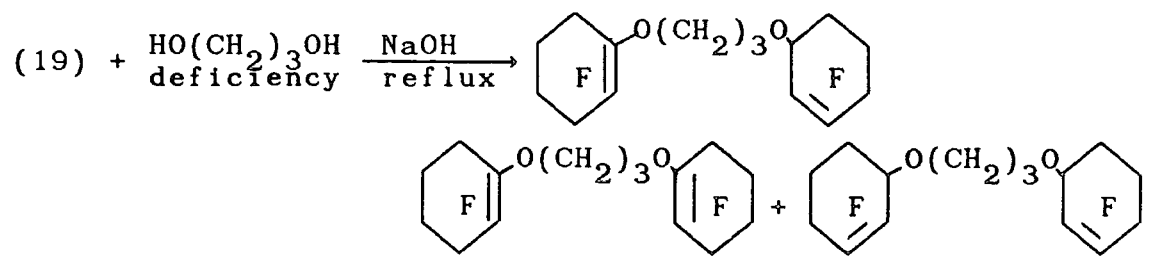
An unusual reaction between saturated 1,2-dichlorodecafluorocyclohexane (75) with ethylene glycol in the presence of potassium hydroxide has been published[64] in which the di-adduct (76) is reported as the sole product. The intermediacy of 1-chloroperfluorocyclohexene has been demonstrated in this case.

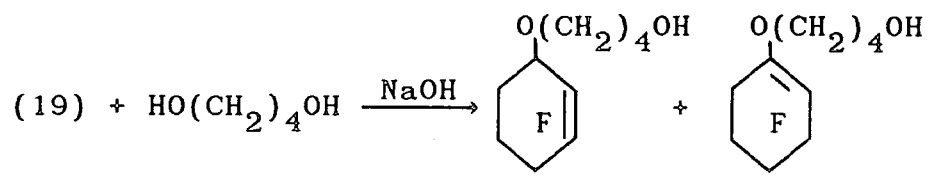
Table 3. Perfluorocyclohexene (19) with bifunctional oxygen nucleophiles[63]

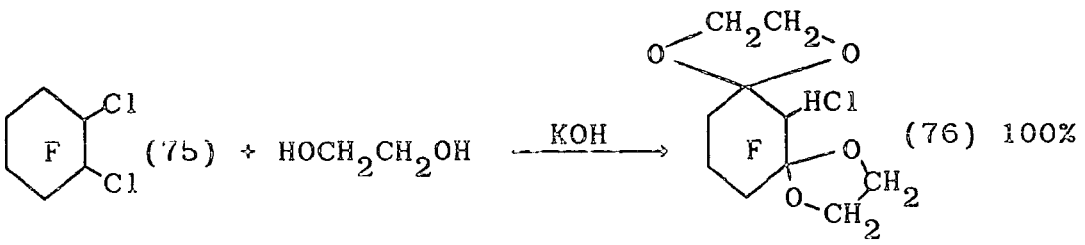




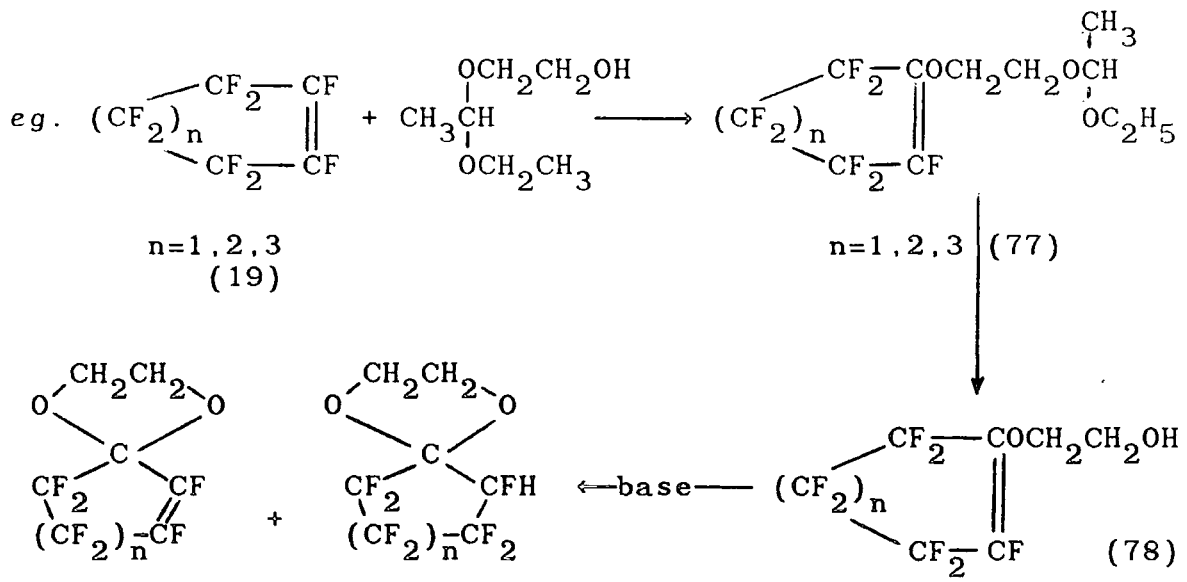








Perfluorocyclo-pentene, -hexene and -heptene have been reacted with 1-ethoxy-1-(2-hydroxyethoxy)ethane in the presence of sodium hydride. Acid labile acetals (77)[65] were produced which could be hydrolysed to the corresponding 1-2(hydroxyethoxy)perfluorocycloalkenes (78). Thus this procedure has lead more cleanly to some of the intermediates in the previous reactions with the simple diols. Cyclisation of these compounds under basic conditions afforded substituted dioxolanes similar to those isolated by Dmowski[59].

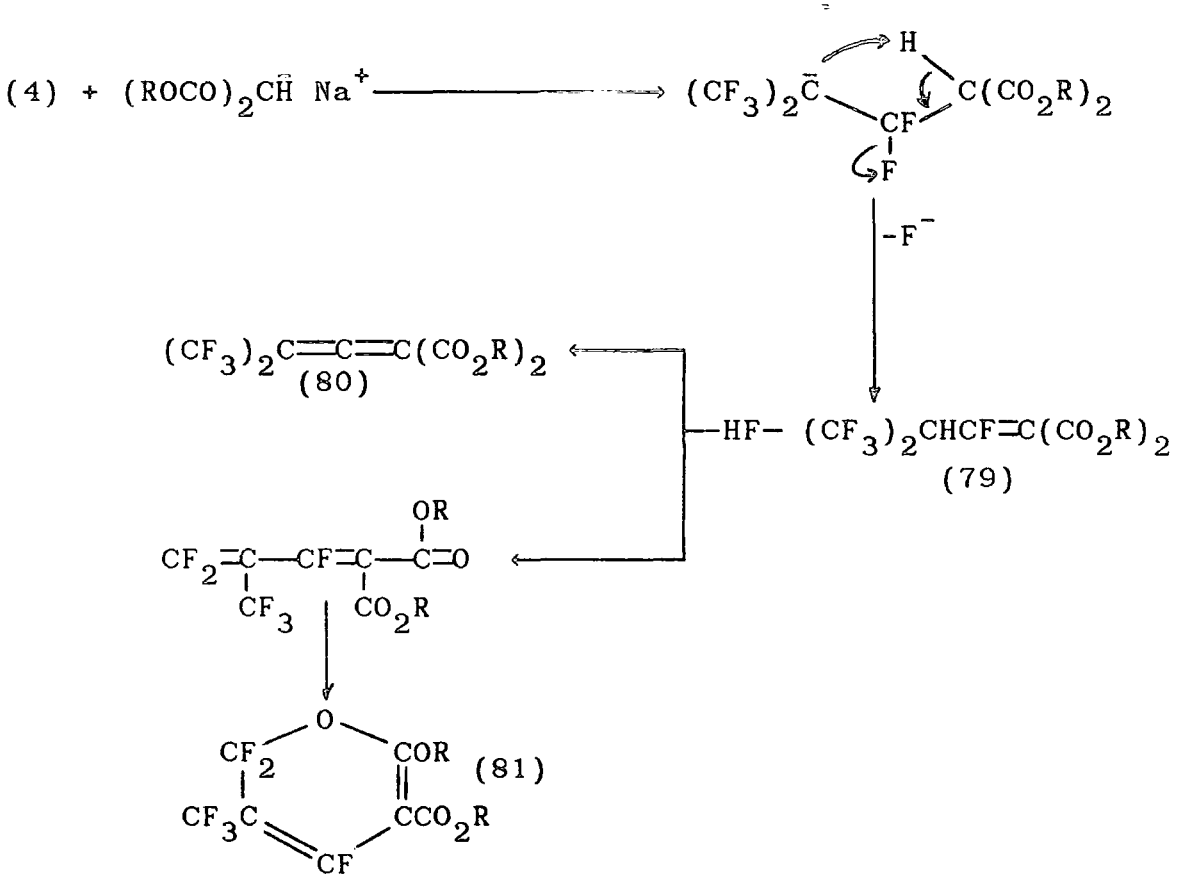


1.C.b Fluorinated alkenes with active methylene compounds

An enolate anion is an example of an ambident nucleophile, *ie.* one which can react through one of two possible sites.

More importantly, in the context of this Chapter removal of a further proton after a nucleophilic substitution process may lead to a second enolate and cyclisation may be effected.

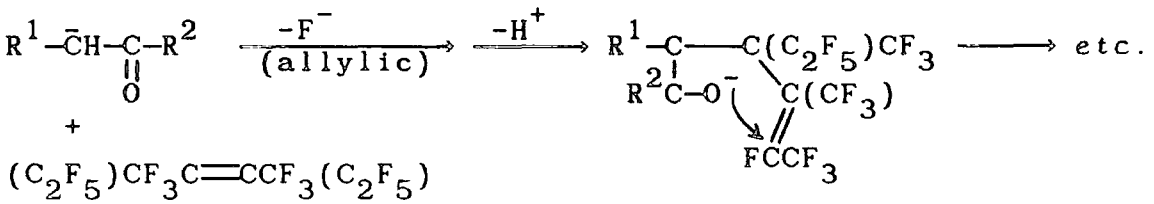
Perfluoroisobutene (4) reacted with malonic ester in the presence of base[66] to give a mixture of products containing the alkylidenemalonic ester (79), the allene (80) and the pyran (81).



Compounds (80) and (81) are formed as a result of the dehydrofluorination of the alkylidenemalonic ester (79) *via* two pathways: with elimination of the vinyl fluorine atom or the fluorine atom from a CF_3-group.

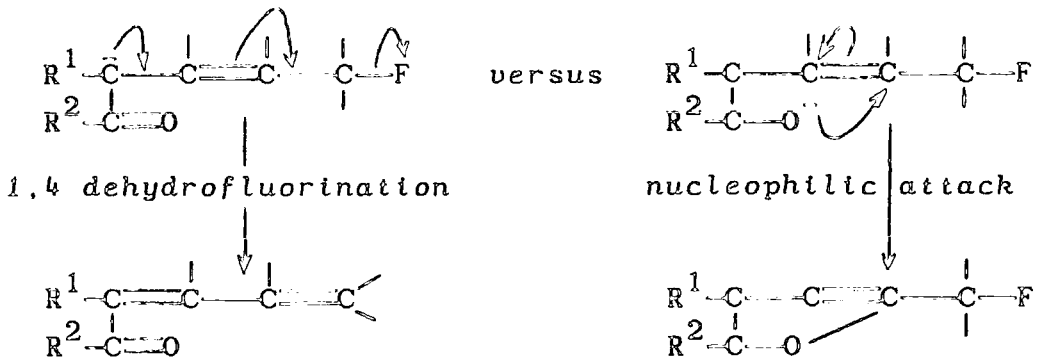
Workers in these laboratories have been actively engaged in a program of research into the novel chemistry of highly substituted perfluoroalkylethylenes,[67,68] and during the last few years a number of publications have emerged

concerning the reactions of such alkenes with active methylene compounds. Perfluoro-3,4-dimethylhex-3-ene (82), the readily available tetrafluoroethylene tetramer, reacted with diethylmalonate, acetylacetone and ethylacetoacetate to yield pyran derivatives (see Table 4).[69] Initial substitution for allylic fluorine by carbon of the primary enolate followed by ring closure through oxygen of the new enolate is the proposed mechanism.



(82)

This investigation was continued[70] with a large number of fluorinated-alkenes and -cycloalkenes and products were formed *via* cyclisation through oxygen to give fluorinated furan and pyran derivatives. With the least acidic of the nucleophiles, diethylmalonate however, the reaction underwent a different course to produce conjugated dienes (see Table 4). This is thought to be a consequence of the relative amount of charge on carbon *versus* oxygen in the relevant enolate. In addition, it is noteworthy that oxygen participates in the reaction at all, as reaction through carbon is by far the most common event. This may be an indication of the *hardness* of the site C=C–F to nucleophilic attack

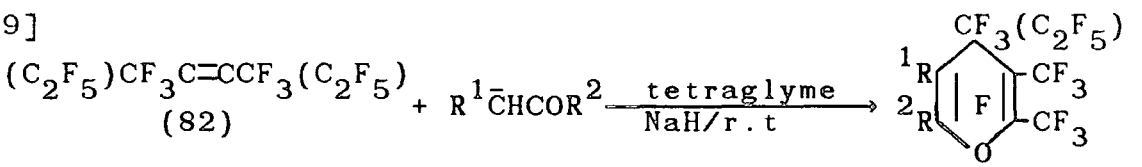


Similar arguments can be used to rationalise the products from perfluoro-3-methyl-4,4-diethylpent-2-ene (83), perfluoro-3-methylpent-2-ene (84) and perfluorobut-2-ene (6), which are displayed in table 4.

Table 4

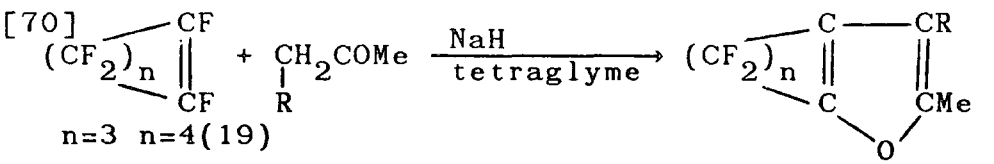
Active methylene compounds with F-alkenes and -cycloalkenes

[69]



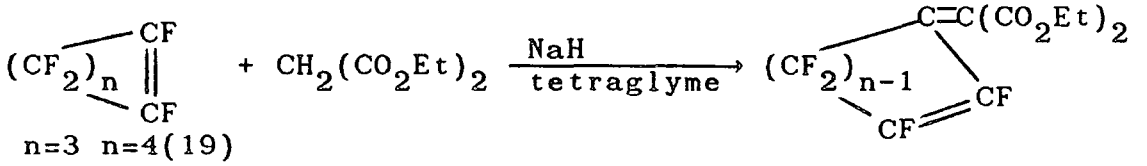
R^1=CO_2Et,	R^1=OEt	42%
COMe,	Me	32%
CO_2Et,	Me	65%

[70]



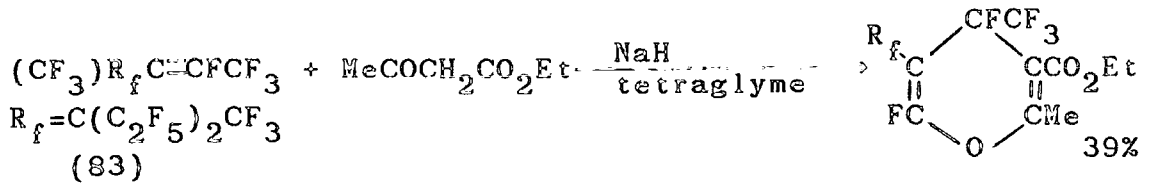
n=3 n=4(19)

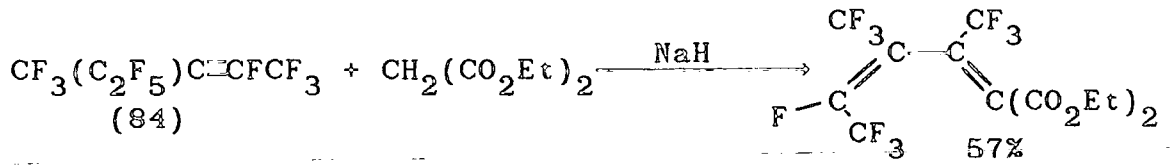
R=COMe,	n=3,4	38-25%
CO_2Et,	n=4	31%

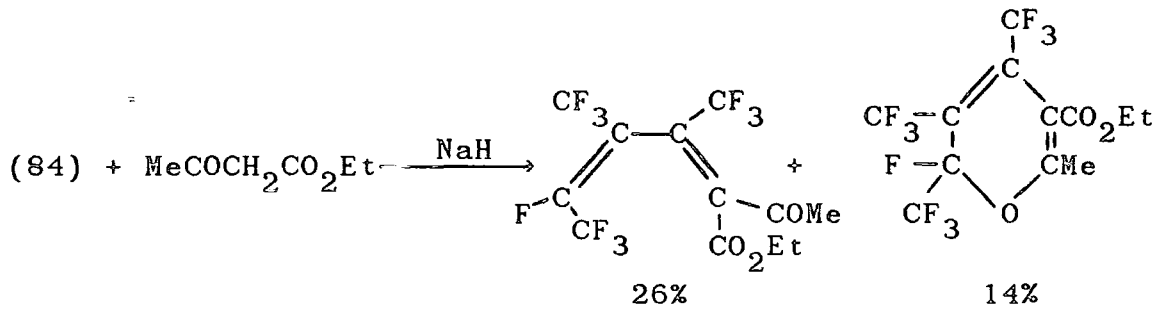


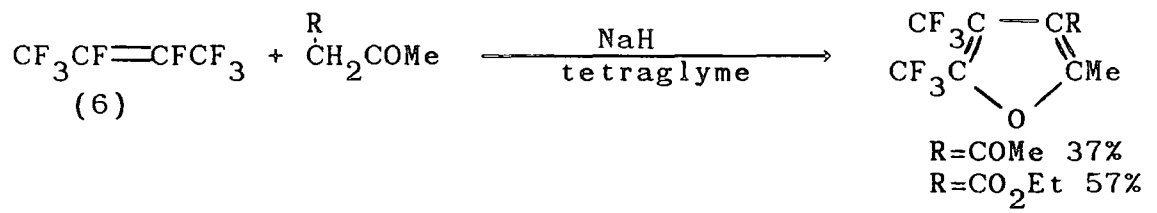
n=3 n=4(19)

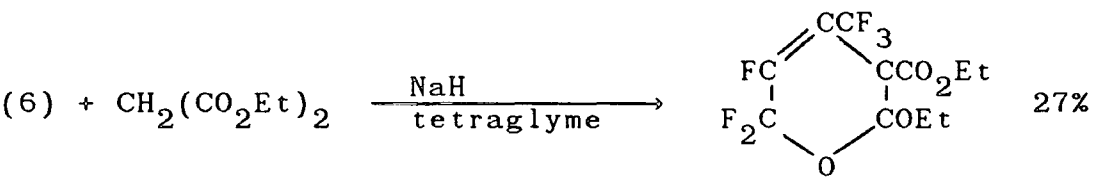
n=3,4 12-31%











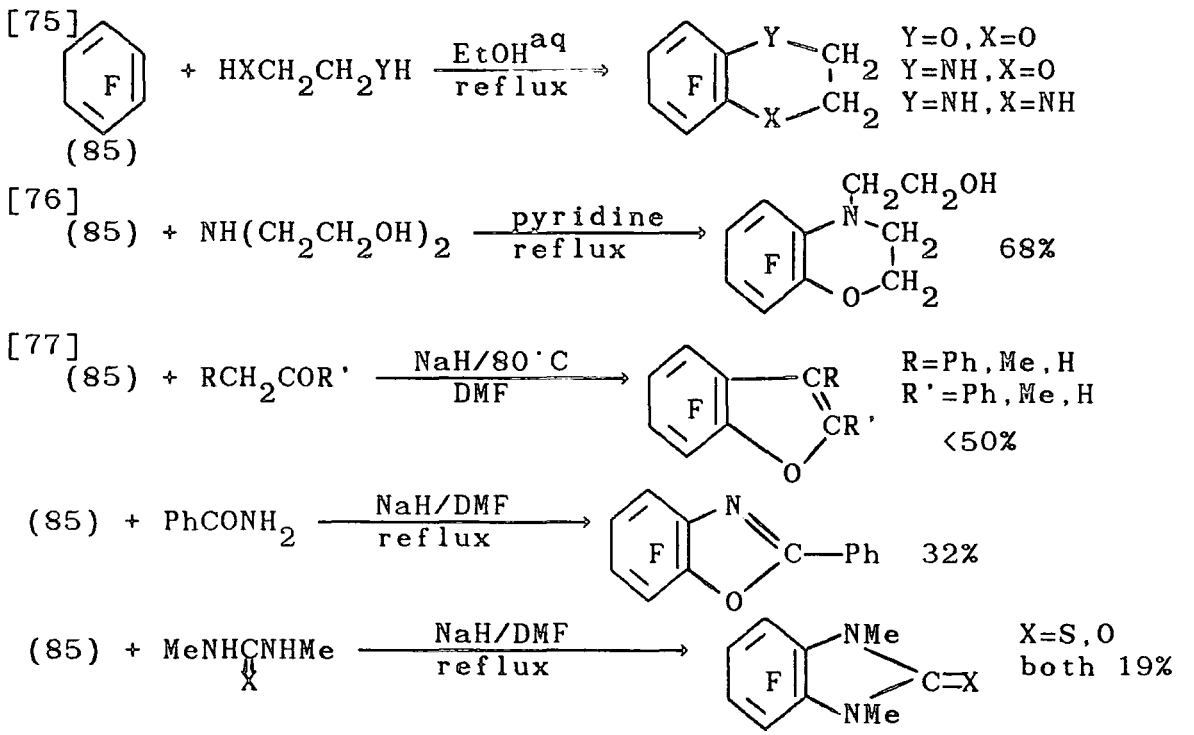
1.C.c Other fluorinated electrophiles

i) Fluoroaromatics Polyfluoroaromatic compounds possess labile C–F units which may be displaced by nucleophiles in a similar manner to substitutions for vinyl fluorine. Clearly, bifunctional nucleophiles may make successive Ar-F substitutions at two adjacent positions, to yield cyclic products in a way analogous to some of the olefin reactions described earlier. The preparation and reactions of polyfluorinated -aromatic and -heteroaromatic compounds has been extensively reviewed.[71-74]

For example, hexafluorobenzene (85) has been reported to react with ethyleneglycol, *ortho*-aminophenol, ethylenediamine[75] and others[76] in the presence of a mild base to yield benzoheterocyclic compounds containing oxygen and nitrogen. Ketones have also been used[77,78] as active methylene compounds in the synthesis of benzo-furans and similar reactions with amides and ureas[77] have been reported.

Table 5

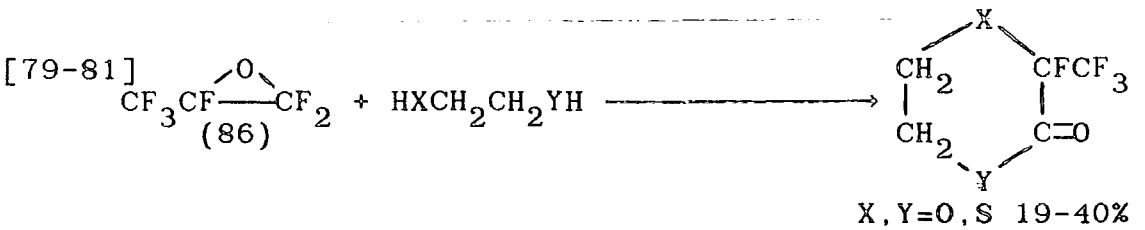
Some ortho-disubstitution reactions of hexafluorobenzene

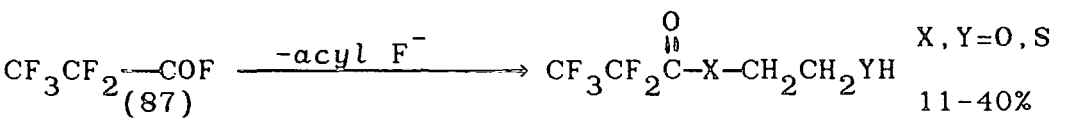


ii) Fluoroepoxides A series of papers has appeared in the literature,[79-81] written by Ishikawa and co-workers on the use of hexafluoropropeneoxide[82] (86) as a fluorinated electrophile in reactions with bifunctional nucleophiles. 1,2-Difunctional benzenes,[81] imidazoles,[79] and 1,2-bifunctional ethanes[80] have all been used. Using the latter

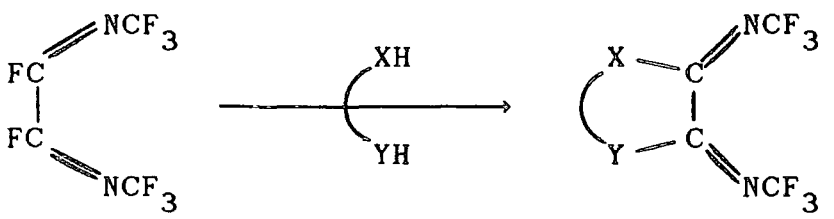
as an example, heterocyclic compounds are formed from reaction of (86) with ethyleneglycol, 2-mercaptoethanol and 1,2-ethanedithiol respectively. Isomerisation of (86) to pentafluoropropionylfluoride (87) under the influence of a strong base results in the formation of side products.

[79-81]





iii) Fluorinated imines Imidoyl fluorides have already been discussed as reactive intermediates in the reactions of bifunctional nucleophiles with fluorinated alkenes. Clearly, therefore, bifunctional imines may react with bifunctional nucleophiles with displacements of the labile fluorines from the N=CF groups to yield heterocyclic compounds. This methodology has received considerable attention from the Bayer Company[39-45] who have studied the reactions of perfluoro-2,5-diaza-2,4-diene (88) with bifunctional nucleophiles.



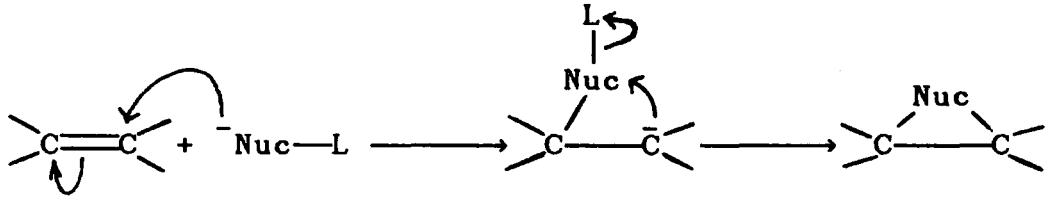
(88)

The resulting trifluoromethyl-substituted heterocycles show exciting biocidal activity.

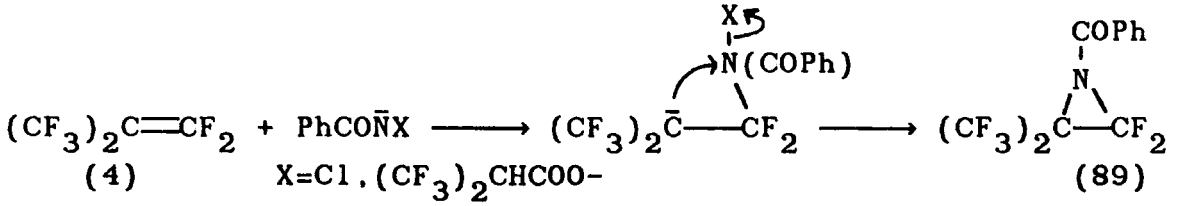
1.D. NUCLEOPHILES CONTAINING LEAVING GROUPS- SYNTHESIS OF FLUORINATED EPOXIDES

1.D.a Introduction

The reaction between fluorinated alkenes and simple nucleophiles has already been discussed (Section 1.B) and shown to occur *via* the intermediacy of carbanionic intermediates. In cases where the original nucleophile contains a substituent of good leaving group ability, this may be displaced by the intermediate carbanion to form a cyclic product.



Such a procedure has been demonstrated for N-chloro and -acetoxy benzamide[83] with perfluoroisobutene (4) where the products are aziridines, *eg.* (89).

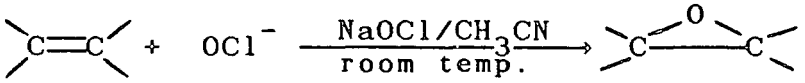


Potassium benzohydroxamate, $Me_3\overset{+}{N}$—NCOPh,[83] N-chloroamides[84] and N-(*para*-nitrobenzenesulphonyloxy)amides[84] also gave aziridine products by a similar process.

In the past, workers in these laboratories have been specifically concerned with reactions of this type, initiated by oxygen nucleophiles which give rise to oxirane products.

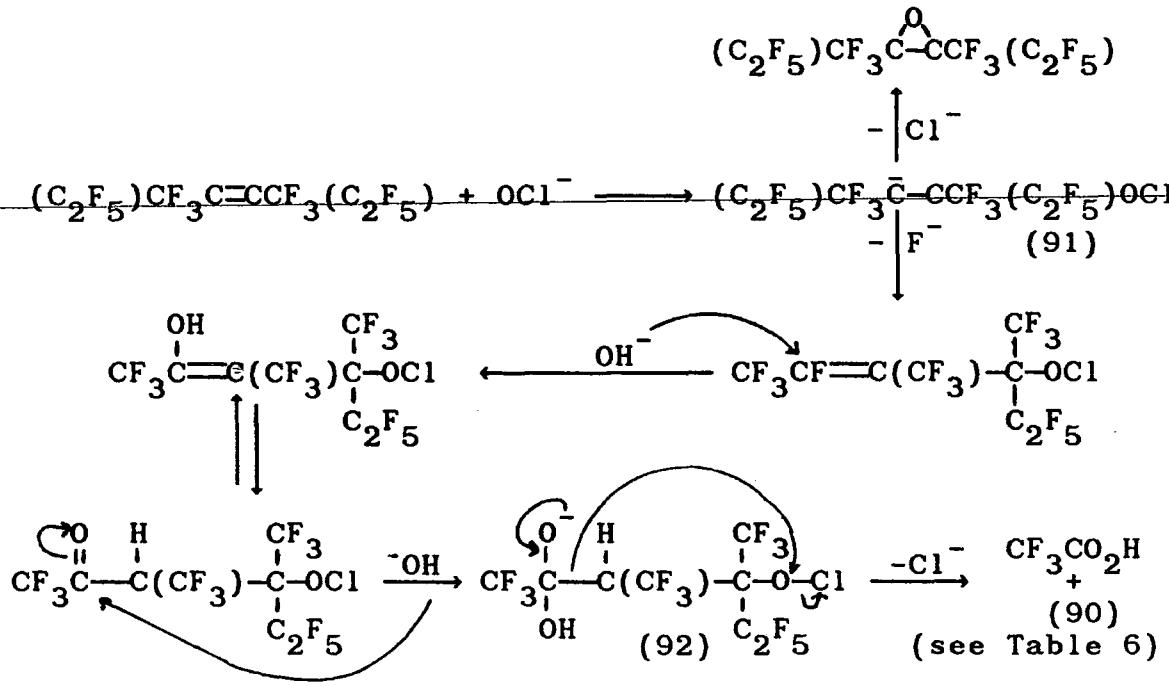
1.D.b Routes to fluorinated epoxides

There exist many routes to fluoro-epoxides[85,86] involving hydrogen peroxide,[87-89] molecular oxygen under severe conditions,[90,91] peracids[92] and alkylperoxides, potassium permanganate,[93] chlorine in the presence of potassium carbonate,[94] and electrochemical methods.[95] None of these processes realised general applicability and were often especially poor for highly substituted fluorinated alkenes. The first nucleophilic epoxidising agents found to be active for a wide range of fluorinated alkenes were hypohalites, discovered in 1979 by Filyakova and co-workers.[96] They reported the use of a aqueous alkali metal hypohalites with a range of co-solvents as epoxidising agents for fluorinated alkenes.



Subsequent work [97-102] extended the number of alkenes and solvent systems available to these reagents. Workers in this laboratory, and elsewhere, have developed a special interest in the chemistry of polyfluorinated alkenes with a high degree of alkyl-substitution and/or with a high degree of strain. They reported[103] the synthesis, using aqueous hypochlorite, of some epoxides derived from tetrafluoroethylene and perfluorocyclobutene oligomers.The novel hydro-derivative (90)(see Table 6), which appears to have originated *via* loss of a pentafluoroethyl group from the target epoxide, in fact occured through initial displacement of allylic fluorine by the hypochlorite reagent (*ie.* in this case fluoride ion elimination from the

intermediate carbanion (91) competed effectively with ring closure)

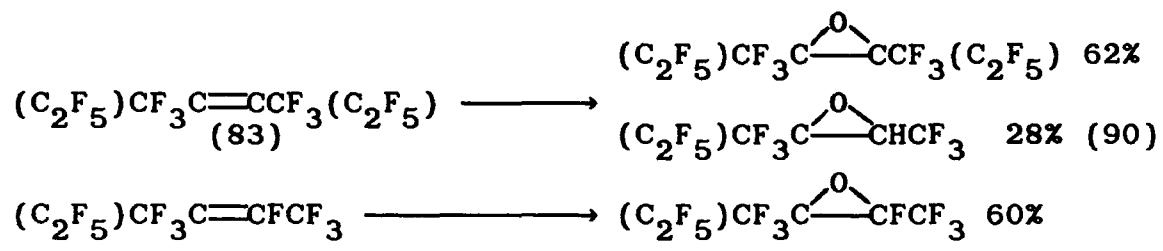


Subsequent hydrolysis of the $=C-F$ site followed by additional attack by OH^- on the keto-form of the enolate leads to oxyanion intermediate (92). Trifluoroacetic acid readily eliminates from (92) to give the observed epoxide (90). Reactions of the epoxide products was also contained but these will be discussed later in the relevant Chapter.

Table 6

Preparation of highly substituted Fluorinated Epoxides

Conditions: $NaOCl, H_2O, CH_3CN$, room temp.



[98] 

X, Y, Z=F or Z, Y=F, X=H, OMe

(19)

[99] $(C_2F_5)CF_3C{=}CFCF_3 \longrightarrow (C_2F_5)CF_3C\overset{O}{\frown}CFCF_3$

$R_fC(CF_3){=}CFCF_3 \longrightarrow R_f(CF_3)C\overset{O}{\frown}CFCF_3$

($R_f=(C_2F_5)_2CF_3C-$, $R_f'=(C_2F_5)CF_3CF-$)

$R_fR_f'C{=}CF_2 \longrightarrow R_fR_f'C\overset{O}{\frown}CF_2$

[100] $(C_2F_5)CF{=}CF(C_2F_5) \longrightarrow (C_2F_5)CF\overset{O}{\frown}CF(C_2F_5)$

[101] $R_fCF{=}CFCF_3 \longrightarrow R_fCF\overset{O}{\frown}CFCF_3$

$R_f=CF_3, C_2F_5, {}^nC_3F_7$

[102] $(CF_3)_2CFCF{=}CFC_3F_7 \longrightarrow (CF_3)_2CFCF\overset{O}{\frown}CFC_3F_7$

$(CF_3)_2C{=}C(C_2F_5)CF(CF_3)_2 \longrightarrow (CF_3)_2C\overset{O}{\frown}C(C_2F_5)CF(CF_3)_2$

$((CF_3)_2CF)_2C{=}CFCF_3 \longrightarrow ((CF_3)_2CF)_2C\overset{O}{\frown}CFCF_3$

1.E FLUOROCARBANIONS

1.E.a Factors affecting carbanion stability

Much of our empirical data derives from kinetic acidity measurements, *ie.* the relative dynamics of the following process:-

$$C{-}H + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C^- + BH^+$$

and this leads to two complications. Firstly, the results relate to the transition state for the process and not directly to the energies of the carbanionic species. More importantly, the degree of internal return, *ie.* the contribution from k_{-1} is difficult to estimate and the necessary corrections are often not made.

i) Fluorine bonded directly to the anionic site

The kinetic acidities of different haloforms[104] has been determined by deuterium exchange studies and has been shown to follow the following series.

For $CHX_3 \longrightarrow \bar{C}X_3$ $\quad X{=}I \approx Br > Cl > F$

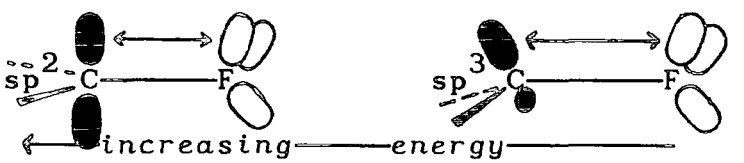
These data have been verified by polarographic measurements[105] and by decarboxylation rates for trihaloacetic acids,[106] and the results are clearly the reverse to that expected from halogen *inductive* effects. The extremely high acidifying influences of the higher halogens may be attributed to *d-orbital participation*,[107] which will be absent for fluorine, but it is not clear why this should

improve from chlorine to iodine.

$\bar{C}\cdots X \longleftrightarrow C{=}\ddot{X}$

X=Br, I, Cl

Other factors which must be considered are *polarisability*, which benefits the heavier atoms and *B-Strain*[104] which is the release of unfavourable repulsions when an sp^3 carbon changes to an essentially sp^2 hybridisation, but this latter effect has been estimated[104] as very small. One final factor which would also be expected to be hybridisation dependent is I_π-*repulsions* (see figure below). Clearly, in a planar (sp^2) arrangement the destabilisation is at a maximum whereas in a trigonal (sp^3) disposition there is some release.



Adolph deduced thermodynamic acidities of substituted nitromethanes[108] through aqueous ionisation constant measurements and discovered that the acidifying influence of directly bonded fluorine increased in the order:-

for $YCNO_2FH \rightleftharpoons Y\bar{C}NO_2F$ $\quad Y=NO_2 < Cl < CONH_2 < CO_2$

—increasing acidity—⟶

Notably, the least acidic compound in the series, $HCF(NO_2)_2$ is the most likely to possess a planar configuration, and yet, the corresponding dinitro compound with H instead of F, $CH_2(NO_2)_2$, is the most acidic in the series:-

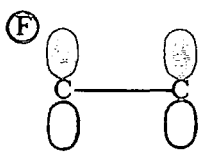
for $YCH_2NO_2 \rightleftharpoons Y\bar{C}HNO_2$ $Y = NO_2 > CONH_2 > CO_2Et > Cl$

decreasing acidity ⟶

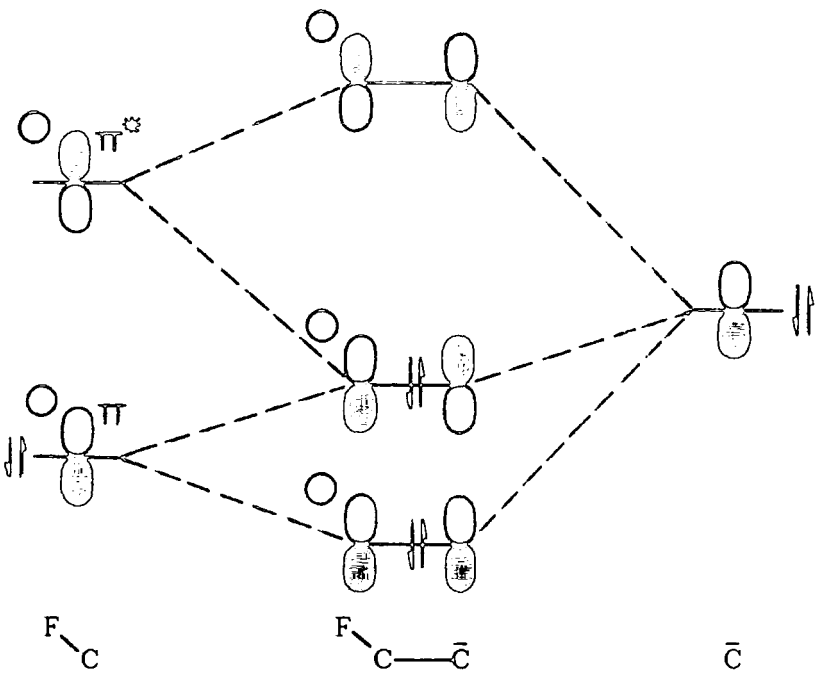
It should be noted that an alternative explanation for the hybridisation dependence of the acidifying influences of directly bonded fluorine has been advanced[109] which is based on the supposed unfavourable bond energy change on moving from sp^3 C—F to sp^2 C—F structures, but the I_π-*effect* has received much more support.

ii) Fluorine or perfluoroalkyl adjacent to the carbanion centre When the substituent in question is adjacent to the carbanionic site the situation is entirely different. *d-Orbital* participation and I_π-*repulsions* are absent, and *polarisibility* and *steric* effects are considerably diminished. The dominant effect would, therefore, be expected to be inductive in nature and, indeed, fluorine is now considerably stabilising with respect to hydrogen,[110] and almost certainly the other halogens. However, in 1950, Roberts and co-workers[111] deduced from physical measurements on trifluoromethyl-substituted aromatic compounds that an inductive mechanism was not sufficient to rationalise their data. They proposed an additional resonance effect, subsequently known as negative hyperconjugation, which quickly found wide and popular acceptance.[112] In valence bond terms this is the participation of forms such as B in the overall stabilisation of anionic molecules possessing an electronegative β-substituent (A).

The equivalent molecular orbital representation involves interaction of the filled p-orbital on the anionic carbon with both the filled π_{C-F} and the vacant π^{*}_{C-F} orbitals of adjacent fluorine.[113,114] If the π^{*}_{C-F} is heavily involved, which would be expected for electronegative elements such as fluorine,[115] the nett effect is considerable stabilisation.



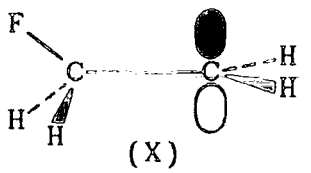
Molecular Orbital diagram for C—CF *system*



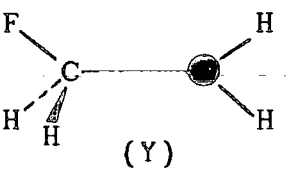
The quantitative energetic consequences of negative hyperconjugation have been readily determined using molecular orbital calculations of increasing reliability.[116-119] In the most common model,[116] the energies of β-substituted ethyl anions may be calculated in two fixed geometrical configurations, (X) and (Y) below; X, in which the C—F bond is ideally situated to participate in a hyperconjugative charge transfer and, Y, in which the relevant orbitals are orthogonal and cannot mix. Other

factors are known to be geometry invariant and, therefore, the energy difference between the two rotamers is an estimate of the absolute contribution made by negative hyperconjugation.

eg.



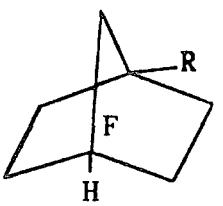
(X)



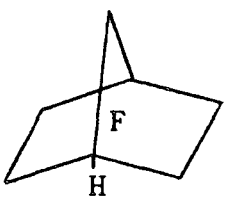
(Y)

The programs also generate optimised structures with the expected manifestations of negative hyperconjugation, namely; i)increased negative charge on fluorine and an extended C—F bond[113,117] and, ii)shorter bond between the two central carbons and greater electron density.

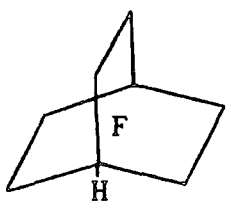
In the past, there have been two facts which have been used to demonstrate that negative hyperconjugation has no significant effect on chemical reactivity. Firstly, mono-hydro perfluorinated bicycloalkanes (93),(94) and (95), synthesised by Tatlow and co-workers[120] were found to be highly acidic[121] despite the fact that the double bond-no bond resonance forms would possess a very unfavourable bridgehead unsaturation.[122]



(93)



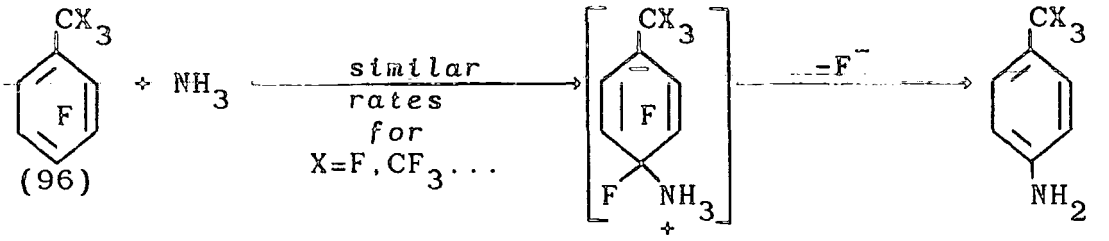
(94)



(95)

Secondly, kinetic measurements performed in Durham[123] on reactions of ammonia with perfluoroalkyl-substituted

fluoroaromatics (96) indicate similar reactivity (for *eg.* X=F and CF_3) and thus, unless hyperconjugative charge transfer to perfluoroalkyl is significant then negative hyperconjugation does not make an appreciable contribution.



Since CF_3H is one of the weakest of all polyfluorinated carbon acids hyperconjugative contributions would seem unlikely, and classical inductive and field effects seem sufficient to explain the data. Nevertheless, Apeliog[117] has performed MO calculations on the $CFH_2\bar{C}H_2$ and $CF_3CH_2\bar{C}H_2$ anions which accurately reflect the similar overall electronic environments of $C(CF_3)_3^-$ and CF_3^- indicated by the kinetic measurements, but which arise, in his calculations, from a similar and significant negative hyperconjugation contribution from both CF_3 and F.

At present, it seems that negative hyperconjugation is an effect which is well supported by molecular orbital calculations. However, these are performed on isolated molecules (in the 'gas phase') and solvent, counterion effects *etc.* are neglected. The genuine influence of anionic hyperconjugation on chemical reactivity can only, therefore, be determined by chemical experiments and, to date, much of the empirical observations can be rationalised by invoking other well established phenomena.

1.F GENERATION AND REACTIONS OF FLUOROCARBANIONS

The area encompassed by the title of this section is far too large to be rigorously discussed in a single thesis and, therefore, the discussion is illustrative rather than thorough.

1.F.a Generation of fluorocarbanions

i) Decarboxylation reactions Carboxylic acids and their respective anions readily cleave under the action of heat to give products derived from the respective carbanions. Thus thermally induced decarboxylation of potassium perfluoroalkanoates[124] in the presence of a protic solvent leads efficiently to the mono-hydroperfluoroalkane. This procedure has been employed in the synthesis of deuterium labelled polyfluorocarbons for exchange experiments.[125]

$$eg.\quad CF_3(CF_2)_6COO^-K^+ + (CH_2OD)_2 \longrightarrow CF_3(CF_2)_6D$$

In the absence of a protic solvent, thermolysis leads to fluorinated alkene products,[124] presumably *via* fluoride ion elimination from the relevant carbanion.

$$eg.\quad CF_3(CF_2)_5COO^-Na^+ + (CH_2OH)_2 \xrightarrow[230\text{-}260^\circ C]{\Delta} C_7F_{14}\ 86\%$$

This procedure has been used in the generation of fluorinated dienes from the corresponding perfluoro-diacids.[126]

Workers in these laboratories have utilised decarboxylation procedures in the synthesis of

perfluoroalkyl-aromatic derivatives[127] from iodobenzene and have provided evidence against a radical mechanism.

$$eg.\ CF_3CF_2COO^-Na^+ \xrightarrow[\text{Å, 170°C, DMF}]{Ar\text{-}Br/CuI} Ar\text{-}CF_2CF_3$$

With acids that give rise, on decarboxylation, to particularly stable carbanions, *eg.* $(CF_3)_3CCO_2H$, then loss of CO_2 may even occur spontaneously at room temperature and the free acid is not readily isolated.[128]

ii) <u>Base induced de-protonations</u> Mono-hydroperfluorocarbons are particularly strong C-H acids. Indeed, nonafluoroisobutane is by far the strongest saturated carbon acid so far discovered; its pKa[129] (*ca.* 11) compares favourably with materials with extensive α,β-unsaturation, *eg.* $CH_3(NO_2)$ pKa 11. Consequently, a variety of intermediate fluorocarbanions have been generated by the action of bases on the relevant hydrogen derivatives. The best studied system is $(CF_3)_3CH/Et_3N$ for which, although no concentration of ionic materials can be detected in solution, characteristic reactions of fluorocarbanions are available.[130]

$$(CF_3)_3CH + Et_3N \rightleftharpoons (CF_3)_3\bar{C}\ Et_3\overset{+}{N}H \rightleftharpoons (CF_3)_2C{=}CF_2 + Et_3\overset{+}{N}H\bar{F}$$

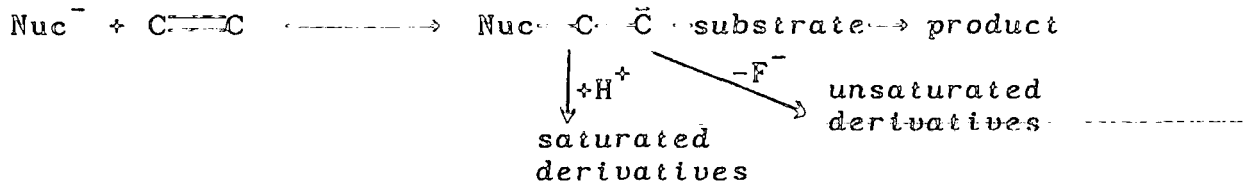
$$\downarrow$$

reactions

iii) <u>Nucleophile with perfluorinated alkene</u>

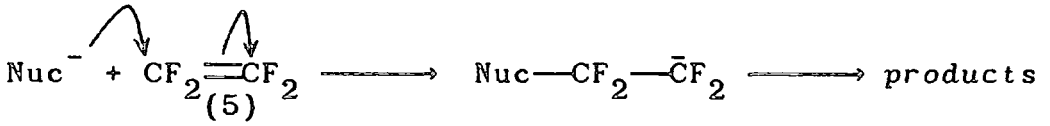
Nucleophiles react readily with fluorinated alkenes to give saturated or unsaturated products *via* fluorocarbanionic

intermediates (see section 1.B.b). This procedure is easily extended to the generation of fluorocarbanions so they may be further reacted with a substrate.



Fluoride ion Sources of fluoride ion exhibit enhanced nucleophilicity when employed in an certain solvents[131] and interact readily with good electrophiles. Alkali metal fluorides are cheap and are best employed in aprotic solvents where complications due to H^+ abstraction may be avoided. It is not surprising, therefore, that addition of fluoride ion to fluorinated alkenes constitutes by far the most convenient and popular method for the generation of fluorocarbanions.

Other nucleophiles Alternative nucleophiles to fluoride ion have been employed as this leads directly to fluorinated molecules with useful functionalities at both ends. Workers from Du-Pont have reported the action of cyanide, azide, alkoxide, mercaptan[132] and other[133] nucleophiles to small fluorinated alkenes, particularly tetrafluoroethylene (5).



Nuc=CN^-, N_3^-, RO^-, RS^-, Cl^-

and the final products are potentially useful

molecules.[134,135] (see Table 6)

1.F.b Reactions of fluorocarbanions

The majority of fluorocarbanions do not have a significant lifetime and, often, the equilibrium for their production lies towards their precursors, so they must be generated in the presence of a substrate. This is not the case, however, for the highly reactive alkenes perfluoroisobutene and perfluoro-2-methylpent-2-ene which form stable complexes with caesium fluoride.[130,136] These are presumed, but not confirmed, to be solutions essentially containing the respective carbanions and thus these may be generated prior to the addition of the substrate.

i) Combination with an electrophile

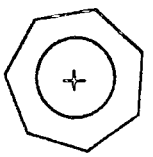
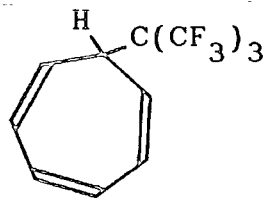
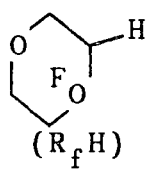
Non fluorinated electrophiles (trapping reactions) In a similar manner to proton capture by a carbanionic intermediate a variety of trapping reactions are available with other simple electrophiles (see Table 7).

$$R_3\bar{C} \xrightarrow{E^+} R_3C{-}E \quad \text{(see Table 7)}$$

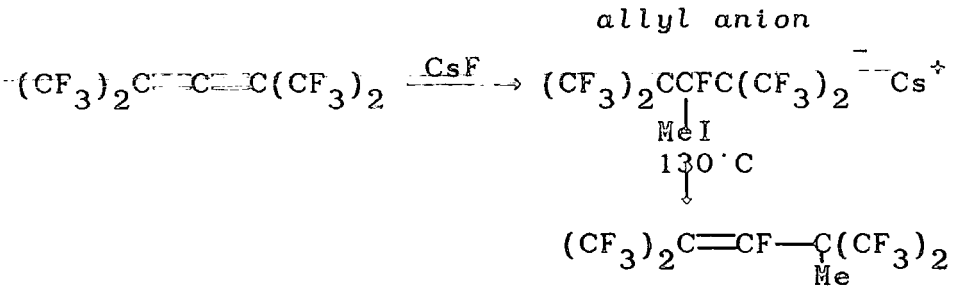
Electrophiles which react in this way include: halogens; tropylium cations; alkyl, benzyl, alkanoyl and allyl halides; carbon dioxide; sulphenyl and silyl chlorides; diazonium salts; simple acids (protonation); and others. Illustrative examples are contained in Table 6, and some reactions of other non-fluorinated electrophiles are discussed in the following text.

Table 7

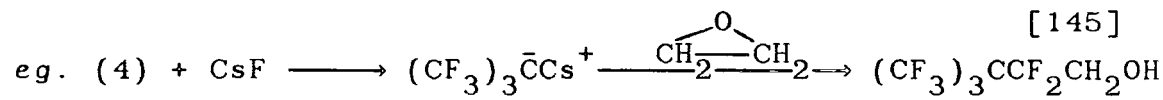
Carbanion trapping reactions with simple electrophiles

Reactants	Electrophile	Product	ref.
$(CF_3)_3CH/Et_3N$	Br_2	$(CF_3)_3CBr$	[130]
"	 Br^-		[138]
$(CF_3)_2C{=}CF_2/CsF$	RX R=Me, C_4H_9, *allyl*, *benzyl*, *etc.*, X=Cl, Br, I	$(CF_3)_3C{-}X$	[139]
 /MeLi	CO_2	R_fCO_2H	
	I_2	R_fI	[140]
	Me_3SiCl	R_fSiMe_3	
$(CF_3)_2C{=}CF_2/KF$	$N{\equiv}\overset{+}{N}{-}Ph$	$(CF_3)_3C{-}N{=}N{-}Ph$	[141]
"	Ar-COF	$(CF_3)_3C{-}COAr$	[142]
$CF_2{=}CFX/KY$ X=F, Cl, $COCF_3$, OC_3F_7 Y=CN^-, N_3^-, PhO^-, $R\bar{S}$ *etc.*	CO_2	$YCF_2{-}CFXCO_2^-\ K^+$	[133]
"	R_fCO_2R	$YCF_2CFXC(=O)O^-{-}R_f$	[132]
$(CF_3)_2C{=}CF(C_2F_5)$	Br_2	$(CF_3)_2C(Br)CF_2CF_2CF_3$	
	$PhCH_2Br$	$(CF_3)_2C(CH_2Ph)CF_2CF_2CF_3$	
	HCl	$(CF_3)_2CHCF_2CF_2CF_3$	[136]
$CF_2{=}CCF_3R/CsF$ R=F, CF_3	R'SCl R'=Me, Et, Ph *etc.*	$R'C(CF_3)_2R$	[143]

In most cases the reactions are carried out under particularly mild conditions, but in cases where the carbanions are very stable, the reaction temperatures are often raised.[137]



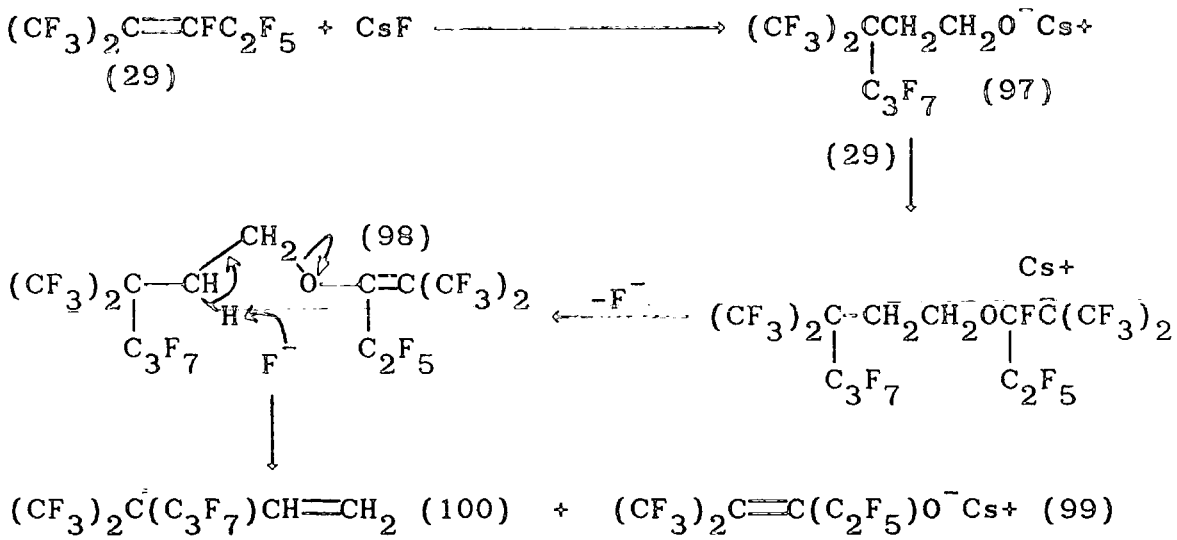
Epoxides Hydrocarban oxiranes are particularly reactive towards nucleophiles and readily react with carbanions derived from perfluoroisobutene (4)[144,145] and perfluoro-2-methyl-2-pentene (29).[146] In some cases, the expected ring opening occurs to give primary alcohol products.



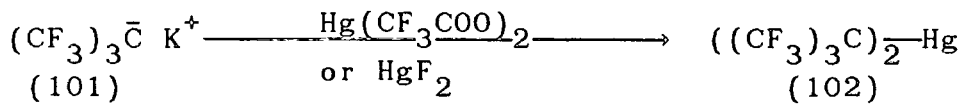
[145]

However, under slightly different conditions (for (29)), alternative products are formed by a mechanism involving further reaction of the oxyanion (97). The key intermediate is the vinyl ether (98) which, under the action of a base, may divide to yield the observed enolate anion (99) and the alkene (100).

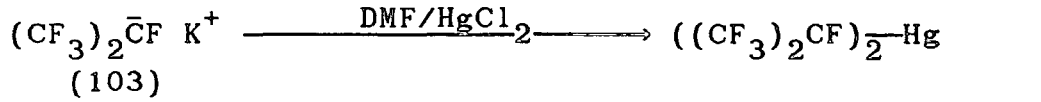
eg. for hexafluoropropene dimer (29).



Mercury salts Mercurations of perfluorocarbanions are easily effected by reaction of the carbanion with a mercury salt containing a good leaving group.[147,148] Thus, contact of the perfluoro^{t}butyl anion (101) with mercury(II)trifluoroacetate or mercury(II)fluoride leads to the bis-perfluoroalkylmercurial (102).



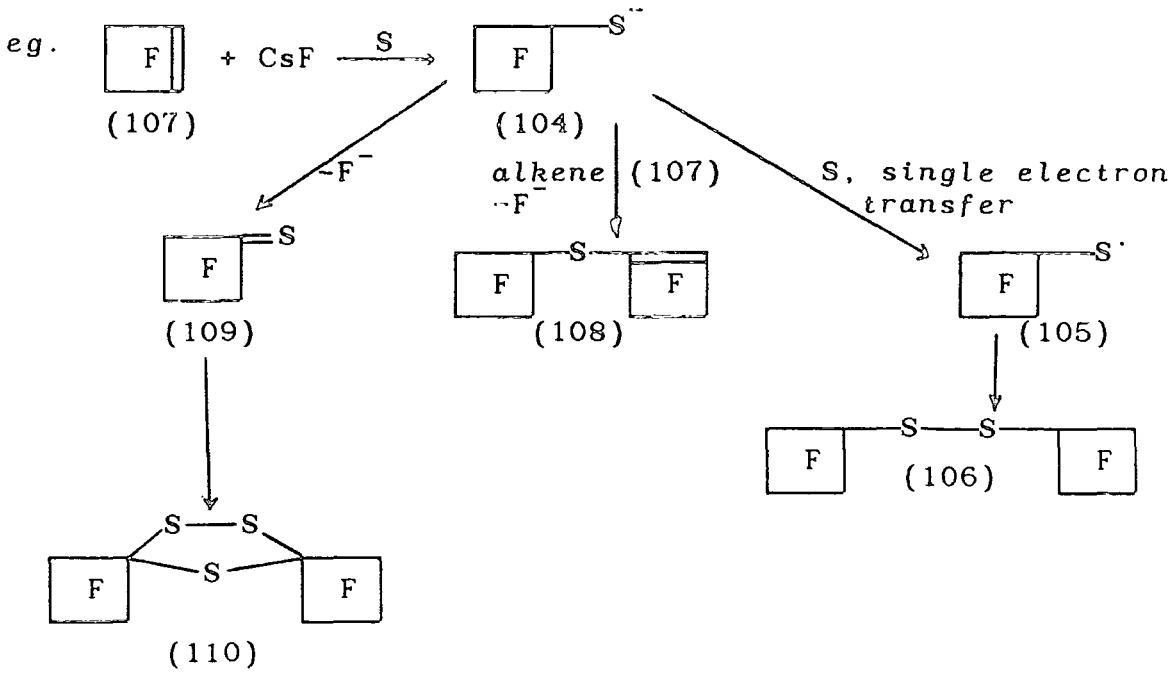
Use of the metal dichloride gives only the mono-perfluoroalkylmercurial, $(CF_3)_3C-Hg-Cl$, but with the perfluoroisopropyl anion (103), full substitution occurs.



Further evidence of the enhanced nucleophilicity of the less stable anion (103) is provided by its ability to substitute for the perfluoro^{t}butyl anion (101) in the organo-mercurials

(*eg.* (102)) themselves.[147]

<u>Sulphur</u> The trapping reactions of perfluorocarbanions with sulphur are complicated by further reaction of the perfluoroalkylmercaptide anion ((104), for perfluoro-cyclobutene).[149]



One electron transfer to sulphur affords the sulphur radical (105) and leads to the coupled compound (106).
Alternatively, since sulphur anions are highly nucleophilic, further reaction of (104) with the precursor alkene (107) to give (108) competes with elimination of fluoride ion to generate the thioketone (109). Interaction of (109) with sulphur afford the novel trithiane (110).

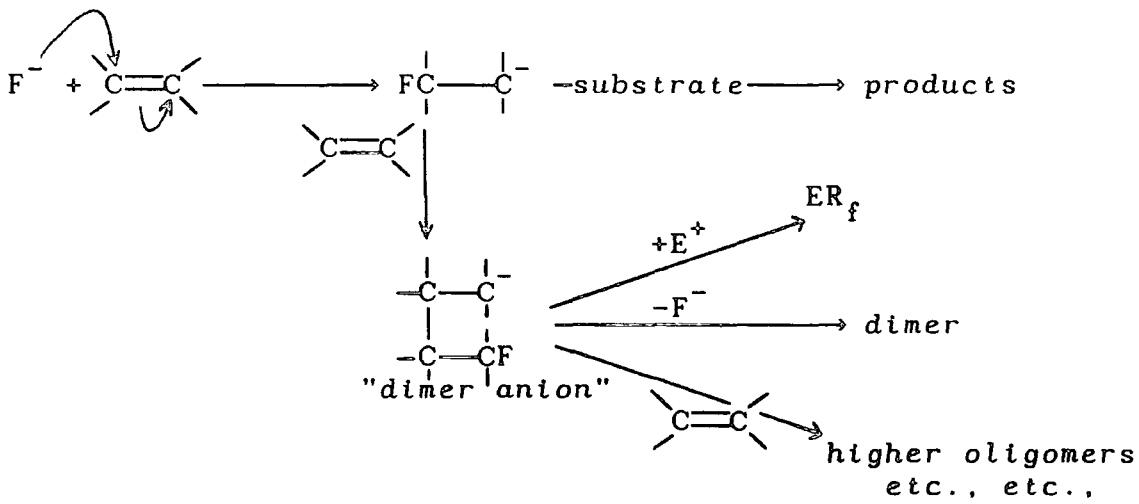
<u>*Michael reactions*</u> Nonafluoroisobutene (112) participates *via* its carbanion (101), in base induced nucleophilic additions to activated multiple bonds.[150,151]

eg. $(CF_3)_3CH + Et_3N + CH_2{=}CHX \longrightarrow (CF_3)_3CCH_2{-}CH_2X$
(112) (113) X=CN, CHO [150]

The adducts have been converted into a series of perfluoroalkyl-substituted organic compounds through the functionalised terminus[152] (*ie.* group X in (113)).

Unsaturated perfluorinated electrophiles

Oligomerisation Reactions In certain cases, the carbanion formed by the addition of fluoride ion reacts readily with its own precursor alkene as an electrophile and the new anion thus formed is capable of further reaction, or termination by elimination of fluoride ion. In this way, fluoride induced processes can lead to the generation of oligomeric materials, and these frequently compete against the intended reactions of the fluorocarbanion.

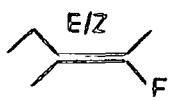
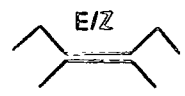
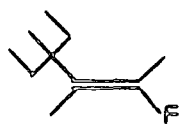
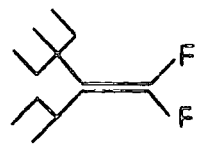
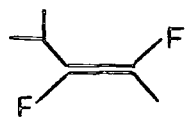
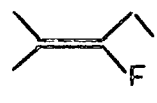
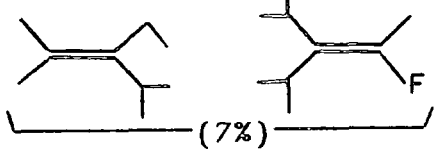
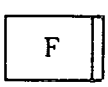
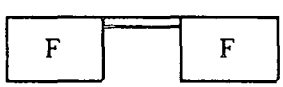
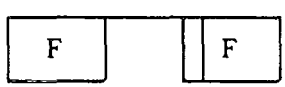
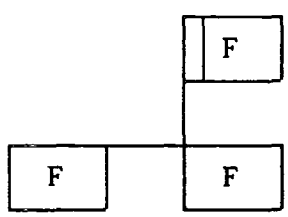
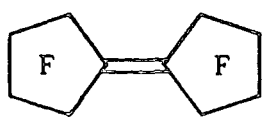


However, the oligomerisation reactions are, themselves, of immense synthetic importance as they allow easy preparation of relatively complex, branched, fluorocarbon olefins from the cheap simpler alkenes. Oligomerisation reactions of

tetrafluoroethylene induced by caesium fluoride;[153] of hexafluoropropene induced by fluoride ion[154] and in the presence of crown ethers,[155] or induced by amines;[156] of fluorinated dienes[157] and of cyclic fluorinated alkenes[158,159] are amongst the wealth of literature available for this type of process. The range of oligomers and their structures are governed by many factors including the nature of the fluoride ion source or nucleophile employed, the configuration of the possible products, solvent and steric effects. Interestingly, for the cyclic fluorinated alkenes the structure of the relevant dimer is determined by conformational interactions[158] except for perfluorocyclobutene where angle strain also becomes important.

Table 8

Products from some typical oligomerisation reactions of simple fluorinated alkenes

Alkene	Conditions	Oligomers	ref
$CF_2{=}CF_2$ (5)	CsF/diglyme 100°C/20psi	trimer(1%)  tetramer(10%)  pentamer(54%)  hexamer(35%) 	[153]
$CF_3CF{=}CF_2$ (1)	KF/CH_3CN room temp.	dimer1(86%)  dimer2(6%) 	[155]
(1)	KF/18-C-6 CH_3CN	dimer2(89%)  trimer1 trimer2 (7%)	
 (105)	CsF/DMF/Ni tube	dimer1(10%)  dimer2(10%)  [160]	
		 trimer(60%)	
	CsF/sulpholan 125°C	 dimer (85%) [159]	

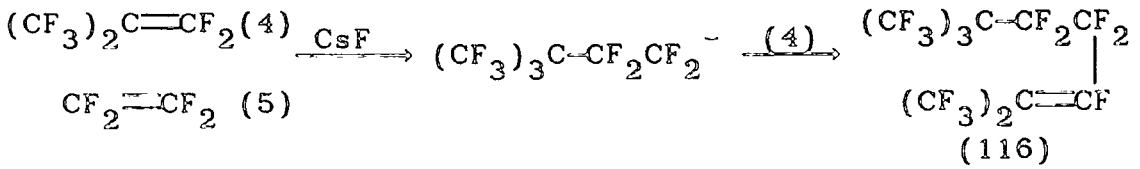
Co-oligomerisation reactions When two different alkenes are introduced to a source of fluoride ion, or an alkene is contacted with a carbanion derived from another, then co-oligomerisation reactions, in addition to the normal oligomerisation reactions are likely. Under conditions of kinetic control the more reactive alkene should act as the addend and the less reactive alkene should act as receptor. In this manner, relative reactivities of fluorinated electrophiles may, in principle, be determined.[161-163] Therefore, the condensation of perfluoroisobutene (4) and hexafluoropropene (1) initiated by fluoride ion produces a co-dimer (114) *via* attack on the hexafluoropropene double bond by the perfluoro^{t}butyl anion (101).[162]

$$\underset{(4)}{(CF_3)_2C{=}CF_2} + \underset{(1)}{CF_3CFCF_2} \xrightarrow{KF} \underset{(101)}{(CF_3)_3\bar{C}Cs^+} \longrightarrow \underset{(114)}{(CF_3)_3CCF{=}CFCF_3}$$

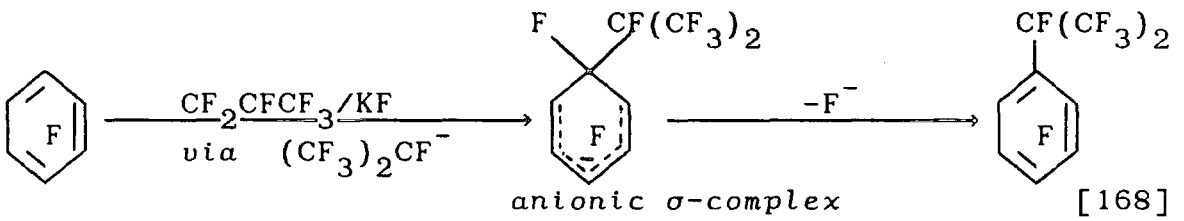
Similarly, carbonyl fluoride may be shown to be a more efficient acceptor of fluoride ion than all of the fluorinated alkenes, including perfluoroisobutene.[164] However, care must be taken in interpreting results of this type as, even under relatively mild conditions, anomalous results can obtain.[165,166]

The reaction of perfluoroisobutene (4) with tetrafluoroethylene (5) follows an unexpected course as the intermediate carbanion (115), formed as a result of the 'normal' attack of the perfluoro^{t}butyl anion (101) on tetrafluoroethylene (5) is sufficiently reactive to effect further reaction with another molecule of (4). Hence, the

major product is the alkene (116).[167]

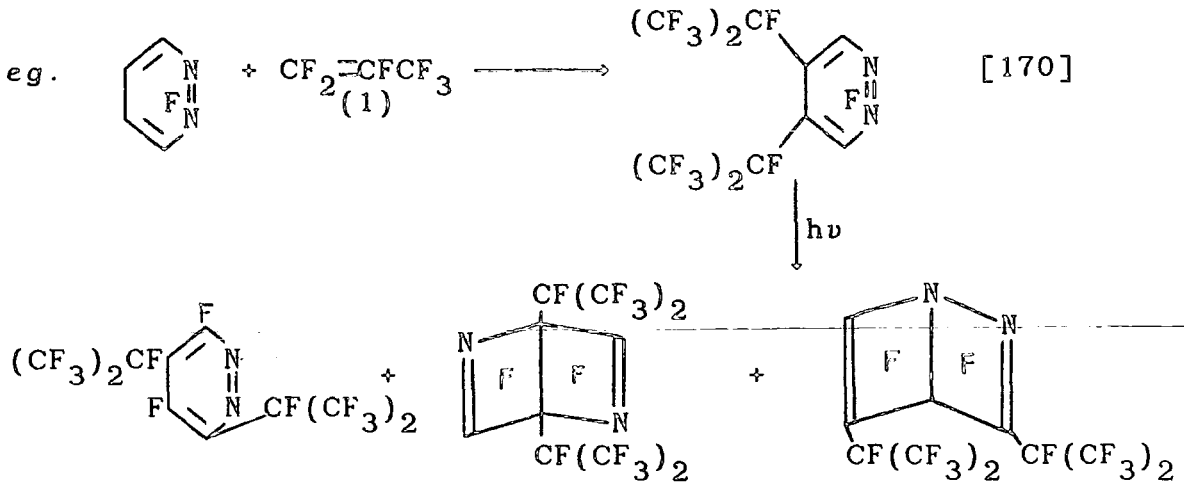


Alkylation of fluoroaromatic compounds Negative Friedel Crafts reactions A synthetically useful procedure has been developed by which highly fluorinated aromatic compounds are reacted with fluorocarbanions to give relevant perfluoroalkylated aromatic derivatives. The reactions are very reminiscent of electrophilic aromatic substitution processes by carbocations (or equivalent) and, hence, they are known as "negative Friedel Crafts reactions".



[168]

Polysubstituted derivatives are also available by, *eg.* using higher pressures *etc.*, and they exhibit extremely interesting behaviour, in that, under photolysis conditions relatively long-lived valence isomers[169] of the aromatic compound are formed.

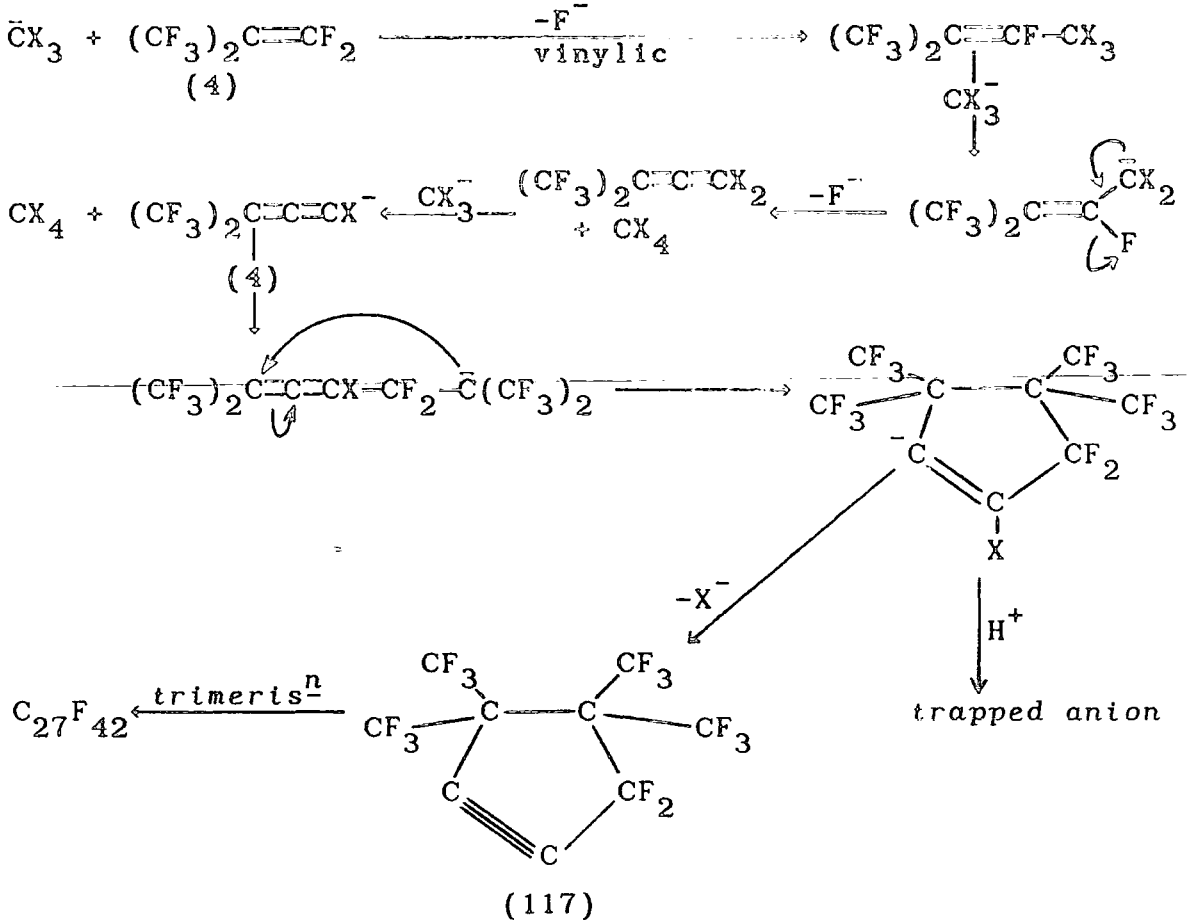


iii) Action as a base

Although monohydrofluorocarbons are very strong carbon acids, their respective conjugate bases, the carbanions, constitute fairly strong bases for initiating alternative organic reactions. It is fairly surprising, therefore, that such a procedure has not been well utilised in the vast area of organic reactions requiring the presence of a strong organic base.

Haloforms In view of the known ability of the perfluoro^{t}butyl anion (101) to substitute $(CF_3)_3C-$ for halogen,[171] Dyatkin and co-workers attempted[172] similar reactions with a number of geminal polyhalogens, such as $PhCHCl_2$, $PhCCl_3$, Ph_2CCl_2, CCl_4 and $CHCl_3$. Only chloroform was found to react and, most unusually, induced the formation of a perfluorocarbon of atomic constitution $C_{27}F_{42}$. The authors proposed a mechanism which involves initial deprotonation of the substrate haloform.

$$(CF_3)_3C^-(101) + CHX_3 \xrightarrow[X=I,Br,Cl]{} (CF_3)_3CH + \bar{C}X_3$$



(117)

Subsequent participation of two molecules of the alkene (4) leads eventually to the acetylenic intermediate (117) where, trimerisation affords the $C_{27}F_{42}$ derivative. Although highly complex, none of the steps are without precedent and several of the key intermediates, or simple derivatives of them, are observed.

Acetonitrile This polar solvent is one of the most common in use for fluoride ion reactions and yet, in 1982, Postovoi *et al*[173] reported that, in the presence of the perfluoro^{t}butyl anion (101) the molecule underwent deprotonation to leave the acetonitrile carbanion (118). Products then derived from attack of this species on perfluoroisobutene (4), the precursor olefin.

$$(CF_3)_3\bar{C} \xrightarrow[(101)]{CH_3CN} (CF_3)_3CH + \ddot{C}H_2CN \xrightarrow[(118)]{(4)} (CF_3)_2C{=}CFCH_2CN$$

$$(CF_3)_2C{=}CFCH_2CN \xrightarrow[(101)]{-(CF_3)_3CH} (CF_3)_2C{=}CF\ddot{C}HCN$$

$$(CF_3)_2C{=}CF\ddot{C}HCN \xrightarrow[-(CF_3)_3CH]{(101)} ((CF_3)_2C{=}CF)_2\bar{C}{-}CN\ Cs^+$$

$$((CF_3)_2C{=}CF)_2\bar{C}{-}CN\ Cs^+ \longrightarrow (CF_3)_2C{=}CF{-}C(CN){-}CFCH(CF_3)_2$$

The result encourages caution in choice of solvent for fluorocarbanion reactions, which at the present time are frequently operated in solvents such as CH_3CN, sulpholan and DMF.

iv) <u>De-halogenations</u> An unusual type of reaction which has been reported[174-176] is the removal of an electropositive halogen atom, usually bromine, by the perfluoro^{t}butyl anion (101). With dibromomethane derivatives containing electronegative substituents the following reaction occurred:-

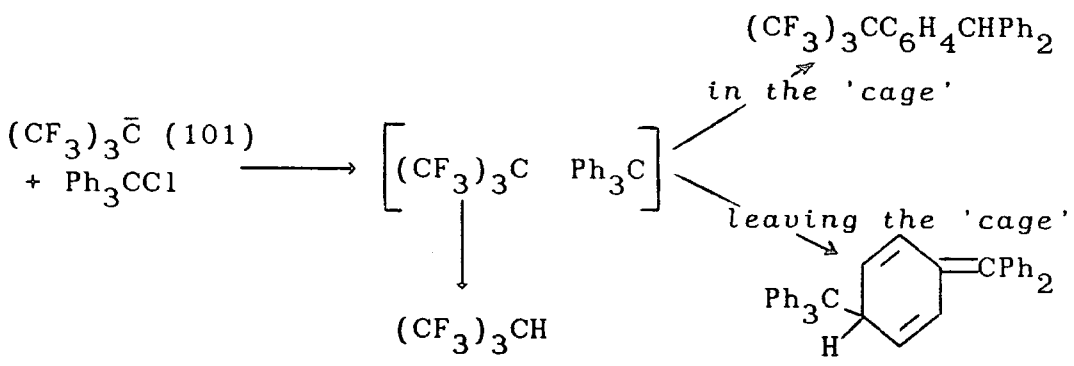
$$(CF_3)_3\bar{C} + Br_2CR_2 \longrightarrow (CF_3)_3C{-}Br + BrCR_2$$
(101) R=CF_3, CN, CO_2Et (4)

$$(CF_3)_2C{=}CFCR_2 \xleftarrow[-(CF_3)_3C{-}Br]{(101)} (CF_3)_2C{=}CCR_2Br$$
$\bar{C}s^+$

Vicinal dihalopolyfluoroalkanes, *ie.* $BrCF_2CFBrCF_3$, effectively lose[175] Br_2 under the influence of the perfluoro^{t}butyl anion (101), to form hexafluoropropene which subsequently co-dimerises with perfluoroisobutene.

v) <u>One electron transfer reactions</u>

Unfortunately, an understanding of the chemistry of organic free radicals has only just begun to take form[177] and, therefore, a "blind spot" exists in the minds of much of the chemical community. Hence, a number of processes previously ascribed to simple 2-electron mechanisms are frequently shown to be connected, at least in part, with one electron transfer. Reactions of fluorocarbanions which have been attributed to one electron transfer include those with diazonium salts, sulphur,[147,149] tetrafluorohydrazine[178] and others.[130] An unambiguous example is provided by the reaction of the perfluoro^{t}butyl anion (101) with triarylmethylhalides, in which e.s.r. evidence is presented.[171]



CHAPTER TWO

FLUORINATED EPOXIDES

CHAPTER TWO

FLUORINATED EPOXIDES

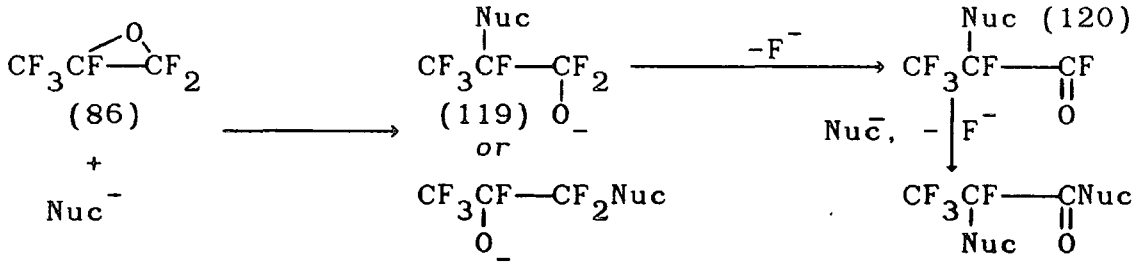
2.A INTRODUCTION

2.A.a Reactions of simple fluorinated epoxides[82,85]

The smaller epoxides are, like their hydrocarbon analogues, readily attacked by nucleophiles. Almost exclusively, the nucleophiles approach the most substituted site which seems unusual as this is the most hindered.[82,87] However, the resulting oxyanion, *eg* (119), would probably be favoured in terms of the relevant C=F bond energies, which follow the order:-

$$CF_3 > CF_2 > CF$$
$$\longrightarrow decreasing\text{-}C\text{-}F\text{-}bond\text{-}strength \longrightarrow$$

Thus, $CF_2\text{–}\bar{O}$ will be more stable than the alternative $CF_3CF\text{–}\bar{O}$ configuration.[103]



Commonly, the oxyanions lose fluoride ion to produce acid fluoride, *eg*. (120), or ketone derivatives. These are themselves strong electrophiles and, therefore, disubstitution becomes a possibility (see section 1.C.c.ii for bifunctional nucleophiles). With fluoride ion as the

nucleophile the reaction product is likely to be a carbonyl isomer of the starting material. Such rearrangements are common for hexafluoropropeneoxide (86) with fluoride ion[179] and other reagents.[180] However, the fluoride ion processes which have received the most attention are polymerisations[181,182] and oligomerisations,[183] in which intermediate oxyanions (*eg.* (119)) participate in a sequence of nucleophilic reactions with the original epoxide.

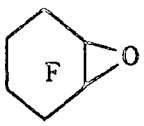
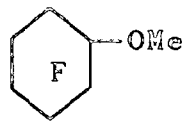
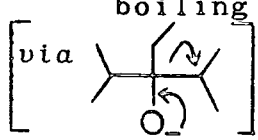
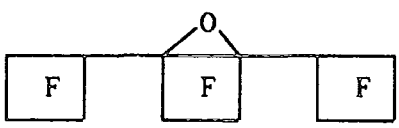
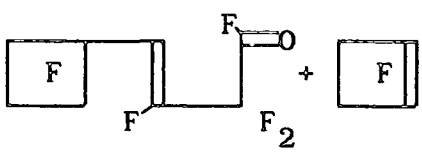
Reactions with electrophiles are notably more difficult to initiate and are often only attainable with powerful electrophiles such as antimony pentafluoride.[184,185]

2.A.b Reactions of perfluoroalkyl substituted epoxides

When compared with the wealth of literature available for reactions of hexafluoropropeneoxide (86)[82] there is relatively little information available on the chemistry of fluoro-epoxides derived from highly substituted internal alkenes. Some examples are shown below.(Table 9) This concentrates on fluoride ion induced reactions of perfluoroalkyl-substituted epoxides and several facts are clear. Firstly, the orientation and mode of nucleophilic attack is the same as previously described *ie.* attack occuring at the carbon of the epoxide ring bearing the least number of fluorine substituents. However, with molecules such as (121)(table 9) with, for example, the structure $R_fCF\overset{O}{\frown}CFR_f'$, where the only difference in environment between the two carbons are inequivalent R_f-substituents, steric effects dominate minor electronic effects, and attack

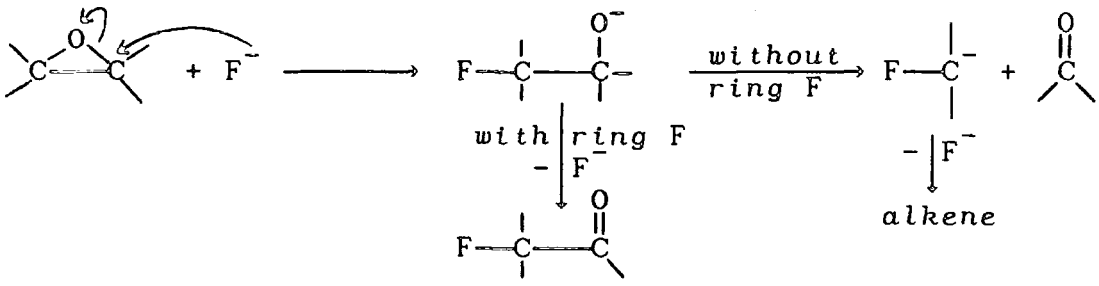
Table 9

Some reactions of perfluoroalkyl-substituted epoxides

Epoxide	Conditions	Products	Ref.
 (122)	i)KF/CH_3CN/55°C ii)MeI		[98]
$(CF_3)_2CF-CF(O)CFCF_3$ (121)	CsF/Tetraglyme	$CF_3CF_2COCF(CF_3)_2$	[185]
$(CF_3)_2C(O)CFC_2F_5$ (124)	CsF/tetraglyme Δ	$CF_3CF_2COCF(CF_3)_2$	[185]
$(CF_3)_2CF-CF(O)CCF_3C_3F_7$	CsF/diglyme 100°C	$(CF_3)_2CFCOF$ + $CF_3CF{=}CFCF_3$	[186]
$(CF_3)_2C(O)C(C_2F_5)CF(CF_3)_2$ (125)	CsF/diglyme boiling 	$(CF_3)_2CFC(=O)C_2F_5$ + $(CF_3)_2C{=}CFC_2F_5$	[102]
$CF_3CF(O)CFCF_3$ (123)	CsF/20°C/solvent	$CF_3CF_2COCF_3$	[101]
C_2F_5 O C_2F_5 C—C E/Z CF_3 CF_3 (126)	CsF/diglyme BuLi/room temp. CsF/200°C	no reaction no reaction $CF_3CF_2C(=O)CF_3$ + $CF_3CF{=}CFCF_3$	[103]
	CsF/200°C		[103]

occurs at the least hindered end of the epoxide.

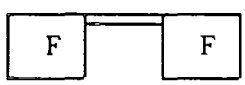
Secondly, increasing perfluoroalkyl substitution confers stability to nucleophilic attack ie. epoxides (122) and (123), with two ring fluorine atoms, react at 50°C with KF and 20°C with CsF, whereas the more substituted epoxide (124), with only one ring fluorine atom needed far higher temperatures for reaction with caesium fluoride. The most remarkable change is to a completely substituted system, where elimination of a ring fluorine is not available. Here, as demonstrated by (125) and (126), extremely high overall stability to nucleophilic attack is observed and reaction only occurs by cleavage of a carbon-carbon bond.



2.B DISCUSSION

Workers in our laboratories have been interested in the reactions of tetraperfluoroalkylethene epoxides, and it was hoped[187] that novel carbene processes would be observed.

However, the compounds were both highly inert to fluoride ion (see table 9) and extremely resistant to high temperatures. *ie.* (126) was recovered unchanged after heating to 530°C.[103] Clearly, the introduction of further ring strain into the epoxide would be useful but Kirk[188] (these laboratories) was unable to obtain the epoxide of perfluorobicyclobutylidene (127) due to extensive hydrolysis by the aqueous reagent.

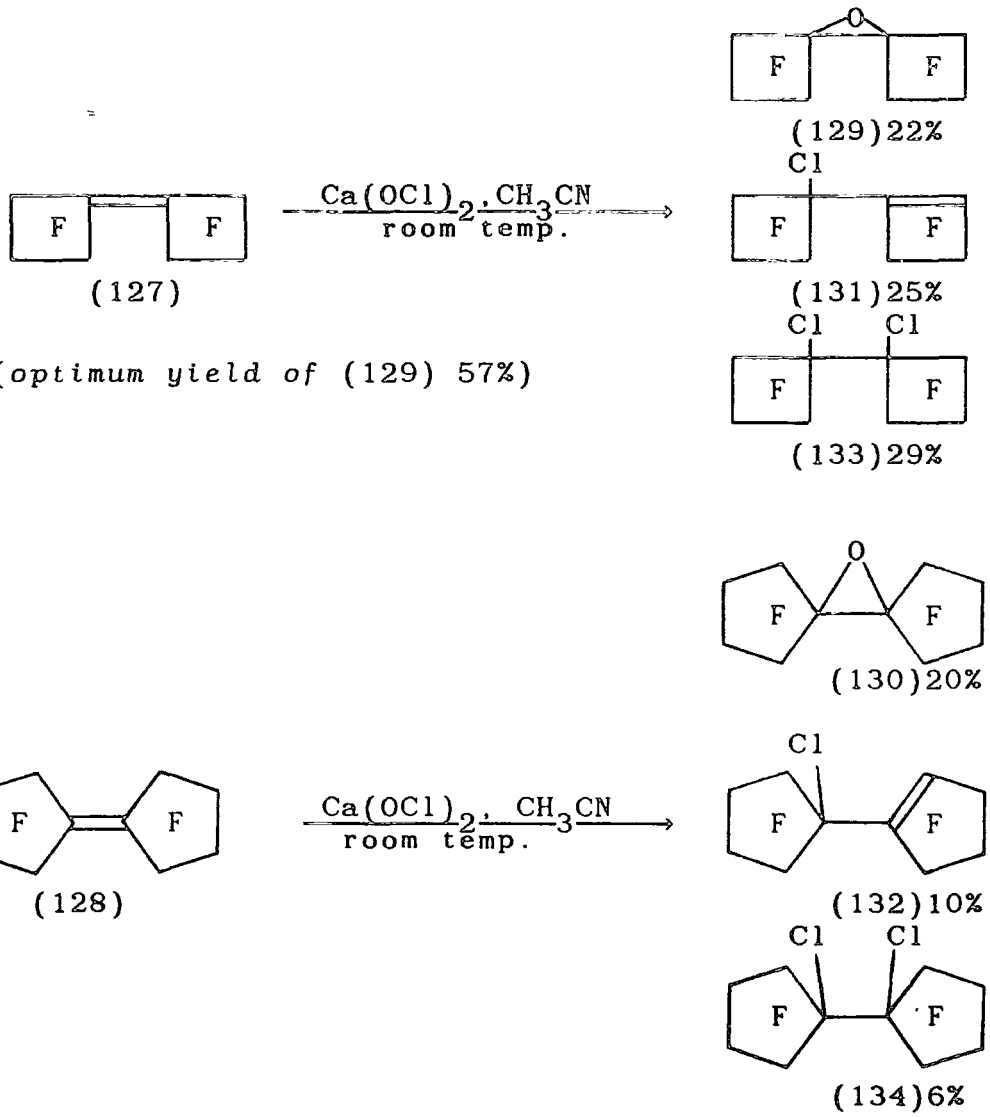
[188]  (127)

$$\xrightarrow{Na(OCl)^{aq},\ CH_3CN,\ room.temp.} X \longrightarrow$$

Other workers from Durham were also interested in epoxidation procedures for very reactive imine systems[189] and they demonstrated the feasability of using anhydrous calcium hypochlorite suspended in acetonitrile by epoxidation of a tetraperfluoroalkylethene (82). This approach was first suggested by Coe.[190]

2.B.a (127) and (128) with calcium hypochlorite

Perfluoro-bicyclobutylidene (127) and -bicylcopentylidene (128), obtained by oligomerisation of the parent cyclic alkenes (see experimental section) reacted with calcium hypochlorite in acetonitrile, to produce the relevant epoxides (129) and (130) along with chlorinated side products (131-134).



(*optimum yield of* (129) 57%)

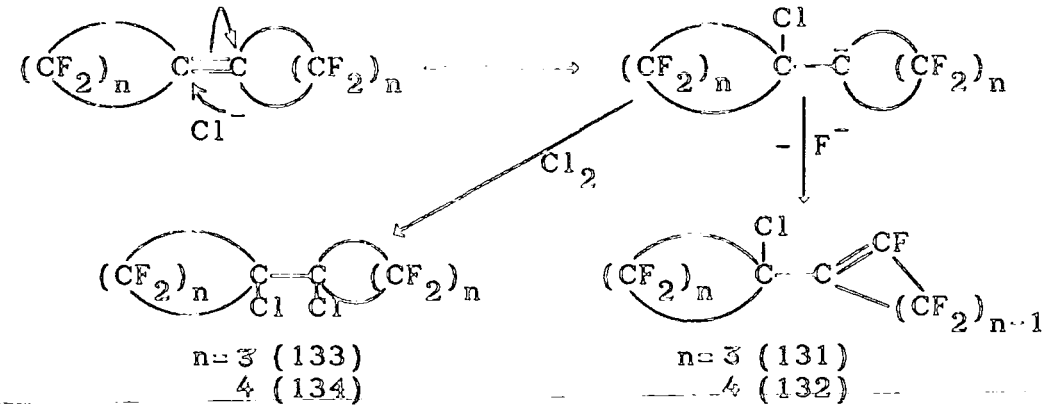
(*optimum yield of* (130) 38%)

The epoxides (129) and (130) were readily identified by the breakdown pattern in their mass spectra, and by their striking ^{19}F n.m.r. spectra. The precursor alkenes (127) and

(128) give two singlets in the CF_2 region whereas their epoxides (129) and (130) do not possess an averaged planar structure, but are forced into a 'bent' shape by the oxygen of the epoxide. Thus, resonances of CF_2 groups close to the ring appear as distinctive AB spin patterns. Similarly, structures of the chloro-compounds (131-134) followed simply from a consideration of their spectral data.

Chlorine containing impurities are not normally found in epoxidations using aqueous hypochlorite reagents, and their presence in this instance is rather curious. Compounds (131) and (132) probably arise from nucleophilic attack by chloride ion on the alkenes (127) and (128) and dichloro-derivatives (133) and (134) appear to result from addition of molecular chlorine across the double bond. Chloride ion is necessarily found in the reaction mixture as it is produced in the epoxidation process and there is precedent for reaction of alkene (127) with lithium chloride.[159]

There appears to be a threshold concentration of reactants (corresponding to *ca.* 0.9 - 1.0 mmol alkene) required before significant by product formation occurs. This presumably corresponds to a critical concentration of chloride ion in the reaction mixture. Notably, dichloro-compounds (133) and (134) are always formed in similar quantities to mono-chloro adducts (see experimental section). A mechanism shown below involving trapping of the common intermediate (135) by free chlorine would, therefore, seem more likely than addition of Cl_2 across the double bond.



2.B.b Reactions of dispiroepoxides (129) and (130)

i) Thermolyses of epoxides (129) and (130)

At the point of acquiring epoxide (129) with its inherent enormous ring strain we were extremely optimistic of discovering novel thermally induced processes. However, (129) withstood thermolyses under static conditions of up to 300°C for prolonged periods.

The hydrocarbon analogue of (129) isomerised smoothly[191] to cyclopentanone derivative (137) at 200°C.

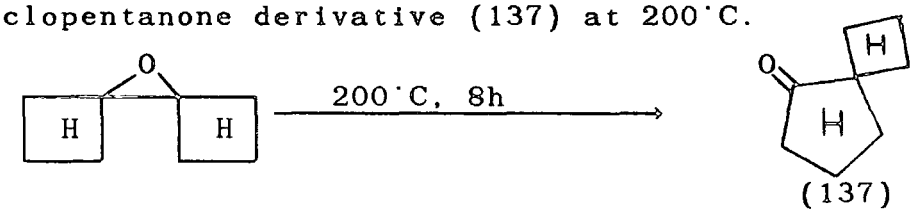
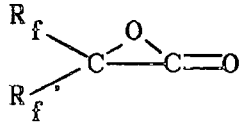


Table 10

Static thermolyses of (129) and (130)

	Time(h)	Temperature(°C)	Recovery(%)
	11	200	100
(129)	2	300	100
	5	300	100
(130)	5	300	100

The quite remarkable high thermal stability exhibited by our strained perfluoroalkyl epoxides (129) and (130) has also been observed for other small ring compounds containing fluorocarbon substituents. The most predominant example is the α-lactone (138),[192] which is the most stable of its class.



(138)

$R_f = C(C_2F_5)_2CF_3$

$R_f' = CF(C_2F_5)CF_3$

The mechanism of the special thermal stabilising influence of perfluoroalkyl groups to small rings is still not entirely clear but, in the course of our work, the effect itself has now been well established.

ii) Caesium fluoride with (129) and (130)

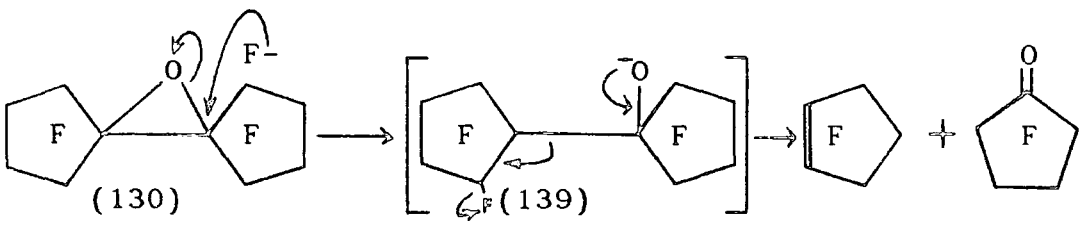
High temperature reactions with a slight excess of active caesium fluoride were attempted in sealed tubes. (see Table 11).

In both cases the threshold temperature for reaction was between 150°C and 200°C, but the more reactive epoxide, (129), afforded little tractable material at the higher temperature. (130) reacted cleanly with CsF at 200°C to give monocyclic products perfluorocyclopentene and perfluorocyclopentanone, and a mechanism for this process is given below.

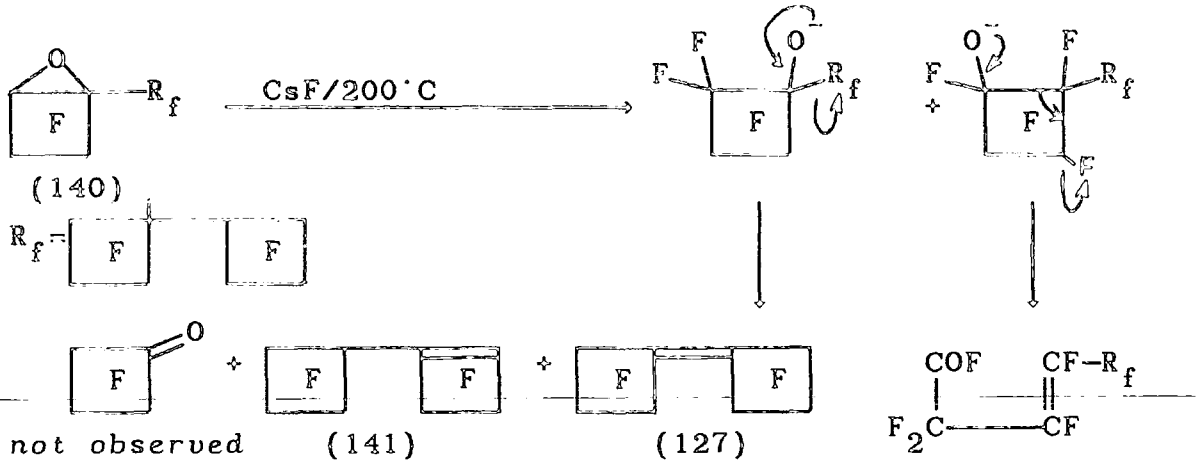
Table 11

High temperature caesium fluoride reactions

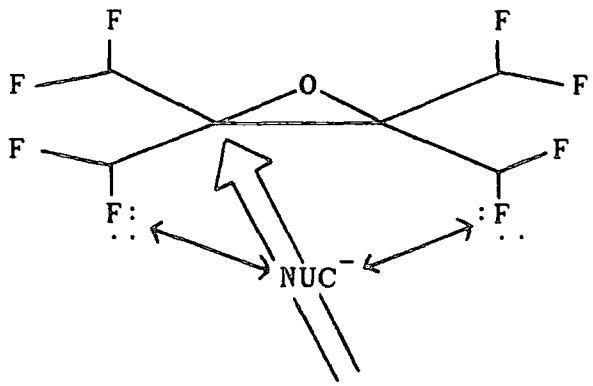
Epoxide	Temperature(°C)	Time(h)	Products or epoxide recovery
(129)	150	16	recovered, 94%
(129)	200	19	recovery, low
			+  , + > 18 other components
(130)	150	16	recovered, 96%
(130)	250	14	multicomponent mixture
(130)	200	16	



Cleavage of the central C—C bond from the intermediate oxyanion (139) to yield a ketone and an olefin occurred in a manner identical to other reported tetraperfluoroalkylethene epoxides.[102,103] It is likely that a similar process was followed for the other epoxide (129) thus giving perfluorocyclobutene and perfluorocyclobutanone. Indeed, the alkene was observed in the product mixture, and a failure to observe perfluorocyclobutanone for a similar process has been reported previously[103] for (140), and attribued to further reaction of the cyclic ketone with fluoride ion.



It is quite remarkable that the very highly strained dispiroepoxides (129) and (130) are approximately as resistant to nucleophilic attack by fluoride ion as acyclic analogue (86)(see Table 9),[103] which also reacted at 200°C. Complete perfluoroalkyl substitution on an epoxide obviously confers substantial resistance to nucleophilic attack and, from our observations, extra ring strain does not significantly influence this stabilisation. This would be consistent with the theory that the kinetic barrier to approach of nucleophiles by the non-bonded electron density on the fluorine atoms, as opposed to any thermodynamic stabilisation of the epoxide, is the dominant effect.[193]



iii) Miscellaneous reactions

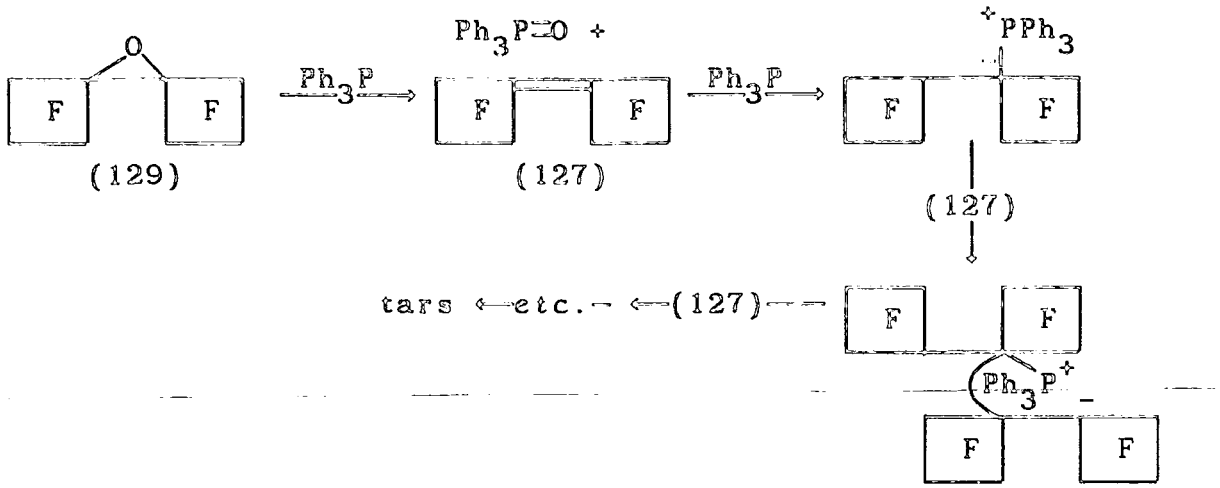
Table 12

Miscellaneous reactions of (129)

Conditions	Products or recovery epoxide
$(Me_2N)_3SMe_3SiF_2$ (142) CH_3CN/room temp.	recovery 76%
Hg/hν/room temp.	recovery 100%
Ph_3P, up to 100°C	recovery 44% + tar

Compound (129) was recovered unchanged after contact with a soluble fluoride source (142) and after prolonged irradiation with a high pressure u.v. source in the presence of mercury.

An unusual result is the rather facile reaction of triphenyl phosphine with (129). As soon as the reaction mixture reached the melting point of the phosphine discolouration was evident and, after *ca.* one hour, significant tarring was observed. Presumably, the phosphine de-oxygenates the epoxide to form triphenylphosphine oxide (the driving force being the formation of the strong P=O bond), and the parent alkene (127). Reactivity of fluorinated alkenes towards phosphines is well established;[194] phosphorus ylids[195] are often formed which may then react further to produce oligomers (and tars). Indeed, a controlled reaction of (127) and triphenylphosphine afforded a brown intractable tar on warming to the melting point of the solid.



It is noteworthy that triphenylphosphine, which is expected to react through oxygen of the epoxide, has a much lower threshold temperature than nucleophiles, such as fluoride ion, which attack the carbon atoms. The carbon atoms receive the maximum protection from the perfluoroalkyl substituents whereas the oxygen atom is somewhat more isolated.

2.B.c Attemted epoxidations of novel fluorinated alkenes and dienes

i) Hypochlorite with (143) and (144)

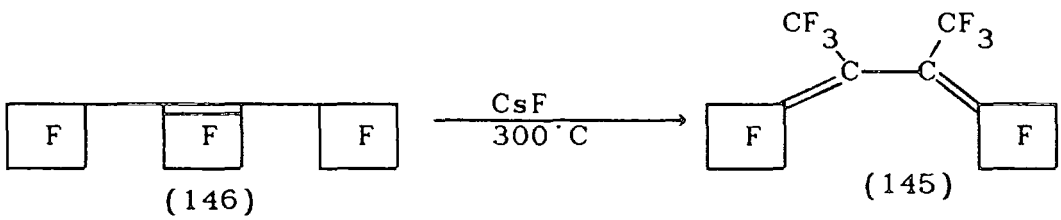
Although aqueous hypochlorite epoxidising agents have been well established for olefins with fluorine and fluorocarbon substituents, we are unaware of any studies on tolerance to other groups such as hydrogen. We have a current interest in the chemistry of alkenes (143) and (144), so their reaction with hypochlorite reagents was attempted.

$CF_3CF{=}CHCF_3$ (143) $(CF_3)_2C{=}CHCF_3$ (144)

Alkene (143) was recovered after stirring with aqueous sodium hypochlorite, calcium hypochlorite, and calcium hypochlorite in the presence of a phase transfer catalyst. Alkene (144) was not affected by contact with anhydrous calcium hypochlorite. Actual recoveries were often low and sometimes other products were present but could not be obtained pure. However, it is still possible to conclude that epoxidations using hypochlorite reagents are not as efficient with fluorinated alkenes possessing a vinyl hydrogen.

ii) Attempted epoxidation of the diene (145)

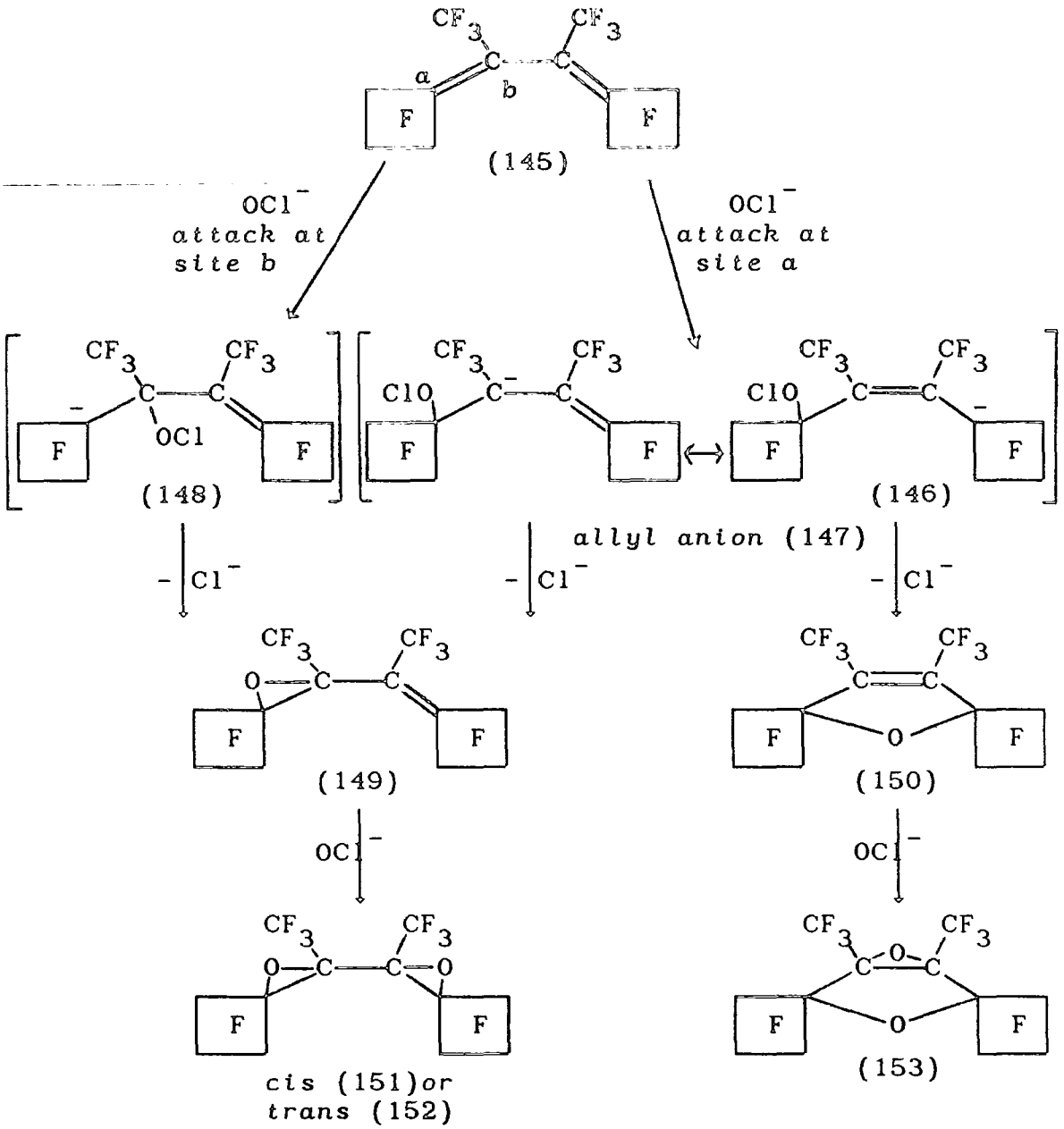
Diene (145) is available from perfluorocyclobutene trimer (146) by reaction with caesium fluoride at elevated temperatures (see experimental section). In our hands, however, yields reported by Taylor[160] were not attained.



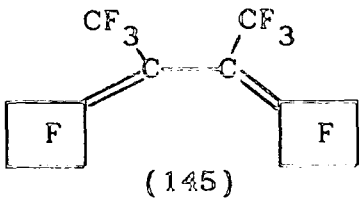
(146) (145)

The chemistry of perfluoroalkyl substituted dienes is relatively underdeveloped, and whether they behave as a conjugated system or as isolated double bonds (forced out of co-planarity by bulky R_f-groups) is the subject of some debate.[196,197] The epoxidation of (145) was expected to prove interesting, in this context, as the degree of conjugation in the system might determine the occurrence of either a simple epoxide, *eg.* (149), or a furan derivative, *eg.* (150). Thus (145) was reacted with calcium hypochlorite

in acetonitrile in a manner similar to the alkenes described earlier.



Four major peaks were observed in the g.l.c. of the product mixture which were identified as (145), two $C_{12}F_{18}O$ isomers (one major) and a $C_{12}F_{18}O_2$ isomer by mass spectroscopy. The major $C_{12}F_{18}O$ isomer was isolated and assigned the mono-epoxide structure (149) on the basis of its ^{19}F n.m.r. spectrum; two distinct $-CF_3$ singlets and complicated $-CF_2$ resonances eliminates the symmetrical isomer (150).



(145)

$\xrightarrow[CH_3CN,\ room\ temp.]{Ca(OCl)_2,}$

(145), 7%
$C_{12}F_{18}O$, 14%
$C_{12}F_{18}O_2$, 57%
$C_{12}F_{18}O$ ca.
unidentified 17%
component

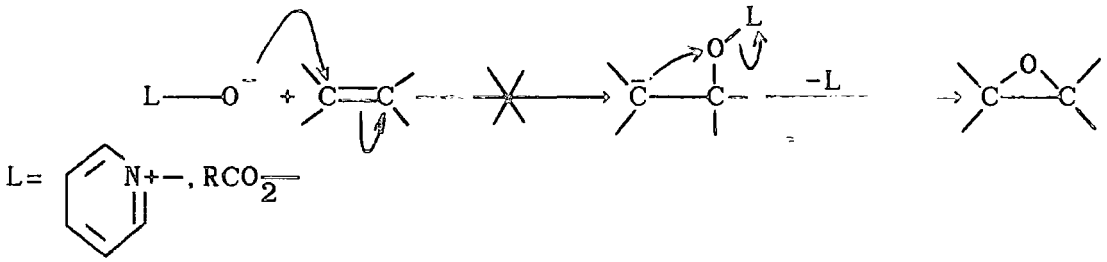
Unfortunately, the major product afforded a ^{19}F n.m.r. spectrum which, by a study of molecular models, could be assigned to all three possible $C_{12}F_{18}O_2$ isomers; the *cis* (151) and *trans* (152) epoxides, and the epoxytetrahydrofuran (153). Compounds (151), (152), and (153) all possess two equivalent CF_3 groups and two equivalent cyclobutyl rings. Therefore, the presence of three overlapping AB resonances in the CF_2 region of the n.m.r. spectrum and a singlet in the CF_3 region is consistent with all the structures. It would seem likely, however, in view of the unambiguous isolation of the mono-epoxide (149), that the unidentified $C_{12}F_{18}O_2$ component derived from it. In addition, the product fluorocarbon from the experiment was further reacted with calcium hypochlorite and the resulting fluorocarbon examined by g.l.c. Complete disappearance of compound (149) and a corresponding increase in the height of the $C_{12}F_{18}O_2$ peak is strong evidence for the assignment of the compound to the di-epoxide (151,152)(*cis* or *trans*).

2.B.d Other potential nucleophilic epoxidising agents

In view of the current interest in general syntheses of fluorinated epoxides, of which OCl^- seemed to be the only example, we sought to develop other reagents which could act in a similar manner. It was thought that pyridine-*N*-oxide and peroxyacid anions were good candidates for oxygen

nucleophiles with leaving group substituents, and so reactions with fluorinated alkenes (1),(143) and (82) were attempted.

$CF_3CF{=}CF_2$ (1) $CF_3CF{=}CHCF_3$ (143) $C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$ (82)



Unfortunately, however, (82) was recovered unchanged after refluxing with pyridine-*N*-oxide and stirring with sodium peroxybenzoate, or *m*-chloroperoxybenzoic acid in the presence of KOH. Similarly, (143) was unaffected by reaction with pyridine-*N*-oxide and (1) was recovered after contact with *m*-chloroperoxybenzoic acid in the presence of KOH.

Despite this, Russian workers have been able to employ peroxyacids, in the absence of base, as epoxidising agents with the highly electrophilic perfluoroisobutene, and claim[198] that a nucleophilic mechanism is in operation.

$$(CF_3)_2C{=}CF_2 \xrightarrow{ArCO_3H} (CF_3)_2C\overset{O}{\diagdown\!\diagup}CF_2 + ArCO_2^-$$
(4)

CHAPTER THREE

BIFUNCTIONAL NUCLEOPHILES WITH FLUORINATED ALKENES

CHAPTER THREE

BIFUNCTIONAL NUCLEOPHILES WITH FLUORINATED ALKENES

Most of the work contained in this Chapter concerns the reactions of aromatic diheteronucleophiles viz catechol, 3,4-dimercaptotoluene, *ortho*-aminophenol and *ortho*-aminothiophenol with fluorinated-alkenes and -cycloalkenes. However, other nucleophiles are also contained and, consequently, this Chapter is structured around the type of alkene where the mechanistic information is best discussed.

We found that potassium carbonate in acetonitrile was the most effective system for reactions of fluorinated alkenes with difunctional aromatic derivatives and was commonly used for reactions described in this section. Acetonitrile is volatile and miscible with water and could be readily eliminated from the reaction mixture but was sufficiently polar to enable the reaction to take place. Potassium carbonate is a good enough base to avoid addition reactions which would destroy the unsaturation and is also non-nucleophilic. As will be shown later, the best results were obtained with careful control of the stoichiometry (nucleophile : alkene = 1 : 1). Unfortunately, a number of the products obtained in this section decomposed fairly rapidly even if sealed under dry nitrogen and refridgerated.

In this Chapter identification of products was aided by a variety of spectroscopic methods including mass spectroscopy, infrared spectroscopy and n.m.r. spectroscopy. Most compounds gave molecular ion peaks in their mass

spectra, especially in electron impact (positive ion) mode, but by far the most instructive technique was ^{19}F n.m.r spectroscopy.

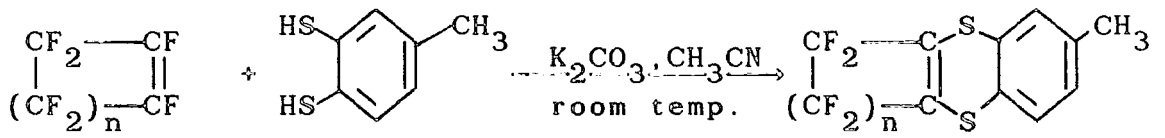
^{19}F N.M.R[199] The fluorine-19 nucleus is 100% abundant and almost as sensitive as the proton. The great difference between the two nuclei lies in the range of chemical shifts available. The majority of proton signals appear in the range 0-10ppm (relative to TMS) whereas, relative to $CFCl_3$, ^{19}F resonances occur anywhere between -20 and +200ppm. Relatively low field analysis of the ^{19}F nucleus, therefore, affords spectra which are sharp and first order. Perhaps the most important practical advantage of ^{19}F n.m.r. spectroscopy is that normal hydrocarbon *etc.* solvents and standard reagents are 'transparent' to radiation in the ^{19}F frequency range and, therefore, crude reaction mixtures may be effectively studied. With instruments that are able to compute multiple transients then extremely small quantities of material can be studied, even down to the level that are eluted from an analytical injection into a standard gas chromatograph.

Resonances due to ^{19}F nuclei of $-CF_3$ groups appear in a different region of the spectrum (typically 60-90ppm) to $-CF_2-$ groups (110-140ppm) which, in turn, occur distinct from $-\dot{C}F-$ resonances (170-210ppm). Application of this crude picture together with spectral integration and coupling constant data yields an enormous amount of information concerning molecular structure and forms the basis for much of the compound identification contained in this Chapter. Several books on ^{19}F n.m.r. spectroscopy are available.[199]

3.A PERFLUORO-CYCLOPENTENE AND -CYCLOBUTENE

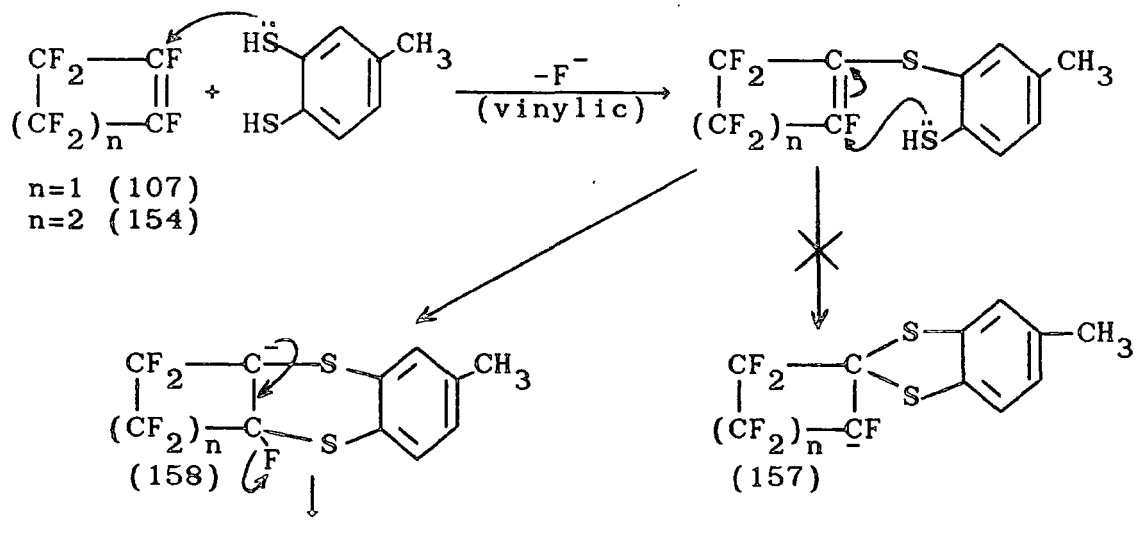
3.A.a With 3,4-dimercaptotoluene

Perfluoro-cyclopentene (154) and -cyclobutene (107) react readily with 3,4-dimercaptotoluene in the presence of potassium carbonate to afford dithiin products (156) and (155), respectively, in good yield.



n=1 (107) *perfluorocyclobutene* n=1 (155) 79%
n=2 (154) *perfluorocyclopentene* n=2 (156) 96%

An exothermic reaction was noticed immediately the reactants were brought into contact. Nevertheless, the reaction mixtures were agitated for at least a further 16 hours before isolation of the product. The yields of the dithiin (156) dropped to 60% when a 50% excess of the alkene (154) was employed and this is probably due to the participation of intermolecular processes prior to cyclisation. A mechanism for the reaction is proposed below:-



n=1 (107)
n=2 (154)

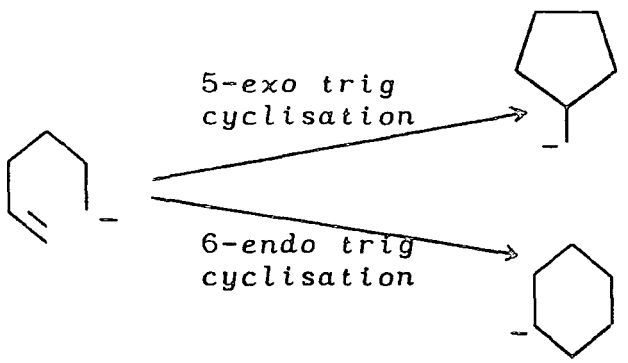
(158)

(157)

n=1 (155), n=2 (156)

After initial displacement of vinylic fluorine, cyclisation is available *via* two possible anionic intermediates (157) and (158). Mesomeric stabilisation through directly bonded sulphur favours (158) over alternative (157) in which the negative charge is localised adjacent to fluorine.

Baldwin[60] has defined a set of empirical rules for the relative facility of ring forming reactions, the physical bases of which lie in the stereochemical requirements of the transition state for the ring closure process. The 'disfavoured' cases require severe distortions of bond angles and distances to achieve the appropriate trajectory. In his analysis, ring closure at an sp^2 (trig.) carbon is preferred for formation of a five membered ring, in which the breaking bond is exocyclic (5-exo trig), over formation of a six membered ring, in which the breaking bond is endocyclic (6-endo trig).

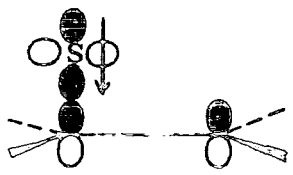


[60]

This is supported by ring forming reactions of relevant radicals in which thermodynamically disfavoured 5-membered ring products are observed.[200]

Clearly, formation of the dithiin derivatives (155) and (156) through six-membered intermediates (158)(6-endo trig cyclisation) is in contradiction to these observations.

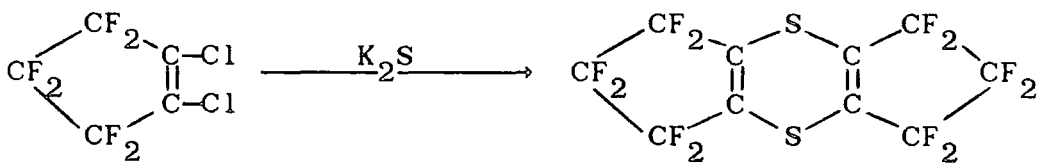
However, Baldwin[61] has achieved disfavoured ring closure processes for sulphur nucleophiles and ascribes the anomalous behaviour of second-row elements to two phenomena. Larger radii and bond lengths for the larger atoms may allow them to obtain conformations which are difficult for the corresponding first row-elements. Alternatively, overlap of filled orbitals on the unsaturated carbon with available unfilled orbitals on the second row-element may reduce the geometric constraint for the desired ring closure.



approach 90°

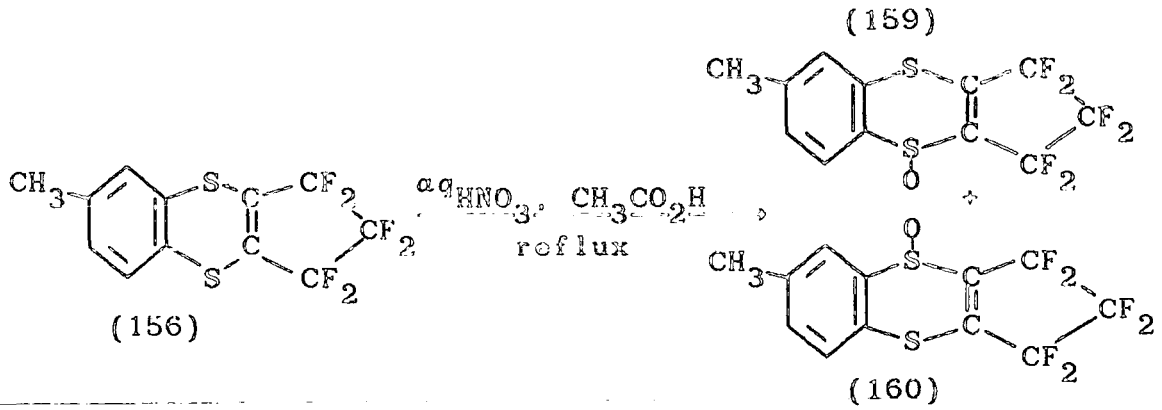
approach 109°

Krespan and England have obtained cyclic sulphides similar to (156) by treatment of 1,2-dichloroperfluorocyclopentene with sulphide ion.[201]



<u>*OXIDATION OF (156)*</u>

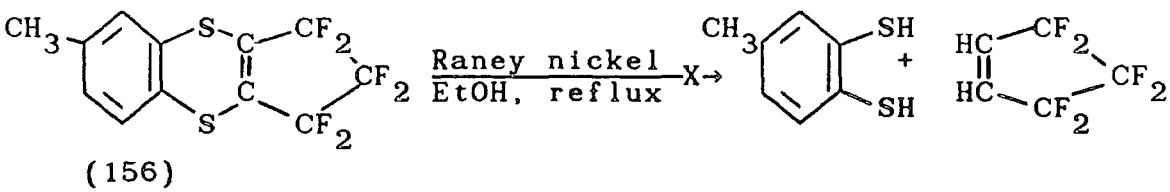
According to the procedure of Gilman and Swayampati,[202] dithiin (156) was treated with boiling nitric acid in acetic acid in order to attempt oxidation.



A low yield of a material with an accurate mass corresponding to $C_{12}H_6F_6S_2O$ was obtained and presumed to be a mixture of the two sulphoxide derivatives (159) and (160).

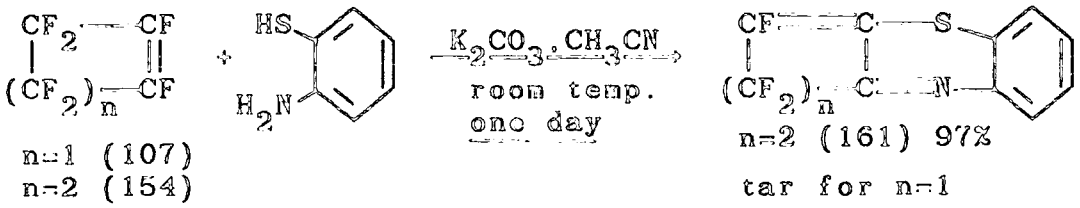
(156) WITH RANEY NICKEL[203]

Vinylic di-hydro derivatives of fluorinated cyclic alkenes are often only produced in low yield by $LiAlH_4$ reductions of the parent perfluoro-compounds.[204] Raney nickel hydrogenations of sulphides are well precedented[203] so we attempted the reaction of this reagent with dithiin derivative (156). Following the procedures of Mozingo and co-workers[205] a mixture of the dithiin (156) and Raney nickel was refluxed in ethanol for one hour,

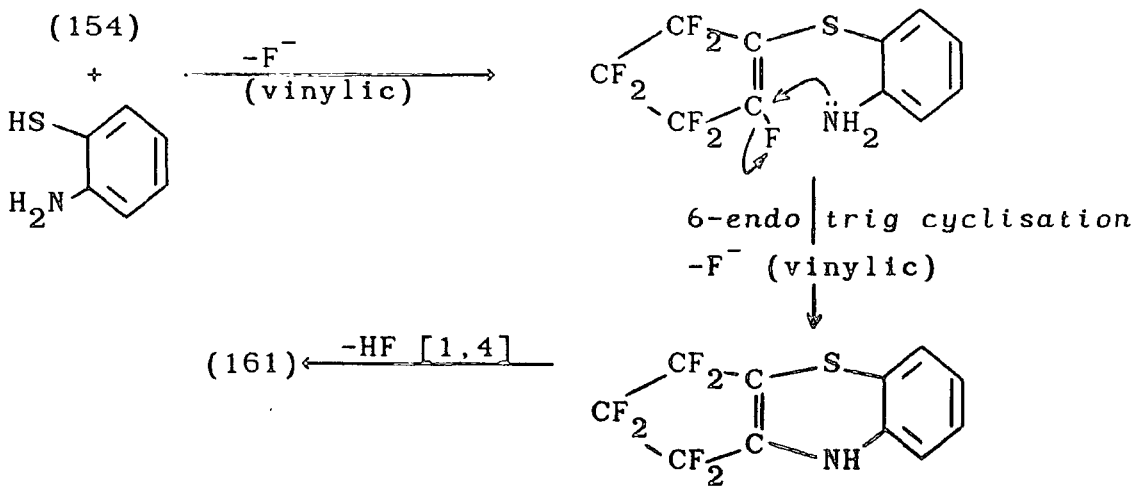


Unfortunately, only a small amount of volatile material was formed and the starting material (156) was entirely consumed. Raney nickel is stabilised by a strongly alkaline medium and it is possible that hydrolysis of (156) was effected.

3.A.b With Ortho-aminothiophenol



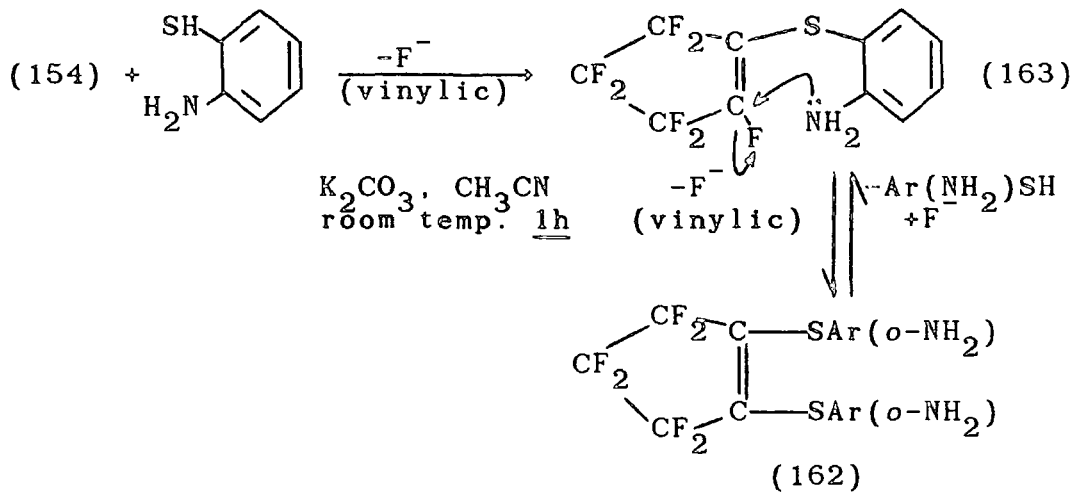
Under the usual conditions *ortho*-aminothiophenol reacted with perfluorocyclopentene (154) in a different manner to perfluorocyclobutene (107). A virtually quantitative yield of an azadiene (161) was obtained in the former case, whereas the latter alkene simply afforded an intractable tar. Again the reaction appears to have occured *via* the less favoured 6-endo trig cyclisation, although in this case nitrogen is the relevant atom and the reasons proposed for the similar behaviour of sulphur are not valid.



There could be two possible explanations for this phenomenon. i) The driving force for localising charge adjacent to sulphur is sufficient to overcome any distortions arising from the 6-endo trig cyclisation, even though a first-row element promotes the ring formation.

ii) Cyclisation through the amino-group is reversible and, although kinetically favoured for the 5-membered ring, leads to the 6-membered product.

As with dimercaptotoluene, an initial exotherm was detected immediately the reagents were brought into contact. In this case, however, a crystalline solid was observed to form which was subsequently isolated and shown to be di-adduct (162), occurring *via* a second intramolecular attack by an *ortho*-aminothiophenol molecule on original intermediate (163).



(162)

Given the activating influence of directly bonded sulphur in intermediate (163) and the known nucleophilicity of the original mercaptide nucleophile, formation of the disulphide (162) is not surprising. Clearly, the final stage is reversible as (162) is not detected in the final product after 24 hours reaction time and disappears gradually on increasing reaction times.

Table 13

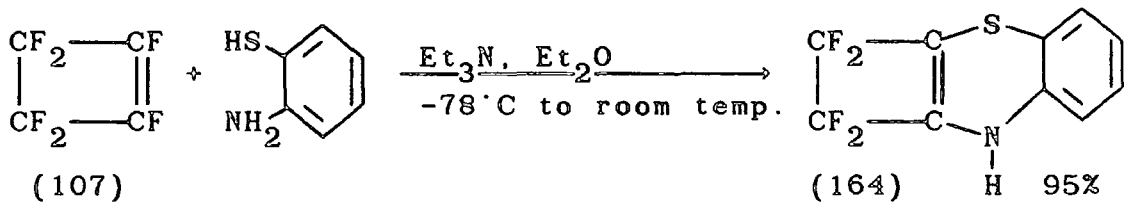
ortho-aminophenol + (154) $\xrightarrow[\text{room temp.}]{K_2CO_3,\ CH_3CN}$ (162) + (161)

Time (hours)	%(162)	[a] %(161)
1	52	——[b]
2	38	28
8	7	33
24	——	97

a *proportions calculated by* ^{19}F *n.m.r.*

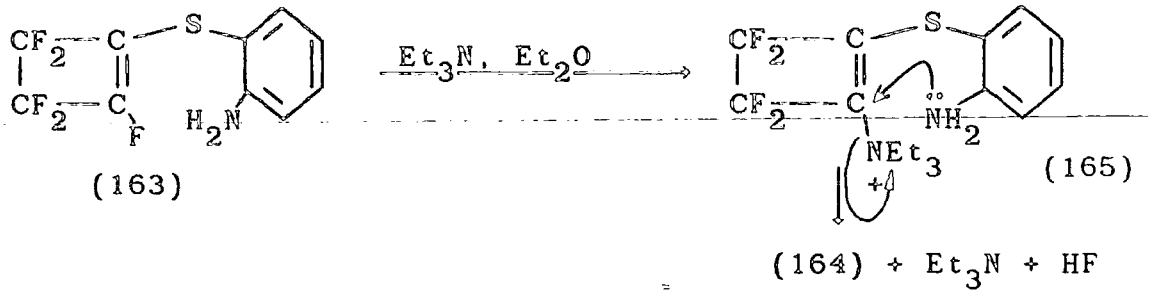
b *crude mixture not analysed. Isolated yield of* (162)

Also, treatment of disulphide (162) with potassium carbonate in acetonitrile at room temperature does not lead to the formation of the expected azadiene (161) and, therefore, it is very likely that free F^- is required for conversion of (162) to (161). Since the addition of sulphur nucleophiles to (163) is a reversible process it is not a large step to assume that intramolecular reaction through the amino-group within (163) will also be reversible under the same conditions. However, when perfluorocyclobutene (107) was reacted with *ortho*-aminothiophenol under conditions mild enough to avoid the final 1,4-dehydrofluorination, where the product of kinetic control would be expected to dominate, a very high yield of six-membered ring product (164) was isolated.



(107) (164) 95%

In this case, it is also possible that triethylamine reacted with the relevant intermediate to generate alkenylammonium compound (165)(see p 26).

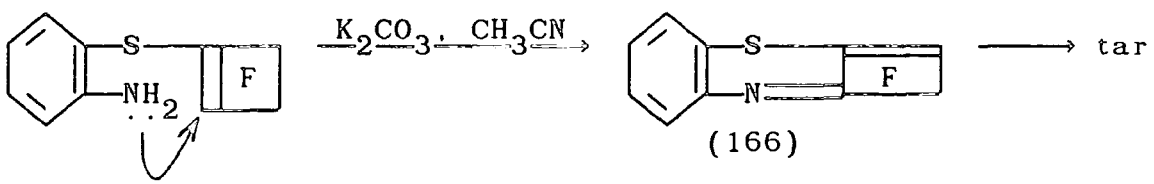


(163) (165)

(164) + Et_3N + HF

This would further activate the position opposite the sulphur substituent and could lead to adduct (164).

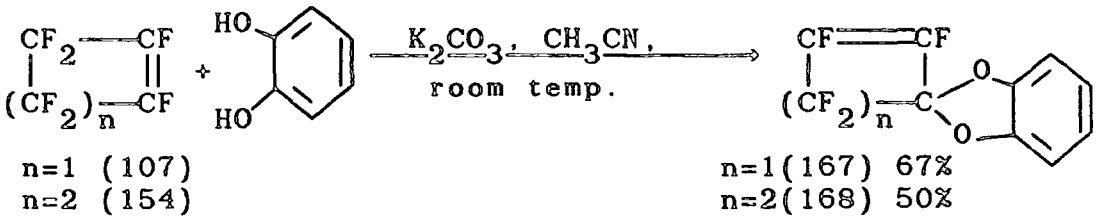
It is almost certain that, under the former conditions, an azadiene (166) analogous to (161), was formed but was too reactive with a four-membered ring containing exocyclic and endocyclic unsaturations and did not survive.



(166)

3.A.c With Catechol

Reactions of cyclic alkenes (107) and (154) with catechol gave five-membered spiro-ketals (167) and (168) in contrast to the previously described six-membered adducts.

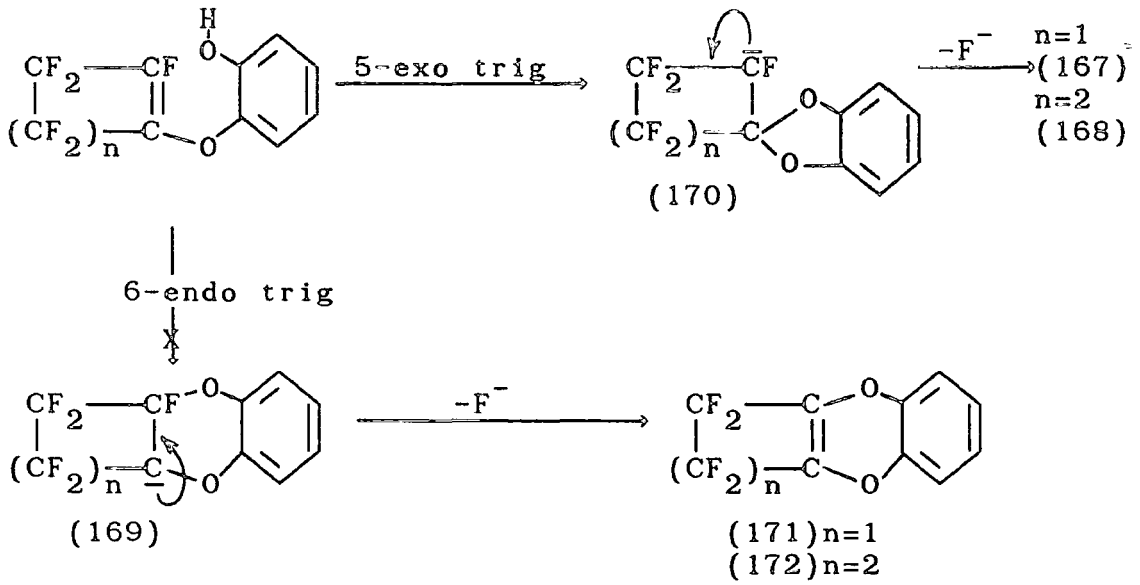


n=1 (107)
n=2 (154)

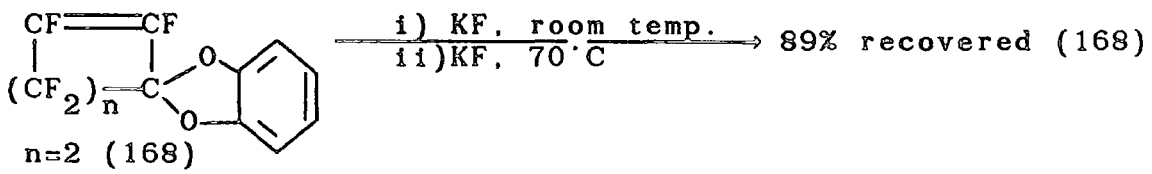
n=1(167) 67%
n=2(168) 50%

Intermediate carbanion (169) with a $R_{f2}\bar{C}$—O structure and

alternative (170) with a $R_{f2}\dot{C}-F$ configuration are structurally very similar. Thus, the stereochemically favoured 5-exo trig cyclisation would be expected to dominate. It is noteworthy that products (167) and (168) contain two vinylic fluorines, whereas alternative 6-membered products would possess an internal double bond and would most probably be more stable.[62]



Hence, if thermodynamic control was operating we would expect adducts (171) and (172) to dominate. Further evidence of the irreversibility of the cyclisation to form the ketals (167) and (168) is found in the stability of (168) to treatment with potassium fluoride at higher temperatures.



It is reasonable that for the more conformationally mobile ethylene glycol, used under more forcing conditions,

selectivity observed in our systems would not be found. This could account for the product mixtures observed by Stephens and co-workers (see p. 34) with their reactions of decafluorocyclohexene. In addition, the Birmingham workers employed excess of the glycol reagent and in our systems this lead to more complicated product mixtures.

Table 14

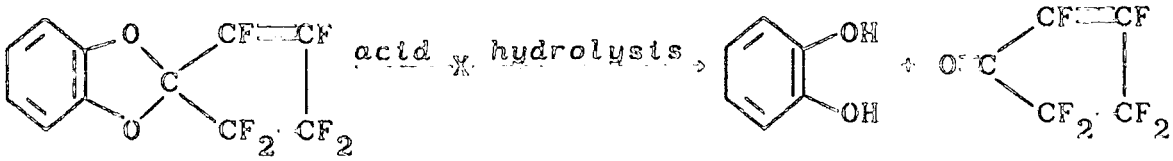
Product formation versus reactant stoichiometry

Catechol : (154)		Description of products
1	1	(168) 50%[a]
1	2.2	recovered (154) 74%[b] (168) 40% $C_{11}H_5F_7O_2$ 3% $C_{11}H_5F_7O_2$ 1% $C_{16}H_4F_{14}O_2$ 6% $C_{16}H_4F_{15}O_2$ 9%
1	0.2	several solid[c] components (unidentified).

a) *isolated yield (no evidence of significant formation of side products)* b) *based on g.l.c./m.s.* c) *based on t.l.c. and n.m.r.*

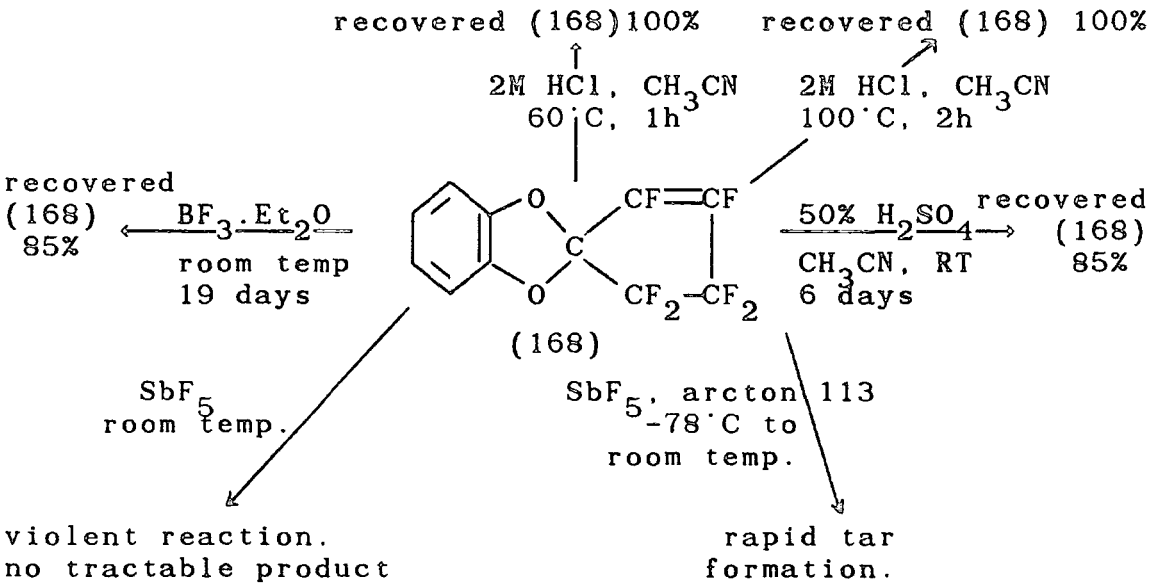
(168) *With acids* Ketals are readily hydrolysed to ketones by the action of aqueous acids under mild conditions.[206] This constitutes part of the 'protecting group procedure' for sensitive carbonyl functions. Typical conditions for cleavage of the ketals are refluxing with 2% HCl for a few hours. α,β-Unsaturated fluorinated cyclic ketones are not readily accessible and it was hoped that acid induced hydrolysis of spiro-ketal (168) would be a

convenient route to perfluorocyclopentenone.



(168)

Remarkably, however, (168) withstood a range of mineral acids[206] (various strengths and different temperatures) and Lewis acids.[207]



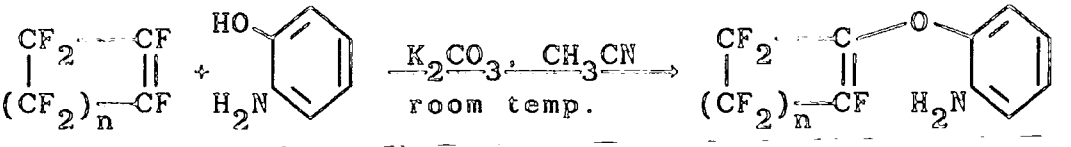
(168)

Only antimony pentafluoride was able to effect reaction and in this case the ketal (168) quickly decomposed to form an intractable tar. No formation of the target alkenone was detected.

3.A.d With Ortho-aminophenol

Compounds (107) and (154) were treated with ortho-aminophenol under the usual conditions with the expectation that oxygen-nitrogen heterocycles would be formed.

Unusually, however, the reactions terminated after initial substitution for vinylic fluorine to afford unstable aromatic ethers (173) and (174) respectively.

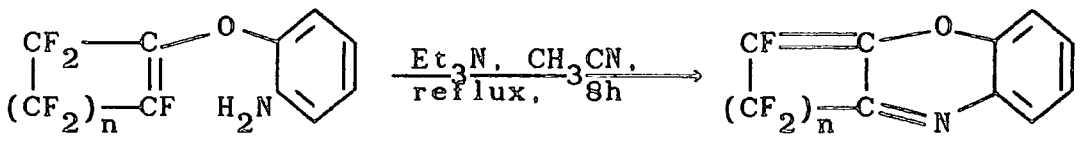


n=1 (107)
n=2 (154)

n=1 (173) 22%
n=2 (174) 98%

The O-H group competed effectively with $-NH_2$ for reaction at the $=CF$ site, a well established phenomenon for base induced nucleophilic processes (see section 1.C). Corresponding reactions with the sulphur analogue (*ortho*-aminothiophenol) gave cyclic products, so failure of the oxygen derivative to cyclise under the same conditions is further evidence of the activating influence of sulphur.

Ethers (173) and (174) decomposed rapidly, even at -15°C, presumably through successive reactions initiated by the free amino-group. However, immediate treatment of a crude reaction mixture containing (174) with triethylamine in boiling acetonitrile lead to isolation of cyclised adduct (175) in good yield. Assignment to structure (175) was made by clear evidence of a $CF_2CF_2CF=$ group in the ^{19}F n.m.r. and ^{13}C n.m.r. spectra and an unsaturated nitrogen in the ^{15}N n.m.r.

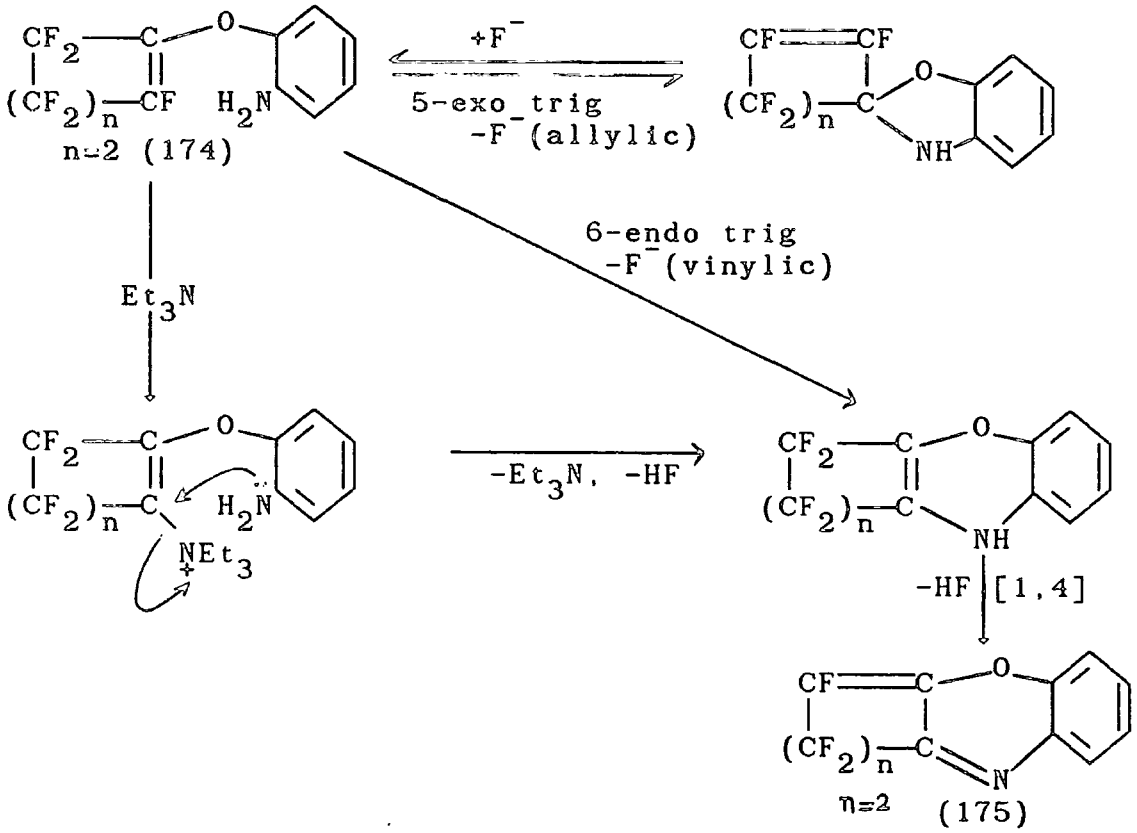


n=2 (174)

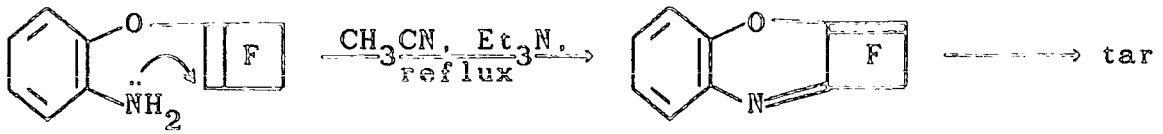
n=2 (175) 59%

The preference for sulphur analogues of (174) to undergo 6-

endo trig cyclisation has been discussed earlier, but we would have expected (174) to mirror the reactions of catechol, as in both cases the system $R_fFC{=}C{-}O{-}Nuc^-$ is being considered. However, the conditions employed in the present case are entirely different. Clearly, with elevated temperatures, (175) could be the product of thermodynamic control. Alternatively, with triethylamine as base alkenylammonium compounds could have been formed (see section 3.A.b).



Under the same conditions, perfluorocyclobutene derivative (173) simply afforded an intractable tar, thus providing further evidence of the supposed instability of the structure (176).

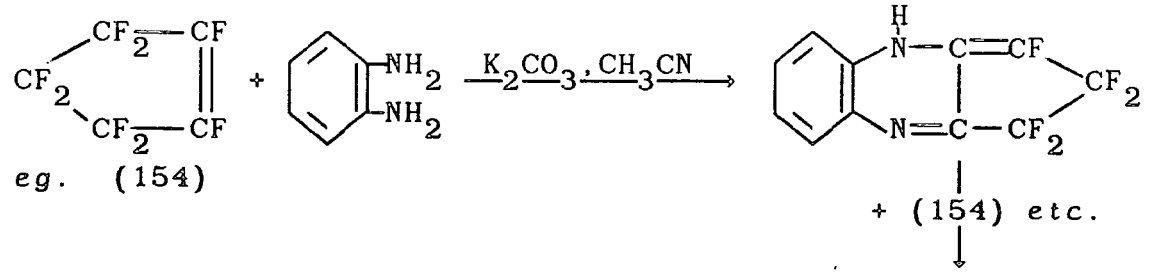


(173) (176)

Treatment of (173) with sodium hydride as an alternative to triethylamine was not successful due to extensive tar formation.

3.A.e Miscellaneous nucleophiles

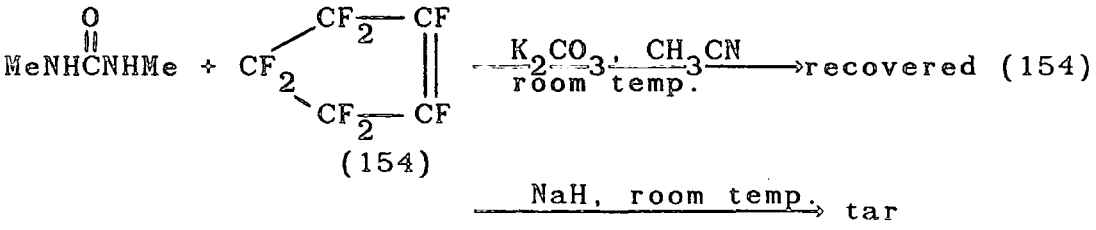
Ortho-phenylenediamine Unlike the previous aromatic difunctional derivatives, *ortho*-phenylenediamine did not give any tractable material on reaction with perfluorocyclopentene under the usual conditions. This may be understood as it is not possible to remove all residual acidic protons by intramolecular dehydrofluorination processes. Further reaction of the cyclised adducts by participation of the ring nitrogens in intermolecular nucleophilic processes is therefore likely.



eg. (154)

Benzamidine Benzamidine hydrochloride appeared to react smoothly with perfluorocyclopentene (154), in the presence of potassium carbonate and acetonitrile, to generate a product with a 'clean' ^{19}F n.m.r. spectrum. Unfortunately, however, attempts at isolation were thwarted by significant tarring of the material on work-up.

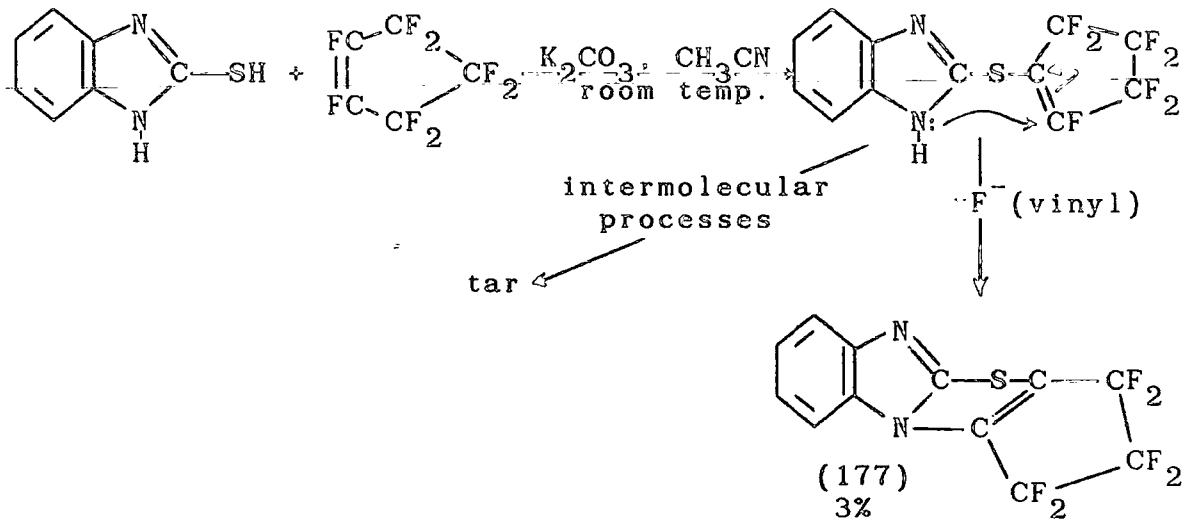
N,N'-dimethylurea Clearly, one way to avoid intramolecular processes occurring is to 'block off' the relevant sites on the nitrogen by methyl substitution. However, this also leads to reduced nucleophilicity of the nitrogen atom and, under the usual conditions, only starting material was recovered from the reaction between perfluorocyclopentene and N,N'-dimethylurea. Under more forcing conditions, *ie.* with sodium hydride as base, the only recovered material consisted of tarry matter.



1,2-Ethanedithiol No pure material could be isolated with the title reagent and perfluorocyclopentene, reacted in the presence of potassium carbonate in acetonitrile, due to decomposition of the product with various work-up procedures. These include attempted sublimation, vacuum distillation, column chromatography *etc.* Further reactions of this nucleophile with perfluorocyclo-olefins were not pursued.

2-Benzimidazolethiol This nucleophile is similar in structure to *ortho*-aminothiophenol with SH and NH groups. The reaction with perfluorocyclopentene afforded the adduct (177) derived from attack by nitrogen at the opposite carbon to the initial sulphur substituent, but by a particularly

disfavoured 5-endo trig cyclisation. This could account for the low yield obtained, as intermolecular processes may have been preferred, resulting in extensive formation of intractable material.



3.A.f Conclusions

The results from this section may be summarised in the following scheme, in which:-

compounds underlined have been isolated, compounds not underlined are intermediates.

The following letters refer to notes and reaction conditions as follows:-

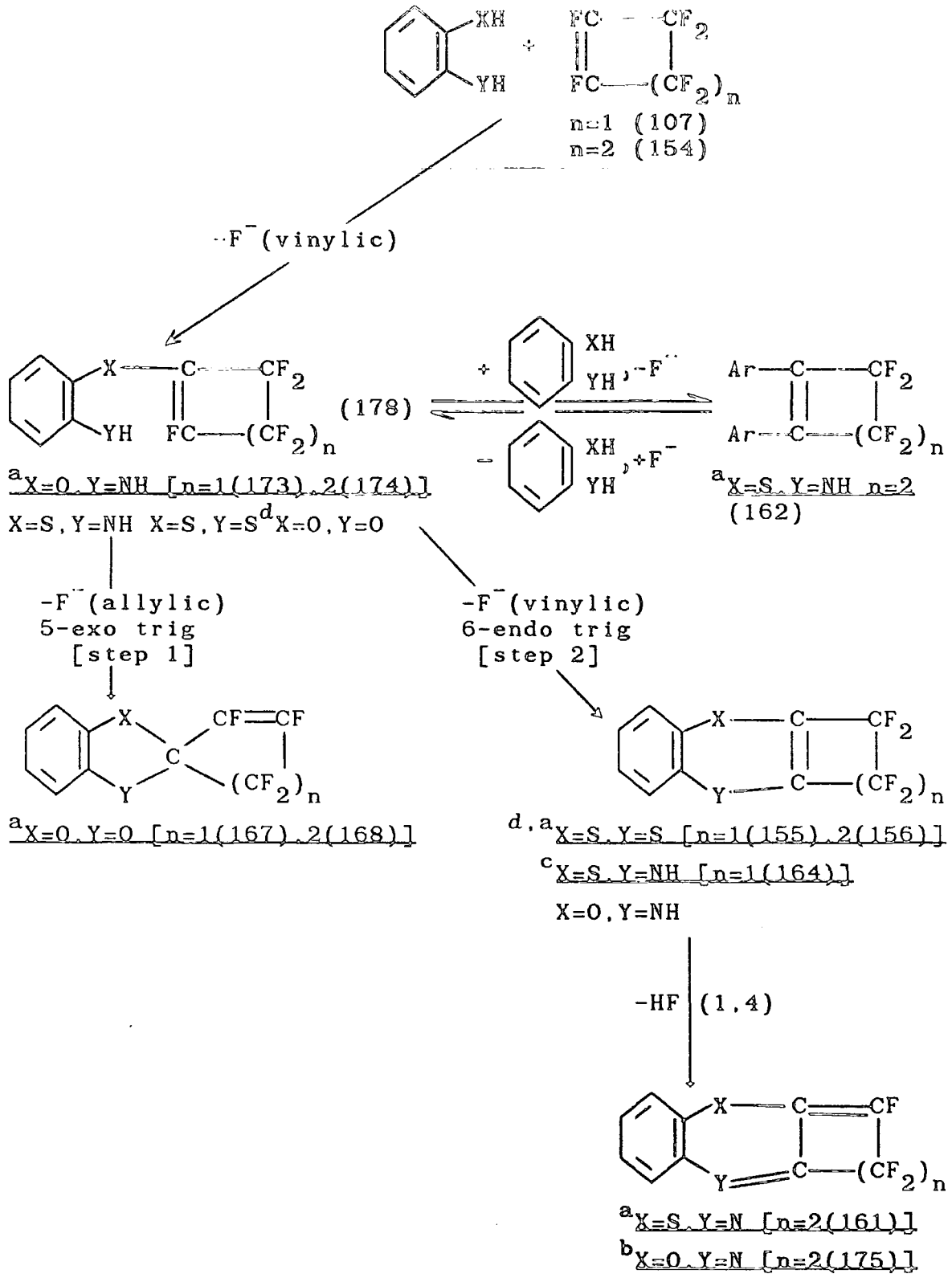
a. K_2CO_3, CH_3CN, room temperature.

b. Et_3N, CH_3CN, reflux.

c. Et_3N, Et_2O, -15°C to room temperature.

d. *4-methyl derivative*

SCHEME: PERFLUORO-CYCLOPENTENE AND -BUTENE WITH AROMATIC BIFUNCTIONAL NUCLEOPHILES



A summary of the available information and conclusions are given below.

1. In the absence of any clear driving force for 6-membered ring formation the stereochemically favoured 5-exo trig cyclisation (step 1) dominates.

2. If the initial substituent does not sufficiently activate the double bond (*eg.* intermediate (178), X=O), then the least reactive group, $-NH_2$, does not initiate cyclisation.

3. Application of triethylamine at higher temperatures to uncyclised adduct (174) leads directly to six-membered ring compound (175). This is in contrast to the reactions of catechol and indicates that either
i) the higher temperatures lead to the product of thermodynamic control, *or*
ii) triethylamine forms an alkenylammonium salt with intermediate (174) and this further activates the relevant carbon to nucleophilic attack.

4. Cyclobutene derivatives analogous to (161) and (175) are not isolated almost certainly as a result of the enhanced reactivity of the more strained system.

5. With sulphur as the initial substituent ((178), X=S, Y=NH *or* S) the double bond becomes more susceptible to nucleophilic attack, as evidenced by
i) Cyclisation occuring in all cases, including the least reactive amino-derivative ((178), X=S, $Y=NH_2$) *and*
ii) Formation of di-adducts (162) by a reversible attack of a second $Ar-S^-$ unit.

6. All the molecules with sulphur as the initial substituent afford 6-membered ring compounds *via* the less

favoured 6-endo trig cyclisation. This could be due to

i) (*in all cases*) the activation of the opposite double bond carbon by stabilisation of the relevant intermediate

ii) (*for* (178), X=S,Y=S) the ability of second row elements (*eg.* sulphur) to undergo stereochemically less favoured cyclisations

iii) (*in all cases*) the possible participation of thermodynamic reaction control. This is especially unlikely for (164) which is formed under particularly mild conditions.

iv) (*for* (164)) the intermediacy of an alkenylammonium compound thus further activating the relevant carbon atom.

7. Bis-amine nucleophiles are particularly unsuitable to heterocyclisation syntheses of this type as a result of the availability of further intermolecular reactions.

3.B OTHER FLUORINATED ALKENES

In this section reactions of alkenes other than perfluoro-cyclopentene and -cyclobutene with bifunctional nucleophiles are discussed. Dimers of perfluorocyclobutene (127) and (141) are contained here because they behave in a similar way to the acyclic alkenes of this study. Reactions involving nucleophiles other than catechol were notably less successful with these alkenes because, frequently, complicated mixtures resulted which could not be purified.

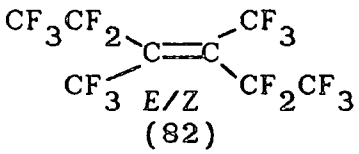
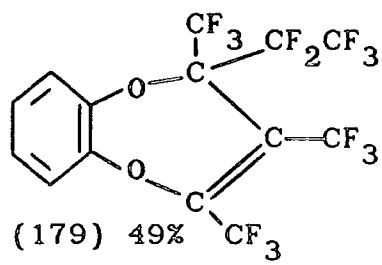
3.B.a With Catechol

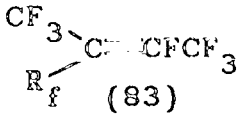
Various fluorinated alkenes were reacted with catechol using the standard conditions, *eg.* potassium carbonate and acetonitrile at room temperature. The results are summarised in table 15.

Table 15

Fluorinated alkenes with Catechol

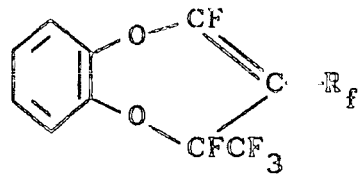
Conditions: K_2CO_3, CH_3CN, room temp.

ALKENE	PRODUCTS
 (82)	 (179) 49% + 2 other $C_{14}H_4F_{14}O_2$ isomers (total 29%)



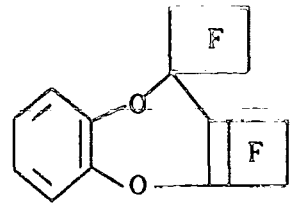
(83)

R_f = $CCF_3(C_2F_5)_2$

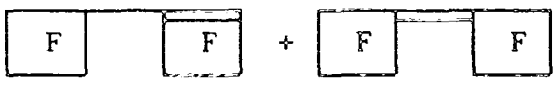


(180) 65%

(141)



(181) 31%

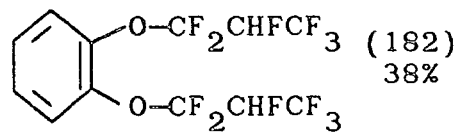


(141) (127)

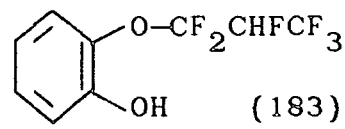
" (181) 75%

$CF_3CF{=}CF_2$

(1)



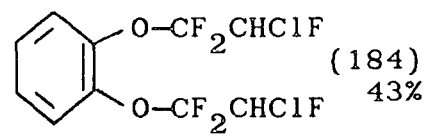
(182) 38%



(183) 16%

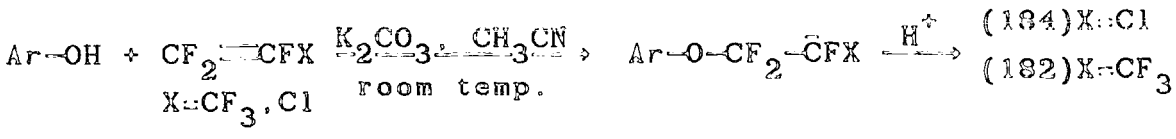
$CFCl{=}CF_2$

(50)



(184) 43%

The less electron deficient alkenes hexafluoropropene (1) and chlorotrifluoroethylene (50) gave products derived from addition rather than substitution processes. This is well understood as the corresponding intermediate carbanions are more basic than higher substituted analogues.

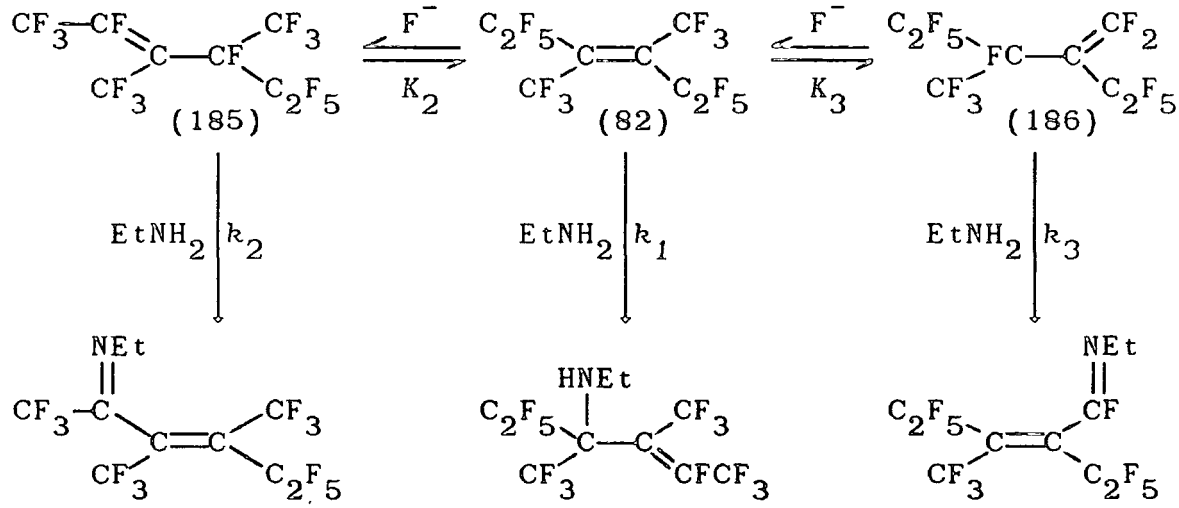


The other alkenes employed in this study (82), (83), (141), and (127) all afforded seven-membered ring products.

i) TFE Tetramer. In the presence of fluoride ion this alkene (82) generates low concentrations of isomers (185) and (186)[208] which are very much more reactive than their precursor and are preferentially selected by nucleophiles.

eg. with ethylamine in the presence of CsF

all mixtures E/Z isomers

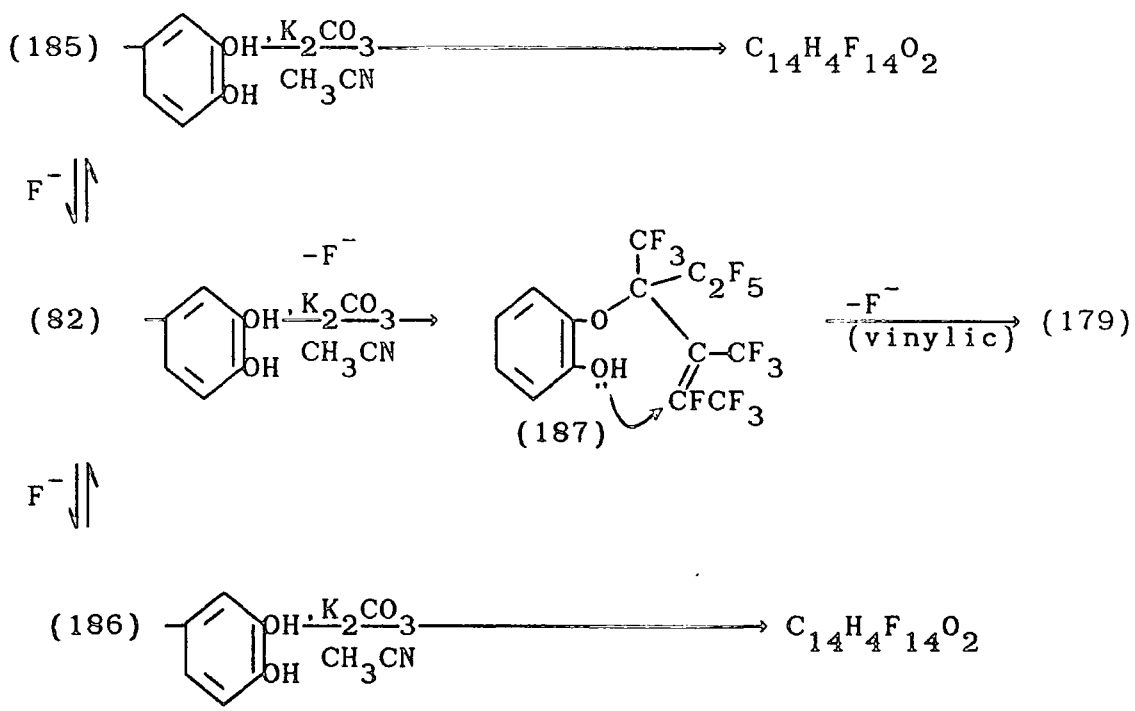


reaction rates $k_3 >> k_2 >> k_1$

equilibrium concentrations [(82)] >> [(185)] >> [(186)]

The final product distribution is governed by a combination of the relative reactivities of the isomeric alkenes and their equilibrium concentrations.

When (82) was reacted with catechol in the presence of potassium carbonate the major product derived from the parent alkene (82), but minor isomers were observed which could not be separated by preparative scale g.l.c. Clearly, (179) occured *via* initial displacement of *allylic* fluorine (no *vinyl* fluorine) from the $-CF_2$ site rather than the less preferred $-CF_3$. Intermediate (187) is then able to cyclise through an 'allowed'[60] 7-endo trig process, with loss of *vinylic* fluorine. During this reaction hydrogen fluoride is eliminated which then reacts with potassium carbonate to give potassium fluoride. The (now) available F^- is able to generate small concentrations of the other isomers (185) and (186) which could then lead to alternative cyclic products.



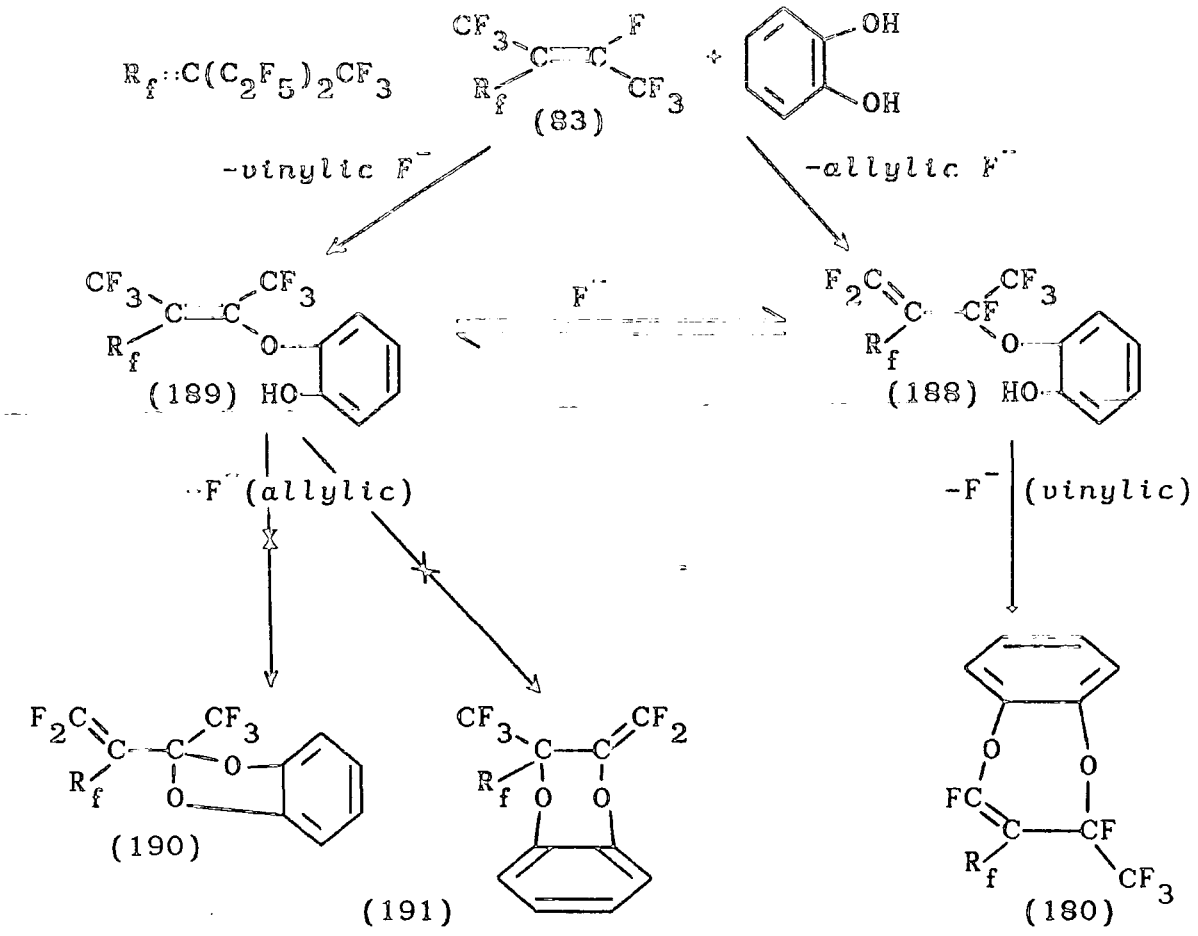
Confirmation of the participation of the isomers (185) and (186) is provided by the result of using lithium carbonate as base. Lithium fluoride formed during the major reaction is a far poorer source of fluoride ion than potassium

fluoride[209] and, therefore, we might expect a reduction in the concentrations of (185) and (186). The ratio of product (179) to competing isomers increases from 1.7 to 3.8 on moving to Li_2CO_3 as base.

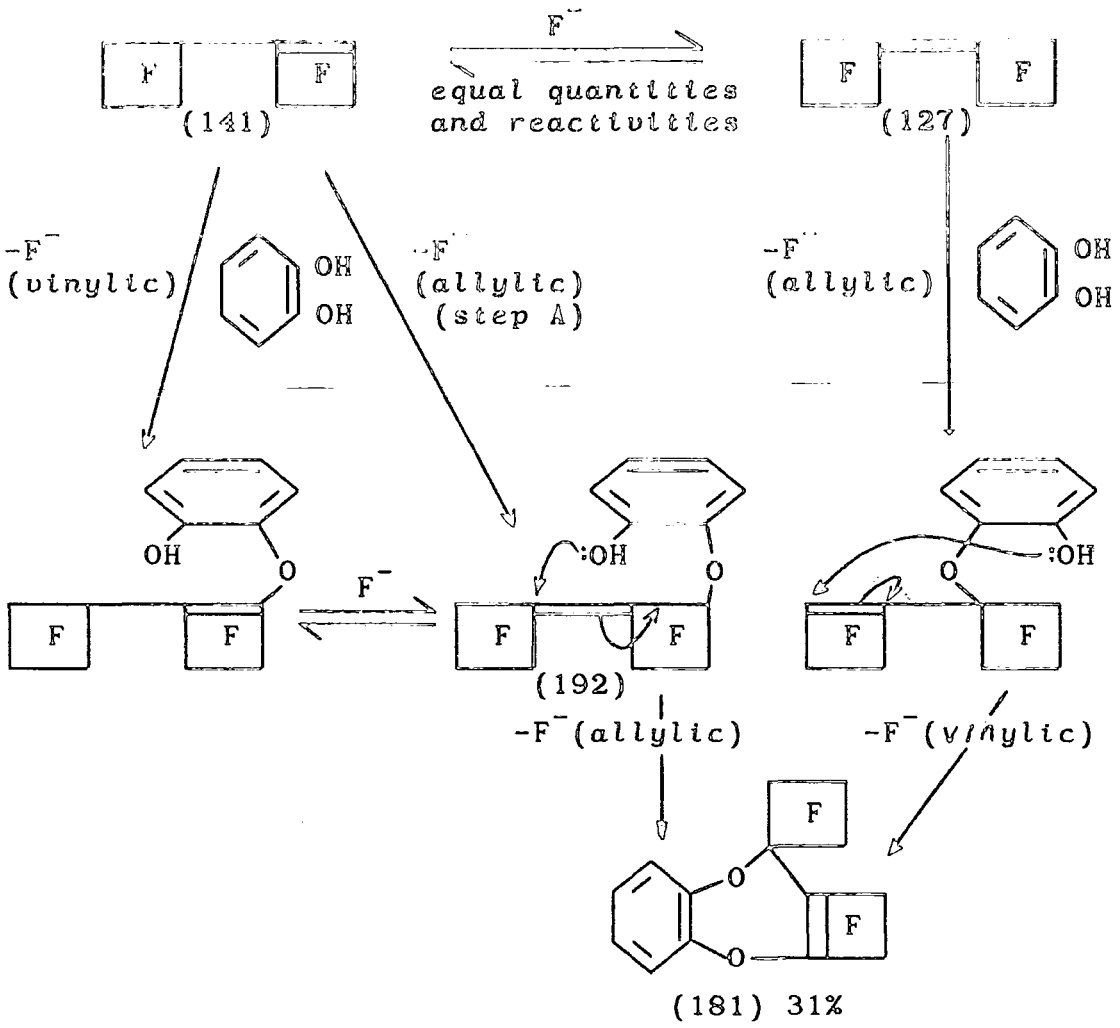
BASE	%(179)	%other $C_{14}H_4F_{14}O_2$	(179):others
K_2CO_3	49	29	1.7
Li_2CO_3	57	15	3.8

A product analogous to (179) has been reported for the reaction of (82) with ethyleneglycol.[210]

ii) TFE Pentamer (83) (83) Reacted with catechol to give compound (180) apparently *via* primary displacement of *allylic* fluorine and ring closure through substitution for *vinylic* fluorine. However, the loss of *allylic* fluorine in preference to the available *vinylic* site is slightly unusual, especially when the unstable terminal difluoromethylene intermediate (188) would result. It is more likely that preferred intermediate (189) was formed but did not cyclise since high energy derivatives (190) and/or (191) would have been produced. The fluoride ion available in the reaction medium could then have induced a low concentration of the more reactive isomer (188), (see previous compound) and ring closure through (188) pulled the equilibrium through to product (180).



iii) Perfluorocyclobutene dimer (141) The title alkene reacted with catechol under the usual conditions to produce seven-membered cyclic adduct (181). The mechanism for this process is unclear. (141) Could have undergone substitution for *allylic* fluorine to give (192) followed by cyclisation by displacement of a second *allylic* fluorine (sequence A, scheme below). Alternatively, the *vinylic* fluorine could have been substituted first and the resulting alkene isomerised to produce internal alkene (192). It is also probable that the other dimer of perfluorocyclobutene (127) was generated in the reaction mixture; this isomer is present in all F^- equilibrated systems involving (141).[211] Indeed, reaction of a 1:1 mixture of (127) and (141) with catechol afforded a good yield of the adduct (181) as the sole product.



Taylor has isolated similar adducts using ethyleneglycol with the perfluorocyclobutene dimers (127) and (141).[160]

3.B.b With di-lithio catechol

In an attempt to avoid saturated adducts with the simpler alkenes (1) and (50), the dilithio-derivative of catechol was employed in acetonitrile solvent. This was generated by the dropwise addition of ^{n}butyl lithium at -78°C to catechol in ether, but ether itself was found to be a poor solvent for the reaction.

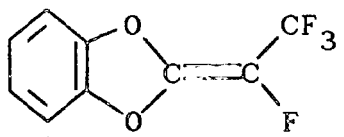
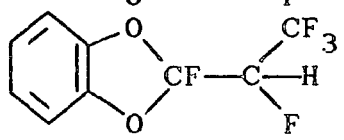
With the less reactive alkene (50) no tractable material could be obtained on several attempts but

hexafluoropropene (1) afforded two products (193) and (194).

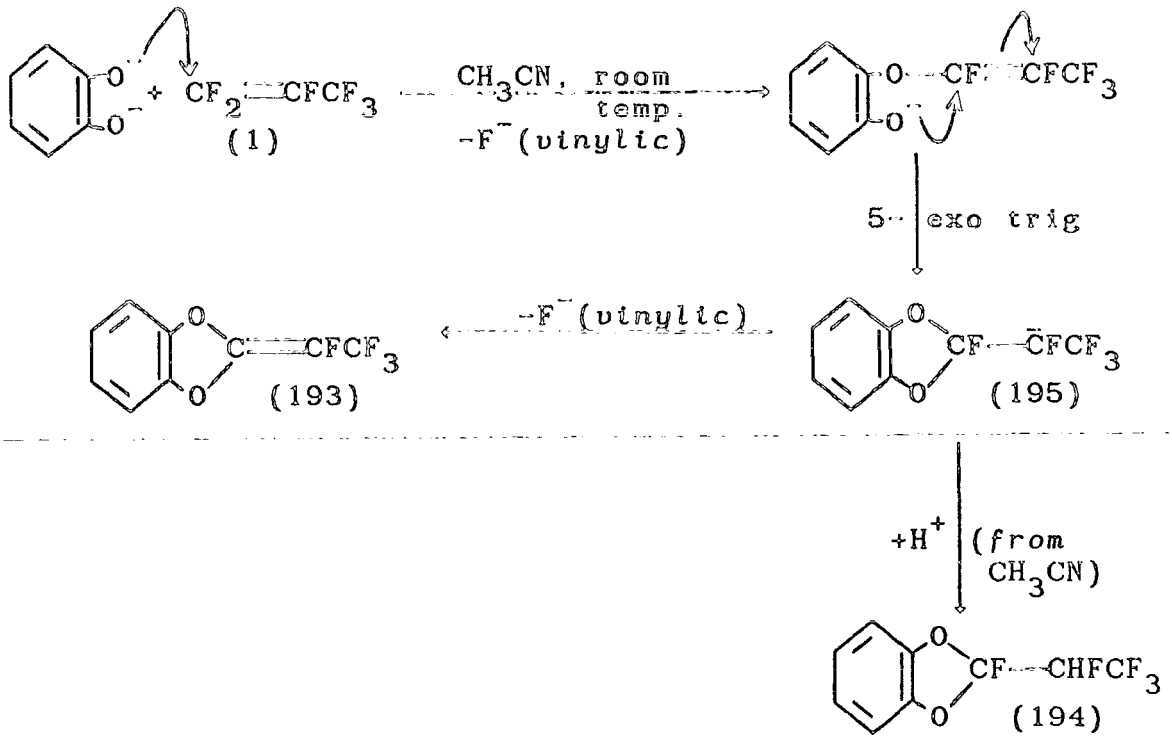
Table 16

Di-lithio catechol with (1) and (50)

Conditions: Di-lithio catechol + CH_3CN + alkene , room temp.

ALKENE	PRODUCT
$CF_3CF{=}CF_2$ (1)	 (193) 54%
	 (194) 29%
$FClC{=}CF_2$ (50)	*None isolated*

The unsaturated cyclic ether (193) resulted from successive displacements of vinylic fluorine from the most reactive terminus of the olefin. In addition, the 5-exo trig cyclisation is preferred over the alternative 6-endo trig ring formation. The saturated cyclic ether (194) is formed from common intermediate carbanion (195) *via* proton capture, probably from solvent. Small quantities of material corresponding to $C_5H_2NF_5$ can be observed in the crude product liquid by g.l.c./m.s. and are probably due to participation of the acetonitrile carbanion.

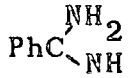
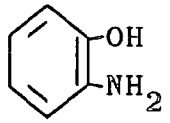
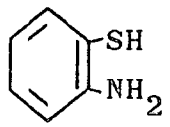
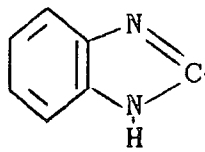


3.B.b Miscellaneous Nucleophiles

i) With TFE tetramer (82) Various nucleophiles other than catechol were reacted with (31) but, due to either significant tar formation or difficulty in isolation, pure products could not be obtained. Table 17 records the information.

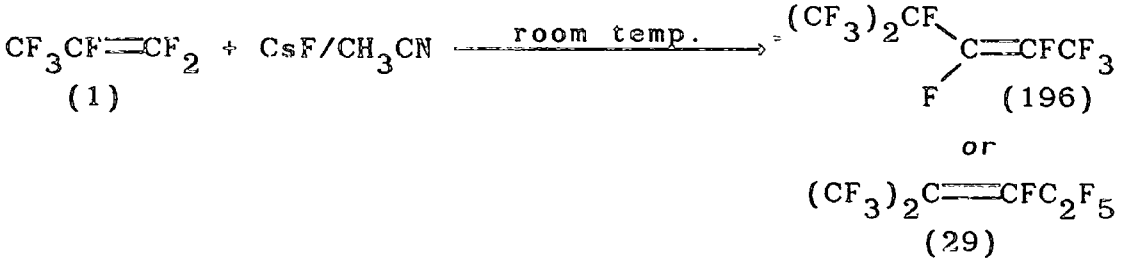
Table 17

(82) with bifunctional nucleophiles

NUCLEOPHILE	CONDITIONS	NATURE OF PRODUCT (RECOVERED (82))
CH_3CONH_2	NaH, dioxan room temp.	tar + (82) >40%
NH_2CONH_2	i) K_2CO_3, tetraglyme, 33°C	
	ii) K_2CO_3, THF, reflux	multicomponent product + (82)
	iii) K_2CO_3, 1,4-dioxane	
MeNHCONHMe	NaH, tetraglyme, room temp.	(82) 100%
	K_2CO_3, CH_3CN, room temp.	compound tarred on work-up
$SHCH_2CH_2SH$	K_2CO_3, CH_3CN	unstable white solid + others
K_2SO_3	H_2O, CH_3CN, reflux	(82) recovered
	i) K_2CO_3, CH_3CN, room temp., 120h	(82)20% +number of other components
	ii) K_2CO_3, CH_3CN, room temp., 24h	(82)39% + complicated product mixture
	K_2CO_3, CH_3CN, room temp., 24h	> 5 compounds
	K_2CO_3, CH_3CN, room temp., 48h	multicomponent product

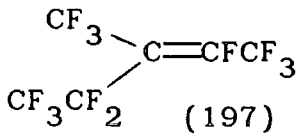
This series of results serves to illustrate the considerable difficulties that may be found in some heterocyclisation methods.

ii) With (29) and (196) We have established that perfluoro-4-methyl-2-pentene (196), the kinetic dimer of hexafluoropropene, may be obtained in good yield by caesium fluoride induced dimerisation in the absence of any agitation. Efficient agitation leads wholly to the thermodynamic dimer (29), and so very similar procedures may be operated in the synthesis of both isomers.



$CF_3CF{=}CF_2$ (1) + CsF/CH_3CN —room temp.→ $(CF_3)_2CF(F)C{=}CFCF_3$ (196) or $(CF_3)_2C{=}CFC_2F_5$ (29)

Compound (196) is an analogue of the cyclic alkenes described in section 3.A but no tractable material could be isolated on reaction with *ortho*-aminophenol in ether with triethylamine as base. Similar reactions were observed with isomer (197) a trimer of tetrafluoroethylene (see experimental section).



$(CF_3)(CF_3CF_2)C{=}CFCF_3$ (197)

CHAPTER FOUR

FLUOROCARBANIONS

CHAPTER FOUR

FLUOROCARBANIONS

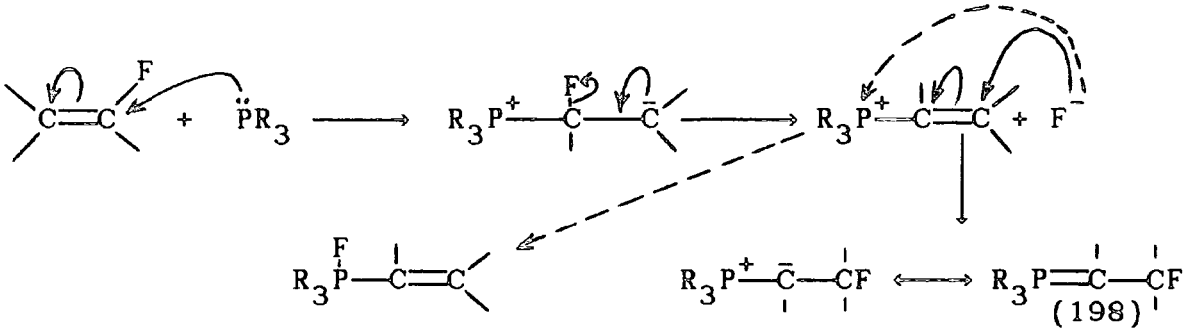
4.A INTRODUCTION

Since the pioneering work of Miller many years ago reactions involving fluorocarbanions have occupied a central role in the reactions of unsaturated polyfluoro-compounds. Olah and co-workers made a huge contribution to Chemistry with their studies relating to long-lived carbocations in the hydrocarbon field,[212] but at the onset of our work relatively few reports were available on studies of long lived carbanions in fluorocarbon systems. The purpose of this section is to review progress in this area up to the point at which we initiated our work.

4.A.a Long Lived Carbanions

i) Ylids

Probably the largest class of highly fluorinated 'carbanionic' species which have been directly observed are ylids.[213] Many have been obtained by the reaction of fluorinated alkenes with tertiary phosphines, amines or arsines although other methods are available,

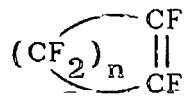
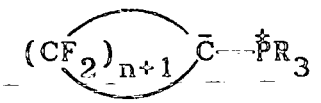
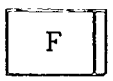
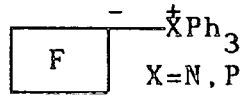


(198)

Some examples are contained in Table 18.

Table 18 Synthesis of stable highly fluorinated ylids

Precursor + R_3N, R_3P or R_3As

PRECURSOR	YLID	REF.
 n= 1,2,3,4	 *eg.* R=Bu	214
$CF_3CF{=}CFCF_3$	$CF_3CF_2\bar{C}(CF_3)\text{—}\overset{+}{P}Bu_3$	215
	 X=N, P	216
"	" (X=As)	217
CF_2Br_2	$\bar{C}F_2\text{—}\overset{+}{P}Ph_3$	218
$[BrCF_2PPh_3]^+Br^-$	"	
$CFBr_3$	$\bar{C}FBr\text{—}\overset{+}{P}Ph_3$	219

In keeping with known factors affecting carbanion stability, ylids which would require a fluorine atom α to the anionic site are generally not formed by usual methods; in the case of phosphorus compounds fluoride ion recombines with the positive heteroatom to yield fluorophosphoranes.[211] Alternative routes to α fluoroylids are available which do not produce fluoride ion in the reaction medium.[218,219] With heteroatoms such as phosphorus, which are able to expand their valence shells, contributions such as (198) greatly enhance the stability of the salts. In examples with particularly unstable carbanion centres, *eg.* $\bar{C}F_2\text{—}\overset{+}{P}Ph_3$, the alkylidene phosphorane form, *eg.*(198), is almost certainly the dominant contributary structure and the question arises

as to whether such materials should be regarded as carbanions. Ammonium ylids do not have an available resonance interaction and the salts are notably less stable. The ylids described in this section often undergo reactions typical of fluorocarbanions, they are isolable and may be studied by a variety of spectroscopic methods including ^{19}F n.m.r.

ii) Other Mesomerically stabilised observable fluorocarbanions

Fluorinated allenes are highly electrophilic and react readily with nucleophiles *via* formation of intermediate carbanions (specifically allyl anions). Workers from Knunyants' group have reported[137] the interaction of caesium fluoride with the tetrakistrifluoromethyl allene (199) in diglyme with warming, which leads to the formation of the salt (200).

$$\underset{(199)}{(CF_3)_2C{=}C{=}C(CF_3)_2} \xrightarrow[35\ C]{CsF,\ diglyme} \underset{(200)}{(CF_3)_2C\!\left(\!\!\begin{array}{c} \\ \\ \end{array}\!\!\right)\!C(CF_3)_2} \quad Cs^+,\ F$$

Attempts to isolate the salt (200) resulted in regeneration of the precursor allene. However, (200) was stable in solution up to 150°C and could be readily observed by ^{19}F n.m.r.

Recently, the extremely stabilised bis(trifluoromethyl)fluorosulphonyl carbanion (201) has been claimed[220] through both deprotonation of the conjugate C–H acid (202) and fluoride addition to terminal

difluoromethylene compound (203).

$$(CF_3)_2CHSO_2F \underset{}{\overset{R_3N}{\rightleftharpoons}} (CF_3)_2\bar{C}SO_2F\ \overset{+}{H}NR_3$$

(202) (201)

equilibrium wholly to right by n.m.r. with > 1.5 eq. NR_3

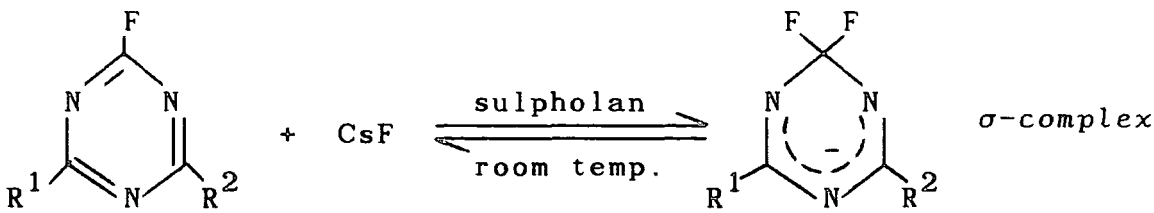
$$CF_2{:}\ C(CF_3)SO_2F \underset{}{\overset{CsF}{\rightleftharpoons}} (CF_3)_2\bar{C}SO_2F\ Cs^+$$

(203) (201)

equilibrium wholly to right by n.m.r. with 1.0 eq. CsF

Again the carbanion may be quenched with a variety of electrophiles and also may be observed by ^{19}F n.m.r. which gives a well coupled spectrum.

Fluorinated heteroaromatic compounds are also highly reactive towards nucleophiles and derivatives of 1,2,3-triazines were shown, by workers from these laboratories,[221] to form solution stable complexes with caesium fluoride.



R^1, R^2 = F, $CF(CF_3)_2$ (204)

^{19}F n.m.r analysis at room temperature gave broadened spectra consistent with the σ-complex (204) with no evidence of starting material, but also indicative of a system undergoing exchange. Cooling to 0°C dramatically sharpened the spectrum, *ie.* exchange kinetics were slowed to a point where they became insignificant on the n.m.r.

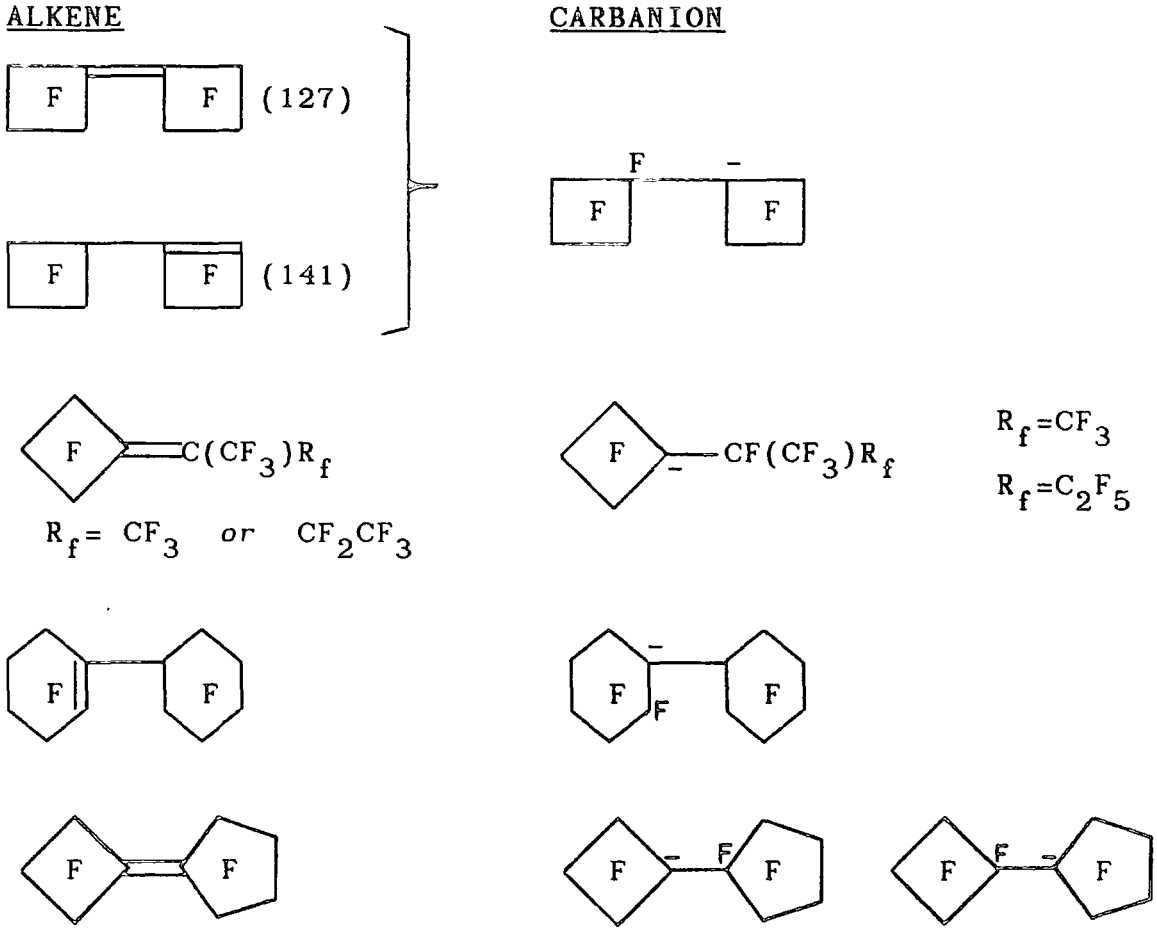
timescale.

iii) Simple perfluoroalkyl carbanions

The title compounds are known to be intermediates in the reactions of unsaturated organofluorine compounds with fluoride ion, a class of reactions now comprising a large proportion of the fluorine literature. However, there have been only a few reports of direct studies on the intermediates even though we have subsequently demonstrated that some are readily produced and stored for long periods.

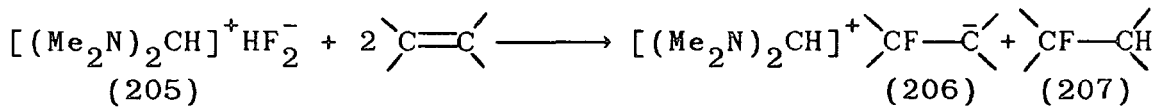
Table 19 Long-lived perfluorocycloalkylcarbanions[222]

Conditions: alkene + CsF/DMF, room temp.



One of the first reports of direct observation of long-lived perfluoroalkyl carbanions was produced in these laboratories with a variety or perfluorocycloalkenes.[222] A mixture of some electrophilic cyclic alkenes and caesium fluoride dissolved in DMF or tetraglyme to produce coloured solutions. These were shown by ^{19}F n.m.r. to contain no starting material and the spectra were consistent with the relevant carbanions (see Table 19). The dissolved carbanions could be quenched with a variety of electrophiles to give characterisable products with virtually no reversion to precursor alkenes.

In 1981, Russian workers reported the use of α-fluoroalkylamides[223-225] as new sources of non-hydrated fluoride ion. N,N,N',N'-Tetramethylformidinium bifluoride (205) reacted with fluorinated alkenes[225] by both addition of fluoride ion and hydrogen fluoride to the double bond. The resulting mixture, therefore, contains both the relevant carbanion (206) and its conjugate C–H acid (207).

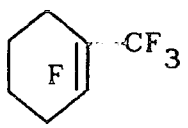


(205) (206) (207)

Carbanion (206) competes for the proton on (207) and the system is too dynamic at room temperature to observe the discrete species. However, cooling between -50°C and -100°C leads to resolution, in the ^{19}F n.m.r., of the resonances corresponding to (206) and (207).

Table 20 Carbanions observable at low temperatures from (205)

Conditions: (205) + alkene, room temp., CH_3CN

ALKENE	PRODUCTS
$(CF_3)_2C{=}CFC_2F_5$ (29)	$(CF_3)_2\bar{C}{-}C_3F_7$ + $(CF_3)_2\overset{H}{\underset{\vert}{C}}{-}C_3F_7$
$(CF_3)_2C{=}CF_2$ (4)	$(CF_3)_3\bar{C}$ + $(CF_3)_3C{-}H$
$C_3F_7(CF_3)C{=}CFC_2F_5$	$(C_3F_7)_2\bar{C}CF_3$ + $(C_3F_7)_2\overset{H}{\underset{\vert}{C}}CF_3$
	

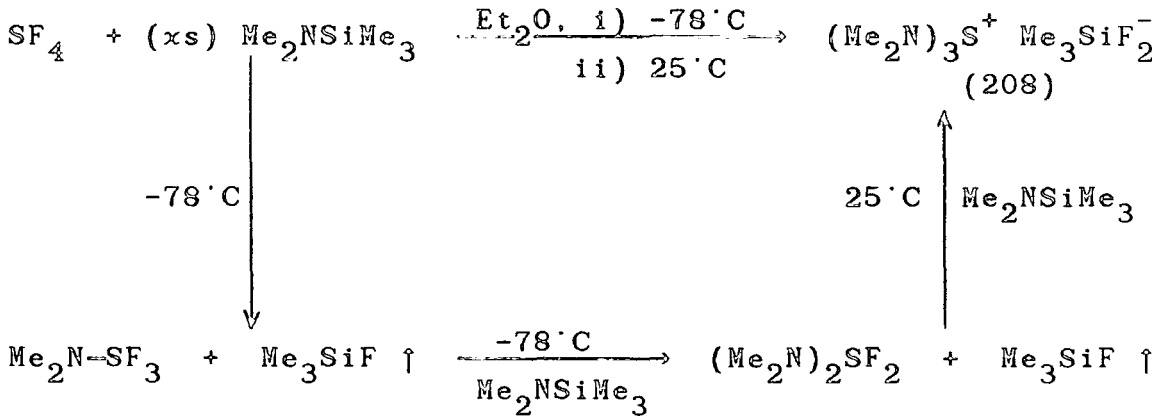
It has been known for some time that perfluoroisobutene (4)[130] and hexafluoropropene dimer (29)[136] form stable complexes with caesium fluoride in suitable solvents. Curiously, however, spectroscopic studies of these materials were not presented in the open literature. A report of the ^{19}F n.m.r. of $CF_2{=}C(CF_3)_2$/CsF/diglyme system is made in a review article[130] in which a very broad single resonance at *ca.* 50 ppm (upfield from $CFCl_3$) is observed. Since this spectrum is also produced by the addition of a deficiency of caesium fluoride and in the light of our recent studies this clearly results from a rapidly exchanging system not containing solely the perfluoro^{t}butyl carbanion (101).

4.A.b TAS-F (208)

During the course of our work we became aware of a similar investigation by workers from Du-Pont using

trisdimethylaminosulphonium trimethylsilyldifluoride (208), or TAS-F for short, as a potent soluble fluoride ion donor.

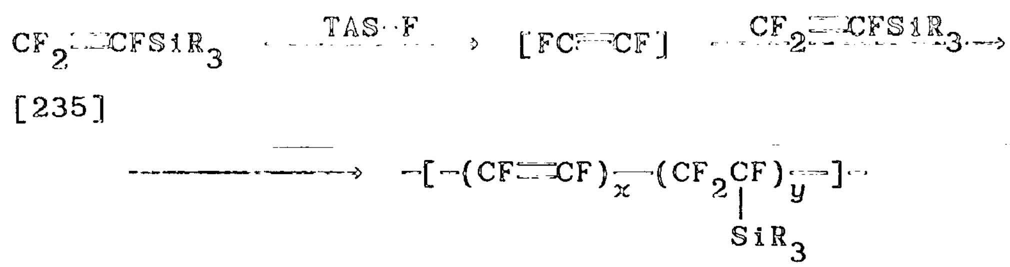
The family of tris(substituted amino)sulphonium salts, including the title compound, were reported in 1976.[226] TAS-F itself is readily synthesised by the reaction of an ethereal solution of sulphur tetrafluoride with N,N-dimethyltrimethylsilylamine, initially at low temperatures. The resulting white solid may be stored under dry nitrogen in glass apparatus and used as required in acetonitrile solution.



We have operated the synthesis of TAS-F using this procedure on a number of occasions (see experimental section) and have found that, for the scale of material (*ca.* 5g) we required, the use of a Schlenk tube (for both manufacture and storage) facilitates the use of dry nitrogen and vacuum essential for the handling of the material.

TAS-F has been employed in halogen exchange reactions,[226] as a catalyst in the group transfer (living) polymerisation of acrylate monomers,[227-229] as a reagent for desilylation reactions[230-235] and recently with unsaturated polyfluoro-compounds. Hiyama and co-workers have used TAS-F

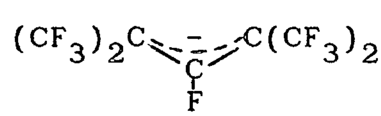
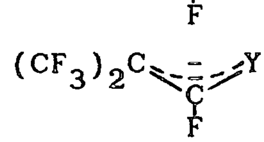
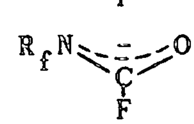
in the de-silylation of trifluorovinyl silanes and obtained conjugated polymers containing the difluoroacetylene monomer unit.[235]



Since the start of our work the Du-Pont workers have brought out publications on the synthesis and characterisation of TAS-fluorinated allyl and heteroallyl compounds,[236] TAS-fluorinated alkoxides[119] and very recently on TAS-fluorocarbanion salts.[237] In the first case, TAS-F was added to trifluoromethyl substituted allenes, ketenes, thioketenes and isocyanates to produce TAS^+ salts of the relevant allyl and heteroallyl derivatives.[236]

<u>Table 21</u> <u>Synthesis of TAS/allyl and heteroallyl salts</u>[236]

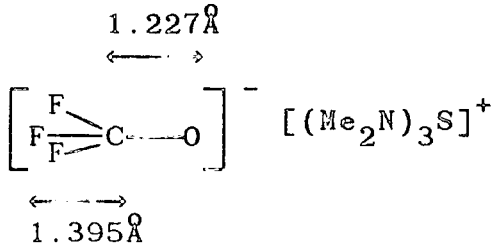
Conditions: electrophile + TAS-F, THF, 0°C

<u>ELECTROPHILE</u>	<u>ANION</u>
$(CF_3)_2C{=}C{=}C(CF_3)_2$	
$(CF_3)_2C{=}C{=}Y$ Y=O,S	
$R_f{-}N{=}C{=}O$ $R_f=CF_3, {}^nC_3F_7$	

The systems were examined by ^{19}F n.m.r. spectroscopy which was used to calculate rotational barriers in the products.

Carbonyl difluoride was reported to react with

TAS$^+F^-$[119] to yield isolable salts of crystallographic quality. The trifluoromethoxide ion was shown by the resulting X-ray data to contain extraordinarily long C-F bonds and an unusually short C-O bond. This has been used to infer substantial contributions from negative hyperconjugation to the crystallographic environment of CF_3-O^- and constitutes by far the best evidence so far as to the structural importance of the effect.



$[(Me_2N)_3S]^+$

Compare:

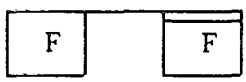
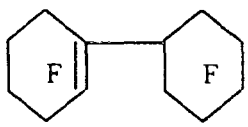
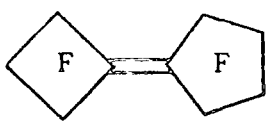
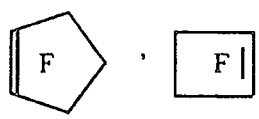
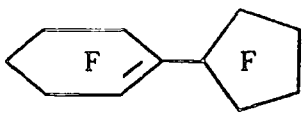
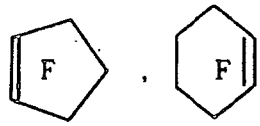
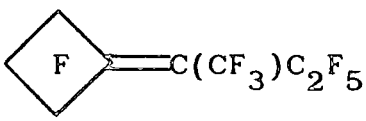
CF_3OR	C—F	1.32Å
	C—O	1.37Å

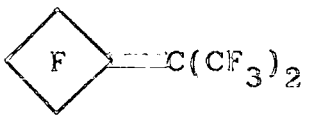
4.B DISCUSSION

4.B.a Sources of Fluorinated Alkenes

The alkenes which were used frequently in this study are shown in Table 22 (below) together with their method of preparation. Most were available through simple oligomerisation procedures, as described in Chapter One.

Table 22 Sources of fluorinated alkenes[1]

ALKENE	METHOD OF PREPARATION	REF.
 (127)	 , pyridine, RT	[160]
 (141)		
	 , CsF, DMF, 150°C[2]	[160]
	 , pyridine, RT	[160]
	 , CsF, DMF, 80°C[2]	[160]
	 , $CF_3CF{=}CFCF_3$, CsF, DMF, RT[2]	[160]



$CF_2{=}CFCF_3$, CsF, DMF, RT [2] [160]

$C_2F_5(CF_3)C{=}CFCF_3$ (197)

$C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$ (82)

$R_f(CF_3)C{=}CFCF_3$
$R_f{=}CCF_3(C_2F_5)_2$ (82)

3

$CF_2{=}CF_2$, CsF, diglyme, 200°C, 20psi [3] [153]

3

$(CF_3)_2C{=}CFC_2F_5$ (29)

$CF_2{=}CFCF_3$, CH_3CN, CsF, RT with agitation

$(CF_3)_2CFCF{=}CFCF_3$ (196)

$CF_2{=}CFCF_3$, CH_3CN, CsF, RT no agitation

$CF_2{=}C(CF_3)_2$ (4)

$CF_2{=}CFCF_3$, Ni tube, 650°C [4] [238]

1. *Perfluoro-propene, -cyclobutene and -cyclopentene (and the fluoroaromatics) are commercially available and are routinely synthesised by technical staff.*
2. *Performed by Dr. G. Taylor (these laboratories).*
3. *We acknowledge a kind donation by ICI plc (Mond Division)*
4. *Perfluoroisobutene (4) is extremely toxic by inhalation. Rigorous time consuming precautions including complete containment in a vacuum line and efficient fumes hood and the wearing of breathing apparatus were considered essential for the handling of this material.*

We are indebted to Mr. T. F. Holmes for help during this experiment.

4.B.b Generation and attempted generation of perfluoroalkyl carbanions

i) With caesium fluoride

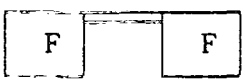
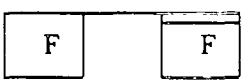
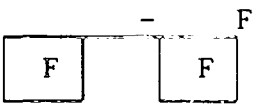
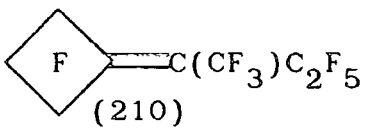
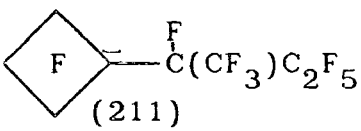
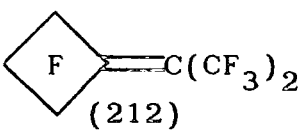
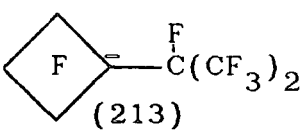
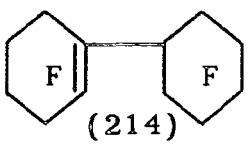
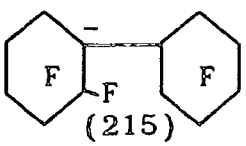
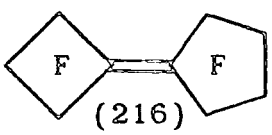
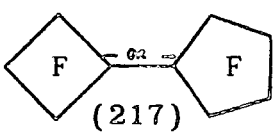
As described earlier, many workers have noted stable complexes with fluorinated alkenes and caesium fluoride. Virtually none of these observations have been supported by spectral observations which could be attributed to the respective carbanions. We are now able to report that by simply choosing the best solvent many perfluorocarbanions are available. Chambers and Taylor (these laboratories)[160] obtained observable cyclic fluorocarbanions by stirring the alkenes with caesium fluoride in DMF solvent at room temperature. In the current investigation, tetraglyme was found to be the superior solvent *ie.* CsF/DMF did not generate appreciable concentrations of anion (220) on prolonged contact. Simply stirring the alkene precursor with dried and ground caesium fluoride in tetraglyme at room temperature lead to sometimes total dissolution of the normally insoluble starting materials and formation of brightly coloured transparent solutions. These could be removed, studied by ^{19}F and ^{13}C n.m.r. and then used for further reactions. If care was taken the perfluorocarbanion solutions could be stored indefinitely under dry nitrogen and used as stock solutions when required.

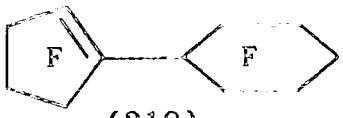
It is important to note that Taylor[160] has demonstrated that, with the most readily available cyclic carbanion (209), one molecular portion of caesium fluoride is dissolved for each portion of the alkene (127) and all the carbanions described in this study afforded clean, well coupled, characteristic spectra containing no trace of the

precursor materials. We can conclude, therefore, that within the limits of detection, the sytems are wholly in the form of the respective anions. The spectroscopic proof and trapping experiments of the carbanion structures will be described later.

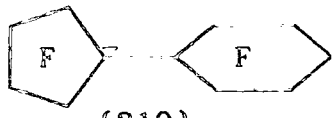
Table 23 Generation and attempted generation of caesium perfluorocarbanions

Conditions: alkene + CsF $\xrightarrow[\text{solvent}]{\text{room temp.}}$ carbanion$^-$ Cs^+ solution

ALKENE	SOLVENTS[1]	CARBANION
 (127)	tetraglyme DMF	 (209)
 (141)	tetraglyme DMF	
 (210)	DMF[2]	 (211)
 (212)	DMF[2]	 (213)
 (214)	tetraglyme DMF[2]	 (215)
 (216)	tetraglyme DMF[2]	 (217)


(218)

DMF[2]


(219)

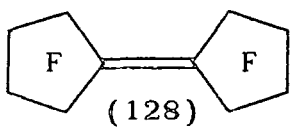
$CF_2{=}C(CF_3)_2$ (4) — tetraglyme — $(CF_3)_3C^-$ (101)

$C_2F_5(CF_3)C{=}CFCF_3$ (197) — tetraglyme DMF CH_3CN — $(C_2F_5)_2\bar{C}CF_3$ (220)

$(CF_3)_2C{=}CFC_2F_5$ (29) — tetraglyme DMF CH_3CN — $(CF_3)_2\bar{C}C_3F_7$ (221)

$CF_3R_fC{=}CFCF_3$ (83) $R_f{=}CCF_3(C_2F_5)_2$ — tetraglyme CH_3CN — $CF_3R_f\bar{C}C_2F_5$ (222)

$C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$ (82) — tetraglyme DMF[2] — *not formed*


(128)

tetraglyme — *not formed*

1. *Solvents tolerated are underlined.*
2. *Systems studied by Dr. G. Taylor see ref.*[160].

Several observations are worthy of note in this section of work:-

a) Under no circumstances have any long-lived α-fluorocarbanions been formed with the CsF/tetraglyme system (or any other F^- source reported to date). This seems to reiterate the known destabilising effect of fluorine bonded directly to an anionic centre (see Chapter One). Hence, all the perfluorocarbanions described in this section have a $R_{f3}\bar{C}$ structure in which a fortuitous combination of

electronic stabilisation and steric hindrance to further reaction, ie. oligomerisation, are found.

eg. $CF_2{=}C(CF_3)_2$ (4) $\overset{(CsF)\ K}{\rightleftharpoons}$ $(CF_3)_3\dot{C}$ persistent $\xrightarrow{(4)\ k}$ *oligomers*

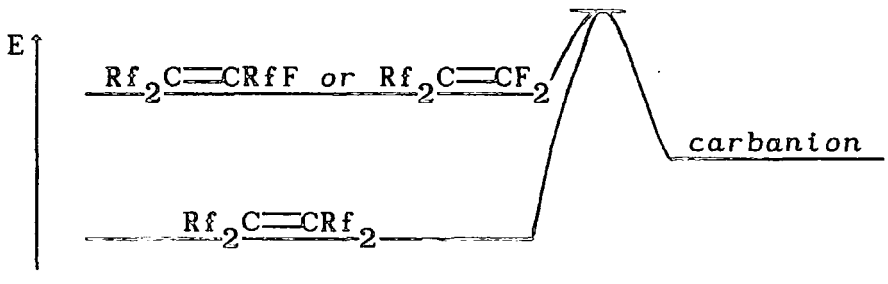
$CF_2{=}CFCF_3$ (1) $\overset{(CsF)\ K}{\rightleftharpoons}$ $(CF_3)_2\dot{C}F$ transient $\xrightarrow{(1)\ k}$ *oligomers*

For (4), K large and k slow

For (1), K smaller and k faster

b) Unusually, internal alkenes which are not connected to a four-membered ring have never been induced to generate significant concentrations of the respective carbanions even though they possess favourable tertiary structures. Thus compounds (83) and (128) (see Table 23) appear unaffected by stirring with caesium fluoride in tetraglyme at room temperature.

It seems likely that, in these cases, the initial state energies of the alkenes are sufficiently low (see Chapter One) to bias the equilibrium in favour of the starting materials.



initial state energies

$$\text{Alkene} \underset{K}{\overset{CsF}{\rightleftharpoons}} \text{carbanion} \longrightarrow \text{prods.}$$

Only when the olefins possess vinyl fluorine atoms or small

rings to raise their initial energy will the equilibrium favour the required carbanion.

c) Solvents tolerated by the caesium perfluorocarbanion salts appear very limited and the reason for this is not entirely clear. The two solvents which have been successful in this study, tetraglyme and DMF, are unfortunately particularly involatile and attempts made to isolate crystals of high quality from (221), (220) and (209) by various methods have not been profitable. Simple cooling of solutions of (221), (220), and (209) down to *ca.* -40°C did not produce any solid material. In addition, controlled diffusion of a non-solvent (toluene) into a tetraglyme solution of (220) only served to regenerate precursor alkene (197) and caesium fluoride.

d) The solution of the perfluoro^{t}butyl carbanion (101) was one of the most concentrated of those made in the study as evidenced by the short period required to accumulate a high quality ^{13}C n.m.r. spectrum. Simply cooling the solution to about +15°C lead to the formation of needle like crystals which, in time, resulted in almost complete solidification of the mixture. Residual solvent could be removed by pipette under a nitrogen plume and the resulting solid readily re-dissolved in tetraglyme to produce an identical carbanion spectrum. The precursor alkene (4) is a gas at room temperature (b.p. *ca.* 5°C) and had it been present would have been driven off during the procedure described. Since caesium fluoride is almost completely insoluble in the solvent and no solid residue was

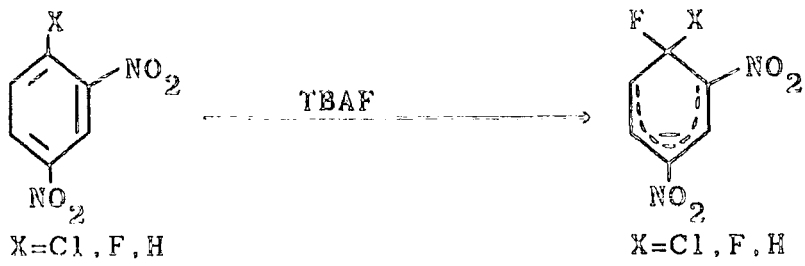
observed in the re-dissolution we can conclude that this constitutes the isolation of a *solid perfluoroalkyl caesium* salt with no detectable reversion to alkene and caesium fluoride. As far as we are aware, this is the first reported case of such an observation with a saturated perfluorocarbanion. Similar observations have been made with Meisenheimer complex (204)(see page 121)[221] which could even be isolated as a glass by heating the relevant aromatic compound with caesium fluoride in the absence of solvent.

ii) Potassium fluoride

Potassium fluoride is a poorer fluoride donor than caesium fluoride and was only effective in our systems with perfluorobicyclobutylidene (127). Notably, the relatively readily available alkene (29) did not generate substantial concentrations of the respective carbanion (221) with KF in both DMF and tetraglyme and in the presence and absence of added 18-crown-6 ether.

iii) Tetrabutylammonium fluoride

In our search for new soluble fluoride sources which would provide different counterions for the perfluorocarbanions we occasioned by literature claims that commercial tetrabutylammonium fluoride (TBAF) trihydrate could be 'dried' without significant decomposition.[239] The resulting oil was found to be a material of high fluoride ion activity in halogen exchange and base induced reactions. Clark and co-workers[240] even claimed long-lived Meisenheimer complexes by fluoride addition from TBAF to activated aromatic compounds.



X=Cl, F, H X=Cl, F, H

Closely following the literature procedure,[239] we subjected commercial $Bu_3NF.3H_2O$ to high vacuum at temperatures between 40 and 45°C for 24 to 48 hours. In our hands the sample thus treated lost a variable proportion of its original weight (lit.[239] 20%) up to about 50%. Clearly, in these cases significant decomposition of the fluoride had occured, most probably by the mode reported by Sharma and Fry.[241]

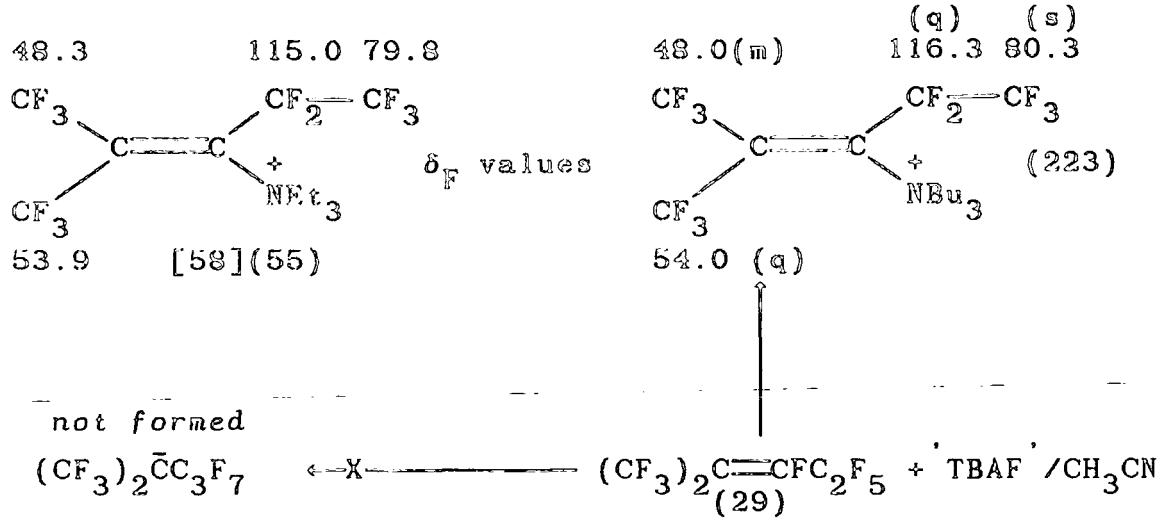
$$^{n}Bu_4NF.3H_2O \xrightarrow{40\text{-}70^{\circ}C} {}^{n}Bu_4NF \xrightarrow[elimination]{immediate\ E_2} {}^{n}Bu_4N^{+}\ HF_2^{-} + {}^{n}Bu_3N$$

[241]

$$+\ 3H_2O$$

$$CH_3CH_2CH{=}CH_2\uparrow$$

Nevertheless, the resulting oils showed high fluoride ion activity in the oligomerisation of hexafluoropropene in acetonitrile at room temprature to give predominantly trimers and higher oligomers. In addition, an immediate reaction was noted between alkene (29), which is a stable carbanion precursor, and an acetonitrile solution of the dried TBAF. The resulting straw coloured solution afforded a curiously broad n.m.r. spectrum clearly not containing any of the desired carbanion (221). However, reduction of the solution volume by application of vacuum lead to considerable sharpening of the spectrum which then bore a striking resemblance to that reported by Ishikawa[58] for alkenylammonium derivative (55).



Compound (55) resulted simply from contact of triethylamine in acetonitrile with (29)[58] and it is almost certain, therefore, that large amounts of tributylamine in the 'dried' TBAF lead to the product assigned the structure (223). Similar observations were noted for isomeric alkene (197) and an unusual spectrum was obtained for perfluorocyclobutene. In none of the cases in the study were carbanions identified and the reactions of TBAF were not persued further.

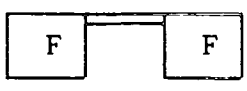
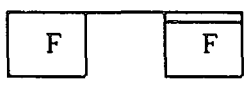
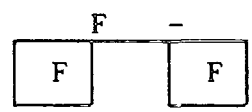
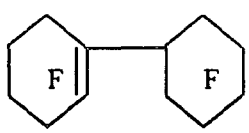
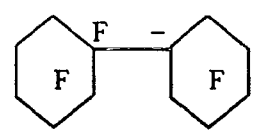
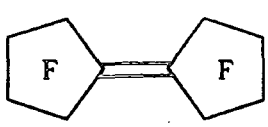
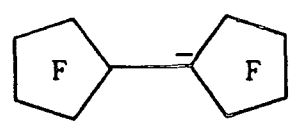
Table 24 Reactions between 'anhydrous' TBAF and fluorinated alkenes

ALKENE	DESCRIPTION OF REACTION
$CF_2{=}CFCF_3$ (1)	Majority of material oligomerised: predominant isomer-trimers. evidence of $(CF_3)_2C{=}C(C_2F_5)\overset{+}{N}Bu_3$ in solvent.
F (107)	unidentified crystalline solid formed.
$(CF_3)_2C{=}CFC_2F_5$ (29)	Almost quantitative conversion to (223).
$C_2F_5(CF_3)C{=}CFCF_3$ (197)	n.m.r. spectrum consistent with $C_2F_5(CF_3)C{=}CCF_3\overset{+}{N}Bu_3$ *ca.* 50%
$CF_3(C_2F_5)C{=}C(CF_3)C_2F_5$ (82)	Immediate exothermic reaction but only (82) recovered (83%).

iv) With TAS-F As soon as we became aware of claims for a high fluoride activity[242] from TAS-F and potential use in polyfluorinated electrophiles we undertook to generate the persistent carbanions observed in the caesium fluoride study. In parallel with this workers from Du-Pont made a similar investigation and published their results very recently.[237]

Table 25 Generation and attempted generation of stable fluorocarbanions using TAS-F

Conditions: Alkene + TAS-F $\xrightarrow[\text{room temp.}]{CH_3CN}$

ALKENE	PERFLUOROCARBANION
$(CF_3)_2C{=}CFC_2F_5$ (29) $(CF_3)_2CFCF{=}CFCF_3$ (196)	$(CF_3)_2\bar{C}C_3F_7$ (221)[1]
 (127)  (141)	 (209)[1]
 (214)	 (215)[1]
 (128)	 (224)
$C_2F_5(CF_3)C{=}C(CF_3)C_2F_5$ (82)	$C_2F_5(CF_3)CF{=}\bar{C}(CF_3)C_2F_5$ (225)[1]
$C_2F_5(CF_3)C{=}CFCF_3$ (197)	*not formed in our hands* $(C_2F_5)_2\bar{C}CF_3$ (220)

1. *Also recently produced by workers from Du-Pont see refs.* [237 *and* 243].

The mode of action of TAS-F with a fluoride receptor

molecule (X) is shown below:-

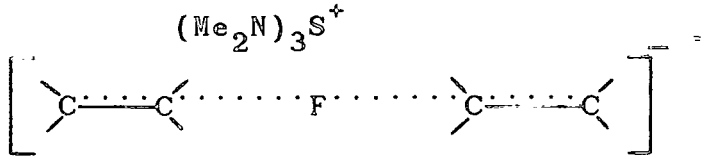
$$TAS\text{-}F + X \longrightarrow XF^- + (Me_2N)_3S^+ + Me_3SiF\uparrow$$

The volatile trimethylfluorosilane fragment appears to act as a fluoride ion carrier and is ejected on fluoride donation. Compound $(Me_2N)_3S^+ F^-$, as opposed to the hypervalent silicon compound (208)(TAS-F), is not available and attempts[244] to isolate it have so far been unsuccessful. Clearly, on loss of Me_3SiF, the simple reverse reaction, *ie.* loss of fluoride ion from the substrate, is no longer able to take place and this may be partly responsible for the claimed high F^- activity of TAS-F. It is also noteworthy, however, that this may negate the application of TAS-F in the mass of reactions of synthetic utility which require fluoride ion catalysis.

The generation of caesium perfluorocarbanion salts in solution is particularly insensitive to reaction stoichiometry. Thus a large excess of either the alkene or caesium fluoride does not appear to affect the spectrum as the excess material is not soluble in the relevant solution. This is not the case with TAS-F and the first observation we made was that very broad spectra of the perfluorocarbanions, especially for resonances corresponding to β-positions, were generated when the reagent was used in deficiency. The ^{19}F n.m.r. spectra on page 140 show the result of the addition of excess TAS-F (upper spectrum) and a deficiency of TAS-F (lower spectrum) to hexafluoropropene dimer (29). A clearly coupled sharp spectrum is evident in the former case, whereas in the latter case coupling is absent and resonances


1. CsF or excess TAS-F
$(CF_3)_2C{=}CFC_2F_5$
F^-
CF_3 a CF_3
C
(2.2.1)
CF_2 b
CF_2 c
CF_3 d
1
d
a
b
c
$CFCl_3$
2. deficiency TAS-F
0
25
50
75
100
100
125
ppm

attributed to groups adjacent to charge are severely broadened. Also, with excess alkene we were surprised to find that all the alkene was taken up into solution. The most likely explanation for this phenomenon is that rapid exchange for the fluoride ion donated (by TAS-F) holds more than a single molecular equivalent of alkene in solution and gives the observed n.m.r. spectrum.



This could involve some form of bridged fluoride species akin to the iodinides isolated recently by Chemists from Du-Pont.[245]

$$(Me_2N)_3S^+ \qquad\qquad (Me_2N)_3S^+$$
$$(CF_3)_3\bar{C} + (CF_3)_3CI \longrightarrow [CF_3)_3C....I....C(CF_3)_3]^-$$

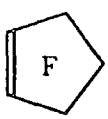
When experiments are being planned which require a deficiency of the fluoride source it is worthwhile to note that obvious problems are to be associated with the TAS-F salts which are not found with the caesium analogues. Addition of excess TAS-F in CH_3CN, however, leads to efficient generation of the perfluorocarbanions and affords clean well coupled spectra, as observed with CsF. Furthermore, alkene (128) which does not give an appreciable concentration of the carbanion (224)(see Table 25) with caesium fluoride does do so with TAS-F. We have been unable, in repeated attempts with different conditions, to observe

the perfluorocarbanion (225)(see Table 25) but the Du-Pont workers claim[237] this species is formed in a manner identical to the others. One curious feature of the n.m.r. spectra generated by the addition of excess TAS-F to fluorinated alkenes is that the excess TAS-F cannot be readily observed in the ^{19}F n.m.r (δ 59.2 ppm); the only extra resonances in the spectra being broad signals around 150 ppm or 80ppm. It is possible that any excess TAS-F is destroyed in some way by a catalytic action of the TAS perfluorocarbanion salt.

Attempts at generating α-fluorocarbanions by the action of excess TAS-F on cyclic fluorinated alkenes (107) and (154) and hexafluoropropene (1) were not successful. Only anions (209, 224, and 221) formed *via* dimerisation of the respective olefins were observed in good yield.

Table 26 TAS-F with (107), (154) and (221)

Conditions: TAS-F(*excess*) + alkene $\xrightarrow[CH_3CN]{\text{room temp.}}$

ALKENE	PRODUCT $[(Me_2N)_3\overset{+}{S}$ salts$]$
 (107)	 (209)
 (154)	 (224)
$CF_2{=}CFCF_3$ (1)	$(CF_3)_2\bar{C}C_3F_7$ (221)

v) With caesium fluoride and added reagents

In view of our observations and spectroscopic studies (section 4.B) it was felt that the TAS-F reagent was, at best, only slightly more potent than conventional

CsF even though the latter acts in a heterogeneous manner. Clearly, any additive which might increase the solubility of CsF in the reaction medium could dramatically improve its effectiveness in carbanion forming reactions. Firstly, we attempted to mirror the action of TAS-F itself, using a hypervalent silicon anion as the fluoride ion carrier until it could be donated to the target electrophile.

Proposed method

$$CsF + Me_3SiF \longrightarrow X \dashrightarrow Cs^+ Me_3SiF_2^-$$

more soluble than CsF ?

Unfortunately, caesium fluoride was found to be unreactive to the fluorosilane when heated at 90°C and 125°C in tetraglyme for prolonged periods.

Very late in the current investigation we became aware of a commercially available cryptand (226) which, it was claimed,[246] aided the solubility of caesium salts in numerous solvents and dramatically improved reaction rates. Alkene (29) was reacted with caesium fluoride in the presence of (226) in CH_3CN, DMSO, and tetraglyme solvents. In all cases, ^{19}F n.m.r. spectra with only a hint of the normal coupling but clearly corresponding to the desired carbanion (221) were obtained.

$$\underset{(29)}{(CF_3)_2C{=}CFC_2F_5} + CsF + \underset{(226)}{N(CH_2CH_2OCH_2CH_2OCH_3)_3}$$

$$\downarrow$$

$$(CF_3)_2\bar{C}C_3F_7 \ (221) \ Cs^+ \quad + \quad (226)$$

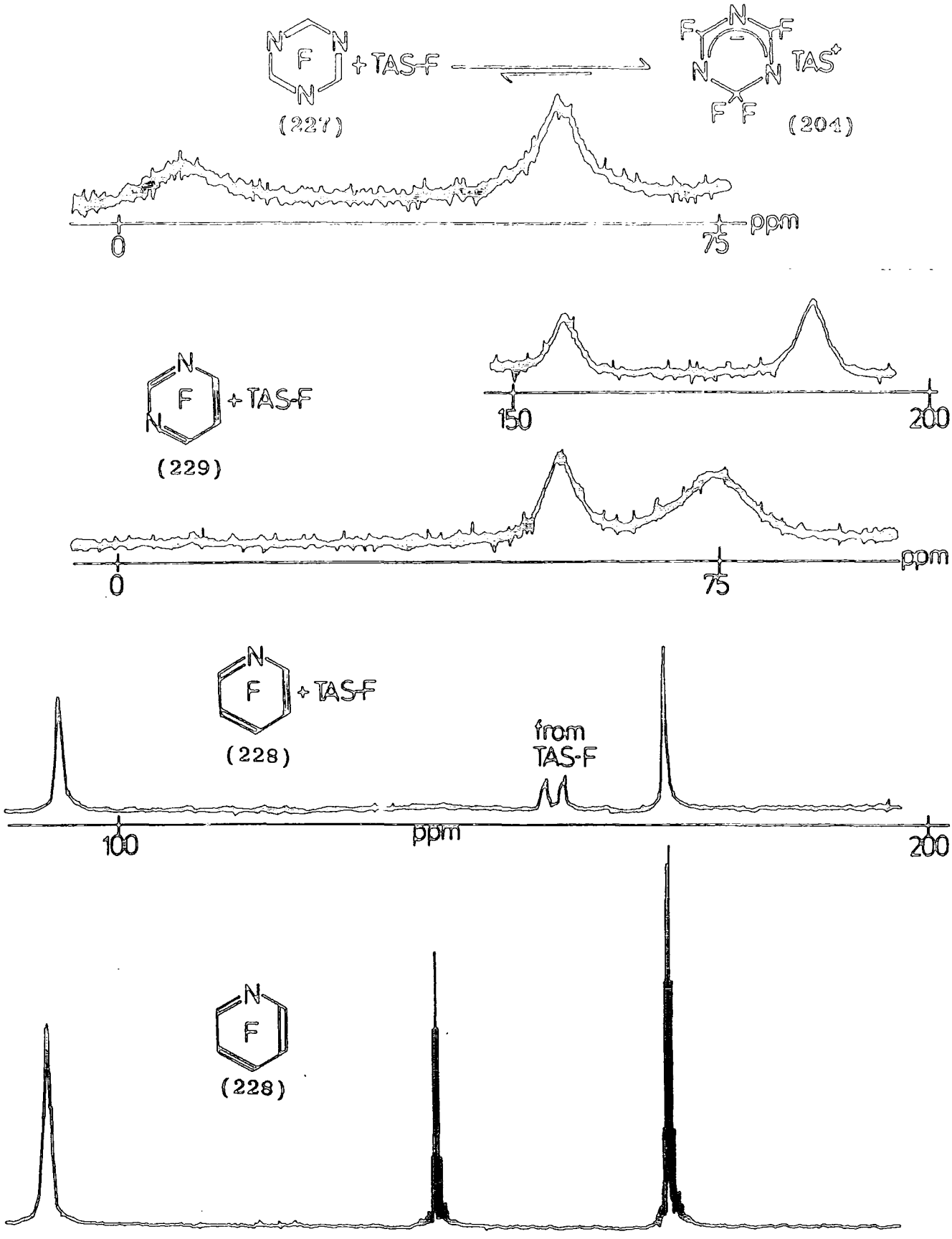
Solvents: DMSO, CH_3CN, tetraglyme

In the absence of (226) in tetraglyme a non-exchanging sharp ^{19}F n.m.r spectrum may be obtained albeit over a longer period of time. The extension of the range of solvents available as determined by these preliminary investigations is potentially of great importance as this opens up new avenues for the isolation of high quality crystals from the caesium perfluorocarbanions.

4.B.c TAS-F with fluoroheteroaromatic compounds

We have also studied the interaction of TAS-F with fluoroheteroaromatic compounds (227-229)(see spectra on page 145). Trifluoro-1,3,5-triazine (227) gave a ^{19}F n.m.r. spectrum very similar to the caesium Meisenheimer complex (204) observed previously[221] in these laboratories. Broad resonances are observed at *ca.* 7 and 56 ppm. corresponding to the C–F and CF_2 groups, respectively. The extent of the broadening exhibited by this species (also observed for the caesium analogue) indicates a measurable rate of exchange, presumably through loss of fluoride ion.

Pentafluoropyridine (228) with TAS-F afforded a spectrum similar to starting material except normal coupling was absent and the *para*-resonance was severely broadened. This is almost certainly a result of rapid exchange, initiated by the soluble fluoride ion, occurring through low concentrations of Meisenheimer complex (230). In this case, the exchange is probably so rapid that only the affected (*para*) position is severely broadened and the other (*ortho* and *meta*) positions remain relatively sharp, although uncoupled. Attack appears to take place at the most reactive *para*-position and this constitutes a rather neat method of

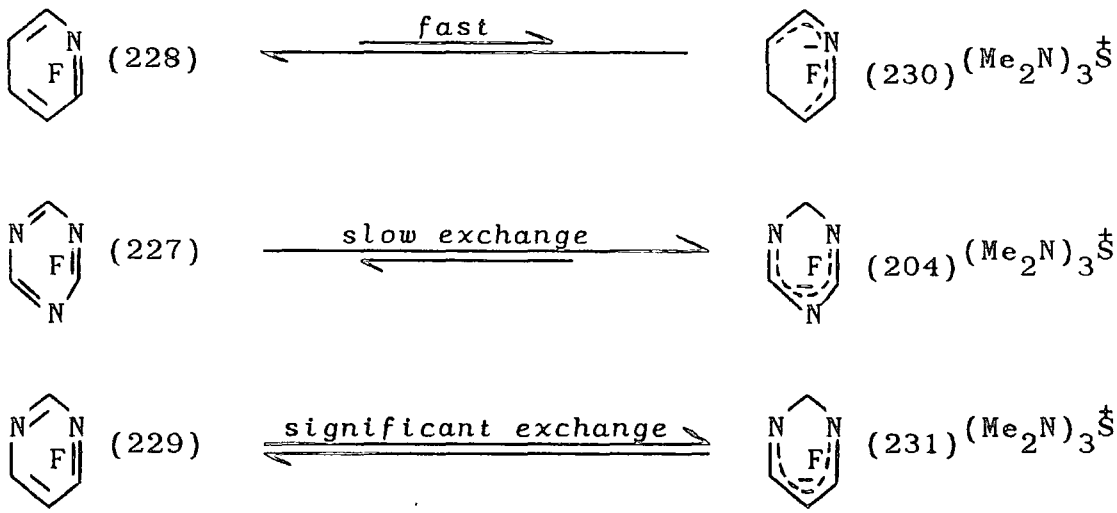


FLUOROHETEROAROMATIC COMPOUNDS WITH TAS-F

determining such information.

Tetrafluoropyrimidine (229) afforded a very broad spectrum which was not obviously either a broadened representation of (229) or an anionic derivative (231) but most likely a balanced average of the two structures. The linewidths are similar to the spectrum obtained for Meisenheimer complex (204) and, therefore, suggest a similar rate of exchange.

The above conclusions are in keeping with the known electrophilicities of the aromatics which follow the order (227) > (229) > (228). The relevant information is summarised by the following scheme in which the lengths of the arrows represent the position of the relevant equilibria.



4.B.d N.m.r. of long-lived perfluorocarbanion solutions

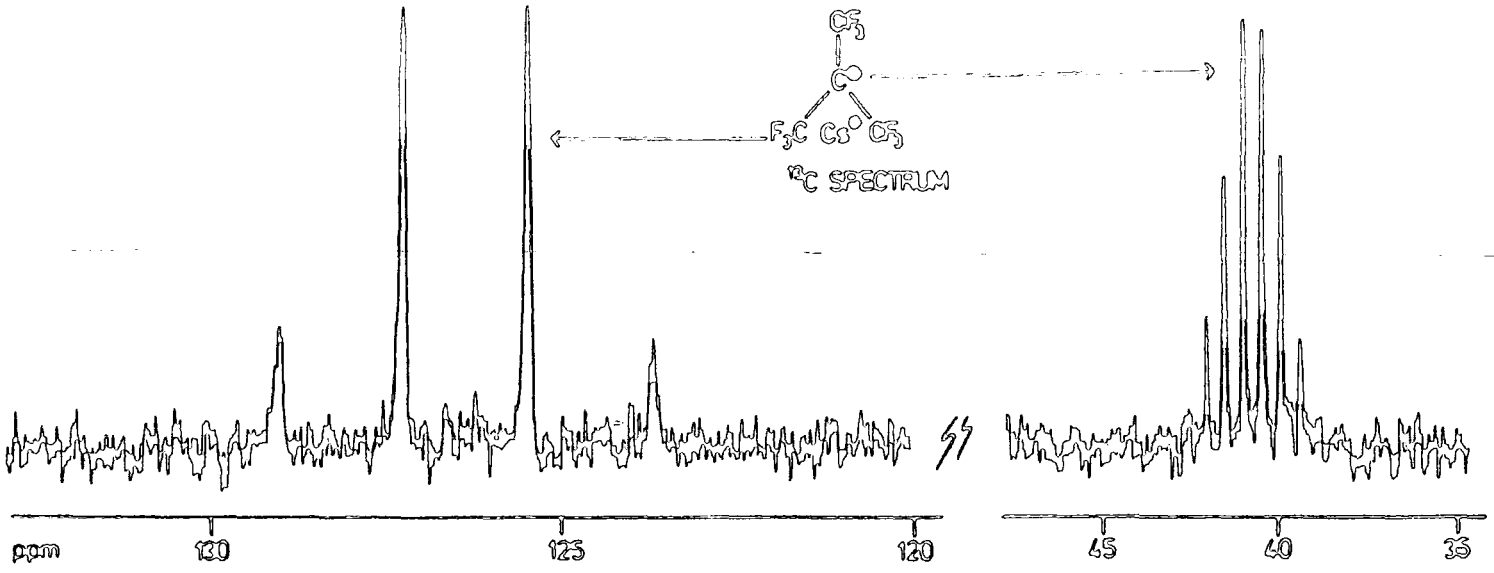
Some of the peculiarities of the ^{19}F n.m.r. spectra obtained during the TAS-F experiments have already been described in the earlier sections but a detailed analysis of the carbanion spectra have been reserved for this section. There are several features of the spectra which are worthy

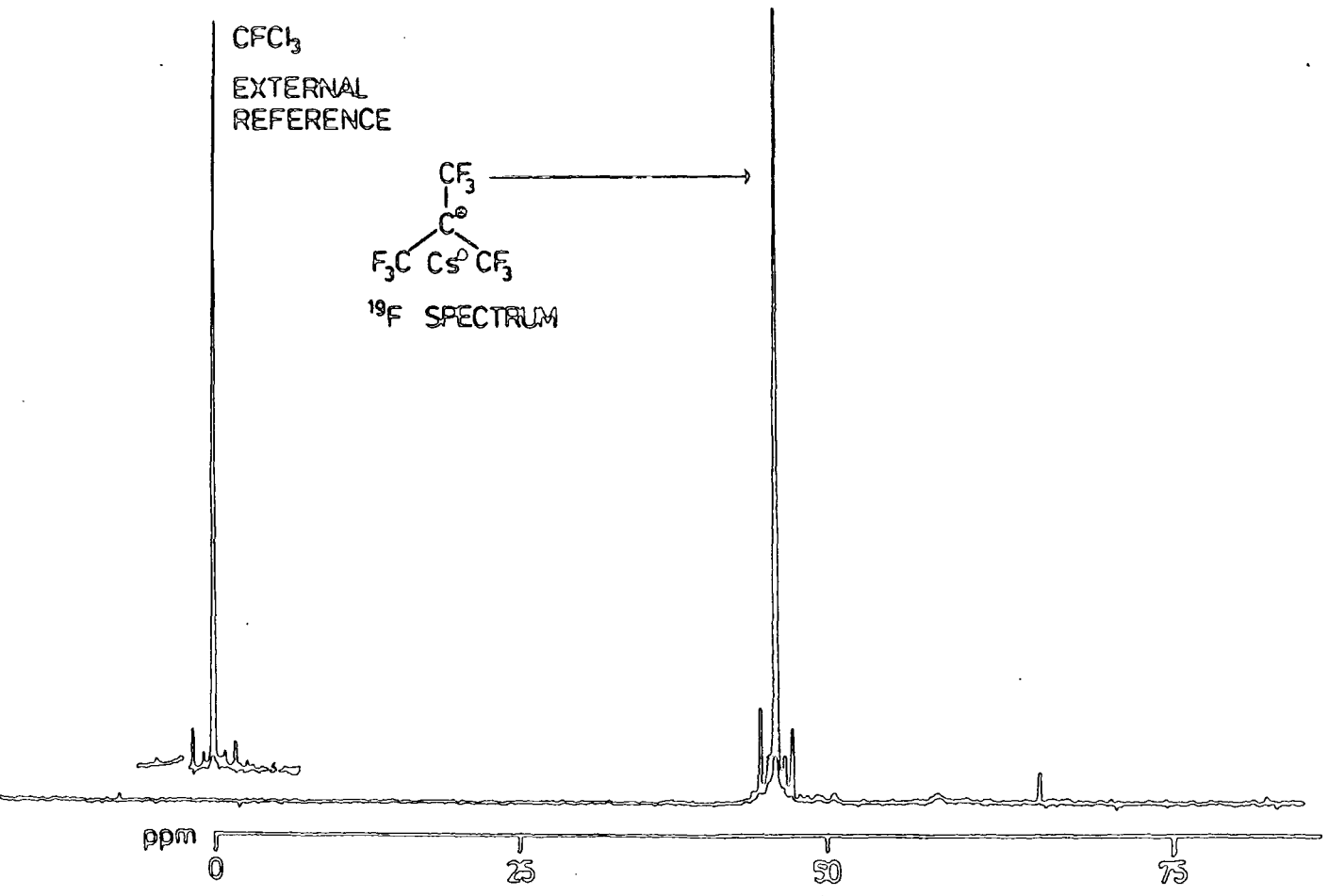
of note:-

i) Firstly, we reiterate that, both ^{19}F and ^{13}C n.m.r. spectra are sharp (low linewidths) and well coupled, indicating a slow (or zero) rate of exchange, and in most cases may be confidently assigned to the respective carbanions. As an example, the simplest case, the perfluoro^{t}butyl anion (101) afforded a single sharp singlet in the ^{19}F n.m.r. spectrum corresponding to the equivalent CF_3 groups, and two ^{13}C n.m.r. resonances. The high field decuplet corresponds to the anionic carbon (coupling to 9 equivalent fluorines) and the low field quartet (major coupling to three equivalent fluorines) to the trifluoromethyl carbons. The perfluoro^{t}butyl carbanion spectra are presented on page 148. No trace of starting materials can be observed in the carbanion solutions even with the sensitivity of the instruments at maximum, and hence, within the limits of detection the systems are wholly within the form of the respective static carbanions.

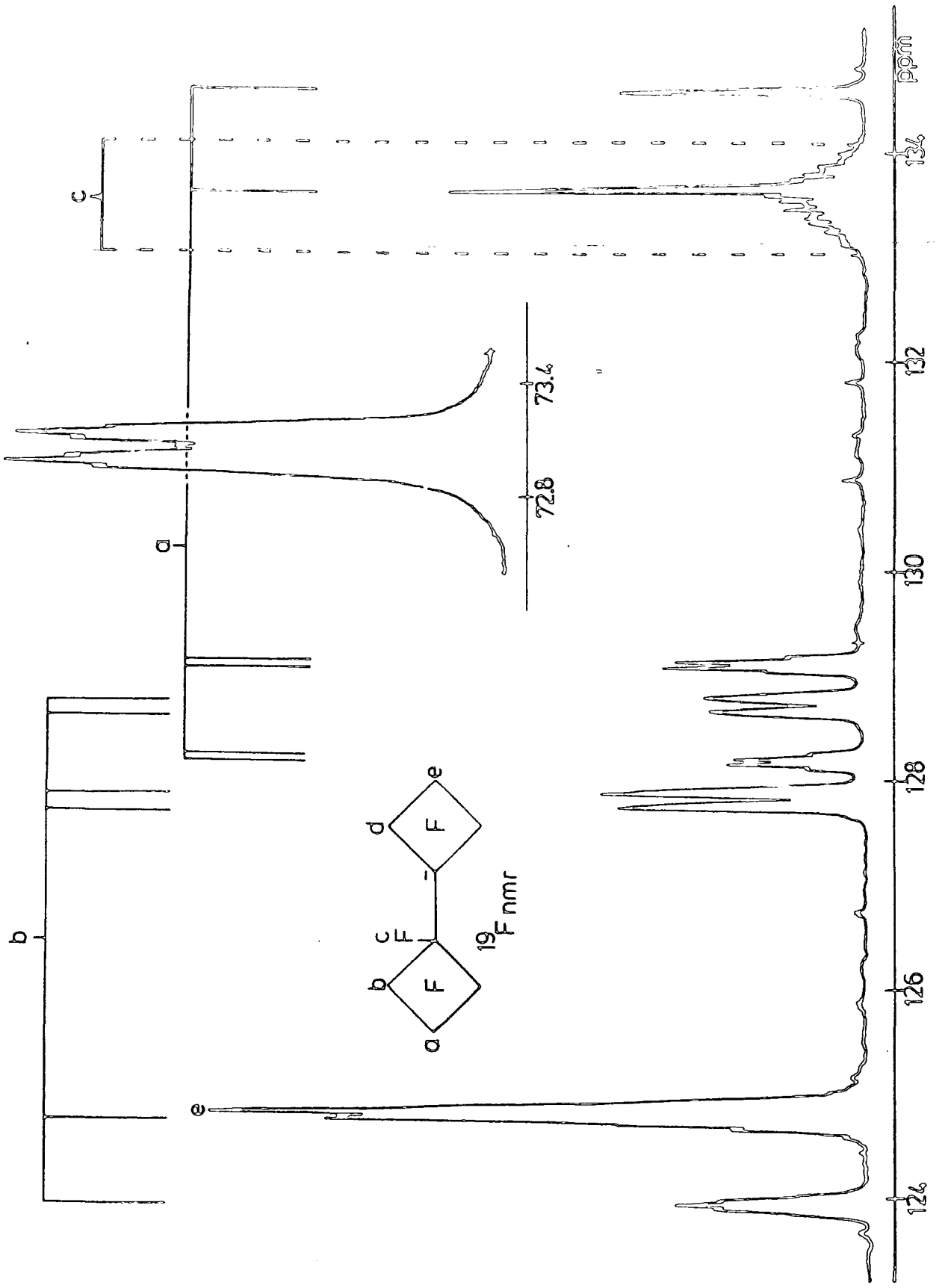
Earlier workers in these laboratories discovered some problems in assigning the ^{19}F n.m.r. spectra of the perfluorocycloalkyl anions (see section 4.A). Firstly, only resonances adjacent to the charged site, occuring at lower field than other resonances could be unambiguously assigned. More importantly, resonances corresponding to the tertiary fluorine (from the added fluoride ion) were conspicuously absent and this induced the authors to postulate dissociation of the carbanions with rapid internal return to the same carbon atom.

THE PERFLUORO t BUTYL CARBANION (101)

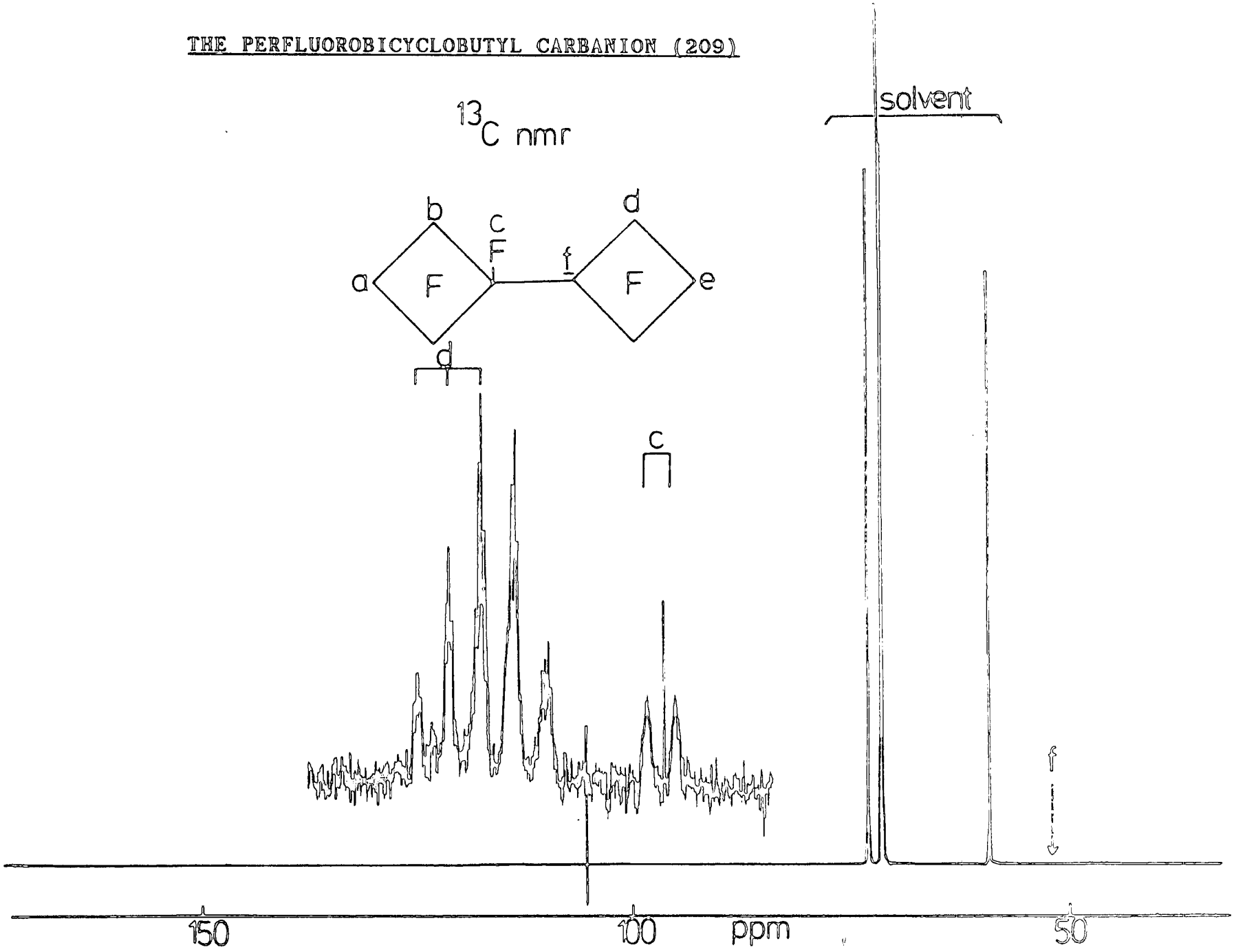




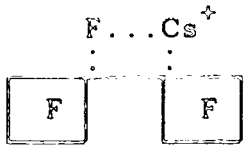
THE PERFLUOROBICYCLOBUTYL CARBANION (209)



THE PERFLUOROBICYCLOBUTYL CARBANION (209)



eg. for carbanion (209)

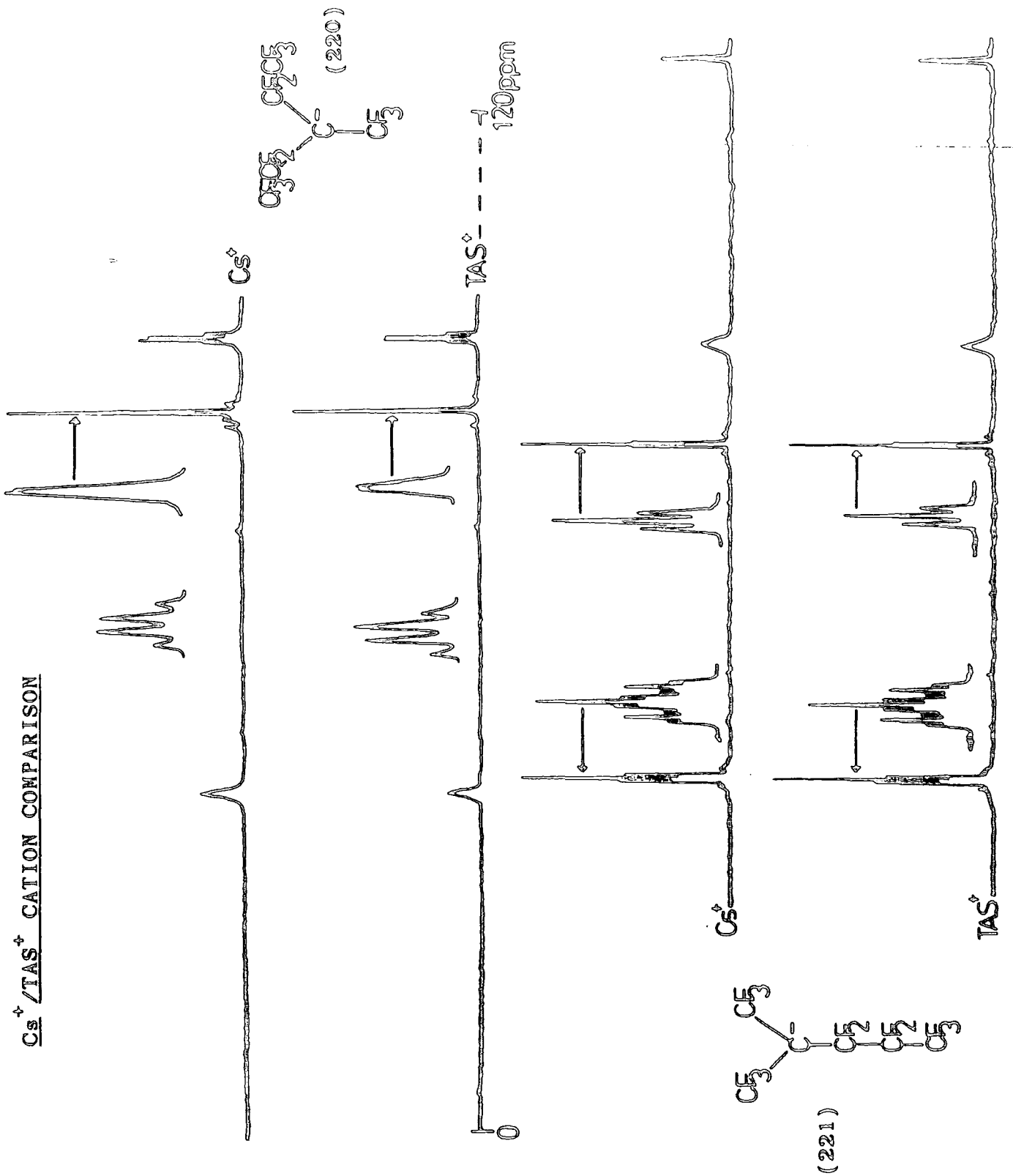


We have recently been able to command use of a higher quality n.m.r. instrument and the re-investigation of the spectra of the perfluorocycloanions initiated our current interest in the area. The perfluorobicyclobutyl carbanion (209) has now been studied in depth with high resolution spectrometers and the early problems associated with failure to observe the added tertiary fluorine have been solved. In addition to all others, this nucleus can be clearly observed in the ^{19}F n.m.r. spectrum at 133.6 ppm, partially hidden by a CF_2 resonance. Moreover, the ^{13}C n.m.r. spectrum picks out the relevant carbon as a distinct doublet centred on 96.5 ppm.

The ^{19}F and ^{13}C n.m.r. of the perfluorobicyclobutyl anion (209) are displayed on pages 149 and 150.

ii) <u>Counterion/solvent dependence</u> Although there are only a few systems available for a comparison of counteranions, there appears to be a striking similarity between the ^{19}F n.m.r. spectra of the carbanions with Cs^+ and TAS^+ cations. Minor concentration dependence of the chemical shifts precludes a very accurate comparison but on a normal sweep width the spectra of all the perfluorocarbanions with TAS^+ and Cs^+ counterions are completely indistinguishable. As an example, the ^{19}F n.m.r. of two isomeric carbanions (221) and (220) are shown on page 152.

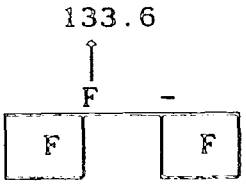
In the single case where we have been able to


Cs+ /TAS+ CATION COMPARISON
Cs+
TAS+
120ppm
(220)
(221)
Cs+
TAS+

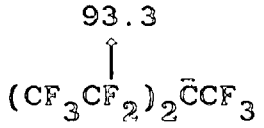
observe a potassium carbanion, *ie.* (209), this is also indistinguishable from its TAS^{+} and Cs^{+} analogues. This rather qualitative comparison is nevertheless quite prominent and strongly suggests that the perfluorocarbanion salts are truly ionic solution species. *ie.* there is a minimum of association $\overset{+}{M}—\ddot{C}$. This is to be contrasted with multitudes of other organometallic materials including the organolithiums in which a high degree of covalency exists in the bonding.[247]

iii) Chemical shift and coupling constant information

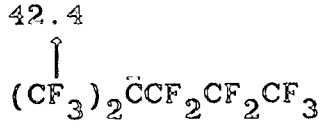
There exists an unusual and striking trend in the chemical shifts observed for all the perfluorinated carbanions we have been able to study. Aside from the expected upfield resonance for the carbon bearing the negative charge, both types of nuclei considered adjacent to the charge give resonances at distinctly lower field than would be expected. This effect is most pronounced for fluorine which may occur more than 30 ppm downfield from a neutral molecule position. Full tabulated chemical shift and coupling constant data for the carbanions and their derivatives are contained in Appendix 1. Examples of this effect for different fluorocarbon groups attached to a carbanionic carbon are shown below, but it should be noted that all the carbanions exhibit the same spectral features.



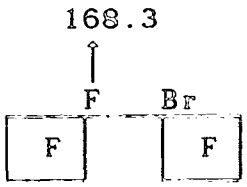
(209)

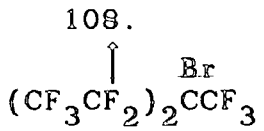


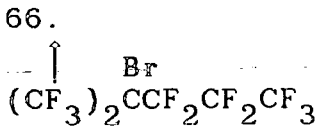
(220)



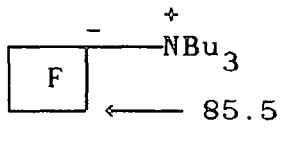
(221)



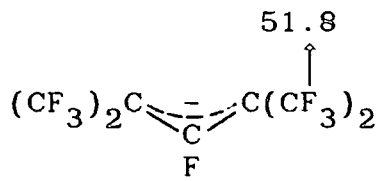




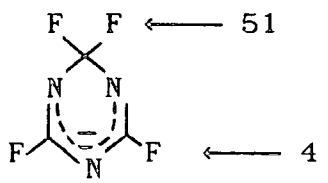
Other polyfluoro-compounds formally possessing a negative charge also display these now clearly defined downfield shifts to some degree. These include stable nitrogen ylids such as (232),[216] allyl anions, *eg.* (200),[137] and observable fluoro-Meisenheimer complexes *eg.* (204).[221]



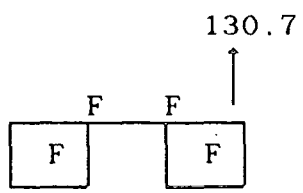
(232)



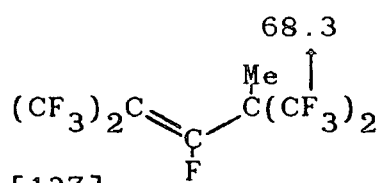
(200)



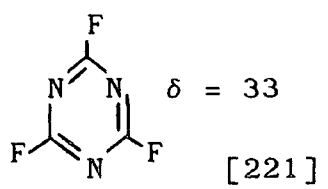
(204)



[30]



[137]

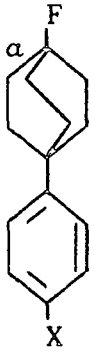


[221]

The prevailing theory[248] indicates that the presence of substituents which donate electronic charge to the local environment of a fluorine nucleus increase shielding and cause upfield shifts. These, however, were largely determined by measurements on aryl fluorides where the effects are believed[248] to reflect primarily changes in

fluorine π-electron density. In contrast, some work available concerning substituent chemical shifts (SCS) in aliphatic fluoride systems[248-250] indicate a *reverse substitution dependence*, *ie.* electron donating substituents cause deshielding and downfield shifts occur. Studies involving phenyl substituted bicyclo[2.2.2]octyl fluorides (233) clearly indicate that electron donating substituents cause downfield shifts in both ^{19}F and, to a lesser extent, ^{13}C n.m.r. and also reduce the $^{1}J_{CF}$ coupling constant.

Substituent chemical shifts and coupling constant changes



	X=H	CH_3	NH_2	$N(CH_3)_2$	CN	NO_2	$C(CN)_3$
^{19}F	0	0.09	0.21	0.33	-0.67	-0.75	-0.81
^{13}C (a)	0	0.02	0.13	0.18	-0.60	-0.63	-0.64
$^{1}J_{CF}$	0	0.0	-0.2	-0.3	0.9	1.0	1.1

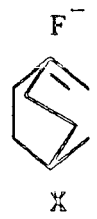
(233)

upfield increments and larger coupling constants are quoted positive

Similar observations were made for metallated bicyclo[2.2.2]octyl skeletons[249] and in both cases the SCS's and the substituent dependent $^{1}J_{CF}$ changes bore a linear relationship to each other. In the metallated derivatives (234) the effects described are reasonably pronounced and are attributed to hyperconjugative interactions exemplified by structures (235) and (236).

X = $PbMe_3$, $GeMe_3$, $SiMe_3$, $SnMe_3$


(234)


(235)


(236)

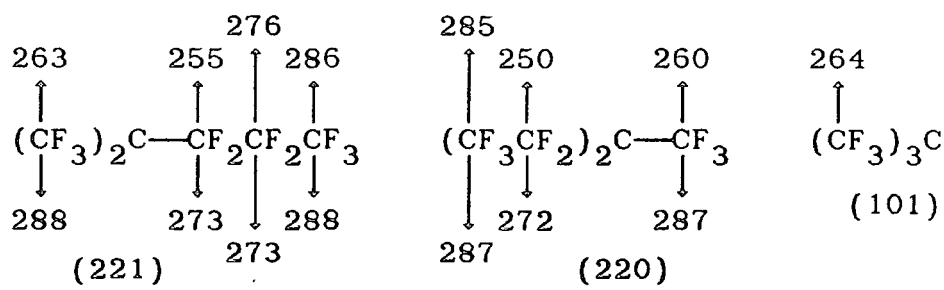
In our systems the downfield shifts observed for positions β-to the charge are dramatic and, by analogy with the above study represent a very high concentration of charge localised at the β-fluorine nucleus. In fluorinated anionic molecules such as (200),[137] where mesomeric stabilisation spreads the formal charge over two carbon atoms the β-downfield shift is clearly present but of a reduced magnitude. It is also noteworthy that without exception in our systems the β-position experiences a significant reduction in the value of the $^1J_{CF}$ coupling constant when compared to neutral models.

Some coupling constant data for simple perfluoroalkyl anions

$^1J_{CF}$

carbanions

bromo-derivatives



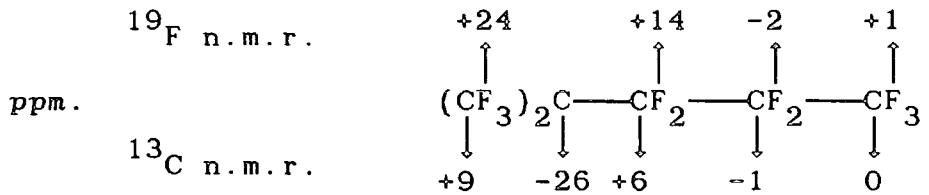
(221) (220) (101)

The mechanism by which the charge is transmitted to the β-position (or by which the chemical shifts are affected) could be inductive, through space or hyperconjugative and it is likely that a more systematic study will be required in order to clearly define the relevant contributions. However, if the primary method of electron delocalisation were

inductive we would expect the spectra to display a steadily decreasing shift difference (on moving from derivative to carbanion) as sites further removed from the charge were considered. This is clearly not the case as, at least for some of the carbanions, there is a hint of alternation of chemical shift changes rapidly attenuated by distance from the charge.

<u>δ(carbanion) - δ(brominated derivative)</u>

+ve values indicate downfield increments from brominated derivatives to carbanion.



Similar phenomena are common[251] for conjugated sytems where alternate carbon atoms constitute nodal points on the relevant molecular orbital, but it is not clear if this could be extended to saturated sytems.

A further trend which is recognised on inspection of the spectra of the acyclic carbanions is that shift positions for the anionic carbon and adjacent trifluoromethyl groups vary smoothly with the number of β-fluorine atoms (see Table 27). Both the ^{13}C (supposedly representing the degree of localised charge) and the ^{19}F chemical shifts of the adjacent trifluoromethyl groups increase with the total number of β-fluorine atoms. The degree of anionic hyperconjugation will depend on this

figure and, therefore, it is now quite tempting to use this information to support a significant contribution from negative hyperconjugation. This is certainly not a firm conclusion and further work will be necessary to establish the true origins of the shift phenomena.

Table 27 Variation of chemical shift data with number of β-fluorine atoms

PARAMETER	NUMBER OF β-FLUORINES(CARBANION)[1]			
	6	7	8	9
^{13}C $\delta(\bar{C})$	-	36.2 (220)	37.0 (221)	40.7 (101)
^{19}F $\delta(CF_3\bar{C})$	36.7 (225)[2]	39.9 (220)	42.4 (221) 41.5 (237)[2]	45.7 (101)

1. *Refer to Tables 23 and 24 for a list of carbanions.*

2. *See reference [237] for compounds (225) and* (237)$[(CF_3)_2\bar{C}CF_2CF_3]$.

iv) Variable temperature behaviour

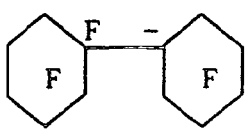
Most of the perfluorocarbanion salt solutions described in section 4.B.b. have been studied by ^{19}F n.m.r. spectroscopy at various temperatures. Cooling the solutions as low as the solvent systems will tolerate (about -45°C for tetraglyme and acetonitrile) has no detectable effect on the perfluorocarbanion spectra and, in the case of the perfluorobicyclobutyl carbanion (in DMF) this could be taken as low as -80°C with no apparent change.[160]

In view of this and the fact that the spectra are well coupled it is clear that, within the defined temperature range, exchange processes are either absent or too slow on

the n.m.r. timescale to be detected. Heating the sample, however, leads to broadening of the signals and a loss of coupling at a temperature which is concentration dependant and specific to the individual M^+ C^- system. The ^{19}F n.m.r. spectrum of Cs^+ $(CF_3)_2\bar{C}C_3F_7$ at various temperatures is shown on pages 162 and 163. By observation of the caesium perfluorocarbanion solutions it may be seen that, at this threshold temperature, regeneration of caesium fluoride and the precursor alkene begins to take place. Thus, the line broadening is in fact an indication that exchange processes of the type $M^+\,\bar{C}-CF \rightleftharpoons M^+F^-\,C=C$ have become significantly fast on the n.m.r. timescale and the threshold temperature at which this takes place is a guide to the perfluorocarbanion salt solution stability. This type of information may potentially be used to compare the effect of counterions and alkene electrophilicities in a manner not previously available. In addition, the temperature above which reactions involving the carbanions may be complicated by other processes may be determined and the information used synthetically (see next section).

The data were acquired by measuring the linewidths of a single resonance in the ^{19}F n.m.r. spectrum adjacent (β) to the anionic centre with 5° or 10°C temperature increments. A graph of linewidth vs temperature was plotted and two distinct lines could be drawn through the points. One line spanned a temperature range prior to the exchange temperature and was approximately straight and parallel to the x-axis, indicating a static sytem. Above the threshold temperature the line climbed steeply and the intersection of the two lines could simply be read off on the x-axis to

Table 28 Threshold temperatures for exchange processes

PERFLUOROCARBANION	COUNTERION	SOLVENT	TEMPERATURE (K)	
 (209)	Cs^+	tetraglyme	343[2]	
"	K^+	DMF	313[1]	
"	TAS^+	CH_3CN	332[2]	
$(CF_3)_2\bar{C}C_3F_7$ (221)	Cs^+	tetraglyme	333[2]	337[3]
"	Cs^+	DMSO	<300[2]	
"	Cs^+	tetraglyme[4]	<300[2]	
"	Cs^+	CH_3CN[4]	<300[2]	
"	TAS^+	CH_3CN	>350[2]	
$(C_2F_5)_2\bar{C}CF_3$ (220)	Cs^+	tetraglyme	329[2]	327[3]
"	TAS^+	CH_3CN	>350[2]	
$CF_3R_f\bar{C}—CF_2CF_3$ (222) $R_f = CCF_3(C_2F_5)_2$	Cs^+	tetraglyme	>350[5,2]	
"	TAS^+	CH_3CN	310[5,2]	
 (215)	Cs^+	tetraglyme	334[6,2]	
"	TAS^+	CH_3CN	320[3]	
 (224)	TAS^+	CH_3CN	>350[3]	

measured over the range 300-350K

1. *Performed by Dr. G. Taylor, see ref.[160]*
2. *Determined for CF_3 resonance.*
3. *Determined for CF_2 resonance.*
4. *With ca. 1 mol. equivalent of cryptand (226) added.*
5. *Peculiar lineshapes on graph. Results only approximate.*
6. *Diluted x20 with solvent and re-run with identical results.*

determine the threshold temperature. In general, the points above this point for the caesium perfluorocarbanions rose linearly whereas for the TAS salts the graph was somewhat curved. This may be a result of simpler exchange kinetics for the heterogeneous fluoride source than for the homogeneous source. It is noteworthy that, in contrast to the caesium salts, the TAS derivatives do not lose from solution either alkene or any solid material even well above the exchange threshold temperature. Full details are presented in the experimental section but the threshold temperatures are contained in Table 28, above and a typical graph is shown on page 164.

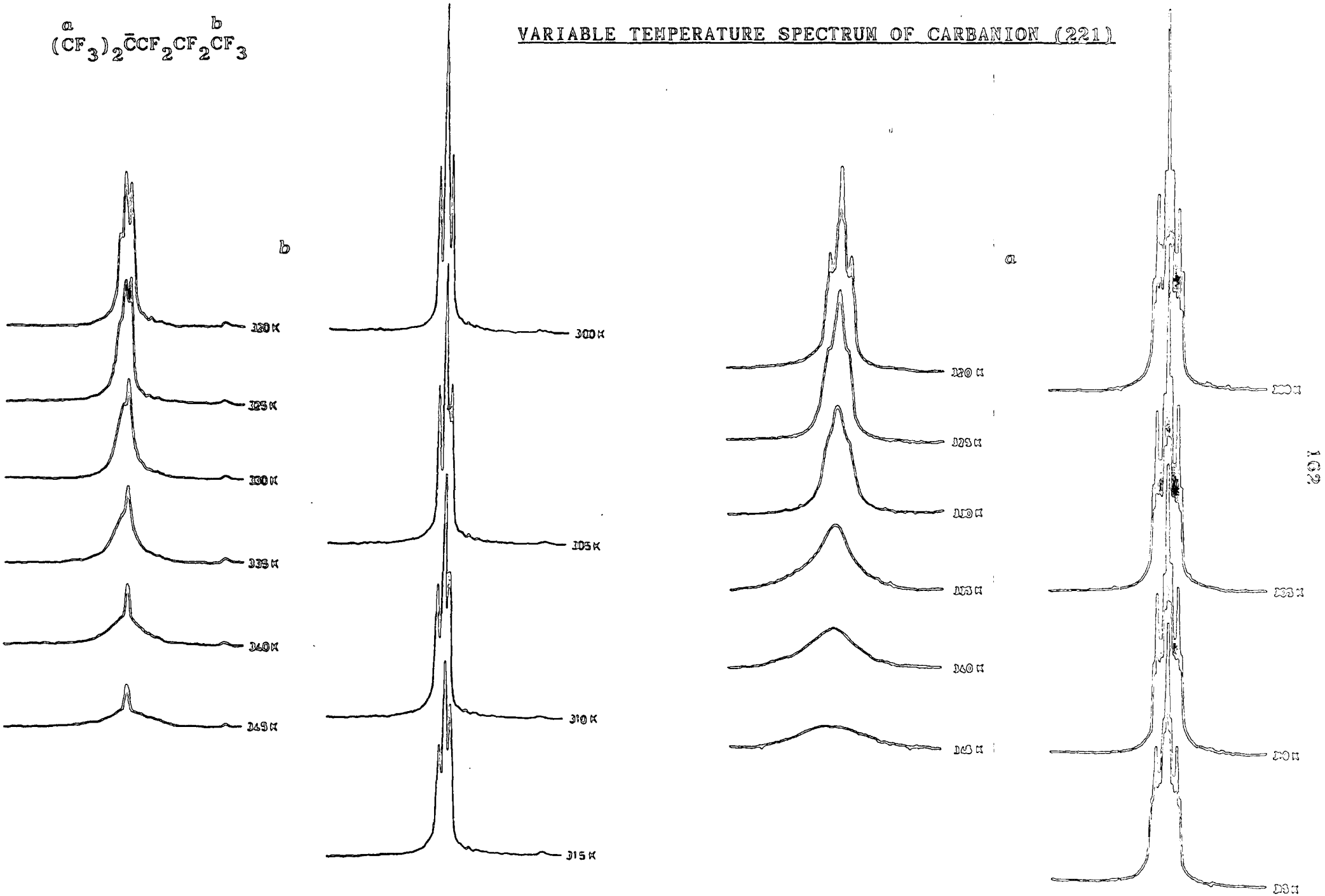
In order to make firm conclusions concerning the effect of solvent, counterion *etc.* on carbanion stability more data with, if necessary, low temperature studies on more transient species will be needed. It should be stressed that this technique is not necessarily restricted to the perfluorocarbanion salts stable at room temperature but potentially is available to many others.

From our data we can conclude that Cs^+ perfluorocarbanion salts are more solution stable than their TAS^+ analogues except for the acyclic carbanions (221) and (220). It is noteworthy that the caesium salt of (224) is not available and forms with difficulty for (222)(probably through steric restrictions). The TAS^+ salt of (224) and the caesium salt of (222) are remarkably resistent to exchange and it may be that salts that are difficult to form are, once obtained somehow stabilised.

We can conclude also that for caesium carbanion salts solvent sytems other than tetraglyme, available with

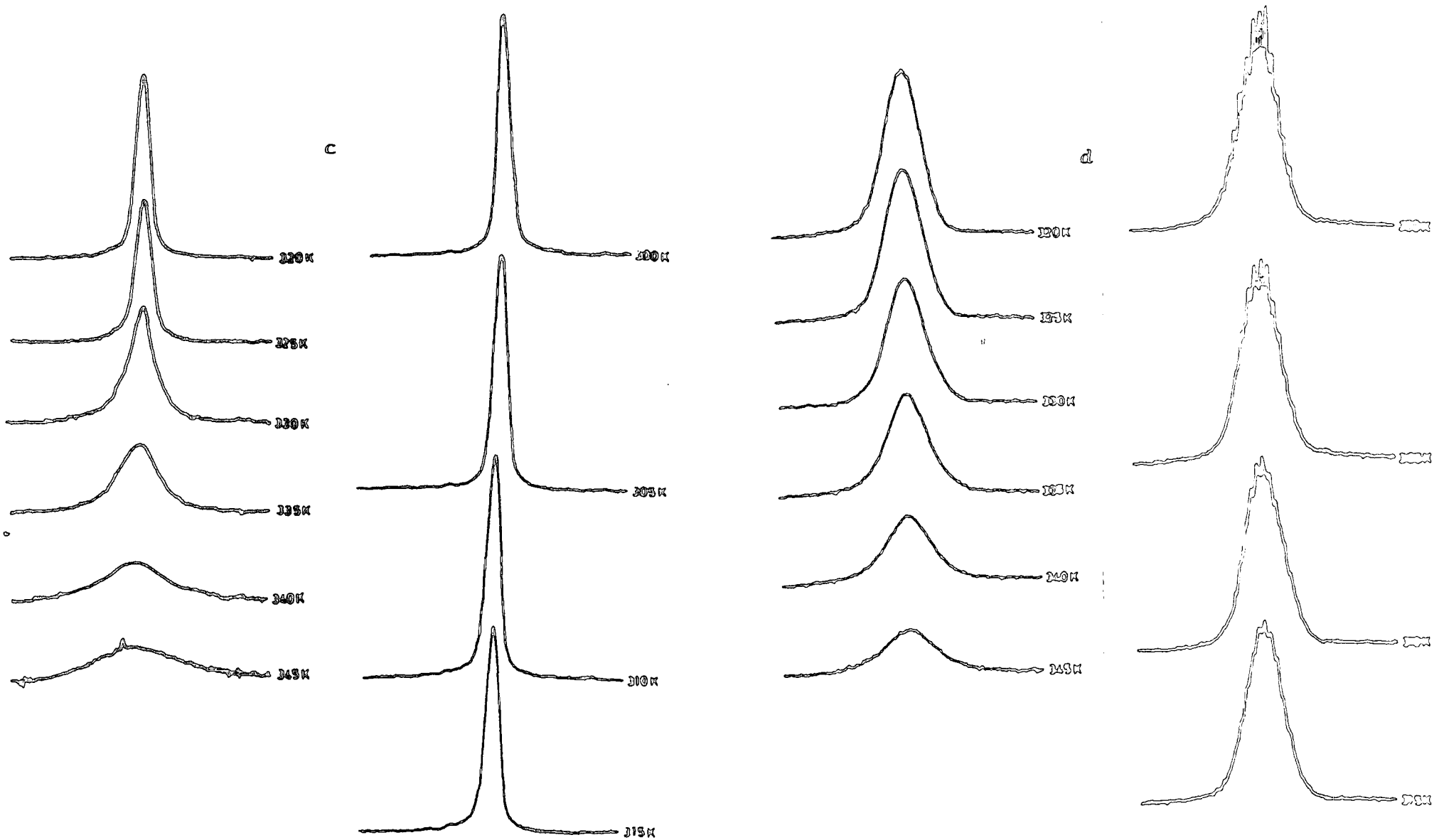
$(\overset{a}{CF_3})_2\bar{C}CF_2CF_2\overset{b}{CF_3}$

VARIABLE TEMPERATURE SPECTRUM OF CARBANION (221)



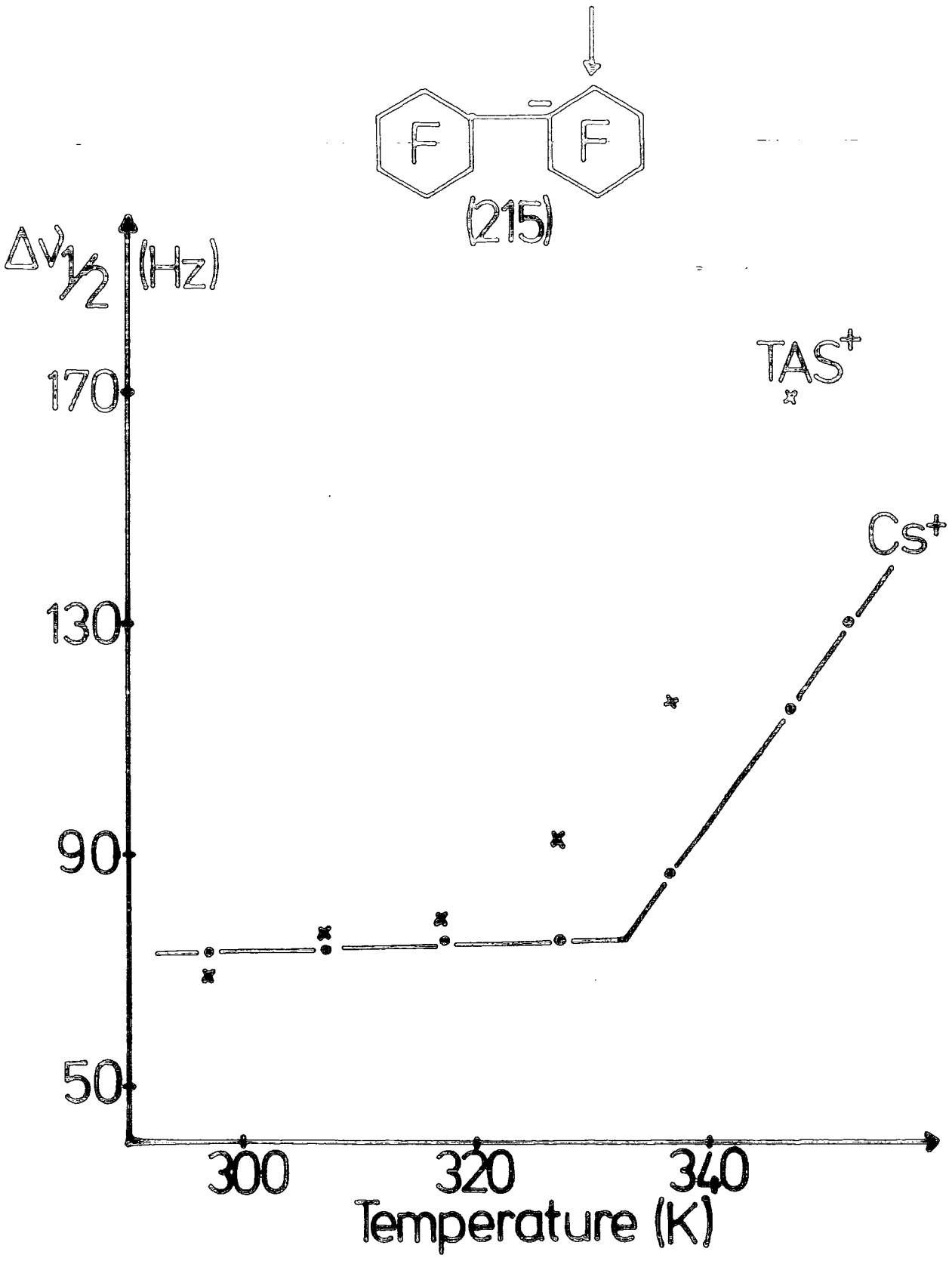
$(CF_3)_2\overset{c}{\bar{C}}CF_2\overset{d}{C}F_2CF_3$

VARIABLE TEMPERATURE SPECTRUM OF CARBANION (221)



LINEWIDTH DATA FOR THE

PERFLUOROBICYCLOHEXYL CARBANION (215)



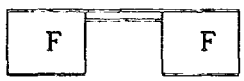
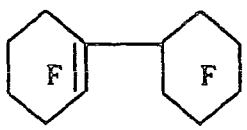
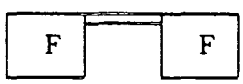
the use of cryptand (236), are not particularly effective and undergo exchange below room temperature.

4.B.e. Competition experiments

Now we are able to directly observe fluorocarbanions in solution that are essentially static on the n.m.r. timescale by simple means, the possibility arises for competition experiments between precursor alkenes and a deficiency of caesium fluoride to be performed. Providing the solubility of the two alkenes is similar, the ratio of the n.m.r. integration for the respective carbanions in solution is a measure of the equilibrium between the two species. Other methods for the analysis of the mixture could include g.l.c. of the residual lower alkene layer or efficient quenching of the upper layer with electrophiles followed by g.l.c. assay. A competition experiment conducted with a deficiency of TAS-F does not work in the same manner as the Cs^+ case because, as described previously, severe broadening of the resonances occurs and more than 1 molecular equivalent of alkene is consumed by the soluble fluoride. However, if two electrophilic fluorinated alkenes are agitiated with caesium fluoride for prolonged periods and then stood for some time to allow the non-dissolved material to settle the experiments work well. Simple analysis of the solvent layer by ^{19}F n.m.r. may be readily conducted at different times and the spectra obtained are sharp and are distinguished readily.

Table 29 Competition experiments

Conditions: xmol alkene A + xmol alkene B, xmol CsF room temp.

ALKENE A	ALKENE B	% ANION A	% ANION B	DAYS
$(CF_3)_2C{=}CFC_2F_5$ (29)	$C_2F_5(CF_3)C{=}CFCF_3$ (197)	45	55	0.3
		48	52	7
		47	53	30
$(CF_3)_2C{=}CFC_2F_5$	 (127)	5	95	0.3
		35	65	7
		33	67	30
$(CF_3)_2C{=}CFC_2F_5$	 (214)	98	2	0.3
		98	2	7
		98	2	30
$(CF_3)_2C{=}CFC_2F_5$	$CF_3R_fC{=}CFCF_3$ (83) $R_f = C(CF_3)_2C_2F_5$	100	0	0.3
		100	0	7
		100	0	30
$C_2F_5(CF_3)C{=}CFCF_3$		14	86	0.3

In view of the changes occuring on further agitation of the mixture containing perfluorobicyclobutylidene (127) and hexafluoropropene dimer (29), it is clear that full equilibration can take up to a week to take place. This could only be the case with systems in which fluoride exchange is extremely slow. From the results we have at the present, it seems that perfluorobicyclobutylidene (127) is very reactive and dominates carbanion mixtures initially. Over a long period of time the full equilibrium is established in which the proportion of the bicyclobutyl anion is reduced but still in the majority. Therefore, not only does the alkene (127) undergo a fast reaction with caesium fluoride but the derived carbanion is also

thermodynamically more stable than its competitors in the study. The less strained bicyclic alkene (214) is particularly ineffective and the anion derived from bulky alkene (83) cannot be observed at all.

We have utilised the results in a qualitative manner only. However, other workers have expressed[252] considerable interest in such experiments to deduce important thermochemical information but have great difficulty in obtaining the data because they use the soluble TAS-F source.

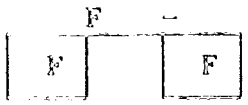
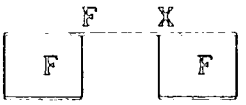
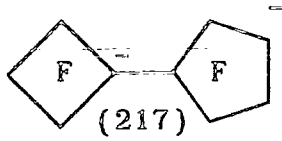
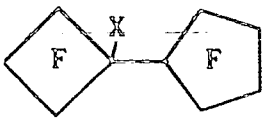
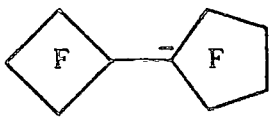
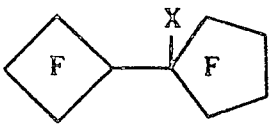
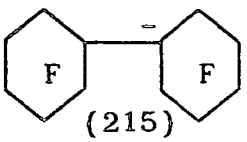
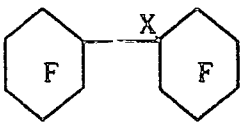
4.B.f Reactions of long-lived fluorocarbanions

i) Trapping reactions

Combination with electrophiles is a reaction type already well established for fluorocarbanions (see Chapter One). As far as could be established most of the persistent carbanions in the present study underwent quantitative conversion to the 'trapped' adducts on treatment at room temperature with suitable electrophiles. The only exceptions were carbanions (215) and (222) in which either the carbanionic centres were too difficult to approach by the bulky electrophiles or introduction of a bulky substituent to the relevant site would constitute unacceptable extra steric strain.

Table 30 Reactions with simple electrophiles

Conditions: Cs^+ carbanion $\xrightarrow[\text{tetraglyme, ca. 1h.}]{\text{electrophile, room temp.}}$

CARBANION	ADDUCT	ELECTROPHILE(ADDUCT)
 (209)		Br_2(X=Br)[1]
 (217)		Br_2(X=Br)[1]
		
 (215)		Br_2(no reaction)[1] Cl_2(X=Cl)[1]
$(CF_3)_2\bar{C}C_3F_7$ (221)	$(CF_3)_2\overset{X}{C}C_3F_7$	Br_2(X=Br), MeI(X=Me) $CH_2{=}CHCH_2I$(X=$CH_2CH{=}CH_2$) $PhCH_2Br$(X=CH_2Ph)
$(C_2F_5)_2\bar{C}CF_3$ (220)	$(C_2F_5)_2\overset{X}{C}CF_3$	Br_2(X=Br), MeI(X=Me) $CH_2{=}CHCH_2I$(X=$CH_2CH{=}CH_2$)
$(CF_3)\bar{C}$ (101)	$(CF_3)C{-}X$	Br_2(X=Br)
$CF_3RfC\bar{}{-}CF_2CF_3$ (222) R_f= $CCF_3(C_2F_5)_2$	$CF_3RfC(\overset{X}{})-CF_2CF_3$ *target*	Br_2(no reaction), Cl_2(no reaction), MeI(no reaction), H_2O(unidentified reaction)

1. *Performed by Dr. G. Taylor, see reference* [160]

With (222) and (215)[160] no reaction could be detected with bromine but (215)[160] afforded the expected adduct with chlorine. Carbanion (222) reacted with boron trifluoride etherate to regenerate its precursor alkene (83) as did the less crowded anion (221). Clearly, $BF_3.Et_2O$ is a better fluoride acceptor than the fluorinated alkenes.

Although simple reactions, these represent extremely clean routes to compounds of interest. Functionalisation of a large saturated perfluorocarbon with non-fluorinated groups such as alkyl, alkenyl, aryl etc. may be routinely performed and the materials are precursors to industrial products.

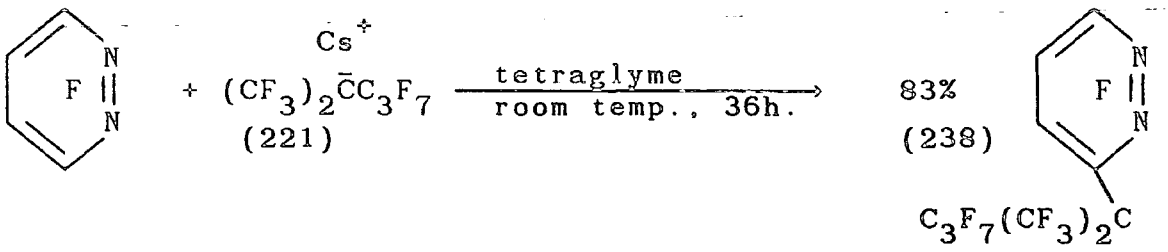
ii) Reactions with fluorinated electrophiles

We decided to ascertain how the bulkier stable fluorocarbanions behaved in some reactions with fluorinated alkenes (co-oligomerisations) and with fluorinated aromatic and heteroaromatic compounds (negative Friedel Crafts reactions). Although well established[253] for transient fluorocarbanions, such as the perfluoroisopropyl anion, there is a current interest in introducing larger inert substituents, especially into fluorinated aromatic compounds. These products constitute ideal sytems for valence isomer study (see Chapter One) and, with 1,2-dinitrogen heteroaromatics, for photolytic elimination of nitrogen to yield observable cyclobutadienes and azetes.

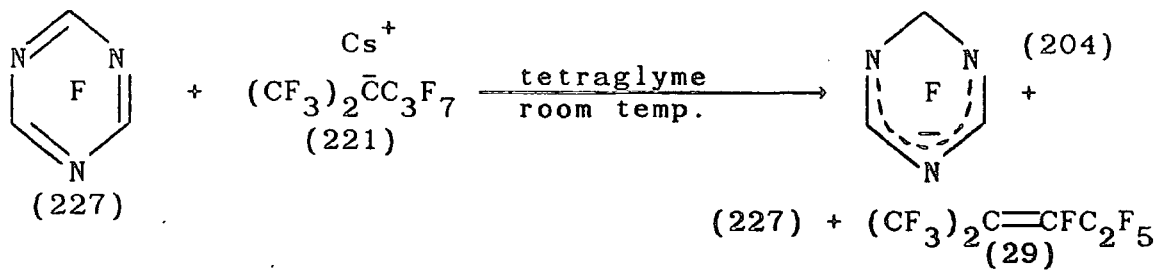
For the following reactions the most available carbanion (221) was used.

(221) with tetrafluoropyridazine The caesium salt of (221) generated in the usual manner was reacted with tetrafluoropyridazine at room temperature. A good yield of the mono-alkylated product (238) was formed but only a hint (g.l.c./ms) of any bis-alkylated material could be detected. Repeated attempts using different temperatures (20°C, 60°C, 100°C, and 120°C) and reaction times between 3 days and 3

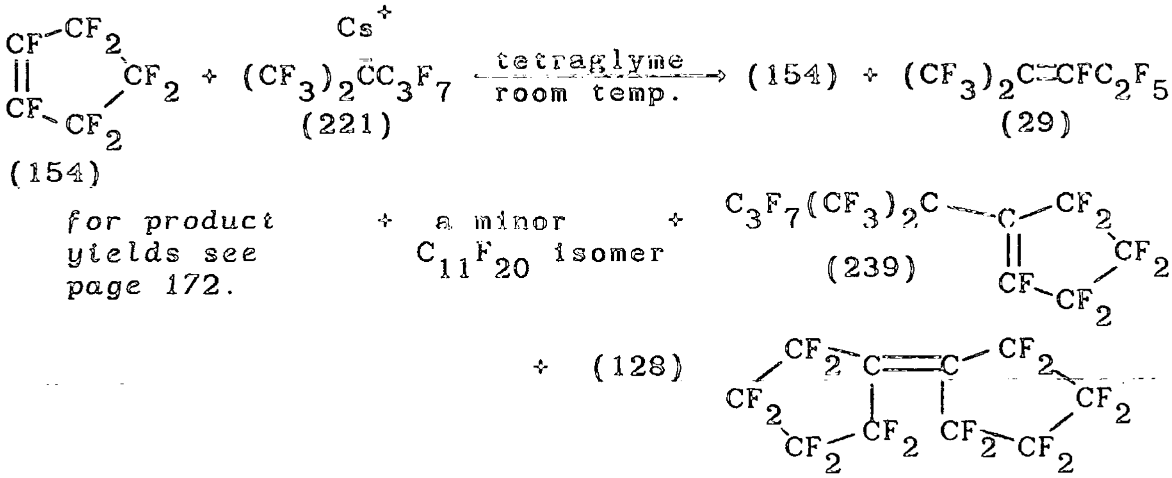
weeks (see experimental section) were made to isolate a bis - perfluoroalkylated compound without success. It was finally concluded that such compounds are too crowded to form readily, or a solubility problem was associated with further reaction of (238).



(221) with trifluoro-1,3,5-triazine In a similar experiment, with the more electrophilic sym-triazine (227) no detectable formation of adducts could be detected. This rather unusual obervation may be explained by the presence of the known Meisenheimer complex (204), detected by ^{19}F n.m.r. of the crude reaction mixture. *ie.* F^- transfer from (221) to (227) was dominant and further reaction involving the aromatic nucleus (227) prevented.

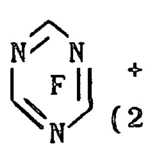


(221) with perfluorocyclopentene (154) The title alkene (154) was reacted at room temperature with the carbanion (221) and, in addition to the alkenes (29) and (154) and alkylated material (239), perfluoro-bicyclopentylidene (128) was also observed.



In a controlled experiment, caesium fluoride (dried and ground) did not react with perfluorocyclopentene (154) in tetraglyme even at 70°C for 36 hours. Thus, in the right circumstances, the long-lived fluorocarbanion solutions can act as potent sources of fluoride ion. This would also explain the observation of the Meisenheimer complex (204) in the reaction between (221) and trifluoro-1,3,5-triazine.

Table 31 Some reactions of fluorocarbanions as F^- Sources

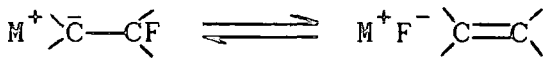
CARBANION	SUBSTRATE	PRODUCT(S)	REF.
$(CF_3)_2\bar{C}F$	$RCOCl$	HFP oligomers, $RCOF$	254
$[(CF_3)_2C{\cdots}CF{\cdots}C(CF_3)_2]^-$	$PhCOCl$	$(CF_3)_2C{=}C{=}C(CF_3)_2$ (200), $PhCOF$	137
 (204)	CH_3COCl	 (227) + CH_3COF	221

Similar observations have been made with the perfluoroisopropyl anion and acid chlorides in which only hexafluoropropene oligomers and the acid fluoride was isolated.[254] Also, the tetrakistrifluoromethylallyl anion

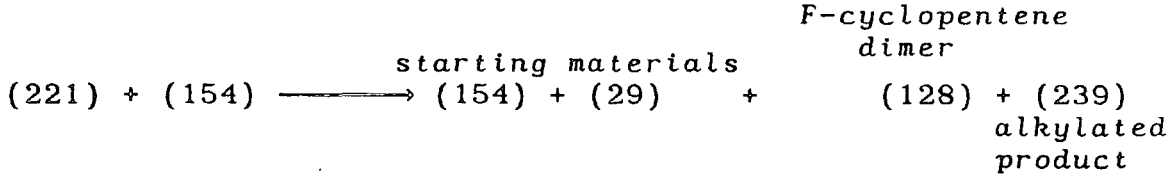
reacted with benzoyl chloride to regenerate the allene (200) and benzoyl fluoride, even though other electrophiles reacted in the usual manner.[137] It, therefore, appears that acid chlorides are particularly susceptible to attack by fluoride but not by perfluorocarbanions and this may be due to the particularly 'hard' nature of the site.

Therefore, there are potentially two factors which may govern, in a long-lived fluorocarbanion/electrophile reaction, whether alkylation or fluoride ion transfer occurs: a)the hardness of the electrophilic site .

b)the temperature of the reaction relative to the threshold temperature for the exchange process



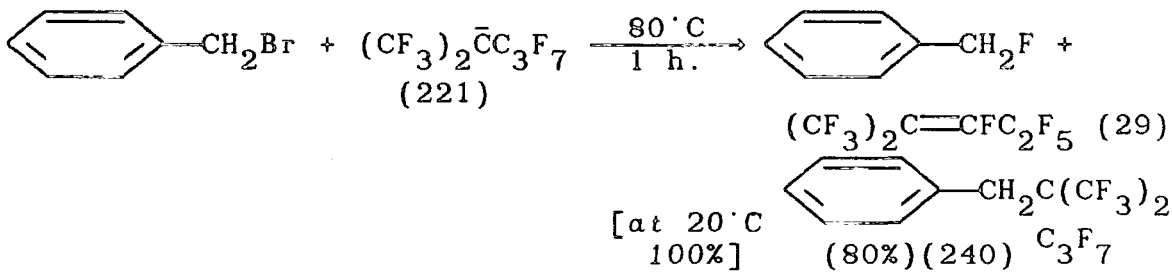
In an attempt to investigate the latter phenomenon the reaction between perfluorocyclopentene (154) and the perfluoro-2-methylpentyl carbanion (221) was re-tried at a temperature above its known exchange threshold, with a catalytic amount of carbanion.



STOICHIOMETRY (154):(221)	TEMP. (°C)	TIME (H)	CONVERSION (%)	PRODUCT DISTRIBUTION (239) : (138)
1 : 1	25	36	>90	1 : 0.6
10 : 1	70	36	*ca.* 20	1 : 3.0
10 : 1	70	36	60	1 : 3.0

1. *small amount of solvent hindered reaction.*

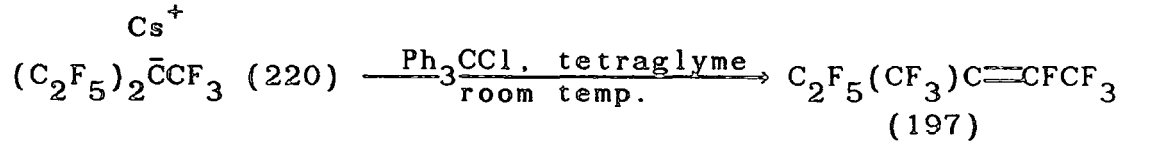
Under these conditions a complete reversal of the product distribution is effected and the product derived from fluoride ion donation dominated. Under identical conditions caesium fluoride is completely unreactive *ie.* (154) is recovered quantitatively. Similarly, at 80°C the carbanion (221) affords a lower yield of the simple trapped compound (240) with benzyl bromide and starting alkene (29) and benzyl fluoride are observed.



Even at room temperature, however, acetyl chloride reacts with (221) to afford mainly precursor alkene (29) and acetyl fluoride thus confirming the previous observations concerning acid halides.

iii) Attempted one-elctron transfer reactions

Russian workers have claimed (see Chapter One) interesting one-electron transfer processes are induced in perfluorocarbanions by triarylmethylhalides. However, the perfluoro-3-methylpent-3-yl anion (220) gave only precursor alkene (197) on treatment with triphenylmethylchloride at room temperature.



Attempts at one-electron oxidation of the carbanions (221) and (222) by lead tetraacetate did not apparently generate radical products and investigation of a tetraglyme solution of (221) by cyclic voltammetry did not provide evidence for any electric potential for the oxidation or reduction of (221) within the constraints of the solvent. One-electron transfer attempts were, therefore, discontinued.

$(CF_3)_2\bar{C}C_3F_7$ (221) $CF_3R_fC{=}CFCF_3$ (222)
$R_f = C(CF_3)_2C_2F_5$

4.B.g Conclusions on perfluoroalkyl carbanions

Fluorocarbanionic species have been postulated as intermediates in a huge variety of organofluorine reactions. For the first time a whole range of persistent fluorocarbanions have been generated using CsF and TAS-F and observed by n.m.r. spectroscopy. These studies indicate that the carbanion solutions contain solely the carbanion (with no detectable concentration of other material) which are essentially static species on the n.m.r. timescale. Curious low field chemical shifts for sites adjacent (β) to the charge and small primary ($^1J_{CF}$) coupling constants are clearly identified. These now well defined and particularly large effects appear to be consistent with a significant degree of charge at the β-position but we are unable to explain a commonly found slight upfield shift at the γ-position. Variable temperature studies indicate a temperature at which exchange processes involving elimination of fluoride ion become significantly fast to be observed by the n.m.r. experiment. These are characteristic

of the M^{+} $\ddot{C}$ system and provide us with a new and novel method for the determination of carbanion/counterion stabilities. Deficiencies of caesium fluoride may be employed with mixtures of two alkenes and the partition of carbanions in the solvent layer, as determined by ^{19}F n.m.r., is an excellent way of ascertaining the position of the relevant equilibrium. A time dependent study of such experiments may also be able to yield useful kinetic information. With minor exceptions that are easily rationalised the carbanion solutions alkylate traditional electrophiles quantitatively to produce potentially useful adducts. Alkylation reactions are also available with unsaturated fluorinated electrophiles such as fluoroheteroaromatics and fluorinated alkenes. With trifluoro-1,3,5-triazine and perfluorocyclopentene there is clear evidence of a competing transfer of fluoride ion from the carbanion. This phenomenon is found to occur when the electrophile is a particularly hard site or, alternatively, above the threshold temperature for the exchange process as determined by n.m.r.

EXPERIMENTAL

INSTRUMENTATION

N.M.R. spectra.— Standard fluorine and proton spectra were recorded on a Varian EM360L spectrometer operating at 56.4 and 60 MHz respectively. Carbon spectra were aqcuired on a Bruker WH-360 spectrometer operating at 90.6 MHz and high resolution/variable temperature spectra were recorded (by the author) on a Bruker AC250 operating at 62.9 MHz (for ^{13}C) and 235.3 MHz (for ^{19}F). Chemical shifts of ^{13}C and ^{1}H signals are quoted in ppm relative to external $(Me)_4Si$ reference with downfield taken as positive. Chemical shifts of ^{19}F signals are quoted in ppm relative to external $CFCl_3$ reference with upfield taken as positive.

Infrared spectra.— Infrared spectra were recorded on a Perkin Elmer 457 grating i.r. spectrophotometer using KBr discs (solid samples) or as thin films between KBr plates (liquids). Gaseous samples were condensed into a cylindrical cell with KBr windows.

Mass spectra.— Mass spectra of pure materials were recorded on a VG 7070E spectrometer with electron impact, chemical ionisation and negative ionisation modes as appropriate, or on a MS9 spectrometer with electron impact ionisation. G.l.c. mass spectra were recorded on a VG Micromass 12B spectrometer fitted with a Pye 104 gas chromatograph (packed columns) or a VG 7070E spectrometer equipped with a capillary column gas chromatograph (25m fused silica column with O_{v1} coating).

Elemental analyses.— Carbon, hydrogen and nitrogen analyses were obtained using a Perkin Elmer 240 elemental analyser. Analysis for halogens was performed as described in the

literature.[255]

Gas liquid chromatographic analysis.— Quantitative analysis was obtained using a Varian aerograph model 920 equipped with a gas density balance detector. Other gas liquid chromatographic analyses were carried out using Pye 104 (packed column), Pye GCD (packed column), and Hewlett Packard 5890A (O_{v1} coated fused silica capillary column) gas chromatographs equipped with flame ionisation detectors. Preparative g.l.c. was performed on a Varian aerograph model 920 (packed column) with a Cathodometer detector. Column packings most commonly used are Col. O (5% or 10% silicone gum rubber) and Col. K (20% Krytox fluid).

Fractional distillations.— Fractional distillation of product mixtures was carried out on a Fischer Spaltrohr MMM 202 concentric tube system.

REAGENTS AND SOLVENTS

Unless otherwise stated, reagents were used as supplied. Solvents were predried by standard methods and stored over molecular seive (type 4A) under dry nitrogen. A current of dry nitrogen was maintained for removal of sovent with an air tight syringe.

CHAPTER FIVE

EXPERIMENTAL TO CHAPTER TWO

FLUORINATED EPOXIDES

CHAPTER FIVE

EXPERIMENTAL TO CHAPTER TWO

5.1 Oligomerisation of perfluorocyclobutene (107) with pyridine

Typically, perfluorocyclobutene (107)(74g, 457mmol) was transferred *in vacuo* to a *rotoflo* tube cooled in liquid air, precharged with pyridine (2.4g, 30mmol). The mixture was agitated in a shaker at room temperature for *ca.* 24h. and then volatile material (53g) was transferred *in vacuo* to a cold trap, washed with water (2x50ml), dried (P_2O_5) and further transferred under vacuum to a cold trap. Distillation (Fischer Spaltrohr, 50 theoretical plates) afforded the *dimers* (127) and (141), b.p. 80-85°C, 30g, 41%

and *trimer* (146) b.p. 145-148°C, 18.5g, 25%, identified by a comparison of mass spectra (number 57) and ^{19}F n.m.r. (number 61) spectra with literature data.[160]

The *dimers* could be separated by preparative scale g.l.c.(Col. 0) to give analytical samples of (127) and (141), identified by comparison of i.r. (numbers 1 and 2) and ^{19}F n.m.r. spectra (numbers 1 and 2) with literature data.[160]

Other reactions, conducted in the same manner, to maximise the production of either dimers or trimer, are detailed in the following table.

(107) (g, mmol)	Pyridine (g, mmol)	time (h.)	Yield dimers (%)	Yield trimer (%)
for dimers (127) and (141)				
74, 457	2.4, 30	24	41	25
34, 209	0.8, 10	18	38	-

for trimer (146)				
103, 635	5.4, 68	15	14	45
51, 315	2.9, 37	15	9	44

5.2 Dimerisation of perfluorocyclopentene (154)

A *Carius* tube was charged with caesium fluoride (6.3g, 41.4mmol) and sulpholan (20ml) and the mixture degassed by the application of vacuum. Perfluorocyclopentene (154)(17.0g, 80.2mmol) was transferred *in vacuo* to the vessel which was cooled in liquid air. The mixture was then heated at 125°C with agitation for 20h. Volatile material (16.0g) was transferred *in vacuo* to a cold trap and subsequently distilled, the fraction collected at 120°-130°C corresponding to the *dimer* (128)(15.8g, 93%) by a comparison of ^{19}F n.m.r. data (number 3) with literature data.[160]

A similar reaction with alkene (154)(18.0g, 84.9mmol), caesium fluoride (7.6g, 49.9mmol) in sulpholan (20ml) for 16h. at 125°C gave the desired *dimer* (128)(14g, 78%).

5.3 Epoxidation of perfluorobicyclopentylidene(128)

A mixture of the alkene (128)(3.1g, 7.3mmol), calcium hypochlorite (1.8g, 12.6mmol) and acetonitrile (6ml) was stirred at room temperature for 36h. Volatile material was transferred *in vacuo* to a cold trap and the resulting lower layer (1.8g) found (by g.l.c., Col. O) to be a mixture of four major components. Preparative scale g.l.c. (Col. O) afforded:-

(a) starting material (128)(13%), identified by ^{19}F n.m.r. (number 3),

(b) *perfluoro-11-oxadispiro(4.0.4.1)undecane*(130)(20%) (Found: C, 27.6; F, 69.3. $C_{10}F_{16}O$ requires: C, 27.3; F,69.1%); m/z (N.I.) 439.9669. $C_{10}F_{16}O$ requires M^{*} 439.9693; mass spectrum numbers 9, 10; n.m.r. spectrum number 7; i.r. spectrum number 7,

(c) *perfluoro-1-(1'-chlorocyclopentyl)cyclopent-1-ene*(132) (10%)(Found: C, 27.3. $C_{10}F_{15}Cl$ requires: C, 27.3%); mass spectrum number 11; n.m.r. spectrum number 8. i.r. spectrum number 8,

and a compound identified as

(d) *1,1'-dichloroperfluorobicyclopentyl*(134)(6%) by consideration of mass spectral and ^{19}F n.m.r. data, and by comparison with the analogous compound 1,1'-dichloro-perfluorobicyclobutyl (131). mass spectrum number 12; n.m.r. spectrum number 9.

A similar reaction with (128)(8.4g, 19.8mmol), calcium hypochlorite (5.7g, 40mmol) and acetonitrile (31ml) conducted at room temperature for 72h. yielded a lower layer (3.3g) which was then shown (g.l.c., Col. 0) to be the *epoxide* (130)(>98% pure)(38%) by a comparison of ^{19}F n.m.r. (number 7) with an authentic sample.

5.4 Epoxidation of perfluorobicyclobutylidene(127)

A mixture of the alkene (127)(4.2g, 13.0mmol), calcium hypochlorite (3.4g, 23.5mmol) and acetonitrile (6ml) was stirred at room temperature for 120h. Volatile material was transferred *in vacuo* to a cold trap and the resulting lower layer (3.4g) purified by preparative scale g.l.c. (Col. 0, 100°C stepwise to 150°C) to yield:-

(a) *perfluoro-9-oxadispiro(3.0.3.1)nonane* (129)(22%) (Found: C, 27.9; F, 66.7. $C_8F_{12}O$ requires: C, 28.2; F, 67.0%); mass spectrum number 6; n.m.r. spectrum number 4; i.r. spectrum

number 4,

(b) *1,1'-dichloroperfluorobicyclobutyl (131)*(25%) (Found: C, 24.5; F, 57.0; Cl, 18.6. $C_8F_{12}Cl_2$ requires: C, 24.3; F, 57.7; Cl, 18.0%); mass spectrum number 7; n.m.r. spectrum number 5; i.r. spectrum number 5,

and (c) *perfluoro-1-(1'-chlorocyclobutyl)cyclobut-1-ene (133)*(29%)(Found: C, 28.2; F, 57.6; Cl, 12.1. $C_8F_{11}Cl$ requires: C, 28.2; F, 61.4; Cl, 10.4%); mass spectrum number 8; n.m.r. spectrum number 6; i.r. spectrum number 6.

Other reactions conducted as before are summarised in the following table;-

ALKENE (127) (g, mmol)	$Ca(OCl)_2$ (g, mmol)	CH_3CN (ml)	TIME (h.)	(129) (%)	(131) (%)	(133) (%)
0.26,0.80	0.17,1.18	0.8	48	24	16	21
1.05,3.24	0.71,4.97	2.0	36	20	19	19
2.13,6.57	1.71,11.9	10	48	52	4	2
4.23,13.1	3.36,23.5	6	120	22	25	29
2.60,8.00	2.10,14.6	60	72	20	3	-
4.95,15.3	4.40,30.3	25	48	57	-	-

yields were measured by n.m.r. integration and g.l.c.

5.5 Static thermolyses of dispiro-epoxides (129) and (130)

5.5.1 Pyrolyses of (129)

The epoxide (129)(0.05g, 0.15mmol), contained in a capillary tube, was heated in a furnace at 200°C for 11h. The product liquid (0.05g) was found to be single component (g.l.c., Col. O) and identified as starting material (129)(100% recovery) by a comparison of a ^{19}F n.m.r. spectrum with an authentic sample (n.m.r. spectrum

number 4)

In a similar manner, epoxide (129) was recovered unchanged after heating at 300°C for periods of 2 and 5h.

5.5.2 Pyrolysis of (130)

The epoxide (130)(0.05g, 0.11mmol), contained in a capillary tube was heated in a furnace at 300°C. The product liquid (0.05g) was identified as pure starting material (130)(100% recovery) by a comparison of a ^{19}F n.m.r. spectrum with an authentic sample (n.m.r. spectrum number 7).

5.6 Dispiroepoxides (129) and (130) with caesium fluoride

5.6.1 Epoxide (129)

The title epoxide (129)(1.0g, 2.9mmol) and caesium fluoride (0.44g, 2.9mmol), contained in an evacuated sealed tube were heated at 150°C for 16h. Volatile material (0.94g) was transferred *in vacuo* to a cold trap, found to be single component (g.l.c., Col. 0) and confirmed to be starting material (129)(94% recovery) by a comparison of ^{19}F n.m.r. and i.r. spectra with an authentic sample (n.m.r. spectrum number 4, i.r. spectrum number 4).

In a second reaction, conducted as before, with (129) (0.94g, 2.8mmol) and caesium fluoride (0.46g, 3.0mmol) heated at 200°C for 19h., volatile material (0.74g) was found (g.l.c., Col. 0) to contain >20 components. Four of the major constituents gave mass spectra corresponding to perfluorocyclobutene (107)(mass spectrum number 13), two C_8F_{12} isomers and starting material (129)(mass spectrum number 6). No material could be obtained pure and the reaction was not persued further.

5.6.2 Epoxide (130)

The title epoxide (130)(2.1g, 4.8mmol) and caesium fluoride (0.64g, 4.2mmol), contained in a sealed, evacuated, glass tube were heated at 150°C for 16h. Volatile material (2.0g) was transferred *in vacuo* to a cold trap, shown (g.l.c., Col O) to consist of one component and identified as starting material (130)(95% recovered) by a comparison of g.l.c. retention times and i.r. spectra (number 7).

Similarly, with (130)(2.0g, 4.5mmol), caesium fluoride (0.62g, 4.1mmol) heated at 200°C for 16h, volatile material (1.6g) was identified as mixture of perfluorocyclopentene (154)(83%) and perfluorocylopentanone (57%) by a comparison of i.r., ^{19}F n.m.r. and mass spectral data with an authentic sample (*for* 154) and literature data[256] (*for* perfluorocyclopentanone).

Mixture of (154) and (perfluorocyclopentanone) (i.r. spectrum number 10)

(154) (mass spectrum number 14, n.m.r. spectrum number 10, i.r. spectrum number 11)

(perfluorocyclopentanone) (mass spectrum number 15, n.m.r. spectrum number 11)

A third reaction conducted similarly with (130) (0.20g, 0.45mmol) and caesium fluoride (0.56g, 3.7mmol), heated at 250°C for 14h. gave volatile material (0.14g) and was subsequently shown (g.l.c., Col. O) to be multicomponent. The reaction was not pursued further.

5.7 Miscellaneous reactions of dispiroepoxides (129) and (130)

5.7.1 Attempted photolysis of (129)

The title compound (129)(0.81g, 2.4mmol) was contained in a

quartz tube with a trace amount of mercury and subjected to u.v. radiation from a high pressure source for 16h. The resulting material (0.81g) was identified as starting material (129)(100% recovery) by a comparison of ^{19}F n.m.r. spectra (number 4) with an authentic sample.

5.7.2 Epoxide (129) with triphenyl phosphine

A mixture of the epoxide (129)(0.81g, 2.4mmol) and triphenylphosphine (0.3g ,1.1mmol) was contained in a sealed glass vessel and heated to 100°C for *ca.* 1h. A residual colourless liquid (0.36g) was removed and found to be starting material (44% recovery) by a comparison of ^{19}F n.m.r. spectra (number 4). An intractable tar remained and was not pursued further.

5.7.3 Alkene (127) with triphenylphosphine

A mixture of alkene (127)(0.2g, 0.62mmol) and triphenylphosphine (0.24g, 0.92mmol) was heated with a hot air blower until the phospine melted. Immediate tarring was observed and, after *ca.* 0.2h no residual liquid was observed.

5.7.4 Epoxide (129) with TAS-F (208)

Epoxide (129)(0.25g, 0.74mmol) was stirred with a solution of TAS-F (208)(0.32g, 1.1mmol) in acetonitrile (1.5 ml) at room temperature for 24h. The lower layer (0.19g) was removed and found (^{19}F n.m.r., number 4) to be (129)(76% recovered).

5.8 Attempted epoxidations of novel alkenes and dienes

5.8.1 *trans*-2-Hydroheptafluoro-2-butene (143)

a) With aqueous sodium hypochlorite.— A mixture of the alkene (143)(7.3g, 39.8mmol), sodium hypochlorite solution (41ml of

10%, 100mmol) and acetonitrile (20ml) was agitated in a sealed glass tube at room temperature for 41h. Excess gas (2.5g) was allowed to enter a flexible gas reservoir and was identified as starting material (34% recovery) by a comparison of i.r. spectra (number 12) with authentic material. Remaining volatile material was transferred *in vacuo* to a cold trap to give a two phase system which was manually separated. The lower layer was found to be water and the upper layer shown (g.l.c., Col. O) to be an acetonitrile solution of volatile fluorocarbon species with mass spectra (number 16) corresponding to starting material (143), and $C_4F_7OH_3$, $C_4F_7HCl_2$ isomers.

b) With calcium hypochlorite.— A mixture of the alkene (143)(0.9g, 4.9mmol), calcium hypochlorite (1.07g, 7.4mmol) and acetonitrile (2.5ml) was contained in a sealed glass vessel and agitated at room temperature for 24h. and for a further 24h. at 60°C. Volatile material was transferred *in vacuo* to a cold trap and found (g.l.c., Col. K) to be mainly solvent and two other major components identified by a consideration of mass spectra as starting material (143)(mass spectrum number 16) and a C_4F_6HO isomer. The mixture could not be purified and was not pursued further.

c) With calcium hypochlorite and a phase transfer catalyst.— As for (a) with the alkene (143)(3.4g, 18.7mmol), cetavlon (0.13g, 4.3mmol), calcium hypochlorite (2.1g, 14.5mmol) and acetonitrile (5ml). Recovered volatile material was shown by i.r.(number 12) to be a solution (in CH_3CN) of starting material (143) and a small amount of an unidentified product.

5.8.2 Attempted epoxidation of perfluoro-2-methyl-3-hydrobut-2-ene (144) with calcium hypochlorite

A mixture of alkene (144)(0.80g, 3.4mmol), calcium hypochlorite (0.65g, 4.5mmol) and acetonitrile (3ml) was stirred at room temperature for 48h. The lower layer (0.71g) was removed and shown to be (144)(89% recovered).

5.8.3 *Diene (145) from perfluorocyclobutene trimer (146)*

A nickel tube was charged with a source of fluoride ion which was then dried under vacuum with heating. After cooling in liquid air, the *perfluorocyclobutene trimer* (146) was transferred *in vacuo* to the tube which was sealed and heated, with agitation, for the required period. Volatile material was transferred *in vacuo* to a cold trap and investigated by g.l.c. (Col. O) and ^{19}F n.m.r., and found to contain starting material (146) and the desired *diene* (145) by a comparison of ^{19}F n.m.r. spectra (numbers 61 and 12) with literature data.[160] Distillation (Fischer Spaltrohr, 50 theoretical plates) afforded *diene* (146), b.p. 134-136°C *ca.*90% pure by g.l.c. (Col. O).

Reactions conducted are detailed in the following table:-

(146) (g, mmol)	F^- source	(g, mmol)	temp. (°C)	time (h.)	*diene* (145) (%)	*trimer* (%)
12.0, 24.7	CsF	7.0, 46.1	330	30	29	16
17.0, 34.9	CsF	12.0, 78.9	330	28	28	12
13.7, 28.2	KF	2.8, 48.2	300	28	59	30
8.3, 17.1	KF	1.2, 20.7	300	24	57	29

Yields based on g.l.c.traces

5.8.4 *Diene (145) with calcium hypochlorite*

A mixture of the diene (145)(3.34g, 6.9mmol), calcium hypochlorite (3.3g, 23mmol) and acetonitrile (15ml) was stirred at room temperature for 5 days. Volatile material (3.2g) was transferred *in vacuo* to a cold trap and shown (g.l.c., Col. O) to consist of five components, identified by mass spectroscopy to be starting material (145)(7% recovered)(by a comparison with literature data),[160] two $C_{12}F_{18}O$ isomers (14% and *ca.*17% (containing a small amount of an unidentified comound)) and a $C_{12}F_{18}O_2$ isomer (57%). One of the $C_{12}F_{18}O$ isomers (a) and the $C_{12}F_{18}O_2$ isomer (b) were isolated by preparative scale g.l.c. (Col. O), and identified as:-

(a) *the mono-epoxide* (149)(14%) m/z (E.I) 432.9466. $C_{12}F_{18}O$ requires M^+-CF_3 432.9709; mass spectrum number 18; n.m.r. spectra number 13; i.r. spectrum number 14,

and (b) either the *cis* (151) or *trans* (152) *diepoxides* (57%) m/z (E.I.) 448.9476. $C_{12}F_{18}O_2$ requires M^+-CF_3 448.9658; 348.9968. $C_{12}F_{18}O_2$ requires $M^+-C_3F_7$ 348.9722; mass spectrum number 19; n.m.r. spectra number 14; i.r. spectrum number 15,

on the basis of n.m.r. and mass spectral data. The compounds were pure by g.l.c. on a variety of column packings (and on a capillary column) but gave variable elemental analyses.

5.8.5 *Further reaction of the mixture from 5.8.4*

The crude liquid from the above (5.8.4) experiment was stirred further with calcium hypochlorite (1.7g, 11.7mmol) in acetonitrile (12ml) for 72h. at room temperature and analysed by g.l.c. The peak due to the *mono-epoxide* (149) had disappeared and that due to the *di-epoxide* (152) was enhanced by a similar amount.

5.9 Other potential epoxidising reagents

5.9.1 Attempted epoxidations using pyridine-*N*-oxide

a) Perfluoro-3,4-dimethylhex-3-ene (82).— A mixture of (82)(5.2g, 13mmol), pyridine-*N*-oxide (1.6g, 16.8mmol) and acetonitrile (4ml) was stirred under reflux for 140h. Volatile material was transferred *in vacuo* to a cold trap and the lower layer (1.6g) was found to be pure starting material (82)(31% recovered) by a comparison of g.l.c. retention times (Col. O) and ^{19}F n.m.r. spectra (number 15).

b) *Trans*-2-hydroheptafluorobut-2-ene (143).— A mixture of (143)(3.2g, 17.6mmol), pyridine-*N*-oxide (1.8g, 18.9mmol) and ether (5ml) was contained in a sealed glass vessel and agitated at room temperature for 308h. Volatile material (7g) was transferred *in vacuo* to a cold trap and found (glc/ms, number 16) to contain starting material (143) as the only fluorocarbon material.

5.9.2 Attempted epoxidations using peroxyacids

a) Perfluoro-3,4-dimethylhex-3-ene (82) with sodium peroxybenzoate.— A mixture of (82)(5.5g, 13.8mmol), aqueous sodium peroxybenzoate (5ml, 15mmol *eq.*) and acetonotrile (5ml) was stirred at room temperature for 48h. The lower layer (4.4g) was removed and shown (g.l.c., capillary column) to consist of one major component (>90%) subsequently identified as starting material (82)(72% recovered) by a comparison of ^{19}F n.m.r. (number 15) with authentic material.

b) (82) with pottasium *m*-chloroperoxybenzoate.— A mixture of (82)(2.0g, 5.0mmol), *m*-chloroperoxybenzoic acid (1.2g, 7.6mmol), water (10ml) and acetonitrile (3ml) was stirred at room temperature

for 3 days. The lower layer (1.9g) was removed and shown by g.l.c. (Col. O) and ^{19}F n.m.r. (number 15) to be pure starting material (82)(95% recovered).

A similar reaction conducted in the absence of potassium hydroxide yielded only starting material (82)(100% recovery).

c) Hexafluoropropene (1) with potassium m-chloroperoxybenzoate Conducted as for (5.9.2.b) with equimolar proportions of (1), m-chloroperoxybenzoic acid and potassium hydroxide only starting material (good recovery) was isolated.

CHAPTER SIX

EXPERIMENTAL TO CHAPTER THREE

BIFUNCTIONAL NUCLEOPHILES WITH FLUORINATED ALKENES

CHAPTER SIX

EXPERIMENTAL TO CHAPTER THREE

6.1 General procedure for bifunctional nucleophiles

When then the fluorinated alkenes were perfluorocyclopentene (154) and perfluorocyclobutene (107) 'rotoflo' tubes were pre-charged with the appropriate solvent and reagents and the tube was then cooled in liquid air. The relevant alkene was subsequently transferred *in vacuo* to the vessel which was then sealed and warmed to room temperature. Agitations were effected using a slowly rotating arm or a standard shaking machine, as appropriate.

With more volatile fluorocarbon alkenes such as hexafluoropropene (1) 'Carius' tubes were employed as above.

Liquid fluorinated alkenes were stirred magnetically in conventional glass apparatus.

6.2 3,4-Dimercaptotoluene with perfluorocyclobutene (107)

A mixture of the alkene (107)(2.0g, 12.3mmol), 3,4-dimercaptotoluene (1.7g, 10.8mmol), potassium carbonate (2.2g, 16.0mmol) and acetonitrile (150ml), contained in a sealed glass vessel, was agitated at room temperature for 24h. Water (150ml) was added and the product extracted with ether (2x100ml) which was dried and evaporated (rotary evaporator) to yield a solid (3.5g). Sublimation *in vacuo* afforded:-

3,4-(3'-methylbenzo)-7,7,8,8-tetrafluoro-2,5-dithiobicyclo(4.2.0)oct-1-ene (155)(2.4g, 79%) m.p. 109-111°C (Found: C, 47.2; H, 2.1; F, 27.7. $C_{11}H_6F_4S_2$ requires: C, 47.5; H, 2.2; F, 27.3%); mass spectrum number 21; n.m.r. spectra number 16; i.r. spectrum number 17.

6.3 3,4-dimercaptotoluene with perfluorocyclopentene (154)

a) Equimolar amounts of alkene (154) and dithiol.— A mixture of the alkene (154)(5.5g, 25.9mmol), 3,4-dimercaptotoluene (3.9g, 25mmol), potassium carbonate (7.0g, 50.8mmol) and acetonitrile (170ml), contained in a sealed glass vessel, was agitated at room temperature for 24h. Solvent was evaporated (rotary evaporator), after filtration, to leave an yellow solid (8.0g) which was subsequently shown to be:- *3,4-(3'-methyl)benzo-7,7,8,8,9,9-hexafluoro-2,5-dithiobicyclo(4.3.0) non-1-ene* (156)(96%) m.p. 53-54°C (Found: C, 44.0; H, 1.6; F, 35.2. $C_{12}H_6F_6S_2$ requires: C, 43.9; H, 1.8; F, 34.7%); mass spectrum number 22; n.m.r. spectra number 17; i.r. spectrum number 18.

b) With excess alkene (154).— A similar reaction with a 3:2 ratio of alkene (154) to 3,4-dimercaptotoluene produced a crude brown solid containing (t.l.c., silica, 60/80 petrol eluent) one major and two minor components. Sublimation *in vacuo* afforded a solid shown to be the desired *dithiin* (156)(3.4g, 60%)(as yellow crystallites m.p. 55-55.5°C) by comparison of ^{19}F n.m.r. spectra with authentic material (number 17).

6.4 *Dithiin* (156) with nitric acid

Nitric acid (0.22ml, 2*M*, 0.44mmol) was added dropwise to a stirred solution of the *dithiin* (156)(0.20g, 0.61mmol) in acetic acid (1.5ml). A further portion of acid (0.20ml) was added and the mixture refluxed for 3h. Water (5ml) was added and the solid thus formed (0.082g) was filtered and found (^{19}F n.m.r.) to contain a small amount (10%) of starting material (156)(n.m.r. spectra number 17). Recrystallisation (CCl_4) afforded a mixture assigned to the twopossible *sulphoxides* (159) and (160)(0.05g, 23%). m/z (E.I.)

343.9776. $C_{12}H_6F_6S_2O$ requires M^+ 343.9764; mass spectrum number 23; n.m.r. spectra number 18; i.r. spectrum number 19.

6.5 *Dithiin (156) with Raney nickel*

A solution of the *dithiin* (156)(2.8g, 8.5mmol) in ethanol (25ml) was added dropwise to a refluxing mixture of Raney nickel (23g) in ethanol (120ml) and heated for a further 1h. A small portion of volatile material was transferred to a cold trap with a stream of nitrogen and shown to by ^1H and ^{19}F n.m.r. to contain more than one component. The mixture could not be separated and was not pursued further.

6.6 *Ortho*-aminothiophenol with perfluorocyclobutene (107)

A mixture of *ortho*-aminothiophenol (6.7g, 53.6mmol), triethylamine (6.6g, 65.3mmol) and ether (100ml) was cooled to -78°C and connected to a flexible gas reservoir containing perfluorocyclobutene (107)(12.5g, 77.1mmol). After stirring for 1h. the mixture was warmed to room temperature and stirred for a further 8h. Ether was partially removed *in vacuo* and the residue was cooled to -15°C and the solid product was collected, washed with water and then sublimed *in vacuo* to give a green solid (2.4g, 18%) identified as:-

3,4-benzo-7,7,8,8-tetrafluoro-2-aza-5-thiobicyclo(4.2.0)oct-1-ene (164) (Found: C, 48.8; H, 2.0; N, 5.3. $C_{10}H_5F_4SN$ requires: C, 48.6; H, 2.0; N, 5.7%); mass spectrum number 24; n.m.r. spectra number 19; i.r. spectrum number 20

Water (250ml) was added to the remaining solution and the ether layer was removed and dried ($MgSO_4$). Evaporation of solvent *in vacuo* yielded a solid (10.8g) shown (^{19}F n.m.r., by comparison

with previous material(164), (number 19) to be the *thiazacyclohexene* (164)(>95% pure)(total yield >95%).

In a separate reaction with potassium carbonate as base conducted at room temperature for 1.5h. no tractable material could be isolated.

6.7 *Ortho*-aminothiophenol with perfluorocyclopentene (154)

a) Quenched after a short period.— A mixture of the alkene (154)(5.0g, 23.6mmol), *ortho*-aminothiophenol (3.0g, 24mmol), potassium carbonate (4.5g, 32.6mmol) and acetonitrile (150ml), contained in a sealed tube, was agitated at room temperature. A crystalline solid was observed to form immediately but agitation was continued for *ca.* 1h. Solid material was filtered, extracted with ether, which was then dried ($MgSO_4$) and evaporated to yield a solid (4.0g). Sublimation *in vacuo* of a portion gave a yellow powder (1.0g) >95% pure by n.m.r. and t.l.c. subsequently identified as :- *1,2-bis(2'-aminothiophenoxy)-3,3,4,4,5,5-hexafluorocyclopentene* (162) (10% isolated) m.p. 120°C; m/z (E.I.) 422.0261. $C_{17}H_{12}N_2S_2F_6$ requires M^+ 422.0348; mass spectrum number 27; n.m.r. spectra number 21; i.r. spectrum number 22.

Variable analysis was obtained for this material but its purity was >95% by n.m.r. and t.l.c.

b) Allowed to proceed for 24 hours.— As in (a) with alkene (154)(4.7g, 22.2mmol), *ortho*-aminothiophenol (2.8g, 22.4mmol), potassium carbonate (4.6g, 33.3mmol) and acetonitrile (150ml) at room temperature for 24h. Water (200ml) was added and the product extracted with ether (2 X 200ml), dried ($MgSO_4$) and the solvent

evaporated *in vacuo* to leave a yellow solid (6.0g) shown by n.m.r. to be a single product (97%). Sublimation of a small portion afforded:-

3,4-benzo-7,7,8,8,9-pentafluoro-2-thia-5-azabicyclo(4.3.0)nona-1,5-diene (161) m.p. 120-121°C (Found: C, 48.0; H, 1.6; N, 5.3. $C_{11}H_4F_5NS$ requires: C, 47.7; H, 1.5; N, 5.1%); mass spectrum number 25,26; n.m.r. spectra number 20; i.r. spectrum number 21.

c) For intermediate times.— As for (a) conducted at room temperature for 2h. The mixture was analysed (by n.m.r. spectroscopy) after the addition of water and extraction with ether, and found to contain the *dithioether* (162)(38%)(^{19}F n.m.r., number 21) and the *thiazole* (161)(28%)(^{19}F n.m.r., number 20) in addition to some small amounts of other unidentified components.

As for (a) conducted at room temperature for 8h. The mixture was analysed by n.m.r spectroscopy after the addition of water and extraction with ether and shown to contain the *dithioether* (162)(7%)(n.m.r. spectra number 21), the *thiazole* (161)(33%)(n.m.r. spectra number 20) and other unidentified resonances.

6.8 Catechol with perfluorocyclobutene (107)

A mixture of the alkene (107)(10.2g, 62.9mmol), catechol (6.9g, 63mmol), potassium carbonate (11g, 80mmol) and acetonitrile (200ml) contained in a sealed glass vessel was agitated at room temperature for 48h. After filtration of solids and solvent evaporation a brown oil (14g) remained which was transferred *in vacuo* to a cold trap and found (g.l.c., Col. O) to contain one major component and a number of unidentified components in small quantities. Purification by preparative scale g.l.c. (Col. O)

afforded:-

1-spirotetrafluorocyclobutenyl-3,4-benzo-2,5-dioxacyclopentane (167)(67%) (Found: C, 51.5; H, 1.5; F, 33.2%. $C_{10}H_4F_4O_2$ requires: C, 51.7; H, 1.7; F, 32.7%); mass spectrum number 28; n.m.r. spectra number 21a; i.r. spectrum number 23.

6.9 Catechol with perfluorocyclopentene (154)

a) With one equivalent of catechol to alkene (154).— A mixture of the alkene (154)(16.0g, 75.5mmol), catechol (7.95g, 72.2mmol), potassium carbonate (13.86g, 100.4mmol) and acetonitrile (200ml) contained in a sealed glass vessel was agitated at room temperature for 24h. Solid material was filtered and the solvent was evaporated to leave a yellow oil (19.3g). Volatile material was transferred *in vacuo* to a cold trap and identified as:-

1-spirohexafluorocyclopent-2-enyl-3,4-benzo-2,5-dioxacyclopentane (168)(50%) (Found: C, 46.8; H, 1.4; F,40.1. $C_{11}H_4F_6O_2$ requires: C, 46.8; H, 1.4; F, 40.4%); mass spectrum number 29; n.m.r. spectra number 22; i.r. spectrum number 24.

b) With excess alkene (154).— A mixture of the alkene (154)(9.4g, 44.3mmol), catechol (2.20g, 20mmol), potassium carbonate (4.60g, 33.3mmol) and acetonitrile (30ml) contained in a sealed glass tube was agitated at room temperature for 48h. Excess gas (7.0g) was allowed to expand into an evacuated space and found to be starting material (154)(74% recovered) by a comparison of ^{19}F n.m.r. (number 10) and i.r. (number 11) spectra with an authentic sample. Water (150ml) was added to the residue and the lower layer (5.0g) thus formed was removed. Volatile material (4.9g) was transferred *in vacuo* to a cold trap and found (g.l.c., Col. O) to be a mixture of several components. Mass spectroscopy identified the *spiro-ketal*

(168)(40%)(mass spectrum number 29), two $C_{11}H_5F_7O_2$ components (3% and 1%), a $C_{16}H_4F_{14}O_2$ component (6%) and a $C_{16}H_5F_{15}O_2$ component (9%). Only the *spiro-ketal* (168) could be isolated pure and the mixture was not pursued further.

c) With excess catechol.— A similar reaction with a five fold excess of catechol and potassium carbonate gave a small quantity of a multicomponent (t.l.c., Et_2O eluent) white solid which could not be purified and was not pursued further.

6.10 *Spiro-ketal* (168) with acids

a) With mineral acids.— A mixture of the *spiro-ketal* (168)(0.52g, 1.8mmol), hydrochloric acid (2*M*, 4ml) and acetonitrile (2ml), contained in a sealed glass vessel, was agitated for 1h. at 60°C and for a further 2h. at 100°C. The mixture was cooled and the lower layer (0.56g) removed and found (g.l.c., Col. O) to be single component and identified by a comparison of g.l.c. retention time and ^{19}F n.m.r. spectra (number 22) as starting material (100% recovered).

Similarly, (168) was recovered (85%) after stirring with excess sulphuric acid (50%) at room temperature for 144h.

b) With strong Lewis acids.— Prolonged stirring with boron trifluoride etherate (excess) gave only starting material (85% recovered).

Neat excess antimony pentafluoride reacted violently on contact with (168) to give an intractable tarry material.

An arcton ($CF_2ClCFCl_2$) solution of antimony pentafluoride was mixed at -78°C with the *spiro-ketal* (168) and warmed slowly to room temperature, upon which the mixture slowly tarred and was not pursued further.

6.11 *Spiro-ketal* (168) with potassium fluoride

A mixture of the *spiro-ketal* (168)(0.98g, 3.5mmol), potassium fluoride (0.38g, 6.7mmol) and tetraglyme (2ml) was stirred at room temperature for 72h. and for a further 1h. at 70°C. The resulting mixture was found (^{19}F n.m.r.,) to contain starting material (168)(89%)(n.m.r. spectra number 22) and an unidentified component (11%).

6.12 *Ortho*-aminophenol with perfluorocyclobutene (107)

A mixture of the alkene (107)(4.8g, 29.6mmol), *ortho*-aminophenol (3.5g, 32.1mmol), potassium carbonate (6.5g, 47.1mmol) and acetonitrile (200ml), contained in a sealed glass tube, was agitated at room temperature for 24h. Water (200ml) was added and the lower layer (10.2g) removed. Mild heating at *ca.* 10mmHg left a viscous oil (4.0g) from which a white solid (1.6g) sublimed *in vacuo*. This was subsequently identified as:-

ortho-2,3,3,4,4-pentafluorocyclobut-1-eneoxyaniline (173)(22%)

(Found: C, 48.1; H, 2.4; N, 5.6. $C_{10}H_6F_5NO$ requires: C, 47.8; H, 2.4; N, 5.6%); mass spectrum number 30; n.m.r. spectra number 23; i.r. spectrum number 25.

6.13 *Ortho*-aminophenol with perfluorocyclopentene (154)

A mixture of the alkene (154)(5.5g, 25.9mmol), *ortho*-aminophenol (2.8g, 25.7mmol), potassium carbonate (5.8g, 42.0mmol) and acetonitrile (200ml), contained in a sealed glass

tube, was agitated at room temperature for 2.5 h. Water (300ml) was added and the lower layer thus formed (11.0g) removed and found (^{19}F n.m.r. and g.l.c., Col. O) to contain solvent, starting material (154)(23%)and one other component. Residual solvent was removed by brief application of high vacuum and then the remaining volatile material was transferred *in vacuo* to a cold trap and found (g.l.c., Col. O) to be single component, identified as:-

ortho-2,3,3,4,4,5,5-heptafluorocyclopent-1-eneoxyaniline (174) (98%)based on consumed perfluorocyclopentene); mass spectrum number 31; n.m.r. spectra number 24; i.r. spectrum number 26.

This material rapidly decomposed on standing at room temperature in air and therefore elemental analysis was unavailable, but could be used immediately in a further reaction..

6.14 *Ether (173) with triethylamine*

The *ether* (173) formed in a separate reaction with *ortho*-aminophenol (3.4g, 31.2mmol), potassium carbonate (8.0g, 57.9mmol), perfluorocyclobutene (107)(4.5g, 27.8mmol) and acetonitrile, conducted as before (6.12) was refluxed in acetonitrile (200ml) in the presence of triethylamine (3.0g, 29.7mmol). Solvent was evaporated *in vacuo* to leave an intractable tar (7.8g) with a very complicated ^{19}F n.m.r. spectrum.

6.15 *Ether (174) with triethylamine*

The *ether* (174) from a separate reaction with *ortho*-aminophenol (5.1g, 46.7mmol) and perfluorocyclopentene (154) (9.7g, 45.8mmol) carried out under conditions identical to previous experiments (6.13), was refluxed with triethylamine (5.0g, 49.5mmol) in acetonitrile (200ml) for 7h. Water (300ml) was added and the

product extracted with ether (2x200ml). After drying ($MgSO_4$) and evaporation of solvent a brown solid remained. Sublimation *in vacuo* afforded a compound identified as:-

3,4-benzo-7,7,8,8,9-pentafluoro-2-oxa-5-azabicyclo(4.3.0)nona-1,5-diene (175)(7.0g, 59% based on consumed perfluorocyclopentene), a white solid m.p. 103-104°C (from CCl_4) (Found: C, 50.9; H, 1.2; N, 5.5; F, 36.0. $C_{11}H_4F_5NO$ requires: C, 50.6; H, 1.5; N, 5.4; F, 36.4%); mass spectrum number 32; n.m.r. spectra number 25; i.r. spectrum number 27.

6.16 *Ether* (173) with sodium hydride

Ether (173) was reacted with one molar equivalent of sodium hydride in acetonitrile at room temperature but only gave an intractable black tar which was not pursued further.

6.17 *Ortho*-phenylenediamine with perfluorocyclopentene (154)

A mixture of the alkene (154)(4.8g, 22.6mmol), *ortho*-phenylenediamine (2.8g, 25.9mmol), potassium carbonate (7.1g, 51.4mmol) and acetonitrile (200ml), contained in a sealed glass vessel, was agitated at room temperature for 24h. Water (200ml) was added and the product extracted with ether (2x150ml), dried ($MgSO_4$) and the solvent evaporated *in vacuo* to leave a black intractable tar which was not pursued further.

6.18 Benzamidine hydrochloride with perfluorocyclopentene (154)

A mixture of the alkene (154)(8.5g, 40.1mmol), benzamidine hydrochloride (5.0g, 32.1mmol), potassium carbonate (16.3g, 118mmol) and acetonitrile (100ml) was agitated in a sealed glass vessel for 24h. at room temperature. The crude material gave only a few well resolved resonances in a ^{19}F n.m.r. spectrum. Solvent was removed

(rotary evaporator) and an attempt to transfer volatile material to a cold trap failed due to severe tarring of the material.

6.19 N,N'-dimethylurea with perfluorocyclopentene (154)

A mixture of the alkene (154)(5.6g, 26.4mmol), N,N'-dimethylurea (2.75g, 31.3mmol), potassium carbonate (5.6g, 40.6mmol) and acetonitrile (250ml), contained in a sealed glass vessel, was agitated at room temperature for 23h. Water (250ml) was added with much effervessence (presence of volatile material) and the diminishing lower layer (0.9g) was removed and found (^{19}F n.m.r., number 10) to be starting material (16% recovered).

In a similar reaction with sodium hydride as base, conducted at -15°C for 3h. only v. volatile fluorocarbon products, presumed to be starting material, were produced on the addition of water.

6.20 Ethanedithiol with perfluorocyclopentene (154)

A mixture of the alkene (154)(4.7g, 22.2mmol), ethanedithiol (2.25g, 23.9mmol), potassium carbonate (6.8g, 49.3mmol) and acetonitrile (80ml), contained in a sealed glass vessel, was agitated at room temperature for 48h. The resulting mixture was filtered and the solvent evaporated *in vacuo* to leave a straw coloured oil (4.4g). A small amount (0.03g) of material was transferred *in vacuo* to a cold trap and found (g.l.c., Col. 0) to contain two components which were not pursued further. The residual solid was found (t.l.c., silica plate, ether eluent) to contain two major components which could not be obtained pure by chromatography on silica (ether eluent).

A similar reaction was performed and a sublimation of the

solid residue attempted. No material could be isolated.

6.21 Benzimidazole-2-thiol with perfluorocyclopentene (154)

A mixture of the alkene (154)(5.6g, 26.4mmol), benzimidazole-2-thiol (3.7g, 24.7mmol), potassium carbonate (7.7g, 55.8mmol) and acetonitrile (200ml), contained in a sealed glass vessel, was agitated at room temperature for 24h. Water (200ml) was added and the product extracted with ether (2x200ml), dried ($MgSO_4$) and the solvent evaporated *in vacuo* to yield a brown solid (8.0g) with a very complicated ^{19}F n.m.r. spectrum. Sublimation *in vacuo* afforded a small amount of a white solid (0.2g) shown (by ^{19}F and ^{1}H n.m.r., and t.l.c.) to be >95% pure and identified as:-

3,4-benzo-2,5-diaza-11-thia-7,7,8,8,9,9-hexafluorotricyclo(4.0.7.0^{6,10})nona-1,6-diene (177)(3%); m/z 322.0028. $C_{12}H_4N_2SF_6$ requires: M^+ 322.0000. mass spectrum number 33; n.m.r. spectra number 26; i.r. spectrum number 28.

Good combustion analysis could not be obtained on this material although other spectroscopic techniques demonstrated it was more than 95% pure.

6.22 Catechol with perfluoro-3,4-dimethylhex-3-ene (82)

a) With potassium carbonate as base.— A mixture of catechol (2.95g, 26.8mmol), the alkene (82) (11.50g, 28.8mmol), potassium carbonate (6.77g, 49.0mmol) and acetonitrile (70ml) was stirred at room temperature for 96h. Water (150ml) was added and the lower layer thus formed removed. Volatile material (9.5g) was transferred *in vacuo* to a cold trap and found (g.l.c., Col. O) to be a mixture of three components; all $C_{14}H_4F_{14}O_2$ isomers (by mass spectroscopy). The major product was isolated by preparative scale

g.l.c. (Col. K) and shown to be:-

6,7-benzo-2,3,4-tristrifluoromethyl-2-pentafluoroethyl-1,5-dioxacycl ohept-3-ene (179)(49%) (Found: C, 36.2; H, 0.7. $C_{14}H_4F_{14}O_2$ requires: C, 35.8; H, 0.9%); mass spectrum number 34; n.m.r. spectra number 27; i.r. spectrum number 29.

The two minor products were formed in a total yield of 29% but neither could be obtained pure and they were not p rsued further.

b) With lithium carbonate as base.— A mixture of the alkene (82)(10.3g, 25.7mmol), lithium carbonate (4.1g, 55.5mmol), catechol (2.8g, 25.5mmol) and acetonitrile (250ml) was stirred at room temperature for 72h. Solid material was filtered and the solvent evaporated. Acetone (3ml) was added (to dissolve remaining lithium carbonate) and the lower layer thus formed (9g) was removed and found (mass spectroscopy/g.l.c., Col. O) to contain the *dioxepene* (179)(57%)(mass spectrum number 34) and the two other $C_{14}H_4F_{14}O_2$ isomers (approximately similar quantity, total yield 15%)

6.23 Catechol with perfluoro-3,4-dimethyl-4-ethylhex-2-ene (83)

A mixture of the alkene (83)(13.9g, 27.8mmol), potassium carbonate (6.4g, 46.4mmol), catechol (2.8g, 25.5mmol) and acetonitrile (70ml) was stirred at room temperature for 144h. Water (250ml) was added and the lower layer thus formed was removed. Volatile material (10.1g) was transferred *in vacuo* to a cold trap and found (g.l.c., Col. O) to contain one major (>94%) component which was isolated by preparative scale g.l.c. (Col. O) and subsequently identified as:-

5,6-benzoperfluoro-3-methyl-2-(1'-methyl-1'-ethylpropyl)-4,7-dioxacyclohept-1-ene (180)(65%)

(Found: C, 33.9; H, 0.4; F, 60.4. $C_{16}H_4O_2F_{18}$ requires: C, 33.7; H, 0.7; F, 60.0%); mass spectrum number 35,36; n.m.r. spectra number 28; i.r. spectrum number 30.

6.24 Catechol with perfluorocyclobutylcyclobut-1-ene (141)

A mixture of catechol (0.34g, 3.1mmol), the alkene (141)(1.00g, 3.1mmol), potassium carbonate (0.94g, 6.8mmol) and acetonitrile (30ml) was stirred at room temperature for 720h. After filtration of solids and evaporation of solvent the remaining oil was transferred *in vacuo* to a cold trap to yield a colourless liquid (0.38g) subsequently shown to be:-

2-spirohexafluorocyclobutyl-3,4-tetrafluorocyclobutenyl-6,7-benzo-1,5-dioxacyclohept-3-ene (181)(31%) (Found: C, 42.9; H, 1.4; F,47.7. $C_{14}H_4F_{10}O_2$ requires: C, 42.7; H, 1.0; F, 48.2%); mass spectrum number 37; n.m.r. spectra number 29; i.r. spectrum number 31.

6.25 Catechol with a mixture of perfluorocyclobutylcyclobut-1-ene (141) and perfluorobicyclobutylidene (127)

In a similar reaction to (6.24) with an equimolar mixture of the title alkenes (127) and (141)(5.3g, 16.4mmol), catechol (1.7g, 15.5mmol), potassium carbonate (4.7g, 34mmol) and acetonitrile (120ml) for the shorter time of 72h, after work up as for (6.24), volatile material (4.8g) was shown to be pure *dioxepene* (181)(78%) by a comparison of g.l.c. retention times and ^{19}F n.m.r. data (number 29) with an authentic sample.

6.26 Catechol with hexafluoropropene (1)

A mixture of the alkene (1)(5.0g, 33.3mmol), catechol (3.9g, 35.4mmol), potassium carbonate (6.2g, 44.9mmol) and acetonitrile (50ml) contained in a sealed glass vessel was agitated at room

temperature for 24h. Water (50ml) was added and the lower layer thus formed (10.8g) was removed. Volatile material (6g) was transferred *in vacuo* to a cold trap and shown (g.l.c., Col. O) to consist of two major components, which were isolated by preparative scale g.l.c. (Col. O) and shown to be:-

(a) *Ortho-1,1,2,3,3,3-hexafluoropropoxyphenol* (183)(38%) (Found: C, 41.4; H, 2.6; F, 43.3. $C_9H_6F_6O_2$ requires: C, 41.6; H, 2.3; F, 43.8%); mass spectrum number 39; n.m.r. spectra number 31; i.r. spectrum number 33.

(b) *Orthobis-1,1,2,3,3,3-hexafluoropropoxybenzene* (182)(16%) (Found: C, 35.4; H, 1.3; F, 51.5. $C_{12}H_6F_{12}O_2$ requires: C, 35.1; H, 1.5; F, 55.6%); mass spectrum number 38; n.m.r. spectra number 30; i.r. spectrum number 32.

6.27 Catechol with chlorotrifluoroethylene (50)

A mixture of the alkene (50)(4.8g, 41.2mmol), catechol (4.2g, 38.2mmol) and acetonitrile (90ml) was agitated in a sealed glass vessel at room temperature for 48h. Water (250ml) was added and the lower layer (12.1g) was removed. Further additions of water (2 X 50ml) were made and the final lower layer was separated, transferred *in vacuo* to a cold trap and found to be:- *orthobis-1,1,2-trifluoro-2-chloroethoxybenzene* (184)(43%); m/z 342, $C_{10}F_6O_2H_6Cl_2$ requires M^+(342); mass spectrum number 40; n.m.r. spectra number 32; i.r. spectrum number 34.

The compound was further purified by preparative scale g.l.c. (col. O) and shown (g.l.c., capillary column) to be pure but repeated elemental analyses were unsatisfactory.

6.28 Dilithio-catechol with hexafluoropropene (1)

^{n}Butyl lithium in hexane (1.6M, 42ml, 67.2mmol) was added dropwise to a stirred solution of catechol (3.7g, 33.6mmol) in dry ether (150ml) under nitrogen at -78°C. After stirring for 1h. at -78°C then for 24h. at room temperature the solvent was evaporated *in vacuo* to leave the dilithio derivative as a white solid. Acetonitrile (100ml) was added and a flexible gas reservoir containing hexafluoropropene (1)(5.5g, 36.7mmol) was attached. After stirring for 48h. at room temperature the solution was filtered and the solvent removed by distillation to leave a colourless liquid (9g). Analysis by g.l.c. (Col. O) indicated the presence of a small amount of solvent and four other components, two of them major. These were isolated by preparative scale g.l.c. (Col. O) and shown to be:-

(a) *4,5-benzo-(1',1',1',2',3'-pentafluoroethyl)-1,3-dioxacyclopentane (194)*(29%) (Found: C, 45.3; H, 2.8. $C_9H_5F_5O_2$ requires: C, 45.0; H, 2.1%); mass spectrum number 42; n.m.r. spectra number 34; i.r. spectrum number 36.

and (b) *4,5-benzo-2-(1',1',1',4'-tetrafluoroetheno)-1,3-dioxacyclopentane (193)*(54%) (Found: C, 48.8; H, 2.1. $C_9H_4F_4O_2$ requires: C, 49.1; H, 1.8%); mass spectrum number 41; n.m.r. spectra number 33; i.r. spectrum number 35.

6.29 Dilithio-catechol with chlorotrifluoroethylene (50)

A flask was charged with catechol (3.65g, 33.2mmol) and dry ether (100ml) and purged with dry nitrogen. ^{n}Butyl lithium in hexane (41ml of 1.6M, 65.6mmol) was added dropwise at -78°C and the mixture was stirred for a 2h. and then for a further 24h. at room temperature. Solvent was evaporated to leave the dilithio

derivative as a white solid. A flexible gas reservoir containing (50)(3.9g, 33.5mmol) was connected and acetonitrile (20ml) admitted and the mixture stirred at room temperature for 72h. Volatile material (15.6g) was transferred *in vacuo* to a cold trap and found to contain no detectable fluorocarbon material by n.m.r. and g.l.c.

6.30 Other reactions of perfluoro-3,4-dimethylhex-3-ene (82)

a) With acetamide.— A mixture of the alkene (82)(5.1g, 12.8mmol), acetamide (0.73g, 12.4mmol), sodium hydride (60% w/w in oil, 0.5g, 12.5mmol) and 1,4-dioxan (25ml) was stirred at room temperature for 48h. After standing for 1h. the lower layer (2.0g) was removed and found to be starting material (82)(40% recovered) by a comparison of i.r. spectra (number 16) with authentic material. Volatile material from the upper layer was transferred *in vacuo* to a cold trap (leaving a significant amount of tarry residue) and shown (g.l.c., Col. K) to consist of starting material (82) and solvent (by a comparison of g.l.c. retention times).

A similar reaction with tetraglyme as solvent only gave starting material (82) as a tractable product.

b) With urea.— A mixture of the alkene (82)(11.7g, 29.3mmol), urea (2.0g, 33.3mmol), potassium carbonate (3.8g, 27.5mmol) and tetraglyme (20ml) was stirred at 33°C for 16h. Water (50ml) was added to give a three phase system. The lower colourless layer (9g) was shown, by comparison of ^{19}F n.m.r. spectra (number 15) with authentic material to be starting material (77% recovered). The middle layer (1.5g) gave a very complicated ^{19}F n.m.r. spectrum and was not investigated further.

Other similar reactions with potassium carbonate as base conducted at various temperatures up to reflux in tetrahydrofuran, acetonitrile and 1,4-dioxan as solvent gave starting material and tarry residues only.

c) With *N,N'*-dimethylurea.— Sodium hydride (60% in oil, 1.0g, 24.9mmol) was added slowly over 1.5h. to a stirred solution of *N,N'*-dimethylurea (2.3g, 26.1mmol) and (82)(11.0g, 27.5mmol) in tetraglyme (40ml) at 0°C. After warming to room temperature and further stirring (72h.), water (100ml) was added and the lower layer thus formed (11.3g) removed and found to be starting material (82)(100% recovered) by a comparison of ^{19}F n.m.r. spectra (number 15) with authentic material.

d) With 1,2-ethanedithiol.— A mixture of the alkene (82)(5.5g, 13.8mmol), potassium carbonate (3.9g, 28.3mmol), ethanedithiol (1.1g, 11.7mmol) and acetonitrile (100ml) was stirred at room temperature for 120h. Water (150ml) was added and the white spongy solid thus formed was filtered but could not be purified by chromatography on silica (ether eluent) and was discarded. A lower layer (0.35g) slowly formed from the aqueous medium and after transferring to a cold trap *in vacuo* was shown (g.l.c., Col. O/mass spectroscopy) to consist of solvent and a $C_{10}H_4S_2F_{14}$ isomer in low yield.

e) With benzamidine hydrochloride.— A mixture of the alkene (82)(9.8g, 24.5mmol), benzamidine hydrochloride (3.7g, 23.6mmol), potassium carbonate (7.1g, 51.4mmol) and acetonitrile (50ml) was stirred at room temperature for 4 days and then at 35°C for 72h. Water (100ml) was added and the lower layer removed and

transferred *in vacuo* to a cold trap to give a yellow oil (8.6g). Analysis by g.l.c./mass spectroscopy (Col. O) confirmed the presence of solvent, an unidentified compound (M=329) and two $C_{15}N_2H_4F_{13}$ isomers. Preparative scale g.l.c. (Col. O) failed to isolate a fluorocarbon product due to decomposition during the separation process. Benzonitrile was found in the cold traps, identified by a comparison of i.r. spectra with authentic material.

In a similar reaction, chromatography on silica (ether eluent) failed to produce pure products.

f) With *ortho*-aminophenol.— A mixture of the alkene (82)(4.2g, 10.5mmol), *ortho*-aminophenol (1.3g, 12.0mmol), potassium carbonate (2.6g, 18.8mmol) and acetonitrile (150ml) was stirred at room temperature for 120h. Water (150ml) was added and the lower layer (5.0g) removed and transferred *in vacuo* to a cold trap and found (g.l.c., Col. O) to contain starting material (82)(identified on the basis of g.l.c. retention time)(20% recovered) and a number of unidentified components which were not pursued further.

A mixture of the alkene (82)(5.1g, 12.8mmol), *ortho*-aminophenol (1.4g, 12.9mmol), potassium carbonate (3.7g, 26.8mmol) and acetonitrile (100ml) was stirred at room temperature for 24h. Water (250ml) was added and three layers were observed to form. The lower (2g) was found (g.l.c., Col. O and ^{19}F n.m.r. number) to be starting material (82)(39% recovered) and the middle phase (8.3g) exhibited a very complicated ^{19}F n.m.r. spectrum and was not p rsued further.

(g) With 3,4-dimercaptotoluene.— A mixture of the alkene (82)(1.65g, 4.1mmol), 3,4-dimercaptotoluene (0.58g, 3.7mmol), potassium carbonate (1.8g, 13mmol) and acetonitrile (100ml) was stirred at room temperature for 24h. Water (100ml) was added and the lower layer (1.8g) removed, transferred *in vacuo* to a cold trap and found (^{19}F n.m.r.) to be a very complicated mixture from which no material could be isolated.

h) With *Ortho*-aminothiophenol.— A mixture of the *ortho*-aminothiophenol (1.6g, 12.8mmol), potassium carbonate (2.7g, 19.6mmol) and ether (200ml) was cooled to -78°C and the alkene (82)(5.0g, 12.5mmol) was added slowly with stirring. On warming to room temperature and further stirring for 24h., water (250ml) was added and the product extracted with ether (2x100ml), dried ($MgSO_4$) and, after evaporation of solvent (3.0g of solid) was shown (^{19}F n.m.r., t.l.c.) to contain at least five components which could not be purified.

i) With benzimidazole-2-thiol.— A mixture of the alkene (82)(4.0g, 10.0mmol), potassium carbonate (2.7g, 19.6mmol), benzimidazole-2-thiol (1.64g, 10.9mmol) and acetonitrile (200ml) was stirred at room temperature for 48h. Water (200ml) was added and the product extracted with ether (2x100ml), dried ($MgSO_4$), shown by ^{19}F n.m.r. spectroscopy to be multicomponent and was not pursued further.

6.31 *Ortho*-aminophenol with perfluoro-3-methylpent-2-ene (197)

A mixture of the alkene (197)(2.4g, 7.9mmol), *ortho*-aminophenol (2.2g, 20.1mmol) and potassium carbonate (6.0g,

43.4mmol) was stirred in acetonitrile at room temperature for 96h. After solvent evaporation (rotary evaporator), sublimation *in vacuo* afforded only a small amount of solid (0.3g). Residue was found (t.l.c. on silica, dichloromethane eluent) to consist of *ca.* 7 components which could not be obtained pure by chromatography on silica (dichloromethane eluent).

A similar reaction with triethylamine as base, ether as solvent conducted at -15°C for 12h. gave a similar result. A small amount (0.2g) of liquid volatile material was also isolated and found (g.l.c., Col. O) to contain five components two of which could be identified as $C_{12}H_5ONF_{10}$ and $C_{12}H_4ONF_9$ isomers by mass spectroscopy.

6.32 Dimerisation of hexafluoropropene (1)

a) <u>with no agitation, giving *kinetic dimer* (196)</u>.— A *Carius* tube was charged with caesium fluoride (1.8g, 11.8mmol) and acetonitrile (38ml), and hexafluoropropene (1)(17.0g, 113mmol) was transferred *in vacuo* to the tube which was cooled in liquid air. The mixture was then stood in the sealed vessel at room temperature for 16h. (NB. *An initial exotherm indicated the relevant dimerisation had taken place and therefore 16h. is probably excessive. Provided no agitation is provided, however, none of the alternative thermodynamic dimer* (29) *is found.*). The lower layer (13.6g) was removed and found by a consideration of ^{19}F n.m.r. (number 35), i.r. (number 37) and mass (number 43) spectra to be the *kinetic dimer* (196)(80%), b.p. 47.5°C.

A number of similar reactions are summarised in the table below.

(1) (g, mmol)	CsF (g, mmol)	CH_3CN (ml)	time (h.)	yield of *dimer* (196) (%)
17.0, 113	1.8, 11.8	38	16	80
6.0, 40	0.5, 3.3	10	24	50
30.0, 200	2.6, 17.1	75	24	77

b) with agitation, giving *thermodynamic dimer* (29).— In reactions conducted as for (a) except efficient agitation in a rotating arm was provided a good yield of the *thermodynamic dimer* (29) could be realised with only minor impurities (^{19}F n.m.r. number 36, i.r. number 38, mass spectra number 44), b.p. 52.5°C.

The reactions are summarised in the following table.

(1) (g, mmol)	CsF (g, mmol)	CH_3CN (ml)	time (h.)	yield of *dimer* (29) (%)
31, 207	2.4, 16	80	24	95
40, 266	4.6, 30	120	24	50
58, 387	5.8, 38	100	22	89

6.33 *Ortho*-aminophenol with perfluoro-3-methylpent-2-ene (196)

In a reaction, conducted as for (6.31) with triethylamine as base and ether as solvent no tractable material could be isolated.

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER FOUR

FLUORINATED CARBANIONS

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER FOUR

7.1 Co-dimerisation of perfluorocyclopentene (154) and perfluorocyclobutene (107)

A *rotoflo* tube was charged with pyridine (2.5g, 31.6mmol) and alkenes (154)(25.3g, 119.4mmol) and (107)(20.5g, 126.5mmol) were transferred *in vacuo* to the tube which was cooled in liquid air. The resulting mixture was agitated in a shaker at room temperature for 16h. and then volatile material was transferred under vacuum to a cold trap, washed with water (2x100ml) and dried (P_2O_5). The liquid was distilled (Fischer Spaltrohr) to yield:-

perfluorocyclobutene dimers (141) and (127), b.p. 80-85°C, 6.0g 29%. and the *co-dimer* (216), b.p. 98-100°C, 2.0 g, 5%.

The syntheses of perfluorobicylobutylidene (127), perfluorocyclobutylcyclobutene (141), perfluorobicyclopentylidene (128), perfluoro-2-methylpent-2-ene (29), and perfluoro-2-methylpent-3-ene (196) have already been described.

7.2 Synthesis of trisdimethylaminosulphonium-trimethylsilyldifluoride (208) (TAS-F)

General procedure.— A 'rotoflo' tube of the desired volume (to contain 0.3 mol. equivalents of SF_4 to Me_2NSiMe_3) was evacuated and the tap was carefully opened to a stream of SF_4 until the tube was full with SF_4 gas. One arm of a *Schlenk* tube was charged with dry ether, cooled in liquid air, and the SF_4 was transferred *in vacuo* to the vessel. The apparatus was allowed to fill with dry nitrogen and warmed to -78°C (acetone/drycold). A pressure

equalising droping funnel containing *N,N*-dimethyltrimethylsilylamine (241)(3 x molar quantity to SF_4) was connected to the apparatus against a countercurrent of dry nitrogen and the *silylamine* was added dropwise (over *ca.* 2h) to the stirred solution and the resulting mixture further stirred at -78°C for *ca.* 2h. Care must be taken when adding the *silylamine* as overzealous additions cause the temperature of the ether solution to rise and significant interference to the reaction may occur. The flask was then warmed to room temperature and stirring was continued under dry nitrogen for *ca.* three days. A white precipitate slowly formed from the ether solution which was filtered on to the *Schlenk* scinter under nitrogen simply by inverting the *Schlenk* tube and reducing the pressure slightly in the opposite arm. This was found to be the desired product (208) by a comparison of ^{19}F n.m.r. and ^{1}H n.m.r. (number 49) with literature data,[228] and by a consideration of ^{13}C n.m.r. data (not reported in the literature)(number 49).

TAS-F may be stored supported on the *Schlenk* scinter for prolonged periods provided moisture is rigorously excluded.

Reactions conducted as above are detailed in the following table:-

silylamine (241) (g, mmol)	SF_4 (g, mmol)	ether (g)	Yield of (208) (%)
10.0, 85.5	2.9, 26.9	21	55
10.0, 85.5	2.3, 21.3	26	85
10.0, 85.5	3.0, 27.8	35	-
10.0, 85.5	2.2, 20.3	30	63

Yields based on SF_4 consumed.

Use of TAS-F All manipulations of TAS-F are made using baked and nitrogen filled apparatus and a countercurrent of dry nitrogen is maintained when the apparatus is open to the atmosphere. A portion of the solid on the scinter of the *Schlenk* tube was caused to fall into the side arm of the *Schlenk* tube and dry acetonitrile was added to dissolve it. The resulting solution was removed and then residual solvent was pumped off. The weight of TAS-F used was calculated by difference and, thus, by the final volume of the acetonitrile solution removed the exact concentration of TAS-F could be determined.

7.3 Synthesis of perfluoroisobutene (4)

Important Note *Pefluoroisobutene is extremely toxic by inhalation* (lc^{50}_{rat} *0.2 ppm for 0.5h.*).[257] *All manipulations with* (4) *should be made with a well ventilated fumes hood and the wearing of breathing apparatus is advised.*

In the course of this experiment, the above conditions were met and, in addition, all volatile material was contained in a vacuum line or apparatus backed up with cold traps. The author gratefully acknowledges the help of Mr. T. F. Holmes during this experiment.

Hexafluoropropene (1) was passed through a nickel tube (bore 2 cm, length 30 cm) previously flushed with nitrogen and maintained at 750°C. The flow rate was preset at 10 ml/minute and maintained for 5h. The products (estimate 20g) were collected in a cold trap and subsequently transferred *in vacuo* to a distillation column. The base of the column was brought up to 0°C and the hexafluoropropene allowed to distill (condensed by an acetone drycold trap) over a period of 1h. The remaining material (7.3g) was transferred *in vacuo* to a cold trap and found, by comparison of i.r. spectra (number 40)

with literature data[258] to be perfluoroisobutene (4) (n.m.r. spectra number 38).

7.4 Generation and attempted generation of caesium perfluorocarbanion salts

	ALKENE (N^{o})g,mmol	CsF g,mmol	SOLVENT[a] ml	TIME days	N.M.R.[b] number
1.	(127) 0.5, 1.5	0.3, 1.9	0.5	3	54
2.	(141) 1.7, 5.2	0.7, 4.6	4	3	54
3.	(127) 0.7, 2.1	0.5, 3.3	(DMF)1.0	3	54
4.	(214) 2.3, 4.4	0.9, 5.9	3	14	53
5.	(216) 0.8, 2.1	0.7, 4.6	2	9	56
6.	(4) 5.3, 26.5	4.2, 27.7	7	3	50
7.	(29) 2.5, 8.3	1.9, 12.5	5	4	51
8.	(29) 6.0, 20.0	4.0, 26.3	20	4	51
9.	(29) 3.2, 10.6	1.9, 12.5	(DMF)3.0	5	*not formed*
10.	(29) 2.4, 8.0	1.1, 7.2	(DMSO)4.0	2	51[c]
11.	(29) 2.2, 7.3	1.8, 11.8	(CH_3CN)2.3	4	*not formed*
12.	(197) 2.7, 8.9	1.5, 10.0	4	4	52
13.	(197) 1.0, 3.3	0.6, 3.9	1.5	2	52
14.	(197) 1.5, 5.0	2.4, 15.7	(CH_3CN)3.0	3	*not formed*
15.	(197) 0.20, 0.66	0.12, 0.78	(DMF)0.5	5	*not formed*
16.	(83) 4.5, 9.0	1.7, 11.2	5	11	60
17.	(83) 4.5, 9.0	2.0, 13.2	5	9	60
18.	(82) 5.2, 13.0	4.9, 32.2	5	5	*not formed*
19.	(128) 1.9, 4.5	0.8, 5.3	3	4	*not formed*

a. Tetraglyme solvent if not stated.
b. Spectra tabulated in Appendix 4.
c. Gave spectrum similar to number 51, but coupling was absent and slight line broadening present.

General procedure.— Unless otherwise stated, the alkene was stirred vigorously with well dried and ground caesium fluoride (approximate molar equivalent) in the required solvent for over 24h. Commonly a deficiency of solvent was employed so that the resulting solutions were as concentrated as possible. The mixture was then stood for *ca*. 0.5h to leave unreacted caesium fluoride and alkene to settle as a lower layer and the transparent coloured homogeneous upper layer was removed by pipette and placed in an n.m.r. tube. The solutions could be stored at room temperature for at least a year without detectable (^{19}F n.m.r.) change, provided moisture was rigorously excluded. Quantities of solvent, caesium fluoride and alkene; approximate reaction times employed and references to n.m.r. spectra for the generation and attempted generation of fluorocarbanions are given above. Table 23, page 131 contains the structures of the respective alkenes and carbanions.

7.5 Attempted crystal growth of caesium perfluorocarbanions

a) The perfluoro-3-methylpent-3-yl anion (220).— A solution of the title carbanion as its caesium salt in tetraglyme (see N°11, section 7.4) was placed in a small dry sample tube and subsequently enclosed in a sealed vessel containing toluene. The toluene was allowed to diffuse over a period of *ca*. 7 days into the tetraglyme solution which then produced a crusty layer on the surface. The soid material was isolated, found to be insoluble in tetraglyme and presumed to be caesium fluoride.

Simply cooling a solution of the carbanion (220)(see N°11, 7.4) to -40°C produced no evidence of any solid species.

b) The perfluoro-2-methylpent-2-yl anion (221).— Cooling a solution of the title carbanion (221)(see N°7, 7.4) to -40°C did not

cause solid material to form.

c) The perfluoro^{t}butyl anion (101).— Cooling the solution of the title carbanion (101)(see N^{o}6, 7.4) to about +15°C (cold water) caused rapid growth of large needles which, in about 2 minutes, caused almost complete solidification of the mixture. Warming the resulting mixture under the hot tap caused complete re-dissolution of the matter in *ca.* 10 seconds. This process could be repeated many times.

On one occasion, the sealed tube was broken and the solid isolated by pipetting residual solvent under a nitrogen plume. After standing at room temperature for about 0.5h, tetraglyme was added which readily re-dissolved the solid to give a ^{19}F n.m.r. spectrum (number 50) indistinguishable from the carbanion (101).

7.6 Attempted syntheses of potassium perfluorocarbanions

a) With perfluoro-2-methylpent-2-ene (29).— A mixture of the alkene (29)(2.0g, 6.7mmol), potassium fluoride (0.5g, 8.6mmol) and tetraglyme (2ml) was stirred vigorously under nitrogen for 7 days. After standing for a further 0.5h the solvent layer was removed and found (^{19}F n.m.r.) to contain no detectable concentration of fluorocarbon.

b) With perfluoro-3-methylpent-2-ene (197).— A similar reaction to (7.6.a) was performed with (197)(0.93g, 3.1mmol), potassium fluoride (2.3g, 39.7mmol) and DMF(10ml). No detectable (^{19}F n.m.r.) concentration of fluorocarbon material was observed in the solvent.

c) With perfluoro-2-methylpent-2-ene (29) and added 18-crown-6 ether.— A mixture of (29)(3.0g, 10.0mmol), potassium fluoride (0.5g, 8.6mmol), acetonitrile (6ml) and

18-crown-6 ether (1.9g, 7.2mmol) were mixed at room temperature. The mixture immediately heated to *ca.* 80°C and, after cooling to room temperature, the solvent layer was reoved and found (^{19}F n.m.r.) to contain no detectable concentration of fluorocarbon.

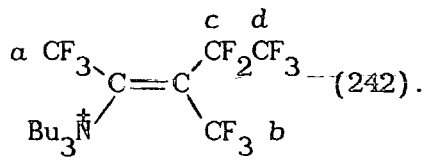
7.7 TBAF reactions

General procedure for drying TBAF.3H$_2$O.— Commercial terabutylammonium fluoride trihydrate (Aldrich) was placed in a dry flask and heated with stirring for 48h at 40 - 45°C under 0.01mm Hg. During this time the sample had liquefied into a straw coloured syrup and lost a proportion of its weight between 22% and 47%. In the following reactions the original weight of the trihydrate and the final weight are quoted. If the sample was divided for separate reactions the quoted weights are reduced in proportion.

a) With perfluoro-2-methylpent-2-ene (29).— 'Dried' tetrabutylammonium fluoride (trihydrate: 3.7g, 11.7mmol; final: 3.08g) in acetonitrile (10ml) was mixed with (29) (2.1g, 7mmol) and stirred at room temperayture for 1h. The resulting homogeneous solution was removed and found to give a broadened ^{19}F n.m.r. spectrum. Dry nitrogen was blown across the solution surface for 3h. and the resulting mixture found (^{19}F n.m.r.) to contain the perfluoroalkenylammonium derivative (223) as the only detectable species, by comparison of the spectrum (see page 137) with literature values[58] for analogous triethylammonium derivative (55).

b) With perfluoro-3-methylpent-2-ene (197).— Alkene (197)(3.16g, 10.5mmol) was added to a solution in acetonitrile (5ml) of 'dried' tetrabutylammonium fluoride (trihydrate: 3.5g, 11.1mmol; final: 2.8g) and stirred for 1h. at room temperature. The residual

solution was studied by ^{19}F n.m.r. and found to contain resonances tentatively assigned to perfluoroalkenylammonium derivative (242) δ_F 48.5(3F, m, a), 54.3(3F, br., b), 84.0(3F, s, d) and 106.6(2F, q, c), along with other unassigned signals (40%).



(242).

In a similar experiment with (197)(0.54g, 1.8mmol), 'dried' tetrabutylammonium fluoride (trihydrate: 1.1g, 3.4mmol; final: 0.56g) and tetraglyme (3.4g) the resulting ^{19}F n.m.r. was complicated but contained resonances as observed above.

c) With hexafluoropropene (1).— Hexafluoropropene (1)(8.8g, 58.7mmol) was admitted to a gas reservoir which was subsequently connected to a flask containing stirred 'dried' tetrabutylammonium fluoride (trihydrate: 4.6g, 14.6mmol; final: 3.8g) and acetonitrile (8ml). After 4 days remaining gas (2.4g) was confirmed to be starting material (1)(27% recovered) by a comparison of i.r. spectra with authentic material. From the remainder, volatile material was transferred *in vacuo* to a cold trap and the resulting lower layer (5.2g) removed and found (g.l.c./mass spectroscopy) to contain mainly (C_9F_{18}) trimers with a trace of ($C_{12}F_{24}$) tetrameric products.

d) With perluoro-3,4-dimethylhex-3-ene (82).— 'Dried' tetrabutylammonium fluoride (trihydrate: 4.6g, 14.6mmol; final: 3.8g) in acetonitrile (8ml) was added to the title alkene (82)(6.0g, 15.0mmol). The resulting mixture heated immediately to boiling and,

after cooling to room temperature was stirred for a further 24h. No significant quantities of fluorocarbon could be detected by ^{19}F n.m.r. in the upper layer. Volatile material was transferred *in vacuo* to a cold trap and the resulting lower layer (5g) was removed and found to be (82)(83% recovered) by a comparison of ^{19}F n.m.r. spectra with authentic material.

e) With perluorocyclobutene (107).— A flexible gas reservior containing perluorocyclobutene (107)(9.5g, 58.6mmol) was connected to a flask containing a stirred solution of 'dried' tetrabutylammonium fluoride (trihydrate: 1.5g, 4.8mmol; final: 1.2g) in acetonitrile (50ml). After 3 days volatile material was transferred *in vacuo* to a cold trap and found (g.l.c., Col. 0) to contain only solvent. Residual material was found to be a crystalline solid which could not be identified.

δ_F (CD_3CN) 120.1(4F, d, J 34Hz) and 138.3 (2F, t, 34Hz).

δ_H (CD_3COCD_3) signals between 0.9 and 3.2 ppm, unassigned.

7.8 Generation and attempted generation of TAS^+ perfluorocarbanion and Meisenheimer complex solutions

(a) *General procedure*.— Unless otherwise stated, a calculated slight excess of a known concentration of TAS-F in CH_3CN (see 7.2) was added in an air tight syringe to the required alkene or fluoroaromatic in a predried n.m.r. tube. After shaking for 10 minutes at room temperature the resulting solution was examined by ^{19}F n.m.r. spectroscopy. The solutions could be stored for weeks at room temperature provided moisture was rigorously excluded but some decomposition was sometimes observed after this period. The details are tabulated below. Refer to table 25, page 138 for a list of alkenes and carbanions.

ALKENE/AROMATIC	TAS-F	CH_3CN	NOTES
(number)g, mmol	g, mmol	ml	
(196) 0.30, 1.0	0.20, 0.7	1.2	*deficiency of TAS-F n.m.r. see page 140*
(196) 0.55, 1.8	0.36, 1.3	5[a]	*deficiency of TAS-F n.m.r. as above*
(196) 0.35, 1.2	0.60, 2.1	0.5	*n.m.r. number 51*
(29) 0.15, 0.50	0.30, 1.1	0.5	*n.m.r. number 51*
(197) 0.19, 0.63	0.30, 1.1	0.5	*n.m.r. number 52*
(127) (141) 0.16, 0.49	0.16, 0.58	0.5	*n.m.r. number 54*
(83) 0.51, 1.0	0.37, 1.3	0.8	*n.m.r. number 60*
(128) 0.38, 0.90	0.60, 2.1	0.6	*n.m.r. number 55*
(227) 0.15, 1.1	0.40, 1.5	0.7	*n.m.r. number 57 see page 140*
(228) 0.19, 1.2	0.49, 1.8	0.3	*n.m.r. number 58 see page 140*
(229) 0.2, 1.3	0.44, 1.6	0.5	*n.m.r. number 59 see page 140*

b) With perfluoro-3,4-dimethylhex-3-ene (82).— A mixture of (82)(0.67g, 1.6mmol), TAS-F(0.3g, 1.1mmol) in acetonitrile (0.5ml) was shaken in an n.m.r. tube for 2h. at room temperature and two layers remained. The lower layer (0.2g) was shown (^{19}F n.m.r. number 15) to be (82)(30% recovery) and the upper layer gave only a broad signal in the ^{19}F n.m.r. spectrum at 81.3 ppm.

In a similar reaction with (82)(0.22g, 0.55mmol), TAS-F(0.3g, 1.1mmol) and acetonitrile (0.5ml) in which the alkene was added dropwise to the fluoride, the alkene was seen to boil on contact with the liquid. the resulting homogeneous solution was studied by ^{19}F n.m.r. δ_F 82.5(*br.*), 146.9(*br.*) and 148.9(*br.*).

A reaction conducted as above at 0°C gave a similar spectrum.

7.9 TAS-F with alkenes (1),(107) and (154)

a) With hexafluoropropene (1).— A flask was charged with a solution of TAS-F(0.45g, 1.6mmol) in acetonitrile (1.1ml). Hexafluoropropene (1)(0.16g,1.1mmol) was transferred *in vacuo* to the flask cooled in liquid air and the resulting mixture stirred at room temperature for 1h. Analysis by ^{19}F n.m.r. confirmed the presence of the *perfluoro-2-methylpent-2-yl anion* (221)(n.m.r. spectra number 51) and small amounts of TAS-F decomposition products.

b) With perfluorocyclobutene (107).— In a reaction conducted as for 7.9.a with perfluorocyclobutene (107)(0.12g, 0.74mmol), TAS-F(0.48g, 1.7mmol) and acetonitrile (1.0ml) the product mixture was shown (^{19}F n.m.r.) to contain the *perfluorobicyclobutyl anion* (209)(n.m.r. number 54) and TAS-F decomposition products.

c) With perfluorocyclopentene (154).— In a reaction conducted as for 7.9.a. with perfluorocyclopentene (154)(0.15g, 0.71mmol), TAS-F(0.46g, 1.7mmol) and acetonitrile (1ml) the product mixture was shown (^{19}F n.m.r.) to contain the *perfluorobicyclopentyl anion* (224)(n.m.r. number 55) and TAS-F decomposition products.

7.10 Synthesis of trimethylfluorosilane

A flask equipped with a mechanical stirrer, a water cooled condenser and a back up trap cooled in liquid air, was charged with dry potassium fluoride (22.0g, 0.38mol), trimethylchlorosilane (35g) and sulpholan (76g). The mixture was stirred under reflux for 12h. and the volatile material in the cold trap (5.3g) was found, by a comparison of ^{19}F and ^{1}H n.m.r. and i.r. spectra with literature data,[259] to be the desired *trimethylfluorosilane*.

δ_F 159.3 (*decuplet*, J 7.3Hz); δ_H -0.6(d, J 7.6Hz); υ_{max} 2979, 1020(br.), 910, 852 and 755 cm^{-1}.

7.11 Attempted reactions of caesium fluoride with trimethylfluorosilane

A Carius tube was charged with caesium fluoride (3.1g, 20.3mmol) and tetraglyme (25ml). Trimethylfluorosilane (1.9g, 20.7mmol) was transferred *in vacuo* to the tube cooled in liquid air which was sealed and heated at 90°C for 24h. Solid material (3.3g) was filtered under nitrogen and shown to be caesium fluoride. The residual solution was found (^{19}F n.m.r.) to contain only the fluorosilane by comparison with authentic material.

In a similar reaction with caesium fluoride (3.0g, 19.7mmol), tetraglyme (18ml) and trimethylfluorosilane (1.6g, 17.4mmol) heated in a steel autoclave at 125°C for 3 days an identical result was obtained.

7.12 Generation of fluorocarbanions using cryptand (226)

General procedure.— A mixture of the alkene (29), caesium fluoride, cryptand (226) and solvent were stirred at room temperature for *ca*. 24h. After allowing to stand for 0.5h., the coloured upper layer was removed and examined by ^{19}F n.m.r. All the spectra corresponded to the carbanions as contained in Appendix 1, except coupling was virtually absent and slight line broadening was evident. Quantities are contained in the table below.

ALKENE (29) g, mmol	CsF g, mmol	(226) g, mmol	SOLVENT, ml
1.8, 6.0	1.0, 6.6	1.9, 5.9	DMSO, 2.5
2.0, 6.7	0.9, 5.9	2.1, 6.5	tetraglyme, 3
1.3, 4.3	0.7, 4.6	1.3, 4.0	CH_3CN, 3

7.13 Variable temperature n.m.r. studies

General procedure.— Unless otherwise stated, homogeneous fluorocarbanion solutions (see sections 7.4, 7.8, and 7.12) contained in pre-dried n.m.r. tubes were placed in the pre-shimmed Bruker AC250 (235MHz) instrument and the spectra accumulated at 10°C intervals above ambient temperature. 0.5h. Equilibration time was allowed before the spectral aquisition. The peak widths (Hz) at half height ($\Delta\nu 1/2$) were measured for resonances adjacent to the charge centre and a graph of temperature vs $\Delta\nu 1/2$ plotted. Refer to table 23, page 131 for a list of fluorocarbanions.

CARBANION	COUNTERION	SOLVENT etc.	TEMPERATURE (K)	$\Delta\nu 1/2$ (Hz)	
				CF_3	CF_2
(221)	Cs^+	tetraglyme	297	46.5	67.5
			313	46.5	69.5
			323	45.5	69.1
			333	53.9	69.5
			343	100.4	88.1
			348	151.8	106.8
				CF_3	CF_2
(221)	TAS^+	CH_3CN	297	46.5	58.8
			313	46.5	66.1
			323	46.7	66.7
			333	46.5	68.1
			343	46.0	66.7
			348	46.0	66.7
(221)	Cs^+	DMSO	300	48.6	
			310	79.8	
			320	194.6	CF_3
			330	603.1	
			340	———	
(221)	Cs^+	tetraglyme,(226)	302	64.2	
			312	79.7	
			322	121.6	CF_3
			332	227.5	
			343	495	
(221)	Cs^+	CH_3CN,(226)	297	39.9	
			307	58.0	
			317	128.7	
			327	357.0	CF_3
			337	644.2	
			347	———	

				CF_3	CF_2
(220)	Cs^+	tetraglyme	297	55.3	33.7
			313	55.3	32.8
			323	60.5	34.8
			333	84.2	61.2
			343	156.7	103.3
			348	195.8	123.4
				CF_3	CF_2
(220)	TAS^+	CH_3CN	297	52.3	31.0
			313	53.8	31.0
			323	53.8	31.8
			333	56.3	34.3
			343	56.3	32.3
			348	53.8	32.2

(209)	Cs^+	tetraglyme	295	89.9	
			305	89.9	
			315	91.1	
			325	90.9	
			335	91.9	CF_2
			345	96.2	
			350	105.5	
			355	113.0	
			360	130.9	
(209)	TAS-F	CH_3CN	296	89.6	
			306	93.3	
			316	94.3	
			326	96.7	CF_2
			336	106.6	
			342	117.9	
			348	136.8	
			352	161.9	
(215)	Cs^+	tetraglyme	294	67.5	
			314	59.9	
			324	67.5	
			334	73.2	CF_2
			344	99.8	
			348	116.9	
(215)	Cs^+	tetraglyme	297	74.6	
	as above but diluted x 20		307	73.6	
			317	75.6	
			327	75.6	CF_2
			337	87.2	
			347	104.7	
			352	130.5	
(215)	TAS^+	CH_3CN	297	69.5	
			307	76.5	
			317	79.8	CF_2
			327	92.9	
			337	116.2	
			347	169.1	

(222)	Cs^+	tetraglyme	297	65.6	
			307	61.0	
			317	60.0	
			327	57.0	CF_3
			337	56.2	
			347	55.1	
			352	57.0	
(222)	TAS^+	CH_3CN	297	69.7	
			307	77.8	
			317	84.3	
			327	105.4	CF_3
			337	141.8	
			347	220.3	
(224)	TAS^+	CH_3CN	297	84.3	
			307	84.3	
			317	86.2	CF_2
			327	89.4	
			337	92.3	
			347	91.3	

7.14 Competition experiments

General procedure.— A small quantity of dry caesium fluoride was carefully introduced into a dry n.m.r. tube and carefully weighed. Equal molar quantities of each alkene corresponding to the amount of caesium fluoride were carefully introduced into the tube by syringe. Tetraglyme (1ml *per* 0.8g CsF) was added to the tube and the resulting mixture agitated efficiently for the required time. Simple ^{19}F n.m.r. analysis of the solvent layer afforded the ratio of the carbanions in solution. Refer to table 23, page 131 for a list of alkenes and carbanions.

ALKENE A g, mmol	ALKENE B g, mmol	CsF g, mmol	TETRAGLYME ml	TIME days	CARBANIONS %A	%B
(29) 0.102, 0.34	(197) 0.102, 0.34	0.0507, 0.33	0.6	0.3	45	55
				7	48	52
				30	47	53
(29) 0.069, 0.23	(127) 0.097, 0.30	0.0337, 0.22	0.35	0.3	5	95
				7	35	65
				30	33	67
(197) 0.087, 0.29	(127) 0.123, 0.38	0.0432, 0.28	0.50	0.3	14	86
(29) 0.078, 0.26	(214) 0.136, 0.26	0.0348, 0.23	0.35	0.3	98	2
				7	98	2
				30	98	2
(29) 0.086, 0.28	(83) 0.145, 0.29	0.0429, 0.28	0.50	0.3	100	0
				7	100	0
				30	100	0

7.15 Trapping reactions of fluorocarbanions

General procedure.— To a homogeneous solution containing the caesium perfluorocarbanion(see section 7.4) an excess of the

electrophile was added and the resulting mixture was shaken manually for 0.5h. A lower liquid layer and a white solid immediately separated from the mixture which was allowed to settle for 0.5h. The lower liquid layer (usually pure even at this stage) was removed with a pipette, washed with water and transferred *in vacuo* to a cold trap and found to contain the trapped species with no detectable level of impurities. The upper layer was examined by ^{19}F n.m.r. spectroscopy and, unless otherwise stated, no fluorocarbon material could be detected even with the sensitivity of the machine at maximum. Thus within the limits of detection the trapping reactions were quantitative.

a) Reactions with bromine

i) With the perfluoro-2-methylpent-2-yl anion (221).—yielded *perfluoro-2-methyl-2-bromopentane* pure by g.l.c. (capillary column) by a comparison of spectra with literature data,[136] mass spectrum number 46; n.m.r. spectra number 39; i.r. spectrum number 41.

ii) With the perfluoro-3-methylpent-3-yl anion (220).—yielded *perfluoro-3-methyl-3-bromopentane* pure by g.l.c. (capillary column, 35°C) (Found: F, 61.0; Br, 20.6. $C_6F_{13}Br$ requires: F, 61.9; Br, 20.0); mass spectrum number 55,56; n.m.r. spectra number 46; i.r. spectrum number 48.

iii) With the perfluoro-2-methylprop-2-yl anion (101).—yielded *perfluoro-2-bromo-2-methylpropane* by a comparison of ^{19}F n.m.r. spectrum (number 47) with literature data.[199]

iv) With perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (222).— gave no reaction at all. The ^{19}F n.m.r. spectrum corresponding to (222)(number 60) could be observed in saturated bromine solution even with slight warming.

b) Reactions of methyl iodide

i) With the perfluoro-2-methylpent-2-yl anion (221).— yielded 2-*methylperfluoro-2-methylpentane* (Found: C, 25.2; H, 1.0. $C_7H_3F_{13}$ requires: C, 25.2; H, 0.9); mass spectrum number 47; n.m.r. spectra number 40; i.r. spectrum number 42.

ii) With the perfluoro-3-methylpent-3-yl anion (220).—yielded 3-*methylperfluoro-3-methylpentane* (Found: C, 25.3; H, 0.7; F, 74.3. $C_7H_3F_{13}$ requires: C, 25.2; H, 0.9; F, 73.9); mass spectrum number 54; n.m.r. spectra number 45; i.r. spectrum number 47.

iii) With the perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (222).— gave no detectable reaction. The ^{19}F n.m.r. corresponding to (222)(number 60) was unchanged by the addition of methyl iodide and warming to 80°C.

c) Allyl iodide with the perfluoro-2-methylpent-2-yl anion (221).— yielded 2-*prop-2-enylperfluoro-2-methylpentane* (Found: C, 29.7; H, 1.1; F,69.0. $C_9H_5F_{13}$ requires: C, 30.0; H, 1.4; F, 68.6); mass spectrum number 48; n.m.r. spectra number 41; i.r. spectrum number 43.

d) Benzyl bromide with the perfluoro-2-methylpent-2-yl anion (221).— yielded 2-*benzylperfluoro-2-methylpentane* pure by

g.l.c.(capillary column, 70°C) by a comparison of spectra with literature data,[136] mass spectrum number 49; n.m.r. spectra number 42; i.r. spectrum number 44.

e) Chlorine with the perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (222).— gave no detectable reaction after *ca.* 1h.

7.16 Reactions with borontrifluoride diethyletherate

a) With the perfluoro-2-methylpent-2-yl anion (221).— Excess boron trifluoride diethyletherate was added to a solution of the title carbanion as its caesium salt in tetraglyme. The resulting lower layer was washed with water, was shown to contain only one component (g.l.c., capillary column) and was found to be *perfluoro-2-methylpent-2-ene* (29) by a comparison of ^{19}F n.m.r. spectra (number 36) with authentic material.

b) With the perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (222).— In a reaction conducted as for 7.16.a. the resulting lower layer was shown to be a single component and confirmed as *perfluoro-3,4-dimethyl-4-ethylhex-3-ene* (83) by a comparison of ^{19}F n.m.r. data with authentic material.

7.17 The Perfluoro-2-methylpent-2-yl anion (221) with tetrafluoropyridazine

A solution of the perfluoro-2-methylpent-2-yl anion (29), formed by stirring a mixture of caesium fluoride (6.2g, 41mmol), perfluoro-2-methylpent-2-ene (29)(8.0g, 26.7mmol) and tetraglyme (19ml) at room temperature for 48h (until no liquid lower layer was evident), was added to tetrafluoropyridazine (243)(2.0g, 13.1mmol) and the resulting mixture stirred at room temperature for 72h.

Volatile material (6.3g) was transferred *in vacuo* to a cold trap with heating and shown (g.l.c., Col.0) to consist of three components. These were shown (mass spectroscopy, g.l.c.) to be *perfluoro-2-methylpent-2-ene* (29)(29%)(mass spectra number 44), *tetrafluoropyridazine* (243)(35% recovered)(by a comparison of g.l.c. retention times) and a $C_{10}N_2F_{16}$ isomer. This was isolated by preparative scale g.l.c. (Col. 0) and identified as perfluoro-4-(2'-methylpent-2-yl)pyridazine (238)(83% based on consumed (243)) (Found: C, 26.3; N, 6.6; F,67.7. $C_{10}F_{16}N_2$ requires: C, 26.6; N, 6.2; F, 67.2); mass spectrum number 52,53; n.m.r. spectra number 44; i.r. spectrum number 46.

Similar reactions were conducted. The table below summarises the information.

CARBANION			(243)	TEMP.	TIME	(29)	(243)	(238)
(29) g, mmol	CsF g,mmol	tetraglyme ml	g, mmol	°C	h.	%	%[a]	%
8.0,26.7	6.2,40.8	19	2.0,13.1	20	72	29	35	83
8.2,27.3	6.3,41.4	20	1.8,11.8	20	500	23	34	71
8.2,27.3	6.3,41.4	20	1.8,11.8	100	144	49	51	—
2.4, 8.0	1.2, 7.9	5	0.7, 4.6	50	48	19	23	89

a. *Recovered material*

7.18 The perfluoro-2-methylpent-2-yl anion (221) with trifluoro-1,3,5-triazine (227)

Trifluoro-1,3,5-triazine (0.6g, 4.4mmol) was added to a solution of the perfluoro-2-methylpent-2-yl anion (221), formed by stirring a mixture of perfluoro-2-methylpent-2-ene (29) (5.1g, 17.0mmol) and caesium fluoride (2.5g, 16.4mmol) in tetraglyme

(30ml), and the resulting mixture stirred at room temperature for 7 days. Analysis by ^{19}F n.m.r. confirmed the presence of *Meisenheimer complex* (204)(n.m.r. spectrum number 57), carbanion (221)(n.m.r. spectrum number 51) and perfluoro-2-methylpent-2-ene (29)(n.m.r. spectrum number 36). Volatile material (3.5g) was transferred *in vacuo* to a cold trap and shown by a comparison of g.l.c. retention times to contain only (29) and (227).

7.19 The perfluoro-2-methylpent-2-yl anion (221) with perfluorocyclopentene (154)

Perfluorocyclopentene (154)(5.0g, 23.5mmol) was added to a a solution of the perfluoro-2-methylpent-2-yl anion (221), formed by stirring a mixture of perfluoro-2-methylpent-2-ene (29)(6.0g, 20.0mmol) and caesium fluoride (3.1g, 20.4mmol) in tetraglyme (20ml), and the resulting mixture was stirred at room temperature for 4 days. Volatile material (8.2g) was transferred *in vacuo* to a cold trap with warming and shown to contain several components. These were identified as *perfluoro-2-methylpent-2-ene* (29)(30%) by a comarison of mass spectra (number 44) with authentic material, *perfluorocyclopentene* (154)(5% recovered) by a comparison of mass spectra (number 14) with authentic material, $C_{10}F_{16}$, and two $C_{11}F_{20}$ isomers. Preparative scale g.l.c. (Col. 0) isolated the $C_{10}F_{16}$ isomer and the major $C_{11}F_{20}$ component and these were identified as:-

(a) *perfluorobicyclopentylidene* (128)(22% based on consumed (154)) (Found: C, 28.4. Calc. for $C_{10}F_{16}$: C, 28.3); by a comparison of spectra with authentic material. mass spectrum number 4,5; n.m.r. spectra number 3; i.r. spectrum number 3.

and (b) perfluoro-(2'-methylpent-2'-yl)-cyclopentene (239) (32% based on consumed (154)) (Found: C, 25.5; F, 74.7. $C_{11}F_{20}$

requires: C, 25.8; F, 74.2); mass spectrum number 50,51; n.m.r. spectra number 43; i.r. spectrum number 45.

Other similar reactions conducted at different temperatures are summarised below:-

CARBANION			(154)	TEMP.	TIME	(154)	YIELD OF	
(29) g, mmol	CsF g,mmol	tetraglyme ml	g, mmol	°C	h.	%[a]	(239), g	(128) g
6.0,20.0	3.1,20.4	20	5.0,23.5	20	96	5	3.7	2.1
0.72,2.4	0.36,2.4	1.5	4.6,21.7	70	24	83	0.27	0.80
0.72,2.4	0.36,2.4	6.5	7.0,33.0	70	72	59	0.77	2.3

7.20 The perfluoro-2-methylpent-2-yl anion (221) with benzylbromide at 80°C

A flask was charged with benzylbromide (2.5g, 14.7mmol) and heated with stirring to 80°C. A solution of the perfluoro-2-methylpent-2-yl anion (221), formed by stirring a mixture of perfluoro-2-methylpent-2-ene (29)(3.8g, 12.7mmol) and caesium fluoride (1.95g, 12.8mmol) in tetraglyme (8ml) at room temperature for 48h., was added slowly and stirring continued for *ca.* 10 minutes. The lower layer (5.3g) thus formed was removed and shown (^{19}F n.m.r.) to contain *2-benzylperfluoro-2-methylpentane* (n.m.r. number 42) and *perfluoro-2-methylpent-2-ene* (29)(n.m.r. number 36) in the ratio 8:2. The upper layer was shown to contain *benzylfluoride* δ_F 207.6 by comparison of ^{19}F n.m.r spectra with literature data.[199]

7.21 The perfluoro-2-methylpent-2-yl anion (221) with acetylchloride

In a reaction conducted according to the general procedure in 7.15, excess acetylchloride was added to the perfluoro-2-methylpent-2-yl anion (221) in tetraglyme. The mixture exothermed and, upon cooling, the lower layer was removed and shown to be *perfluoro-2-methylpent-3-ene* (29) by a comparison of ^{19}F n.m.r. spectra with authentic material (n.m.r. number 36). the upper layer was shown (^{19}F n.m.r.) to contain *acetylfluoride* δ_F -49 by a comparison of ^{19}F n.m.r. spectrum with literature data.[260]

7.22 Reactions of lead tetraacetate

Excess lead tetraacetate was added to solutions of the perfluoro-3,4-dimethyl-4-ethylhex-3-yl anion (222) and perfluoro-2-methylpent-2-yl anion (221)(see section 7.4) and the resulting solutions stirred for 1h. at room temperature. In both cases, ^{19}F n.m.r. analysis of the solutions afforded spectra which could not be assigned. No residual carbanion (222) or (221), or alkenes (83) or (29) could be detected.

7.23 Reactions of triphenylmethylchloride

Excess triphenylmethylchloride was added to a solution of the perfluoro-3-methylpent-3-yl anion (220) in tetraglyme (see section 7.4) and the resulting mixture stirred at room temperature for 1h. Volatile material was transferred *in vacuo* to a cold trap and shown to be *perfluoro-3-methylpent-2-ene* (197) by a comparison of ^{19}F n.m.r. spectra (number 37) with authentic material.

7.24 Cyclic voltammetry of the perfluoro-2-methylpent-2-yl carbanion

Tetraethylammonium tetrafluoroborate (0.15g, 0.69mmol), made by mixing hot aqueous solutions of sodium tetrafluoroborate (3.1g,

28mmol) and tetraethylammonium bromide (5.5g, 26.2mmol), followed by recrystallisation (2xMeOH) and drying, was dissolved in tetraglyme (10ml) with warming. A solution of the perfluoro-2-methylpent-2-yl carbanion (221)(see section 7.4)(ca. 0.1ml, 1M) was added and the resulting solution shaken until homogeneous. The cyclic voltammogram was recorded (50 mV/s) but no clear oxidation or reduction potential (-4 to +4 V) could be observed.

APPENDICES

APPENDIX 1 N.M.R. SPECTRA

1. Perfluorobicyclobutylidene (127)
2. Perfluorocyclobutylcyclobut-1-ene (141)
3. Perfluorobicyclopentylidene (128)
4. Perfluoro-9-oxadispiro[3.0.3.1]nonane (129)
5. Perfluoro-1-(1'-chlorocyclobutyl)cyclobut-1-ene (131)
6. 1,1'-Dichloroperfluorobicyclobutyl (133)
7. Perfluoro-11-oxadispiro[4.0.4.1]undecane (130)
8. Perfluoro-1-(1'-chlorocyclopentyl)cyclopent-1-ene (132)
9. 1,1'-dichloroperfluorobicyclopentyl (134)
10. Perfluorocyclopentene (154)
11. Perfluorocyclopentanone
12. *Diene* (145)
13. *Epoxide* (149)
14. *Diepoxide* (151) or (152)
15. Perfluoro-3,4-dimethylhex-3-ene (82)
16. 3,4-(3'-Methylbenzo)-7,7,8,8-tetrafluoro-2,5-dithiobicyclo[4.2.0]oct-1-ene (155)
17. 3,4-(3'-Methylbenzo)-7,7,8,8,9,9-hexafluoro-2,5-dithiobicyclo[4.3.0]non-1-ene (155)
18. *Sulphoxides* (159) and (160)
19. 3,4-Benzo-7,7,8,8,-tetrafluoro-2-aza-5-thiobicyclo[4.2.0]oct-1-ene (164)
20. 3,4-Benzo-7,7,8,8,9-pentafluoro-2-aza-5-thiobicyclo[4.3.0]non-1-ene (164)
21. 1,2-Bis(2'-aminothiophenoxy)-3,3,4,4,5,5-hexafluorocyclopentene (162)

21a. 1-Spirotetrafluorocyclobutenyl-3,4-benzo-2,5-dioxacyclopentane (167)

22. 1-Spirohexafluorocyclopent-2'-enyl-3,4-benzo-2,5-dioxacyclopentane (168)

23. *Ortho*-2,3,3,4,4-pentafluorocyclobut-1-enoxyaniline (173)

24. *Ortho*-2,3,3,4,4,5,5-heptafluorocyclopent-1-enoxyaniline (174)

25. 3,4-Benzo-7,7,8,8,9-pentafluoro-2-oxa-5-azabicyclo[4.3.0] nona-1,5-diene (175)

26. 3,4-Benzo-2,5-diaza-11-thio-7,7,8,8,9,9-hexafluorotricyclo [4.0.7.$0^{6,10}$]nona-1,6-diene (177)

27. 6,7-Benzo-2,3,4-tristrifluoromethyl-2-pentafluoroethyl-1,5-dioxacyclohept-3-ene (179)

28. 5,6-Benzo-3-methyl-2-(1'-methyl-1'-ethylpropyl)-4,7-dioxacyclohept-1-ene (180)

29. 2-Spirohexafluorocyclobutyl-3,4-tetrafluorocyclobutenyl 6,7-benzo-1,5-dioxacyclohept-1-ene (181)

30. *Ortho*bis-1,1,2,3,3,3-hexafluoropropoxybenzene (182)

31. *Ortho*-1,1,2,3,3,3-hexafluoropropoxyphenol (183)

32. *Ortho*bis-1,1,2-trifluoro-2-chloroethoxybenzene (184)

33. 4,5-Benzo-2-(1',1',1',4'-tetrafluoroethenyl)-1,3-dioxacyclopentane (193)

34. 4,5-Benzo-2-(1',1',1',2',3'-pentafluoroethyl)-1,3-dioxacyclopentane (194)

35. Perfluoro-4-methylpent-2-ene (196)

36. Perfluoro-2-methylpent-2-ene (29)

37. Perfluoro-3-methylpent-2-ene (197)

38. Perfluoroisobutene (4)

39. 2-Bromoperfluoro-2-methylpentane

40. 2-Methylperfluoro-2-methylpentane

41. 2-Prop-2'-enylperfluoro-2-methylpentane

42. 2-Benzylperfluoro-2-methylpentane

43. Perfluoro-1-(2'-methylpent-2'-yl)cyclopentene (239)

44. Perfluoro-4-(2'-methylpent-2'-yl)pyridazine (238)

45. 3-Methylperfluoro-3-methylpentane

46. 3-Bromoperfluoro-3-methylpentane

47. 2-Bromoperfluoro-2-methylpropane

48. Perfluorocyclobutene (107)

49. Trisdimethylaminosulphonium trimethylsilyldifluoride (208)

50. Perfluoro^{t}butyl anion (101)

51. Perfluoro-2-methylpent-2-yl anion (221)

52. Perfluoro-3-methylpent-3-yl anion (220)

53. Perfluorobicyclohexyl anion (215)

54. Perfluorobicyclobutyl anion (209)

55. Perfluorobicyclopentyl anion (224)

56. Perfluorocyclopentylcyclobutyl anion (217)

57. Trifluoro-1,3,5-triazine in TAS-F (204)

58. Tetrafluoropyridazine (229) in TAS-F

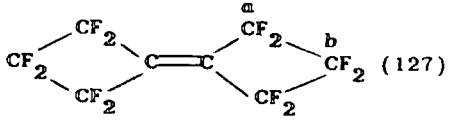
59. Pentafluoropyridine (228) in TAS-F

60. Perfluoro-3,4-dimethyl-4-ethyl hex-3-yl anion (228)

61. Perfluoro-1,2-bis(cyclobutyl)cyclobutene

N.m.r. of liquid products were, unless stated otherwise recorded neat. Solid materials were run as chloroform-*d* solutions except for the fluorocarbanions and Meisenheimer complexes which were taken in tetraglyme (caesium salts) or acetonitrile (TAS salts), unless otherwise stated. Reference compounds were used externally.

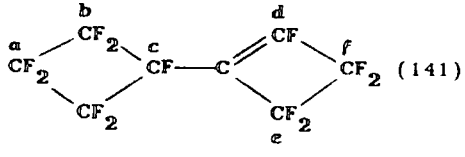
N.M.R. SPECTRA NUMBER 1



(127)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	117.5	s	8	a
	131.8	s	4	b

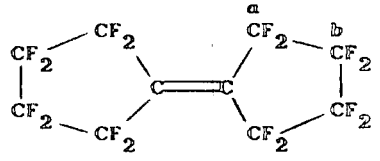
N.M.R. SPECTRA NUMBER 2



(141)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	98.7	broad		1	d
	116.8	m		2	e
	121.8	m		2	f
	131.3 and 134.9	AB	J 232Hz	2	a
	128.4 and 134.5	AB	J 236Hz	4	b
	189.8	s		1	c

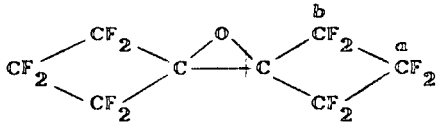
N.M.R. SPECTRA NUMBER 3



(128)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	128.1	s	8	a
	138.8	s	8	b

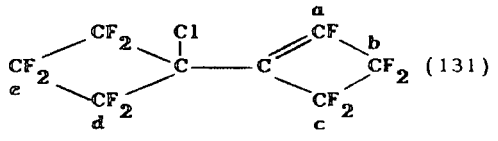
N.M.R. SPECTRA NUMBER 4



(129)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	123.2 and 132.3	AB	J 205Hz	8	b
	135.4 and 138.3	AB	J 225Hz	4	a

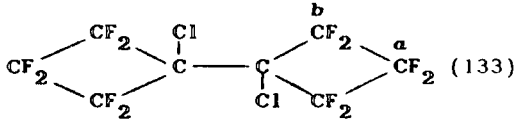
N.M.R. SPECTRA NUMBER 5



(131)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	97.3	s(broad)	1	a
	116.3	m	2	c
	121.3	m	2	b
	122.4	s	4	d
	128.9	s	2	e

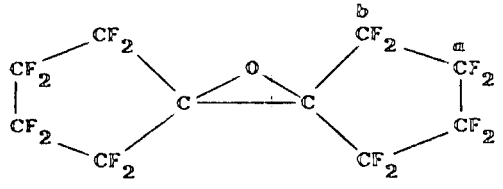
N.M.R. SPECTRA NUMBER 6



(133)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	114.3 and 122.1	AB(broad) J 205Hz	8	b
	127.4 and 129.1	AB J 225Hz	4	a

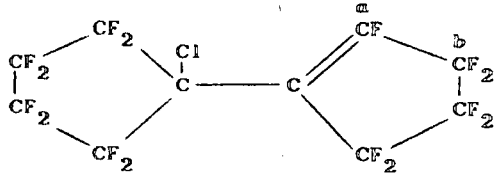
N.M.R. SPECTRA NUMBER 7



(130)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	117.8 and 129.0	AB	J 273Hz	8	b
	137.8	s		8	a

N.M.R. SPECTRA NUMBER 8

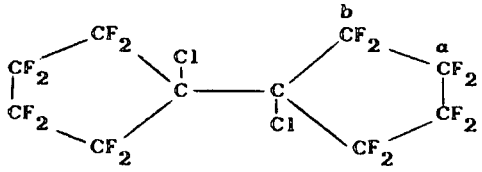


(132)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	107.3	t	J_{ab} 30Hz	1	a
	129.8	d	J_{ba} 30Hz	2	b

signals between 116 and 142 ppm, integrating to 14 F, unassigned

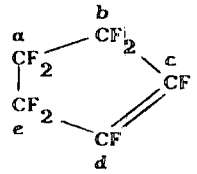
N.M.R. SPECTRA NUMBER 9



(134)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	107.0 and 118.8	AB	J 249Hz	8	b
		low field portion resolved into doublets			
		J 26Hz			
	115.4 and 126.1	AB	J 240Hz	8	a
		of d	J 2Hz		

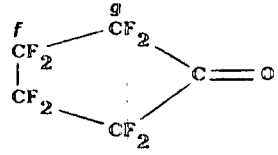
N.M.R. SPECTRA NUMBER 10



(154)

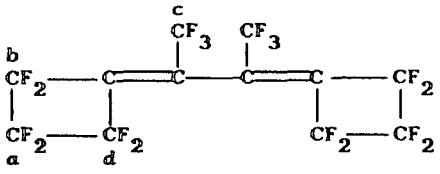
	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	121.3	dd	J_{bc} 11Hz	4	b
			J_{bd} 11Hz		
	133.2	s		2	a
	153.5	tt	J_{cb} 11Hz	2	c and e
			J_{ce} 11Hz		

N.M.R. SPECTRA NUMBER 11



	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	129.0	s	4	g
	140.1	s	2	f

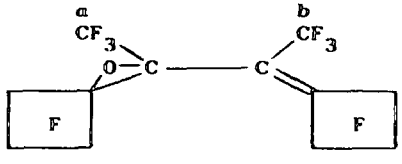
N.M.R. SPECTRA NUMBER 12



(145)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	65.9	s		6	c
	117.8	q	J 9Hz	4	d
	118.6	d	J 25Hz	4	b
	133.6	s		4	a

N.M.R. SPECTRA NUMBER 13

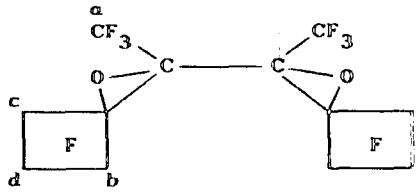


(149)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	63.8	s	3	b
	73.8	s	3	a

signals between 116 and 140, integrating to 12 F, unassigned.

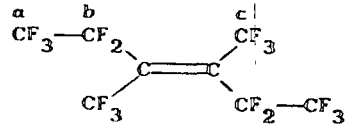
N.M.R. SPECTRA NUMBER 14



cis or trans
(151)/(152)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	71.9	s		6	a
	123.6 and 129.5	AB	J 242Hz	4	b or c
	123.6 and 128.9	AB	J 245Hz	4	b or c
	134.3 and 137.8	AB	J 231Hz	4	d

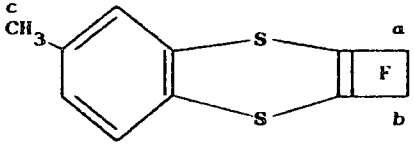
N.M.R. SPECTRA NUMBER 15



E/Z
(82)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	58.3	m(broad)	6	c
	75.3	m(broad)	6	a
	101.0	m(broad)	4	b

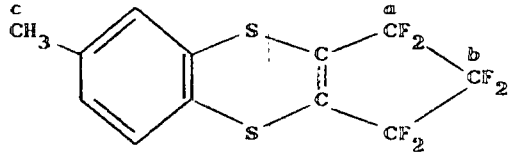
N.M.R. SPECTRA NUMBER 16



(155)

	Chemical shift	Multiplicity	Integral	Assignment
^1H	2.2	s	3	c
	6.8	broad	3	Ar.H
^{19}F	114.7	s		a and b

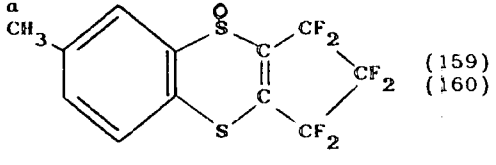
N.M.R. SPECTRA NUMBER 17



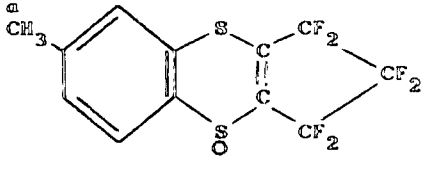
(156)

	Chemical shift	Multiplicity	Integral	Assignment
^1H	2.4	s	3	c
	7.1	broad	3	Ar.H
^{19}F	110.0	s	4	a
	129.5	s	2	b

N.M.R. SPECTRA NUMBER 18

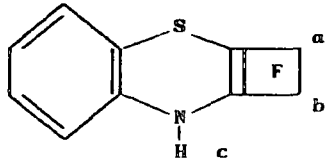


(159)
(160)



	Chemical shift	Multiplicity	Integral	Assignment
^1H	1.2	broad	3	a
	6.9	broad	3	Ar.H
^{19}F	signals between 106 and 132 ppm, unassigned.			

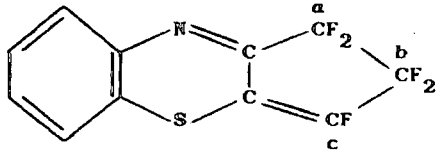
N.M.R. SPECTRA NUMBER 19



(164)

	Chemical shift	Multiplicity	Integral	Assignment
^1H	5.4	s(broad)	1	c
	6.4-7.3	broad	4	Ar.H
^{19}F	110.9	s	2	a or b
	117.4	s	2	a or b

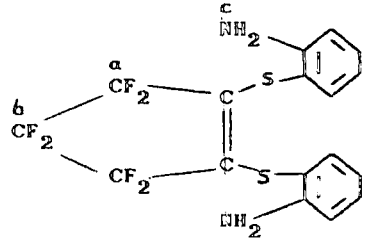
N.M.R. SPECTRA NUMBER 20



(164)

	Chemical shift	Multiplicity	Integral	Assignment
^1H	7.1	broad		Ar.H
^{19}F	120.7	d J_{bc} 14Hz	2	b
	123.6	s	2	a
	137.3	t J_{cb} 14Hz	1	c

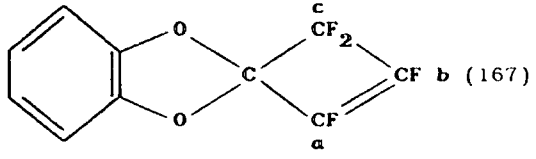
N.M.R. SPECTRA NUMBER 21



(162)

	Chemical shift	Multiplicity	Integral	Assignment
^1H	4.1	s	4	c
	6.9	broad	8	Ar.H
^{19}F	108.0	t J_{ab} 6Hz	4	a
	131.0	pentet J_{ba} 6Hz	2	b

N.M.R. SPECTRA NUMBER 21a

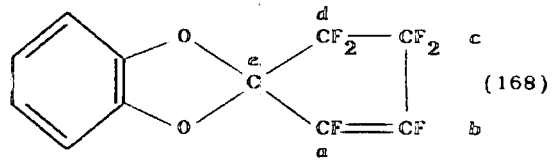


(167)

	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	6.7	m			Ar.H
^{19}F	120.8	dd	J_{cb} 18Hz		c
			J_{ca} 8Hz		

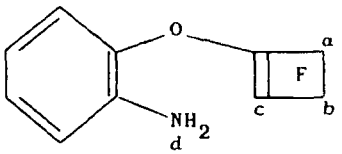
overlapping resonances centred at 133.5, integrating to 2 F corresponding to vinylic fluorines

N.M.R. SPECTRA NUMBER 22



	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	6.7	m			Ar.H
^{19}F	128.9	dd	J_{cb} 12Hz	2	c
			J_{ca} 12Hz		
	139.3	dd	J_{db} 5Hz	2	d
			J_{da} 5Hz		
	159.5	tt	J_{bc} 12Hz	1	b
			J_{bd} 5Hz		
	165.0	tt	J_{ac} 12Hz	1	a
			J_{ad} 5Hz		

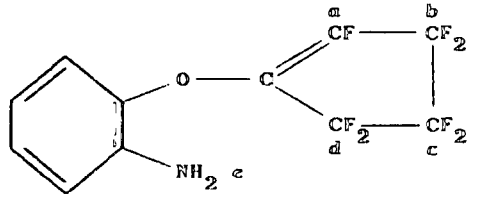
N.M.R. SPECTRA NUMBER 23



(173)

	Chemical shift	Multiplicity		Integral	Assignment
^1H	3.9	s(broad)		2	d
	6.9	broad		4	Ar.H
^{19}F	117.3	d	J_{ac} 7Hz	2	a
	119.3	d	J_{bc} 20Hz	2	b
	134.2	tt	J_{cb} 20Hz	1	c
			J_{ca} 7Hz		

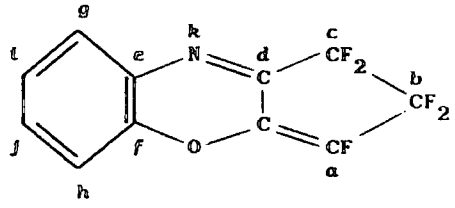
N.M.R. SPECTRA NUMBER 24



(174)

	Chemical shift	Multiplicity		Integral	Assignment
^1H	3.8	s		2	e
	6.6	broad		4	Ar.H
^{19}F	116.8	d	J_{ba} 25Hz	2	b
	116.9	s		2	d
	131.1	s		2	c
	154.6	m		1	a

N.M.R. SPECTRA NUMBER 25



(175)

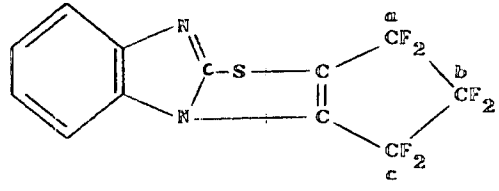
	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	7.6	broad			Ar.H
^{19}F	117.8	d	J_{ba} 13Hz	2	b
	124.3	s		2	c
	158.1	t	J_{ab} 13Hz	1	a
^{13}C	151.3	t	$^{2}J_{CF}$ 26Hz		d
	143.6	s			e or f
	135.9	dt	$^{1}J_{CF}$ 298Hz $^{2}J_{CF}$ 26Hz		a
	134.7	s			e or f

signals at 131.5, 130.3, 126.2, 116.0, all doublets $^{1}J_{CH}$ ca.160Hz corresponding to g, h, i, j

signals at 113, 110, both overlapping triplets $^{1}J_{CF}$ ca 260Hz corresponding to c and b

^{15}N	-80.5	broad			k

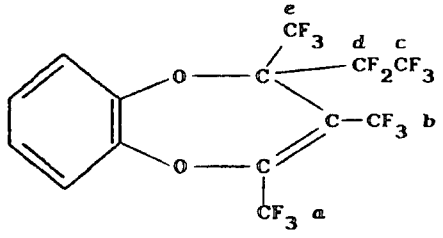
N.M.R. SPECTRA NUMBER 26



(177)

	Chemical shift	Multiplicity	Integral	Assignment
^{1}H	7.2	broad		Ar.H
^{19}F	102.8	s	2	c
	109.7	s	2	a
	124.0	s	2	b

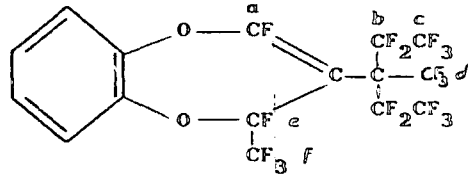
N.M.R. SPECTRA NUMBER 27



(179)

	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	7.8	m(broad)			Ar.H
^{19}F	53.1	m		3	b
	64.9	qt	J_{ec} 12Hz	3	e
			J_{ed} 2Hz		
	69.3	q	J_{ab} 16Hz	3	a
	80.2	s		3	c
	119.0 and 120.4	AB(m)	J 240Hz	2	

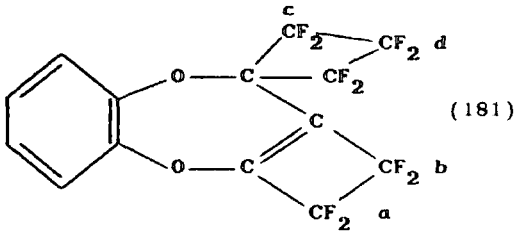
N.M.R. SPECTRA NUMBER 28



(180)

	Chemical shift	Multiplicity	Integral	Assignment
^{1}H	6.9	broad	Ar.H	
^{19}F	38.2	m(broad)	1	a
	55.3	broad	3	f
	76.2	s	3	d
	77.8	v.broad	6	c
	101.4	broad	4	b
	107.0	broad	1	e

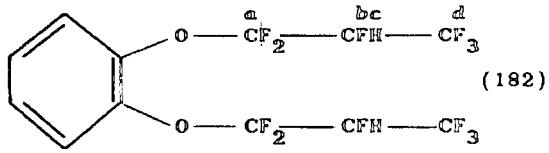
N.M.R. SPECTRA NUMBER 29



(181)

	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	6.8	m			Ar.H
^{19}F	108.8	s(broad)		2	b
	118.6	s		2	a
	122.0 and 130.8	AB	J 224Hz	4	c
	129.2 and 132.9	AB	J 215Hz	2	d

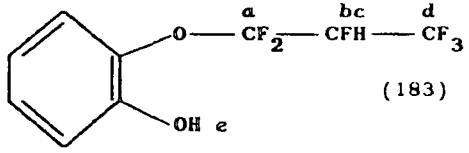
N.M.R. SPECTRA NUMBER 30



(182)

	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	4.3	d	J_{cb} 43Hz	1	c
	6.3	broad		4	Ar.H
^{19}F	75.1	m		3	d
	79.0	m		2	a
	212.0	d	J_{bc} 43Hz	1	b

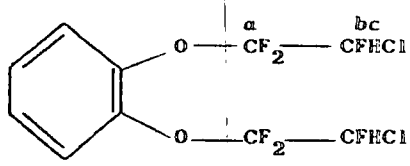
N.M.R. SPECTRA NUMBER 31



(183)

	Chemical shift	Multiplicity		Integral	Assignment
^1H	4.3	d	J_{cb} 43Hz	1	c
	5.3	broad		1	e
	6.3	broad		4	Ar.H
^{19}F	75.1	m		3	d
	79.0	m		2	e
	212.0	d	J_{bc} 43Hz	1	b

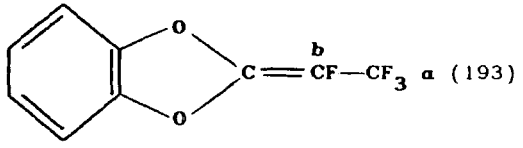
N.M.R. SPECTRA NUMBER 32



(184)

	Chemical shift	Multiplicity		Integral	Assignment
^1H	6.6	dt	J_{cb} 49Hz J_{ca} 4Hz	2	c
	7.5	broad		4	Ar.H
^{19}F	86.7	dd	J_{ab} 11Hz J_{ac} 4Hz	4	a
	155.9	dt	J_{bc} 49Hz J_{ba} 11Hz	2	b

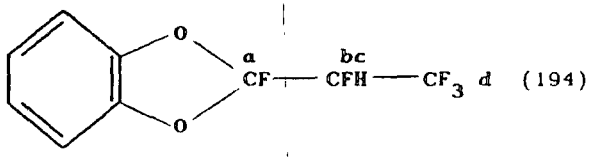
N.M.R. SPECTRA NUMBER 33



(193)

	Chemical shift	Multiplicity		Integral	Assignment
^1H	6.8	s			Ar.H
^{19}F	65.8	d	J_{ab} 16Hz	3	a
	201.3	q	J_{ba} 16Hz	1	b

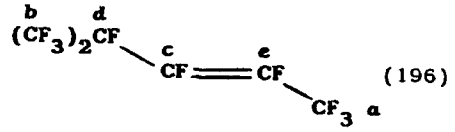
N.M.R. SPECTRA NUMBER 34



(194)

	Chemical shift	Multiplicity		Integral	Assignment
^1H	6.6	m		4	Ar.H
	4.8	dq	J_{cb} 39Hz J_{cd} 6Hz	1	c
^{19}F	68.3	m		1	a
	76.2	ddd	J_{db} 11Hz J_{dc} 6Hz J_{da} 11Hz	3	d
	212.5	dm	J_{bc} 43Hz	1	b

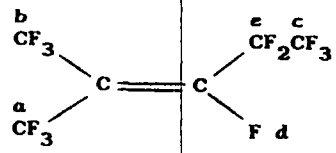
N.M.R. SPECTRA NUMBER 35



(196)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	73.7	dd	J_{ac} 20Hz	3	a
			J_{ae} 5Hz		
	79.9	dd	J	3	b
			J		
	161.1	m		1	c
	162.2	dq	J_{ed} 40Hz	1	e
			J_{ea} 5Hz		
	191.8	dm	J_{de} 40Hz	1	d

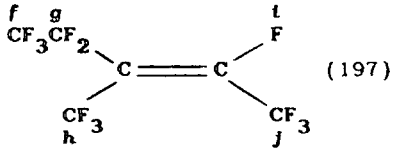
N.M.R. SPECTRA NUMBER 36



(29)

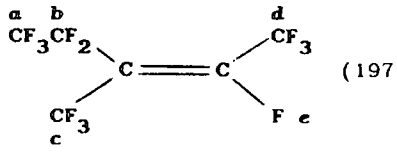
	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	60.2	m		3	b
	62.8	dq	J_{ad} 33Hz	3	a
			J_{ab} 9Hz		
	86.4	m(sharp)		3	c
	100.5	broad		1	d
	119.6	qd	J_{eb} 20Hz	2	e
			J_{ed} 5Hz		

N.M.R. SPECTRA NUMBER 37



(197)

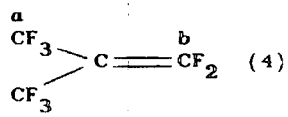
	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	60.1	m		3	h
	70.1	q	J_{jh} 14Hz	3	j
	87.8	m		3	f
	96.3	broad		1	i
	115.0	dq	J_{gi} 30Hz	2	g
			J_{gh} 14Hz		



(197)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	61.3	m		3	c
	69.3	m		3	d
	86.2	m		3	a
	93.2	qt	J_{ec} 25Hz	1	e
			J_{eb} 3Hz		
	111.3	m		2	b

N.M.R. SPECTRA NUMBER 38

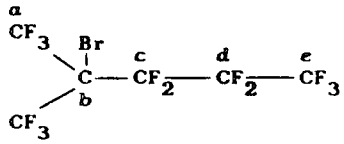


(4)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	59.1	ddd ($AA^{1}BB^{1}$)	6	a
		coupling constants difficult to determine		
	64.0	m	2	b

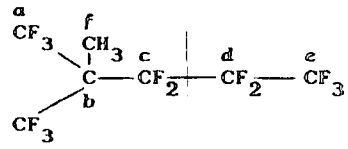
hexafluoropropene impurity <5%

N.M.R. SPECTRA NUMBER 39



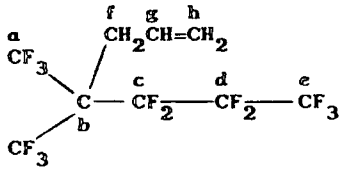
	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	66.4	s		6	a
	82.3	s		3	e
	106.8	m		2	c
	123.7	m		2	d
^{13}C	57.5	t of septets			b
		$^{2}J_{CF_{a,c}}$	ca. 27Hz		
	108.3	thex	$^{1}J_{CF}$ 273Hz		d
			$^{2}J_{CF}$ 37Hz		
	112.1	tt	$^{1}J_{CF}$ 273Hz		c
			$^{2}J_{CF}$ 33Hz		
	116.7	qt	$^{1}J_{CF}$ 288Hz		e
			$^{2}J_{CF}$ 34Hz		
	119.5	q	$^{1}J_{CF}$ 288Hz		a

N.M.R. SPECTRA NUMBER 40



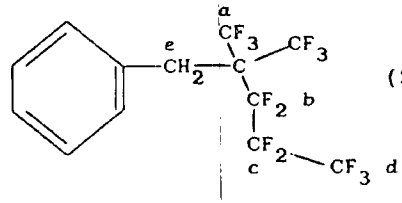
	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	2.0	s			f
^{19}F	69.2	t	J_{ac} 11Hz	6	a
	82.7	t	J_{ec} 11Hz	3	e
	111.8	m		2	d
	124.7	m		2	c

N.M.R. SPECTRA NUMBER 41



	Chemical shift	Multiplicity		Integral	Assignment
^1H					
^{19}F	65.0	t	J_{ac} 11Hz	6	a
	82.0	t	J_{ed} 14Hz	3	e
	108.6	q	J_{ca} 11Hz	2	c
	124.7	m		2	d

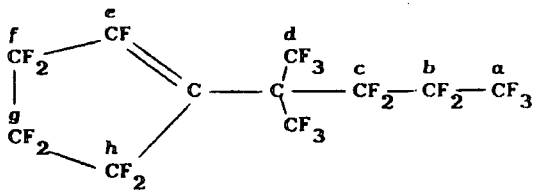
N.M.R. SPECTRA NUMBER 42



(240)

	Chemical shift	Multiplicity		Integral	Assignment
^1H	3.2	broad		2	e
	6.9	broad		5	Ar.H
^{19}F	59.7	t.t	J_{ab} 11Hz	6	a
			J_{ac} 11Hz		
	77.9	t	J_{db} 13Hz	3	d
	103.1	m		2	b
	120.1	m		2	c

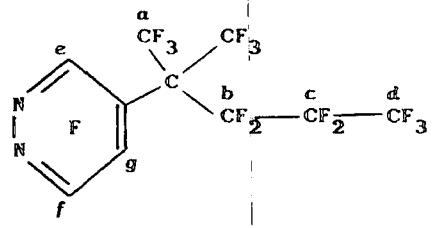
N.M.R. SPECTRA NUMBER 43



(239)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	63.0	dt	J_{de} 20Hz	6	d
			J_{dc} 10Hz		
	72.7	m		1	e
	83.3	t	J_{ac} 13Hz	3	a
	broad resonance centred at 107.7, integrating to 4 F, assigned to f and h				
	124.3	m		2	c
	125.5	d	J_{ce} 18Hz	2	b
	136.0	s		2	g

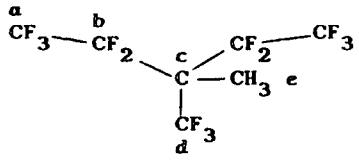
N.M.R. SPECTRA NUMBER 44



(238)

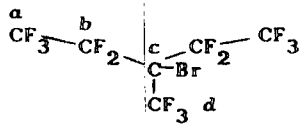
	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	59.7	m		6	a
	63.4	m(broad)		1	e
	82.9	t	J_{db} 17Hz	3	d
	97.7	dd	J_{fg} 32Hz	1	f
			J_{fe} 23Hz		
	105.0	m		2	b
	107.2	m(broad)		1	g
	124.3	m		2	c

N.M.R. SPECTRA NUMBER 45



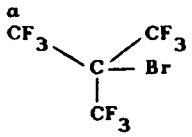
	Chemical shift	Multiplicity	Integral	Assignment
^{1}H	1.8	s(broad)		e
^{19}F	68.0	m	3	d
	81.5	m	6	a
	113.8	m	4	b

N.M.R. SPECTRA NUMBER 46



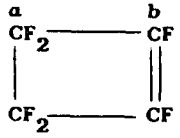
	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	63.9	septet	J_{da} 7Hz	3	d
	77.9	q	J_{ad} 7Hz	6	a
	107.5	m		4	b
^{13}C	72?	m			c
	111.5	tq	$^{1}J_{CF}$ 270Hz		b
			$^{2}J_{CF}$ 40Hz		
	117.5	qt	$^{1}J_{CF}$ 281Hz		a
			$^{2}J_{CF}$ 38Hz		
	120.3	q	$^{1}J_{CF}$ 287Hz		d

N.M.R. SPECTRA NUMBER 47



	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	68.3	s		a

N.M.R. SPECTRA NUMBER 48



(107)

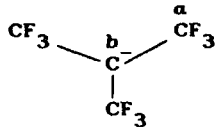
	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	125.1	m	4	a
	136.3	m	2	b

N.M.R. SPECTRA NUMBER 49

$((CH_3)_2N)_3S^{+}$ $(CH_3)_3SiF_2^{-}$ or TAS-F (208)

	Chemical shift	Multiplicity		Integral	Assignment
^{1}H	0.1	s		9	b
	2.7	s		6	a
^{19}F	59.1	s			c
^{13}C	4.0	q	$^{1}J_{CH}$ 430Hz		b
	37.1	q	$^{1}J_{CH}$ 517Hz		a

N.M.R. SPECTRA NUMBER 50

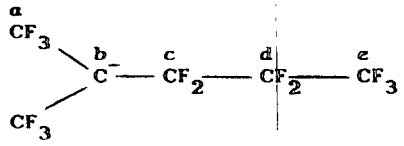


Cs^+ (101)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	45.8	s		a
^{13}C	40.7	decuplet $^2J_{CF}$ 39Hz		b
	127.8	q $^1J_{CF}$ 264Hz		a

See n.m.r. number 47 for model

N.M.R. SPECTRA NUMBER 51

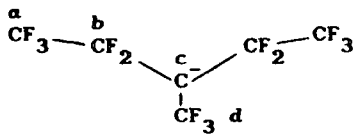


Cs^+/TAS^+ (221)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	42.4	tt J_{ac} 19Hz, J_{ad} 6Hz	6	a
	81.1	t J_{ec} 10Hz	3	e
	92.8	m	2	c
	126.2	m	2	d
^{13}C	37.0	m		b
	107.5	t $^1J_{CF}$ 296Hz		d
	116.6	q $^1J_{CF}$ 286Hz		e
	118.0	tt $^1J_{CF}$ 255Hz, $^2J_{CF}$ 32Hz		c
	128.4	q $^1J_{CF}$ 263Hz		a

See n.m.r. number 39 for model

N.M.R. SPECTRA NUMBER 52

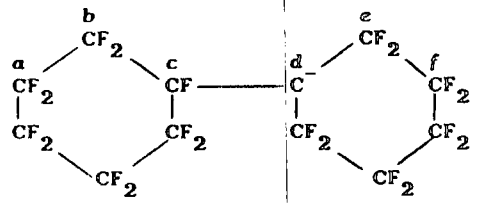


Cs^+-TAS$^+$
(220)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	39.9	m		3	d
	84.6	s		6	a
	93.3	q	J_{bd} 19Hz	4	b
^{13}C	36.2	*octet*	$^2J_{CF}$ 36Hz		c
	119.0	tq	$^1J_{CF}$ 250Hz		b
			$^2J_{CF}$ 37Hz		
	121.0	qt	$^1J_{CF}$ 250Hz		a
			$^2J_{CF}$ 37Hz		
	131.0	q	$^1J_{CF}$ 260Hz		d

See n.m.r. number 46 for model

N.M.R. SPECTRA NUMBER 53

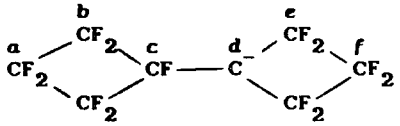


Cs^+-TAS$^+$
(215)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	166.0	s(broad)		1	c
signals between 101 and 149, integrating to 20 F, unassigned.					
^{13}C	33.9	*broad*			d
	94.9	dpentet	$^1J_{CF}$ 196Hz		c
			$^2J_{CF}$ 29Hz		
	118.7	t	$^1J_{CF}$ 244Hz		e
signals between 101 and 113, unassigned					

See n.m.r. number 62 for model

N.M.R. SPECTRA NUMBER 54

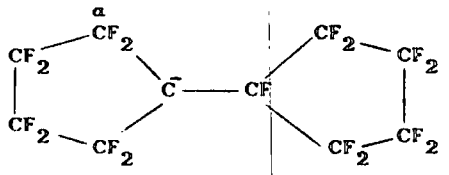


Cs^+ TAS^+
(209)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	87.2	dm	J_{ec} 47Hz	4	e
	124.4 and 128.2	AB	J 218Hz	4	b
	(low field limb	d	J_{bc} 31Hz		
	high field limb	m	all J ca. 10Hz)		
	124.8	s		2	f
	128.7 and 134.0	AB	J 218Hz	2	a
	(low field limb	s			
	high field limb	m	all J ca. 10Hz)		
	133.6	broad m		1	c
^{13}C	52.2	s			c
	96.6	d	$^1J_{CF}$ 233Hz		c
	signals centred at 113.3, overlapping triplets, J ca. 293Hz, corresponding to a, b, e and f				
	121.1	t	$^1J_{CF}$ 284Hz	4	e

See n.m.r. number 63 for model

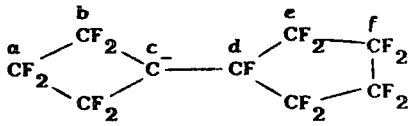
N.M.R. SPECTRA NUMBER 55



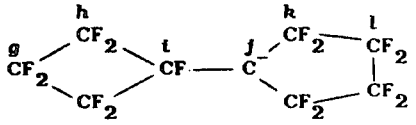
TAS^+
(224)

	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	80.5	d	J 29Hz	4	a
	signals between 107 and 138, integrating to 14 F, unassigned.				

N.M.R. SPECTRA NUMBER 56



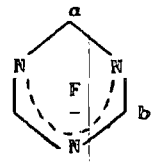
Cs^+ (217)



	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	81.8		4	c
	89.4		4	k
	signals between 117 and 138, unassigned			
	1:4 ratio of anion (a) to (b)			
^{13}C	52.4	s(broad)		c
	47.6	s(broad)		k
	99.7	d	$^1J_{CF}$ 270Hz	d
	signals between 105 and 145 unassigned			
	(spectrum too noisy to observe signal i)			

See n.m.r. number 64 for models

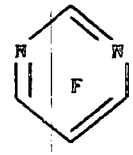
N.M.R. SPECTRA NUMBER 57



TAS^+ (204)

	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	7.0	very braod	2	a
	51.7	very broad	2	b

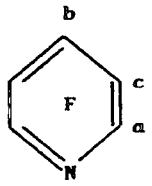
N.M.R. SPECTRA NUMBER 58

(229) 

+ TAS-F

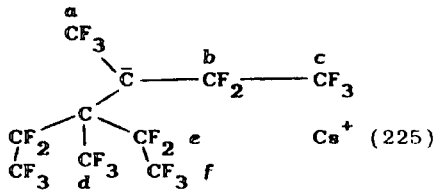
	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	52.0	very broad	1	
	70.3	very broad	2	
	152.7	very broad	1	
	187.2	very broad	1	

N.M.R. SPECTRA NUMBER 59

(228)  in TAS-F/CH_3CN

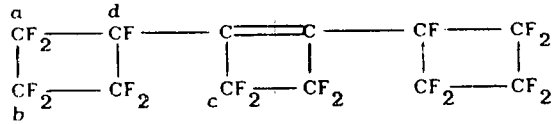
	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	92.0	slightly broad	2	a
	157.6	very broad	1	b
	164.7	slightly broad	2	c

N.M.R. SPECTRA NUMBER 60

 Cs^+ (225)

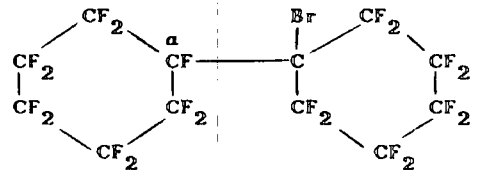
	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	43.0	m	3	a
	54.3	m	3	d
	70.3	q J_{ca} 12Hz	3	c
	77.8	q J_{fd} 11Hz	6	f
	79.0	broad	2	b
	106.0	m	4	e

N.M.R. SPECTRA NUMBER 61



	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	112.5	s		4	c
	127.0 and 133.0	AB	J 234Hz	8	a
	130.3 and 134.1	AB	J 228Hz	4	b
	180.0	s		2	d

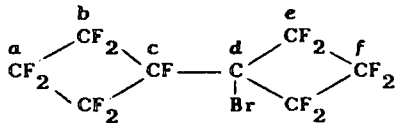
N.M.R. SPECTRA NUMBER 62 [ref. 160]



	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	79.9	s(broad)	1	a

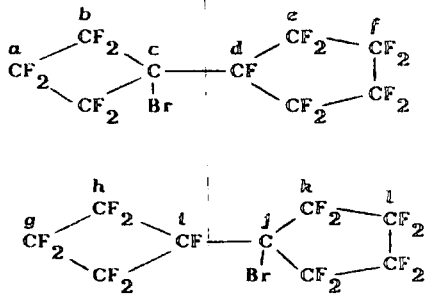
signals between 110 and 145, unassigned

N.M.R. SPECTRA NUMBER 63 [See ref. 160]



	Chemical shift	Multiplicity		Integral	Assignment
^{19}F	122.1 and 108.4	AB	J 220Hz	4	e
	126.3	m		4	b
	130.7 and 125.5	AB	J 230Hz	2	e
	131.1	s		2	a
	168.3	m		1	c

N.M.R. SPECTRA NUMBER 64 [See ref. 160]



	Chemical shift	Multiplicity	Integral	Assignment
^{19}F	106.3	part of AB J 248Hz		k
	107.7	part of AB J 215Hz		b
	135.1	s		f
	164.2	m		d
	168.1	s		i

APPENDIX 2 INFRARED SPECTRA

1 Perfluorobicyclobutylidene (127)

2 Perfluorocyclobutylcyclobut-1-ene (141)

3 Perfluorobicyclopnetylidene (128)

4 Perfluoro-9-oxadispiro[3.0.3.1]nonane (129)

5 Perfluoro-1-(1'-chlorocyclobutyl)cyclobut-1-ene (131)

6 1,1'-Dichloroperfluorobicyclobutyl (133)

7 Perfluoro-11-oxadispiro[4.0.4.1]undecane (130)

8 Perfluoro-1-(1'-chlorocyclopentyl)cyclopent-1-ene (132)

9 Perfluorocyclobutene (107)

10 Perfluorocyclopentene (154) and perfluorocyclopentanone

11 Perfluorocyclopentene (154)

12 *Trans*-2-hydroheptafluorobut-2-ene (143)

13 *Diene* (145)

14 *Epoxide* (149)

15 *Diepoxide* (151) or (152)

16 Perfluoro-3,4-dimethylhex-3-ene (82)

17 3,4-(3'-Methylbenzo)-7,7,8,8-tetrafluoro-2,5-dithiobicyclo [4.2.0]oct-1-ene (155)

18 3,4-(3'-Methylbenzo)-7,7,8,8,9,9-hexafluoro-2,5-dithiobicyclo [4.3.0]non-1-ene (155)

19 *Sulphoxides* (159) and (160)

20 3,4-Benzo-7,7,8,8,-tetrafluoro-2-aza-5-thiobicyclo[4.2.0] oct-1-ene (164)

21 3,4-Benzo-7,7,8,8,9-pentafluoro-2-aza-5-thiobicyclo[4.3.0] non-1-ene (164)

22 1,2-Bis(2'-aminothiophenoxy)-3,3,4,4,5,5-hexafluorocyclpentene (162)

23 1-Spirotetrafluorocyclobutenyl-3,4-benzo-2,5-dioxacyclopentane

(167)

24 1-Spirohexafluorocyclopent-2'-enyl-3,4-benzo-2,5-dioxacyclopentane (168)

25 *Ortho*-2,3,3,4,4-pentafluorocyclobut-1-enoxyaniline (173)

26 *Ortho*-2,3,3,4,4,5,5-heptafluorocyclopent-1-enoxyaniline (174)

27 3,4-Benzo-7,7,8,8,9-pentafluoro-2-oxa-5-azabicyclo[4.3.0] nona-1,5-diene (175)

28 3,4-Benzo-2,5-diaza-11-thio-7,7,8,8,9,9-hexafluorotricyclo [4.0.7.$0^{6,10}$]nona-1,6-diene (177)

29 6,7-Benzo-2,3,4-tristrifluoromethyl-2-pentafluoroethyl-1,5-dioxacyclohept-3-ene (179)

30 5,6-Benzo-3-methyl-2-(1'-methyl-1'-ethylpropyl)-4,7-dioxacyclohept-1-ene (180)

31 2-Spirohexafluorocyclobutyl-3,4-tetrafluorobutenyl-6,7-benzo 1,5-dioxacyclohept-3-ene (181)

32 *Ortho*bis-1,1,2,3,3,3-hexafluoropropoxybenzene (182)

33 *Ortho*-1,1,2,3,3,3-hexafluoropropoxyphenol (183)

34 *Ortho*bis-1,1,2-trifluoro-2-chloroethoxybenzene (184)

35 4,5-Benzo-2-(1',1',1',4'-tetrafluoroethenyl)-1,3-dioxacyclopentane (193)

36 4,5-Benzo-2-(1',1',1',2',3'-pentafluoroethyl)-1,3-dioxacyclopentane (194)

37 Perfluoro-4-methylpent-2-ene (196)

38 Perfluoro-2-methylpent-2-ene (29)

39 Perfluoro-3-methylpent-2-ene (197)

40 Perfluoroisobutene (4)

41 2-Bromoperfluoro-2-methylpentane

42 2-Methylperfluoro-2-methylpentane

43 2-Prop-2'-enylperfluoro-2-methylpentane

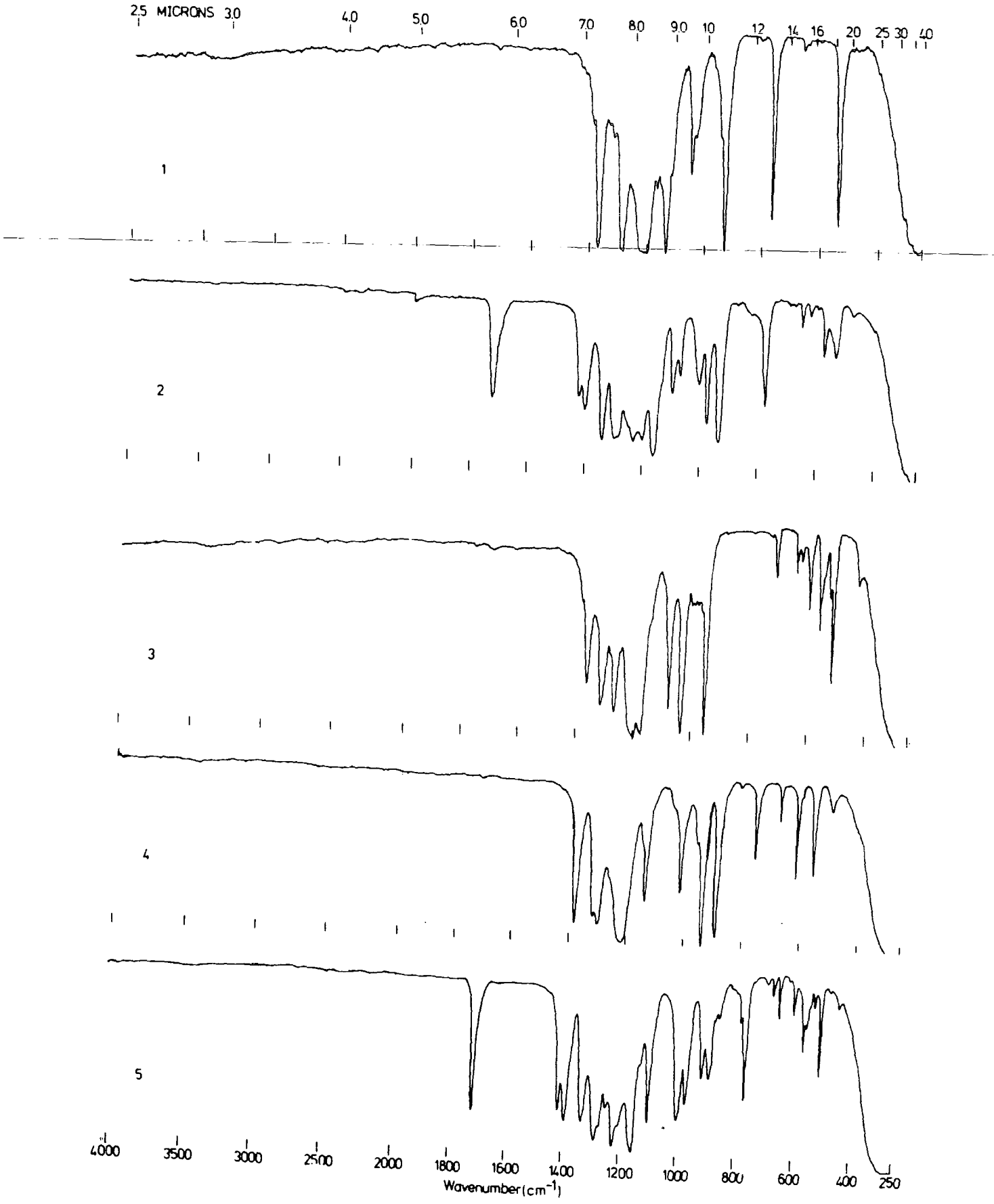
44 2-Benzylperfluoro-2-methylpentane

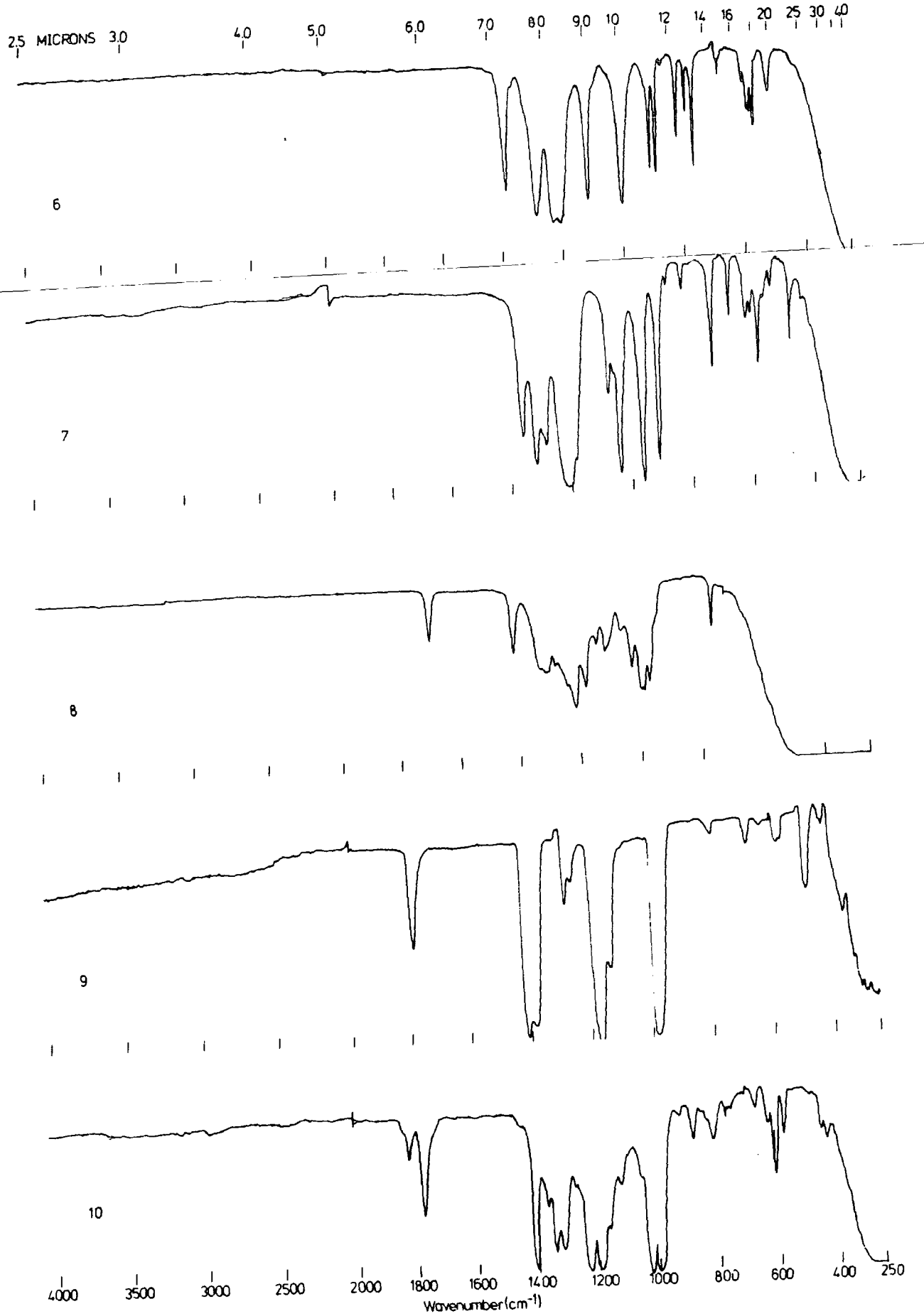
45 Perfluoro-1-(2'-methylpent-2'-yl)cyclopentene (239)

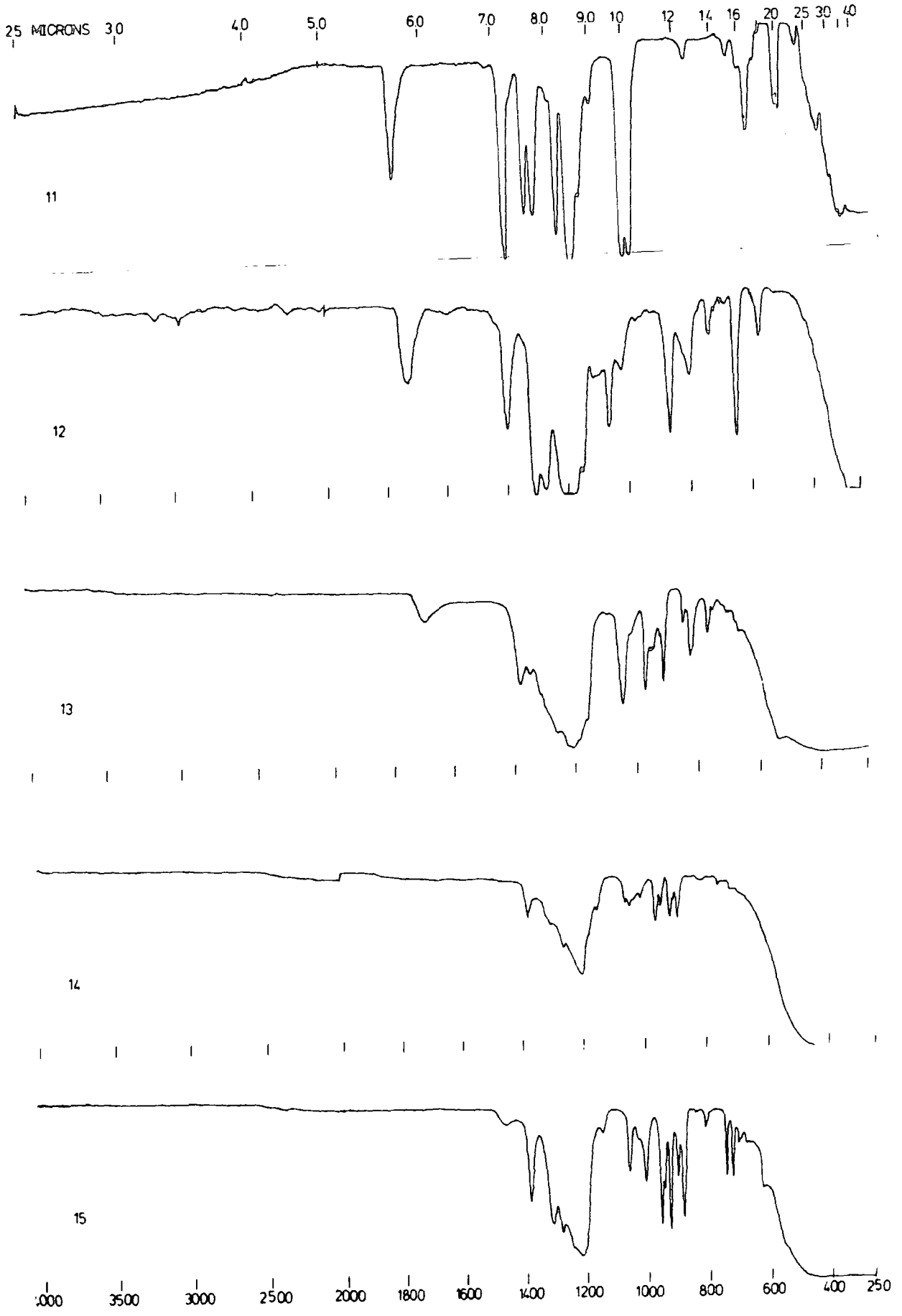
46 Perfluoro-4-(2'-methylpent-2'-yl)pyridazine (238)

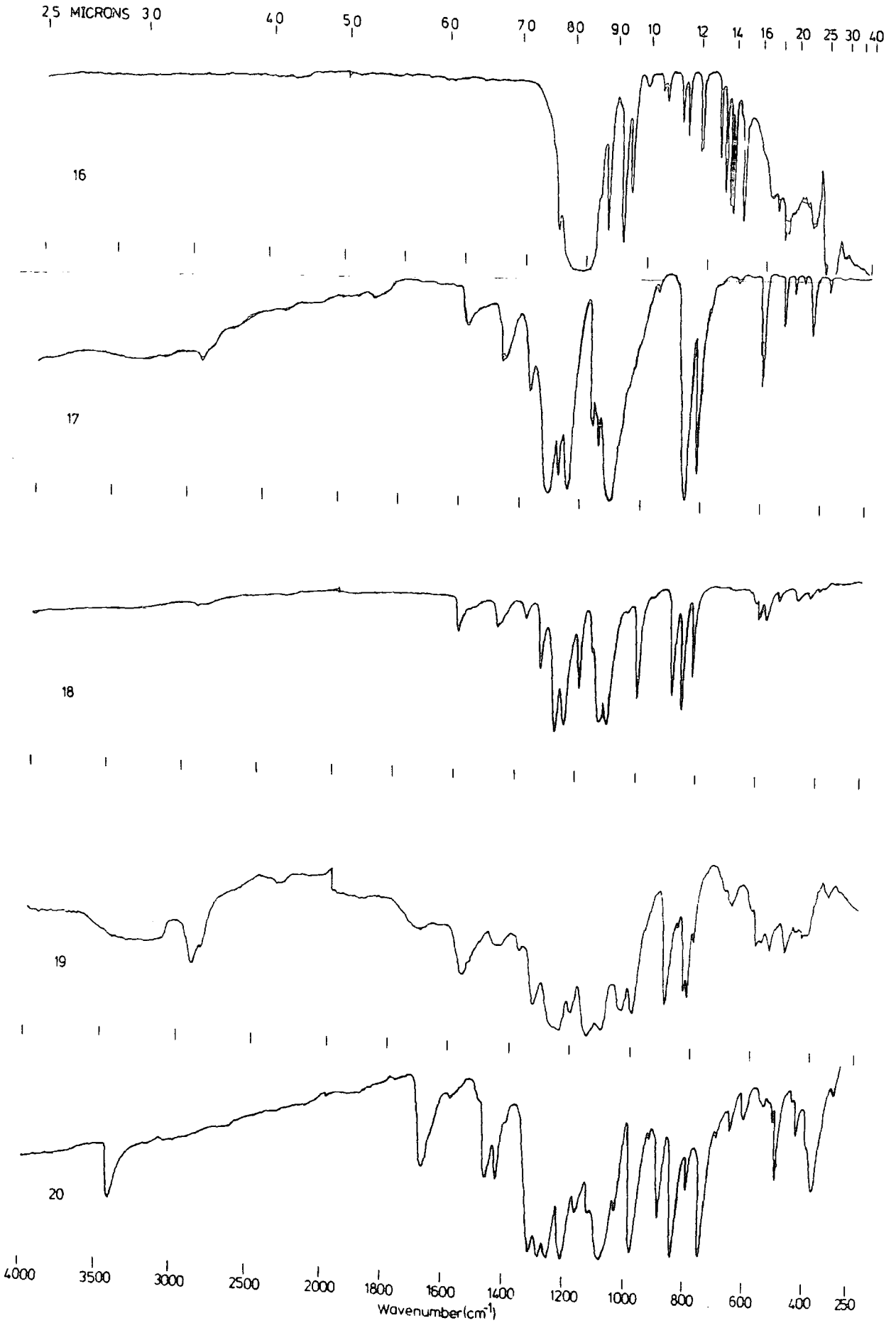
47 3-Methylperfluoro-3-methylpentane

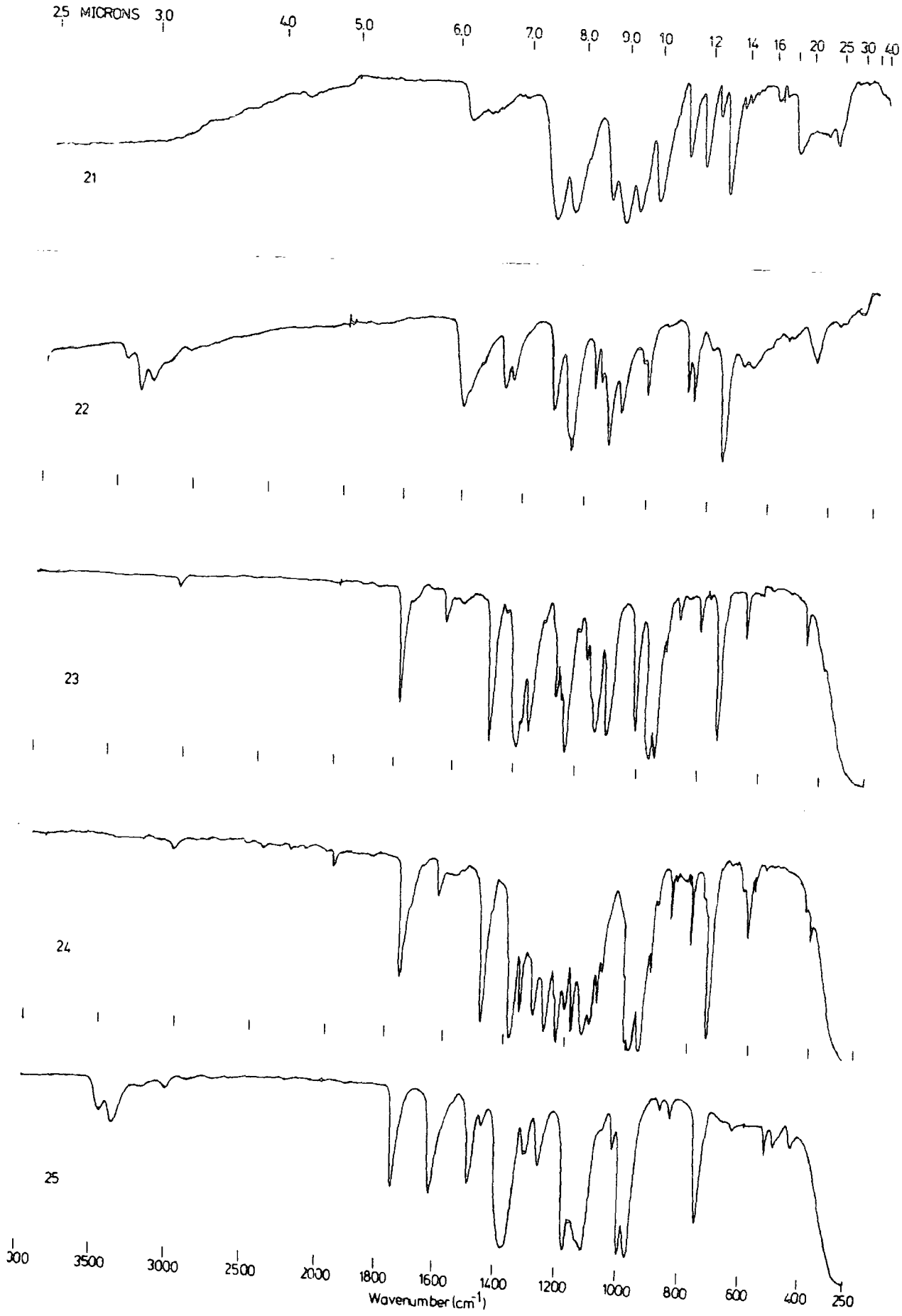
48 3-Bromoperfluoro-3-methylpentane

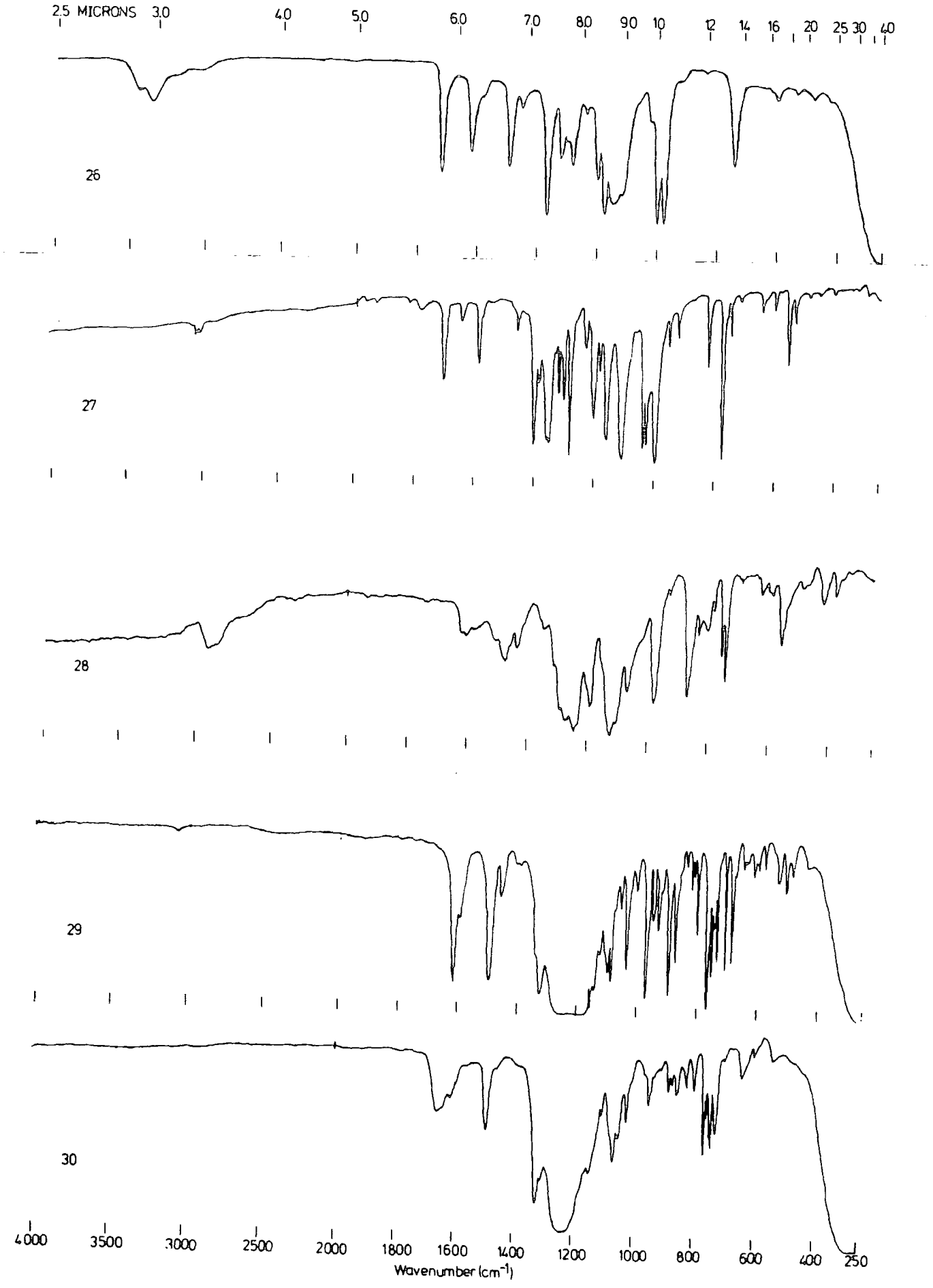

2.5 MICRONS 3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
30
40
1
2
3
4
5
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)

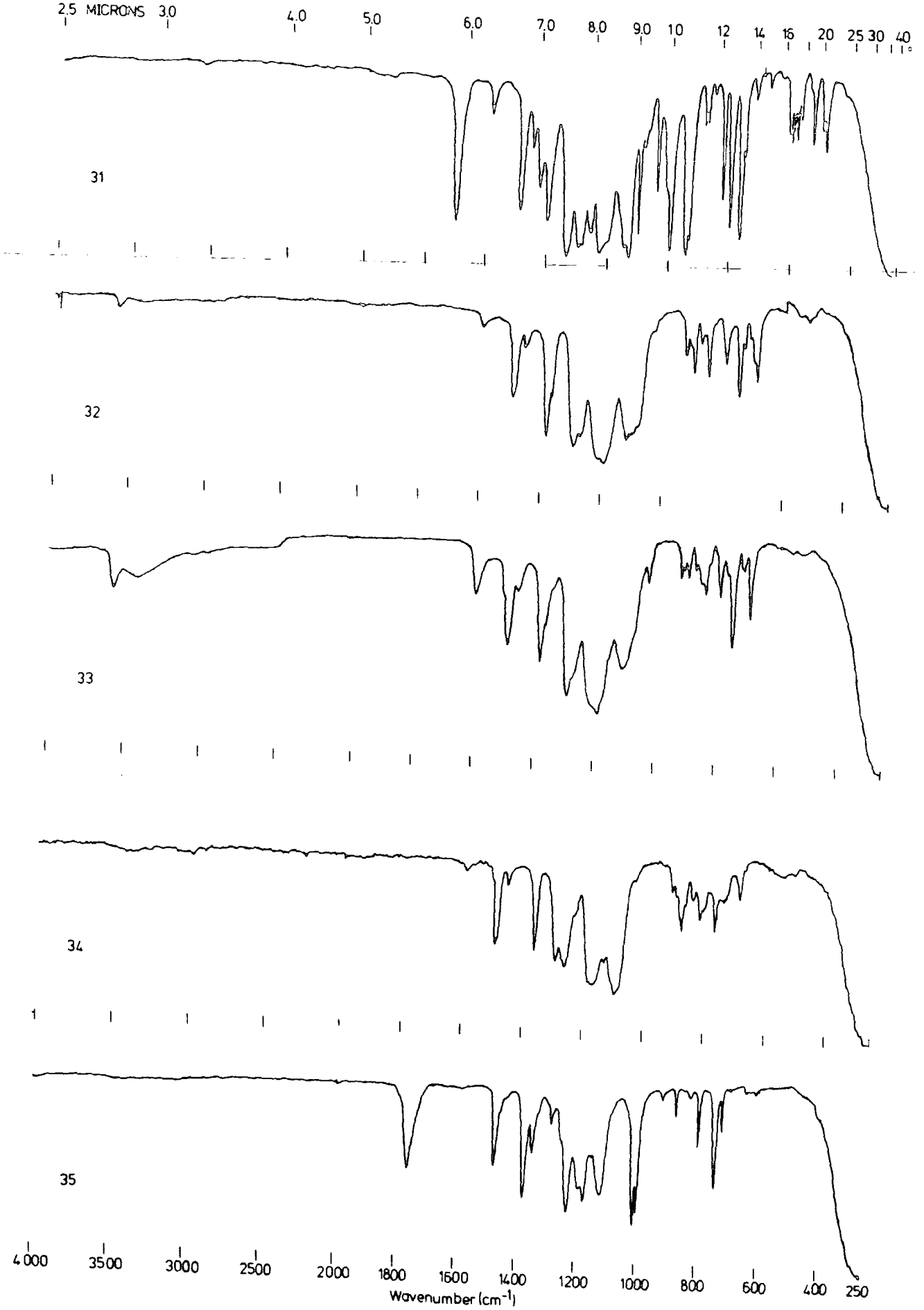

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
6
7
8
9
10
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)

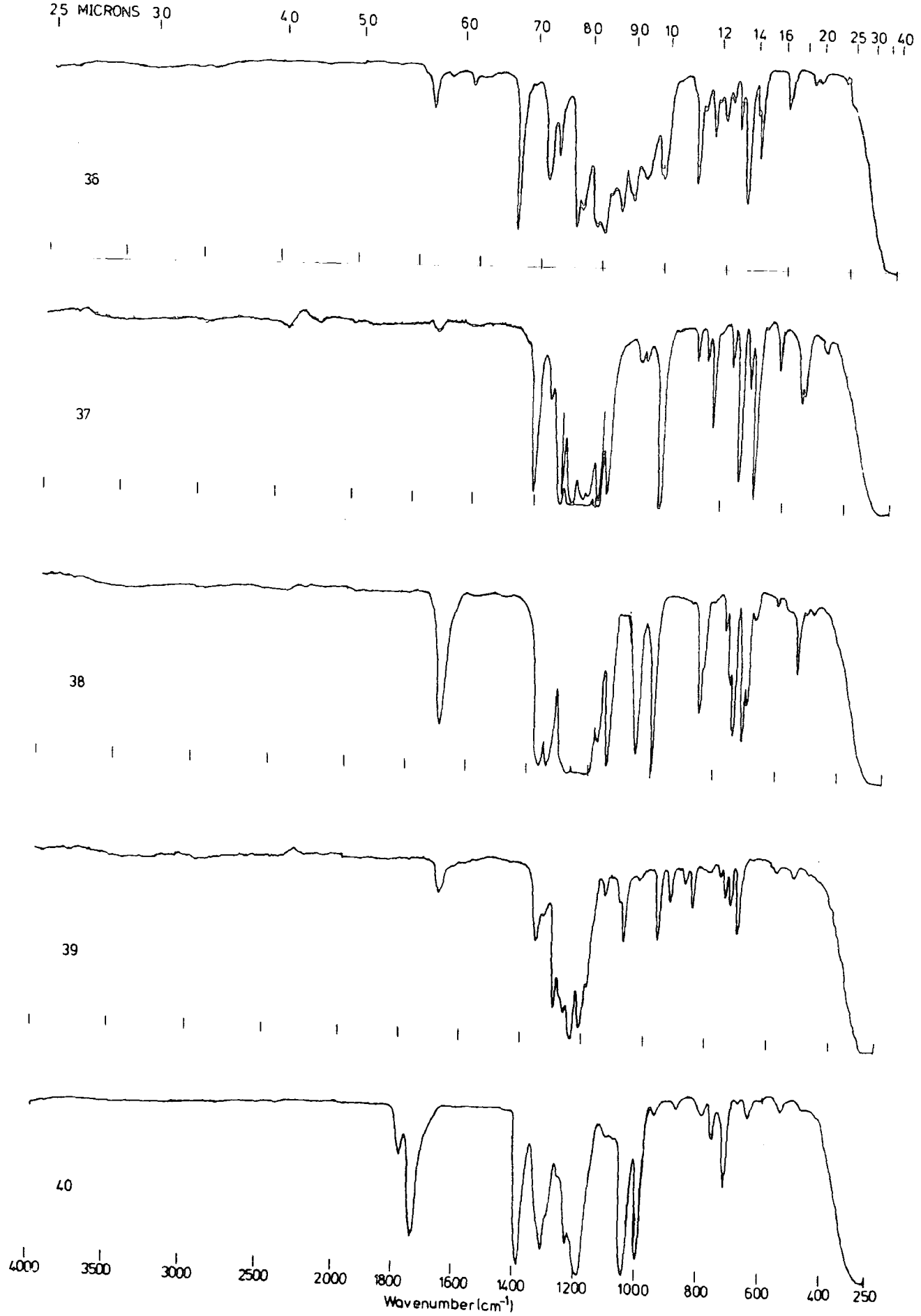

25 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
11
12
13
14
15
3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250

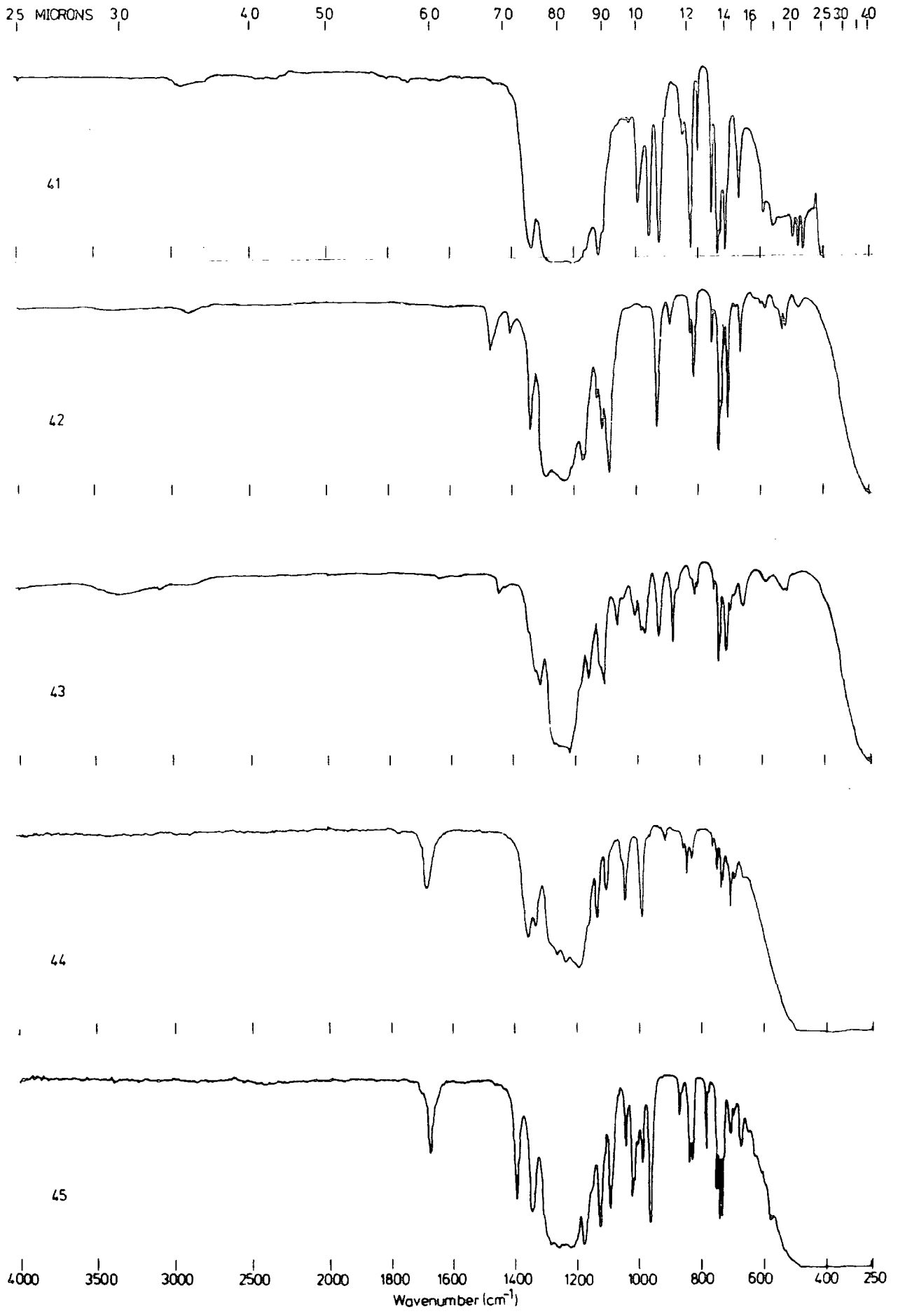

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
16
17
18
19
20
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber(cm-1)

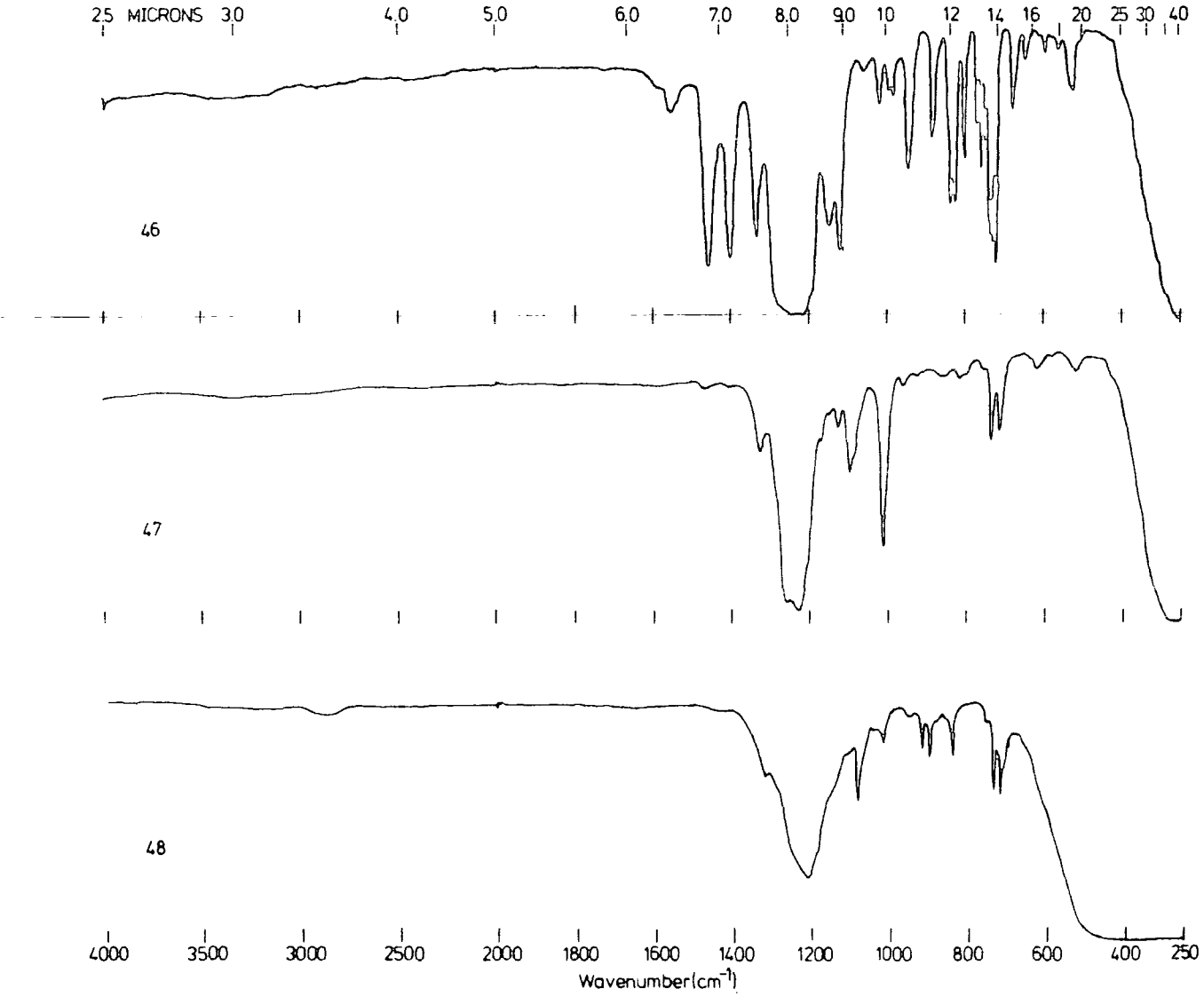

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
21
22
23
24
25
3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)


2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
26
27
28
29
30
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)


2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
31
32
33
34
35
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)


25 MICRONS 30
40
50
60
70
80
90
10
12
14
16
20
25
30
40
36
37
38
39
40
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
Wavenumber (cm⁻¹)


2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
41
42
43
44
45
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber (cm⁻¹)


2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
46
47
48
4000 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250
Wavenumber(cm⁻¹)

APPENDIX THREE MASS SPECTRA

EI IF NOT STATED OTHERWISE

1. Perfluorobicyclobutylidene (127)
2. Perfluorocyclobutylcyclobut-1-ene (141) (EI)
3. Perfluorocyclobutylcyclobut-1-ene (141) (CI)
4. Perfluorobicyclopentylidene (128) (EI)
5. Perfluorobicyclopentylidene (128) (NI)
6. Perfluoro-9-oxadispiro[3.0.3.1]nonane (129)
7. Perfluoro-1-(1'-chlorocyclobutyl)cyclobut-1-ene (131)
8. 1,1'-Dichloroperfluorobicyclobutyl (133)
9. Perfluoro-11-oxadispiro[4.0.4.1]undecane (130) (EI)
10. Perfluoro-11-oxadispiro[4.0.4.1]undecane (130) (NI)
11. Perfluoro-1-(1'-chlorocyclopentyl)cyclopent-1-ene (132)
12. 1,1'-dichloroperfluorobicyclopentyl (134)
13. Perfluorocyclobutene (107)
14. Perfluorocyclopentene (154)
15. Perfluorocyclopentanone
16. *Trans*-2-hydroheptafluorobut-2-ene
17. *Diene* (145)
18. *Epoxide* (149)
19. *Diepoxide* (151) or (152)
20. Perfluoro-3,4-dimethylhex-3-ene (82) (NI)
21. 3,4-(3'-Methylbenzo)-7,7,8,8-tetrafluoro-2,5-dithiobicyclo[4.2.0] oct-1-ene (155)
22. 3,4-(3'-Methylbenzo)-7,7,8,8,9,9-hexafluoro-2,5-dithiobicyclo [4.3.0]non-1-ene (155) (CI)
23. *Sulphoxides* (159) and (160)
24. 3,4-Benzo-7,7,8,8,-tetrafluoro-2-aza-5-thiobicyclo[4.2.0] oct-1-ene (164)
25. 3,4-Benzo-7,7,8,8,9-pentafluoro-2-aza-5-thiobicyclo[4.3.0]

non-1-ene (164) (EI)

26. 3,4-Benzo-7,7,8,8,9-pentafluoro-2-aza-5-thiobicyclo[4.3.0] non-1-ene (164) (CI)

27. 1,2-Bis(2'-aminothiophenoxy)-3,3,4,4,5,5-hexafluorocyclopentene (162)

28. 1-Spirotetrafluorocyclobutenyl-3,4-benzo-2,5-dioxacyclopentane (167)

29. 1-Spirohexafluorocyclopent-2'-enyl-3,4-benzo-2,5-dioxacyclopentane (168)

30. *Ortho*-2,3,3,4,4-pentafluorocyclobut-1-enoxyaniline (173)

31. *Ortho*-2,3,3,4,4,5,5-heptafluorocyclopent-1-enoxyaniline (174)

32. 3,4-Benzo-7,7,8,8,9-pentafluoro-2-oxa-5-azabicyclo[4.3.0] nona-1,5-diene (175)

33. 3,4-Benzo-2,5-diaza-11-thio-7,7,8,8,9,9-hexafluorotricyclo [4.0.7.$0^{6,10}$]nona-1,6-diene (177)

34. 6,7-Benzo-2,3,4-tristrifluoromethyl-2-pentafluoroethyl-1,5-dioxacyclohept-3-ene (179)

35. 5,6-Benzo-3-methyl-2-(1'-methyl-1'-ethylpropyl)-4,7-dioxacyclohept-1-ene (180) (EI)

36. 5,6-Benzo-3-methyl-2-(1'-methyl-1'-ethylpropyl)-4,7-dioxacyclohept-1-ene (180) (CI)

37. 2-Spirohexafluorocyclobutyl-3,4-tetrafluorocyclobutenyl 6,7-benzo-1,5-dioxacyclohept-3-ene (181)

38. *Ortho*-1,1,2,3,3,3-hexafluoropropoxyphenol (183)

39. *Ortho*bis-1,1,2,3,3,3-hexafluoropropoxybenzene (182)

40. *Ortho*bis-1,1,2-trifluoro-2-chloroethoxybenzene (184)

41. 4,5-Benzo-2-(1',1',1',4'-tetrafluoroethenyl)-1,3-dioxacyclopentane (193)

42. 4,5-Benzo-2-(1',1',1',2',3'-pentafluoroethyl)-1,3-dioxacyclopentane (194)

43. Perfluoro-4-methylpent-2-ene (196)

44. Perfluoro-2-methylpent-2-ene (29)

45. Perfluoro-3-methylpent-2-ene (197)

46. 2-Bromoperfluoro-2-methylpentane

47. 2-Methylperfluoro-2-methylpentane

48. 2-Prop-2'-enylperfluoro-2-methylpentane

49. 2-Benzylperfluoro-2-methylpentane

50. Perfluoro-1-(2'-methylpent-2'-yl)cyclopentene (239) (EI)

51. Perfluoro-1-(2'-methylpent-2'-yl)cyclopentene (239) (NI)

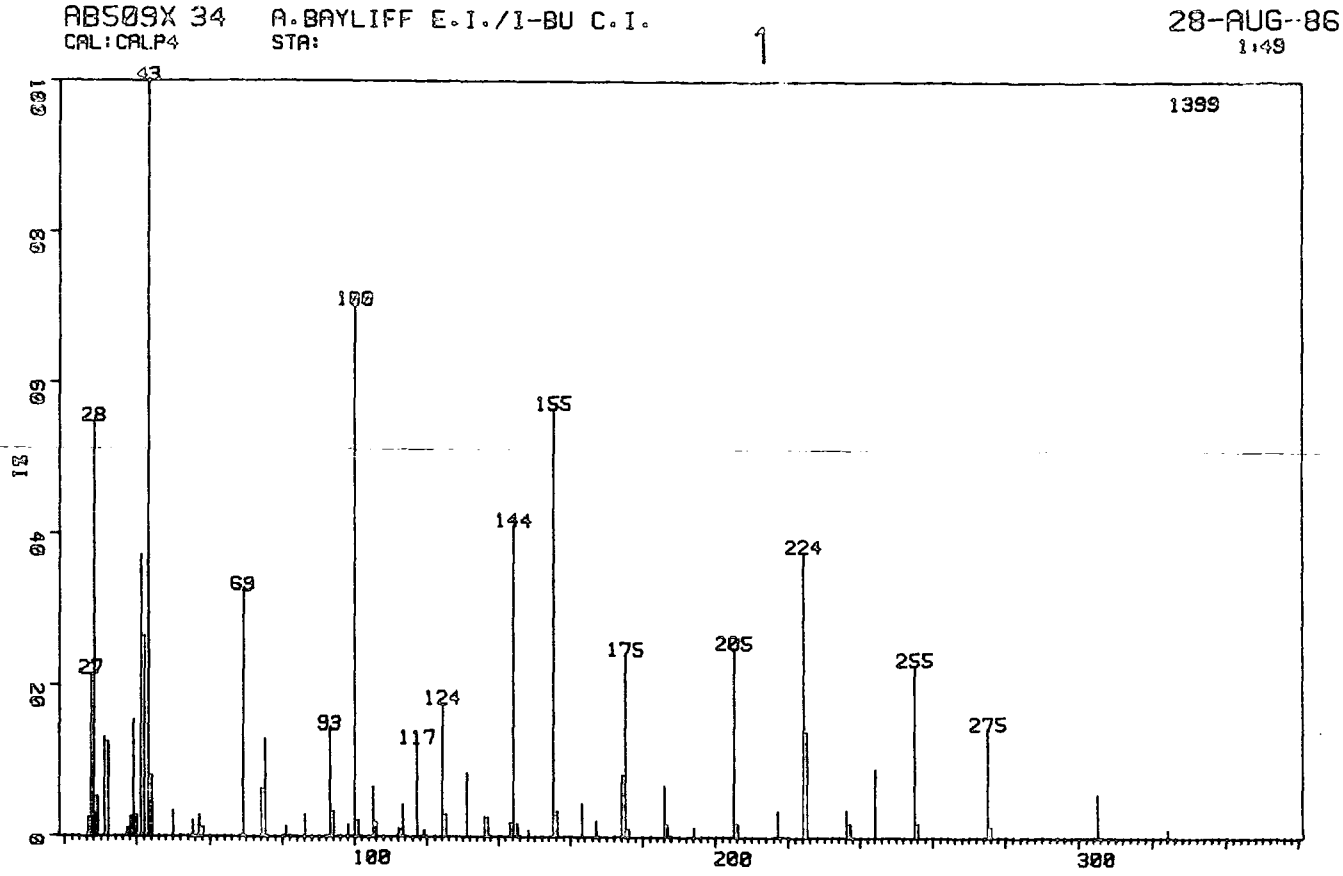
52. Perfluoro-4-(2'-methylpent-2'-yl)pyridazine (238) (CI)

53. Perfluoro-4-(2'-methylpent-2'-yl)pyridazine (238) (EI)

54. 3-Methylperfluoro-3-methylpentane

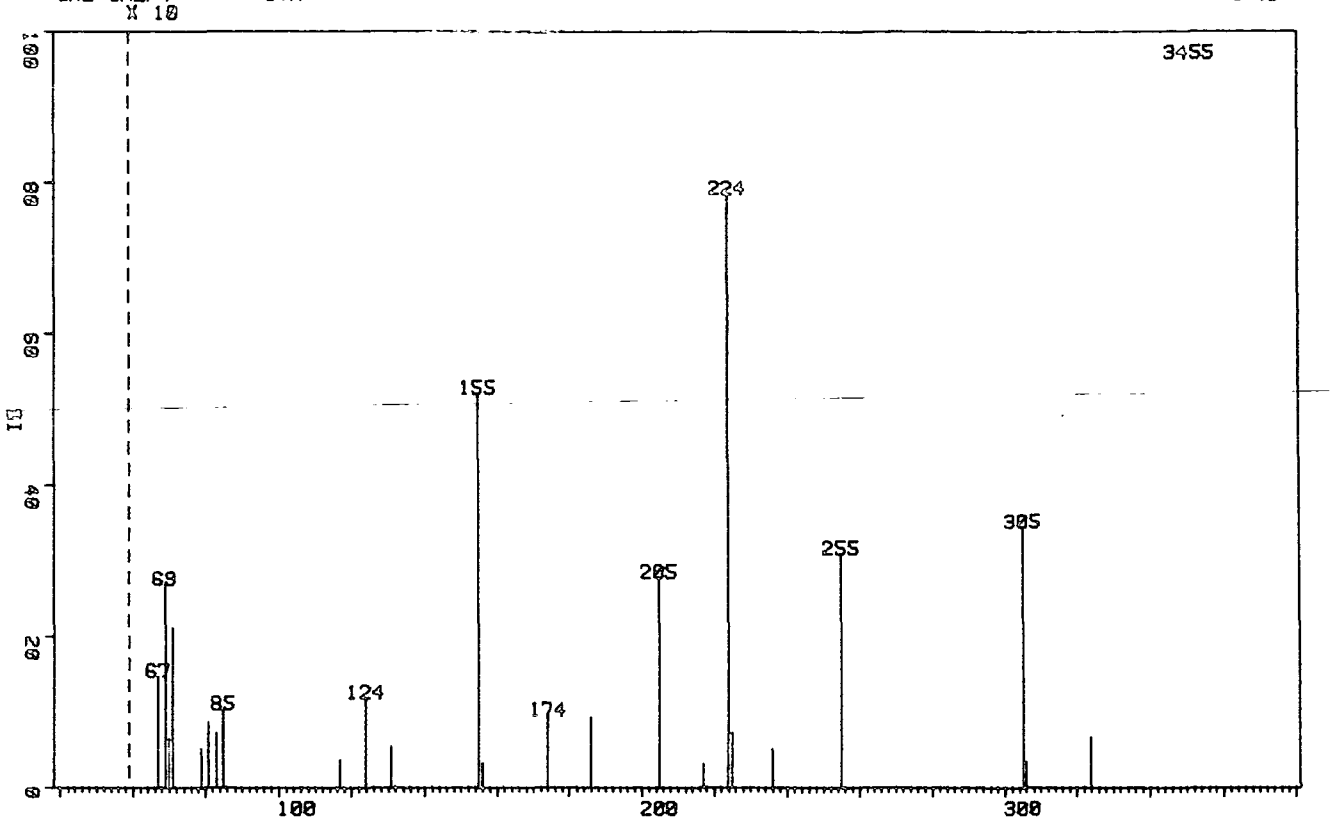
55. 3-Bromoperfluoro-3-methylpentane (EI)

56. 3-Bromoperfluoro-3-methylpentane (NI)



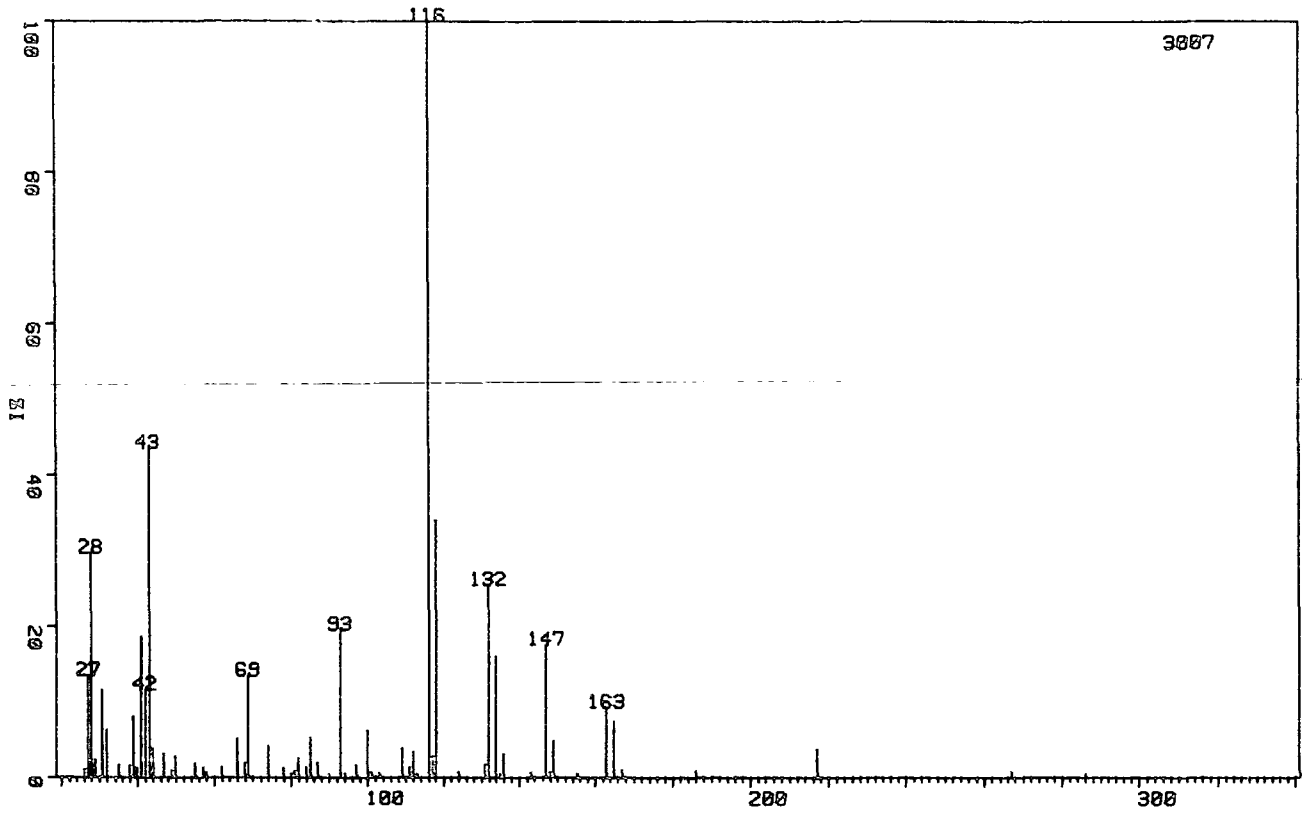
MASS	%HT. BASE	MASS	%HT. BASE
26.2891	2.50	124.0844	17.58
27.2241	21.52	125.1025	2.86
28.1030	54.90	131.0192	8.43
28.1274	2.86	136.0704	2.57
28.9990	5.22	137.0666	2.50
30.8667	13.08	143.0699	1.79
31.9775	12.51	144.0832	41.10
37.1069	1.07	145.0964	1.57
38.0542	2.57	148.0627	0.86
38.9795	15.51	155.0915	56.54
39.8169	2.79	156.0997	3.29
39.8779	2.57	163.1139	4.43
40.9644	37.24	167.0798	2.14
42.0581	26.59	174.0939	8.15
43.1299	100.00	175.0949	24.09
44.1016	8.08		
44.1724	3.22	176.1105	1.07
49.9877	3.36	186.0707	6.79
55.1196	2.07	187.0716	1.64
55.1733	1.14	194.0907	1.22
57.1606	2.79	205.1014	24.95
58.1299	1.22	206.0892	1.79
69.0088	32.59	217.0780	3.50
74.1138	6.29	224.0995	37.74
75.1011	12.87	225.0980	13.87
80.9643	1.36	236.1185	3.57
86.0547	2.93	237.0876	1.86
93.0444	14.22	244.0968	9.08
94.0698	3.29	255.1149	22.80
98.0298	1.57	256.0946	1.86
99.9438	70.34	275.1107	14.30
100.9960	2.14	276.0914	1.43
105.0829	6.58	305.1490	5.93
106.0839	1.86	324.1353	1.07
112.0458	1.07		
113.0737	4.22		
117.0727	12.37		
119.0185	0.86		

AB509X 33 A.BAYLIFF E.I./I-BU C.I. 2 28-AUG-86
CAL:CRLP4 STR: 1:45



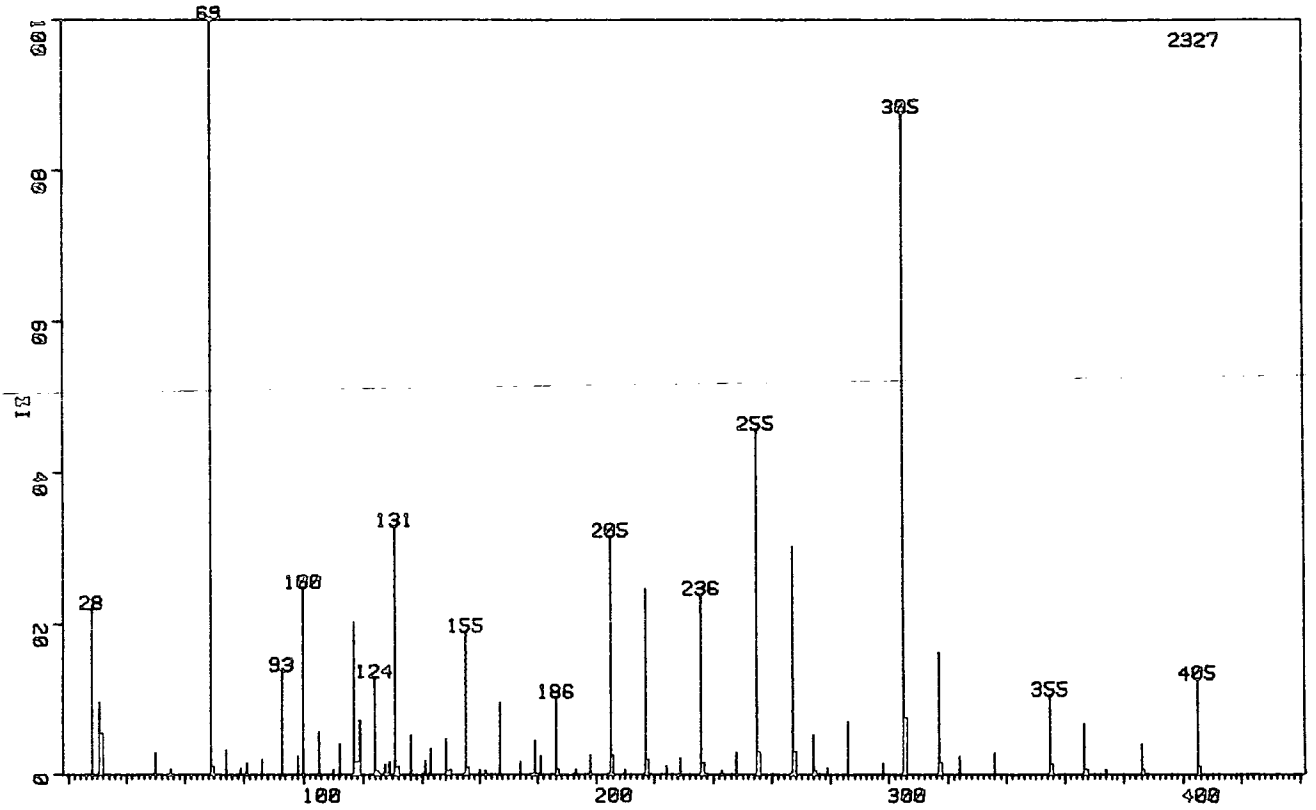
MASS	%HT. BASE
67.1167	1.45
69.0163	2.64
69.9563	0.63
71.0305	2.07
79.0041	0.51
81.0207	0.85
83.1081	0.71
85.1174	1.02
116.9750	0.37
123.9916	1.17
130.9350	0.54
155.0121	5.12
156.0033	0.31
174.0161	0.94
186.0302	0.91
205.0317	2.73
217.0506	0.31
224.0428	7.70
225.0658	0.71
236.0595	0.51
255.0731	3.04
305.1341	3.38
306.1361	0.34
324.1119	0.65

AB509X 38 A.BAYLIFF E.I./I-BU C.I. 3 28-AUG-86
CAL:CALP4 STA: 2:1



MASS	%HT. BASE	MASS	%HT. BASE
26.2866	1.10	111.0011	1.36
27.2217	13.54	112.0607	3.36
28.1030	29.76	113.0324	0.47
28.1250	1.63	116.0719	100.00
28.9673	0.53	117.0778	2.76
28.9966	2.29	118.0397	34.05
30.8642	11.67	124.1115	0.80
31.9726	6.35	131.0294	1.73
35.1099	1.66	131.9864	25.54
38.0542	1.70	134.0153	16.10
38.9746	8.08	135.0358	0.43
39.8169	1.16	136.0294	3.16
39.8755	1.30	143.0802	0.67
40.9595	18.62	147.0475	17.63
42.0581	11.67	148.0461	0.76
43.0688	0.67	149.0153	4.79
43.1274	43.63	155.1164	0.57
44.0967	3.82	163.0146	9.31
44.1675	1.36	165.0263	7.48
47.0557	3.16	167.0551	1.13
48.9404	1.00	186.1053	0.93
49.8804	2.83	217.1093	3.79
55.1147	1.90	267.1502	0.90
55.1733	0.53	286.1434	0.47
57.1557	1.36		
58.1250	0.67		
62.0361	1.50		
66.0815	5.15		
68.0249	1.90		
69.0015	13.44		
74.1064	4.22	89.9221	0.50
78.0056	1.26	93.0617	19.59
79.9075	0.40	94.0896	0.57
80.9817	0.90	97.0388	1.76
81.9680	2.56	99.9636	6.25
84.0115	1.46	100.9523	0.67
85.0539	5.29	103.0153	0.53
87.0339	2.00	109.0016	3.86

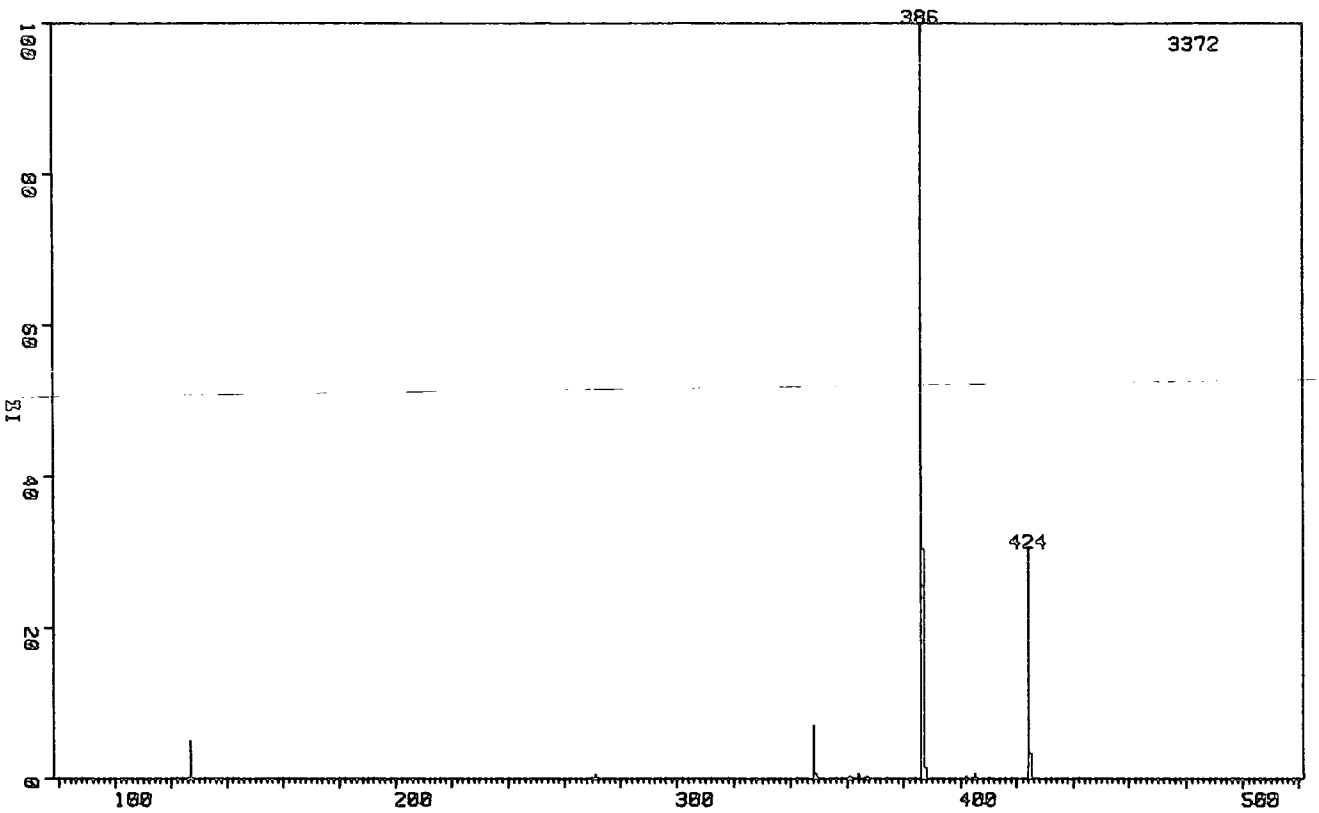
AB214X 47 A.BAYLIFF E.I. CAP.CAL 24C 4 02-APR-85
CRL:CALP21 STR: 3:1



MASS	%HT. BASE
28.09	22.00
30.85	9.58
31.96	5.46
49.85	0.97
55.07	0.82
68.94	100.00
69.88	1.12
74.05	3.22
78.96	0.90
80.93	1.59
86.02	2.02
92.99	13.04
97.97	2.54
99.88	24.84
105.02	5.76
109.91	0.73
111.96	4.13
116.99	20.24
117.97	1.72
118.93	7.26
123.97	12.94
124.99	0.47
127.47	1.38
128.92	1.76
130.90	32.96
131.96	1.07
135.98	5.09
140.93	1.09
142.96	3.52
147.93	4.86
148.92	0.47
149.87	0.64
154.98	19.04
155.98	0.98
159.90	0.64
161.93	0.56
166.95	9.63
173.94	1.76
178.89	4.56
180.89	2.45

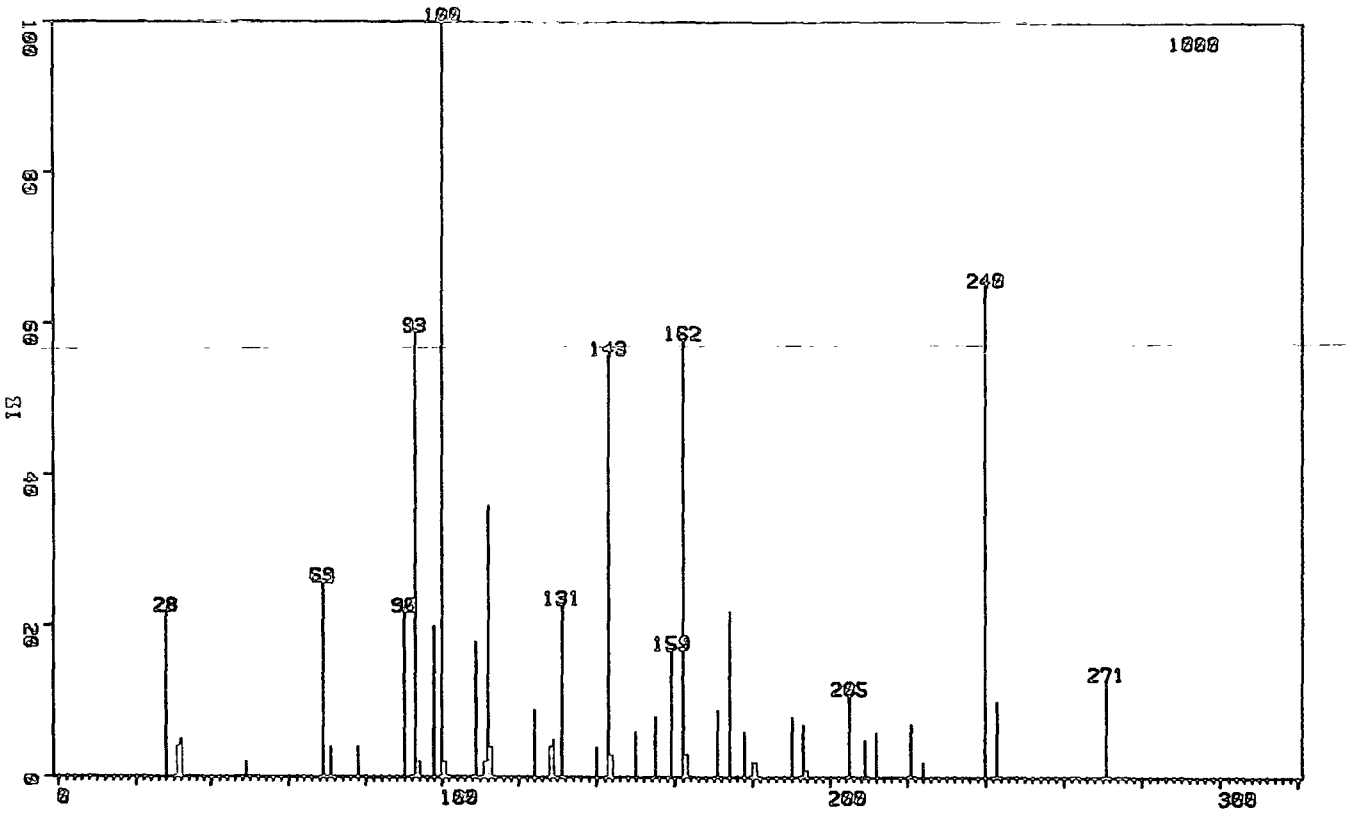
MASS	%HT. BASE
185.97	10.27
186.98	0.77
192.95	0.73
197.93	2.62
204.94	31.63
205.93	2.54
209.87	0.69
216.94	24.71
217.93	1.93
223.93	1.20
228.90	2.28
235.92	23.98
236.91	1.68
242.90	0.60
247.91	3.05
254.92	45.72
255.93	3.05
266.90	30.25
267.90	3.09
273.91	5.29
274.95	0.47
278.90	0.95
285.93	7.13
297.89	1.59
304.90	87.62
305.90	7.52
316.90	16.20
317.93	1.59
323.89	2.49
335.90	2.88
354.86	10.61
355.91	1.38
366.84	6.75
367.90	0.69
373.91	0.69
385.89	4.04
386.92	0.64
404.87	12.76
405.91	1.12

A214CN 60 A.BAYLIFF 214C NEG.(I-BU) 5 28-AUG-86
CAL:CALNEG STA: 3:10



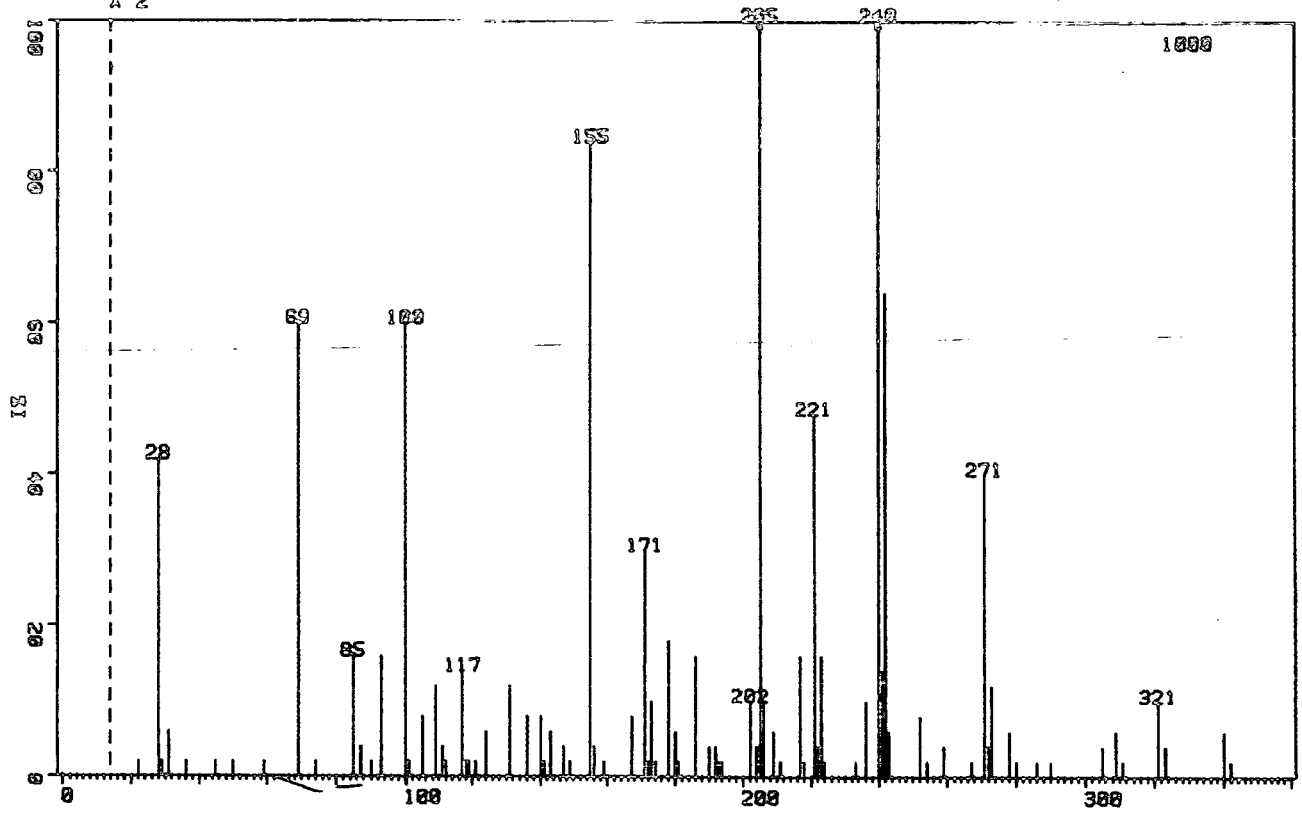
MASS	%HT. BASE
127.0214	5.04
271.1156	0.50
348.2035	7.15
349.1852	0.65
361.1092	0.36
364.1488	0.56
367.0802	0.30
386.0816	100.00
387.0850	30.37
388.1251	1.45
402.1172	0.33
405.1373	0.65
424.0897	30.60
425.1199	3.23

RB6B 0 A.BAYLIFF EI 6 21-AUG-86
CRL:LIB STR: 0:0



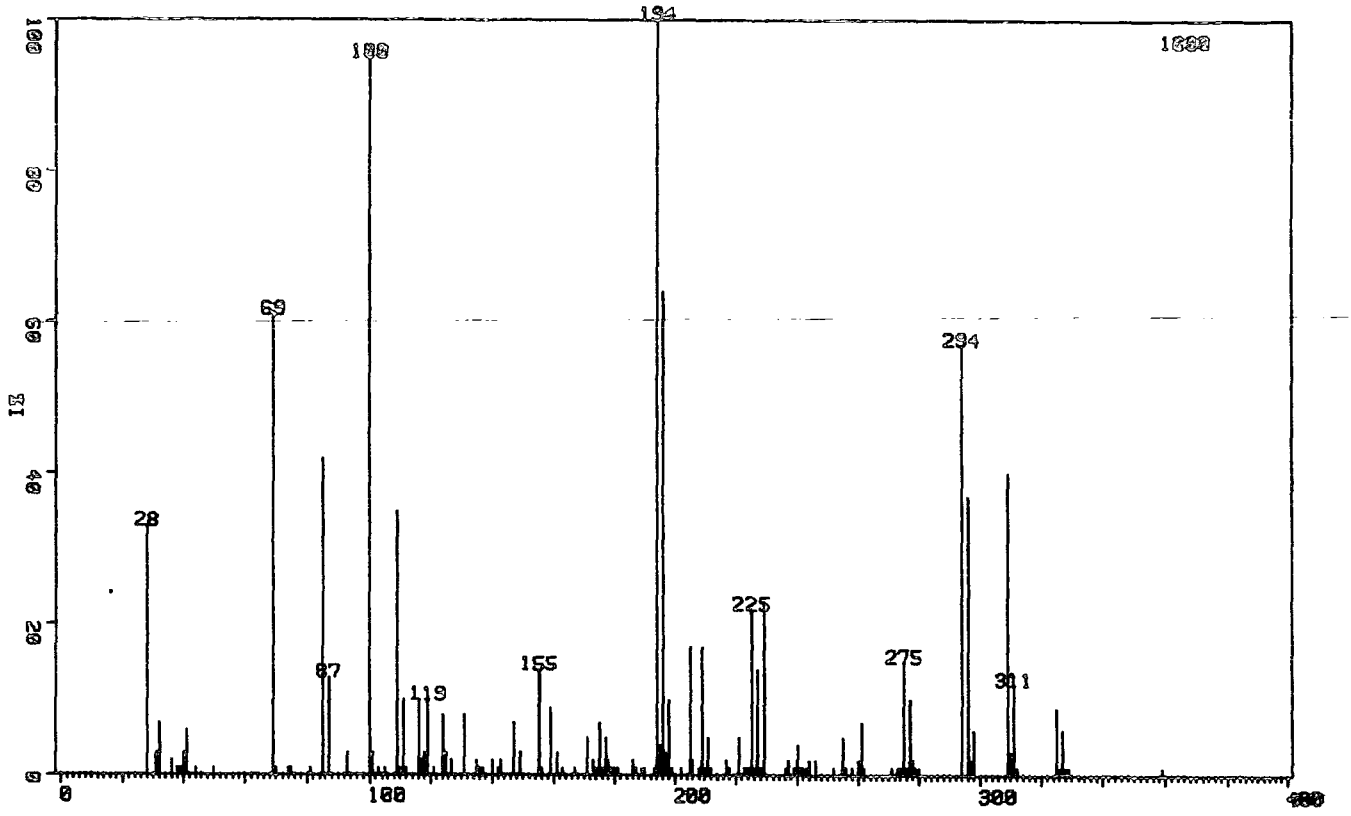
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.07	22.14	36	189.93	8.24
2	30.83	3.51	37	192.96	7.48
3	31.95	4.89	38	205.00	11.60
4	49.86	2.14	39	208.94	4.73
5	58.94	25.95	40	211.94	6.56
6	70.91	3.66	41	220.99	6.56
7	77.95	3.51	42	223.96	2.90
8	89.84	21.98	43	239.84	65.19
9	93.99	59.08	44	240.90	4.58
10	94.01	2.44	45	242.94	10.23
11	97.01	2.14	46	270.94	13.13
12	97.97	20.00			
13	99.91	100.00			
14	100.94	2.29			
15	108.94	18.32			
16	110.93	1.53			
17	111.94	36.18			
18	113.00	3.66			
19	124.00	8.85			
20	127.97	4.43			
21	128.90	4.73			
22	130.95	22.75			
23	139.93	3.82			
24	142.97	56.03			
25	143.98	2.90			
26	149.89	5.65			
27	154.99	8.24			
28	158.94	16.95			
29	161.96	57.86			
30	162.97	2.90			
31	170.92	9.16			
32	173.97	22.44			
33	177.93	5.65			
34	179.88	2.14			
35	180.99	2.14			

ABCPD4 0 A.BAYLIFF EI 7 21-AUG-86
CAL:LIB STA: 0:0
X 2



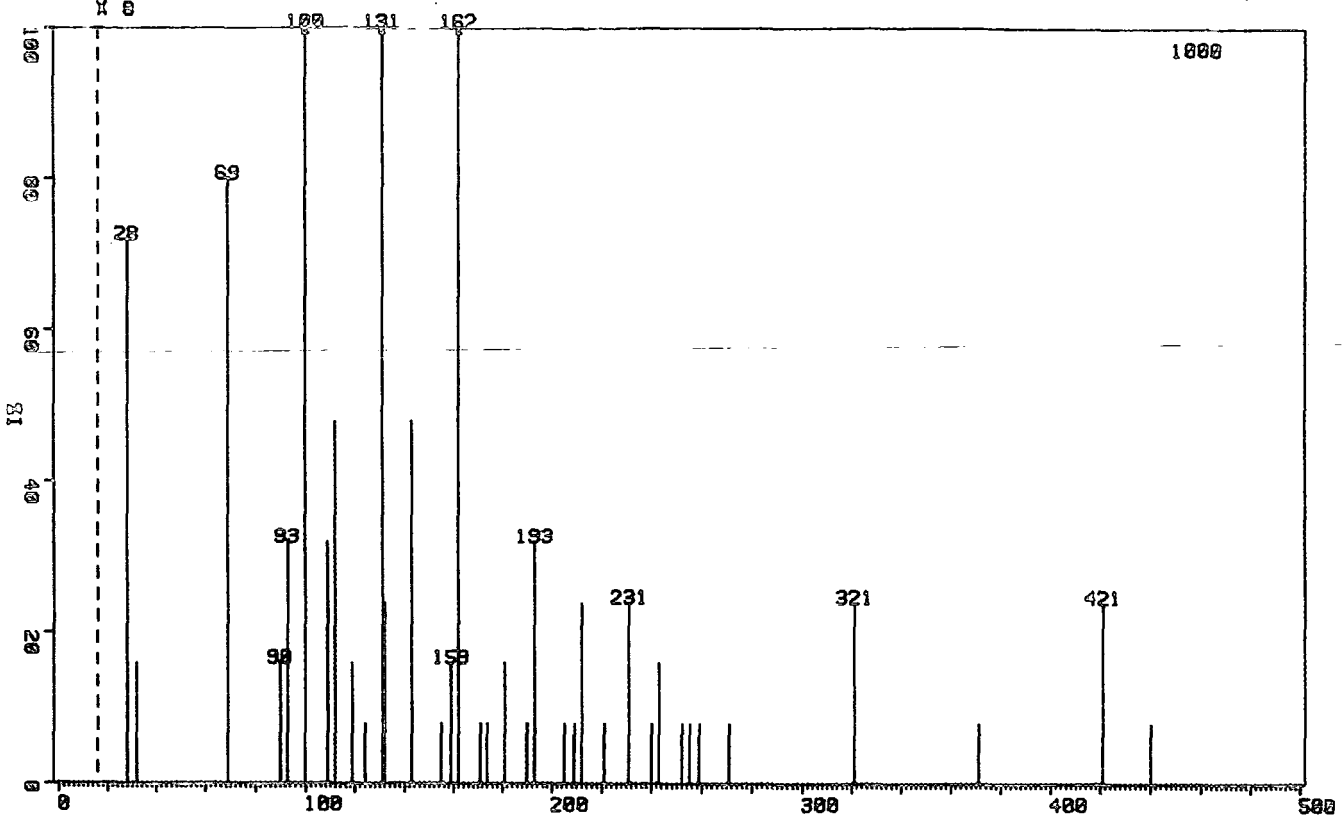
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.06	21.22	36	155.97	2.25	71	240.80	6.75
2	28.96	0.71	37	158.91	1.00	72	241.92	32.08
3	30.84	3.11	38	166.90	4.25	73	242.96	2.97
4	31.94	4.18	39	170.80	15.01	74	251.93	4.32
5	36.09	0.64	40	171.91	0.82	75	252.96	0.39
6	45.13	0.54	41	172.89	4.97	76	253.95	1.39
7	49.84	0.68	42	173.95	0.86	77	254.98	5.97
8	58.96	0.64	43	175.08	0.43	78	256.01	0.46
9	68.89	29.76	44	177.92	9.25	79	258.88	1.54
10	74.02	0.57	45	178.92	0.46	80	266.97	1.07
11	80.82	0.43	46	179.87	2.89	81	270.85	19.97
12	84.90	7.50	47	180.93	0.68	82	271.91	1.64
13	86.89	2.29	48	185.95	7.82	83	272.88	6.47
14	89.81	1.00	49	186.98	0.50	84	273.98	0.46
15	92.97	8.07	50	189.88	2.11	85	277.91	2.82
16	99.88	29.97	51	191.91	0.82	86	279.90	0.89
17	100.94	0.71	52	192.96	0.82	87	285.95	1.29
18	105.00	4.25	53	193.88	0.54	88	289.87	0.82
19	108.88	5.75	54	201.85	4.68	89	304.86	2.22
20	110.88	1.86	55	202.93	0.46	90	308.85	3.04
21	111.97	0.68	56	203.93	1.82	91	310.83	0.96
22	117.00	7.40	57	204.93	78.39	92	320.87	5.11
23	117.97	0.50	58	205.94	5.22	93	321.85	0.50
24	118.95	1.18	59	208.88	5.04	94	322.89	1.61
25	120.89	0.68	60	210.90	0.96	95	339.80	2.68
26	124.01	3.07	61	216.96	7.93	96	341.79	0.89
27	130.92	5.68	62	217.98	0.64			
28	135.98	3.72	63	220.90	24.44			
29	139.84	3.93	64	221.92	1.57			
30	141.92	1.39	65	222.91	7.90			
31	142.97	2.89	66	223.93	0.32			
32	146.92	1.96	67	232.86	0.57			
33	147.94	0.46	68	235.91	4.72			
34	148.87	0.64	69	236.94	0.54			
35	154.95	42.05	70	239.84	100.00			

ABCPD3 0 A.BAYLIFF EI 8 21-AUG-86
CAL:LIB STA: 0:0



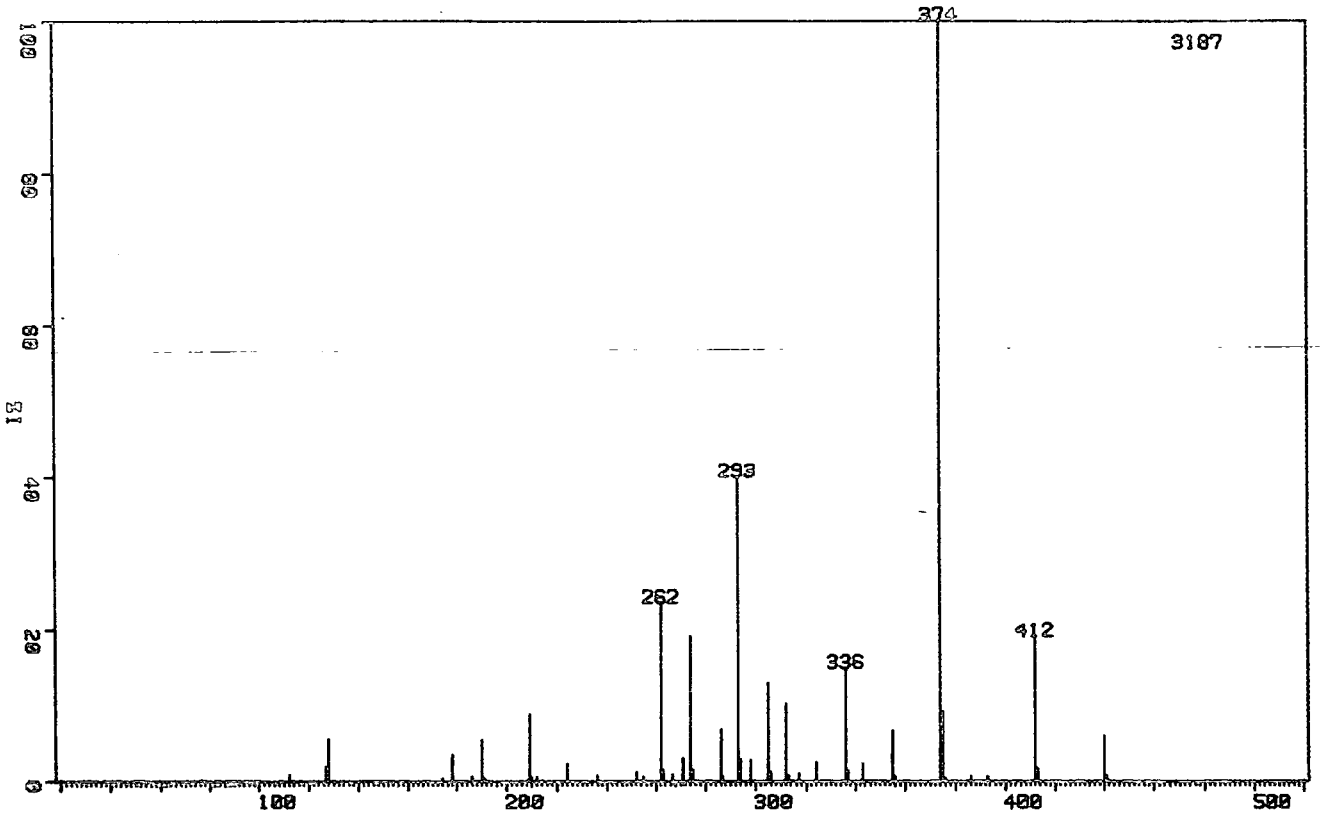
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.06	32.73	36	130.91	8.32	71	196.94	3.36	106	259.93	1.55
2	28.94	0.38	37	134.95	2.31	72	197.89	10.08	107	260.88	7.39
3	28.97	0.46	38	135.99	0.97	73	198.93	0.76	108	261.94	0.59
4	30.84	3.24	39	136.94	0.84	74	201.93	1.13	109	266.99	0.42
5	31.95	5.72	40	139.84	2.06	75	204.97	16.60	110	270.92	1.34
6	36.09	2.06	41	141.93	0.63	76	205.98	1.85	111	272.96	0.59
7	38.01	0.88	42	142.95	1.81	77	207.88	0.59	112	273.98	0.55
8	38.95	1.13	43	146.90	7.48	78	208.91	17.10	113	274.90	15.04
9	39.84	2.61	44	148.86	2.52	79	209.92	1.22	114	275.92	1.26
10	40.92	6.34	45	154.97	13.91	80	210.90	5.25	115	276.89	9.83
11	44.07	0.88	46	155.96	0.88	81	211.92	0.67	116	277.94	2.10
12	49.84	0.92	47	158.89	8.70	82	216.98	0.48	117	278.86	1.76
13	68.91	61.01	48	160.89	2.98	83	217.92	0.55	118	280.01	0.59
14	69.85	0.84	49	162.92	0.59	84	220.88	4.54	119	293.81	57.18
15	74.01	0.80	50	164.92	0.46	85	222.96	1.47	120	295.79	36.85
16	80.84	0.88	51	166.95	1.01	86	223.98	0.97	121	296.93	2.44
17	84.96	41.47	52	168.92	0.50	87	224.93	21.72	122	297.92	5.92
18	86.94	13.49	53	170.87	4.75	88	225.91	1.09	123	298.96	0.46
19	92.97	3.49	54	172.94	1.55	89	226.90	13.66	124	305.00	0.50
20	99.85	95.00	55	173.98	1.18	90	227.94	1.05	125	308.89	39.87
21	100.90	2.55	56	174.93	7.02	91	228.89	2.35	126	309.89	3.32
22	102.91	0.92	57	175.96	0.55	92	235.98	1.18	127	310.95	12.06
23	104.98	0.88	58	176.91	4.83	93	236.93	2.39	128	311.95	0.97
24	108.87	34.58	59	177.94	2.44	94	238.92	1.39	129	324.86	9.12
25	109.87	1.05	60	178.89	0.80	95	239.91	4.20	130	325.93	0.71
26	110.92	10.34	61	179.92	0.88	96	240.91	0.63	131	326.91	5.67
27	111.96	1.43	62	180.96	0.97	97	241.90	1.39	132	327.94	0.50
28	115.98	9.62	63	185.97	2.48	98	242.94	0.71	133	328.92	0.97
29	116.99	1.64	64	186.94	0.84	99	243.89	2.14	134	358.84	1.01
30	117.94	3.24	65	188.90	0.42	100	245.94	1.60			
31	118.94	10.34	66	189.90	0.80	101	251.89	0.67			
32	120.90	0.59	67	192.95	0.55	102	254.97	5.29			
33	124.02	3.19	68	193.87	100.00	103	255.91	1.60			
34	124.96	2.52	69	194.91	4.37	104	257.89	0.76			
35	126.94	1.76	70	195.90	64.45	105	258.90	22.56			

RB6R 0 A.BAYLIFF EI 9 21-AUG-86
CAL:LIB STA: 0:0



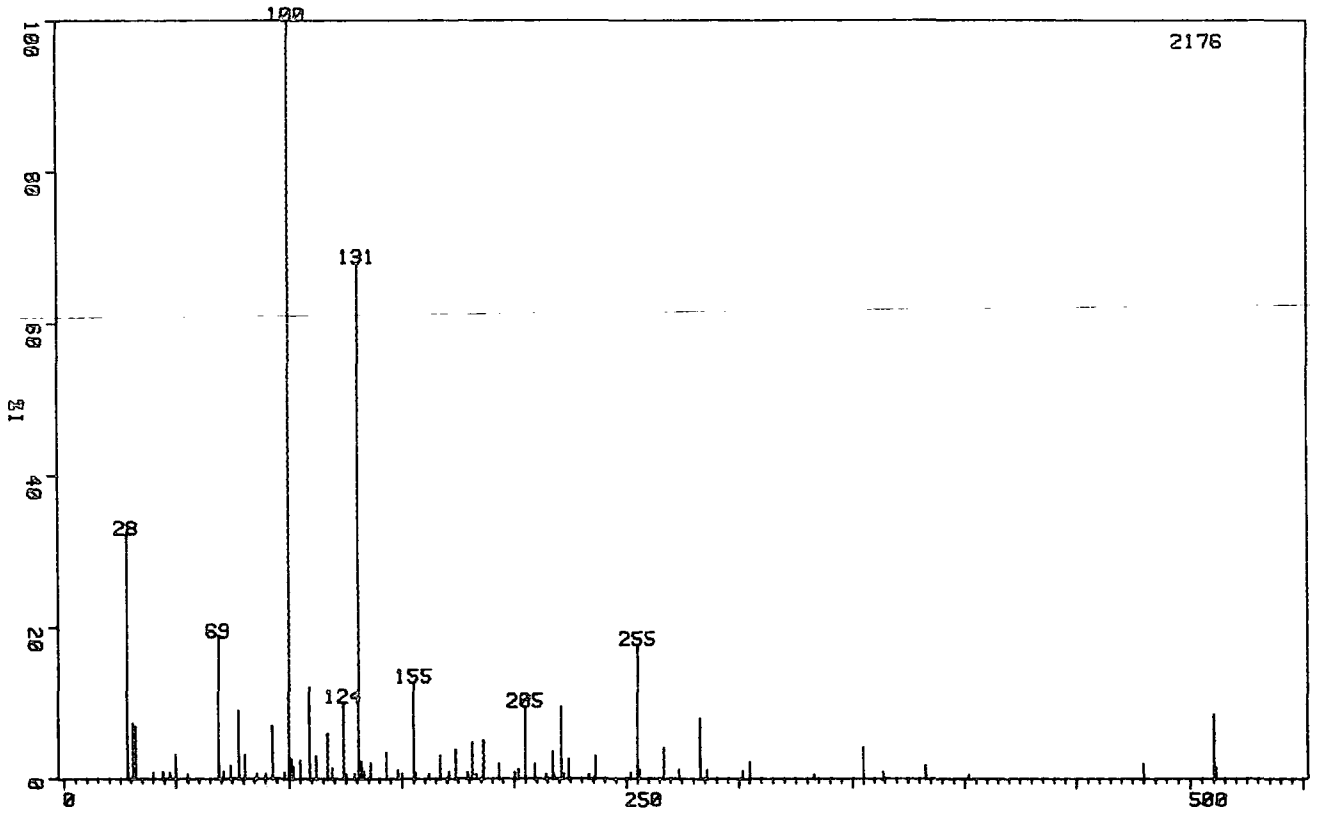
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	28.13	9.46	36	259.05	0.82
2	32.02	1.96	37	271.06	0.57
3	68.98	10.39	38	293.03	0.43
4	89.93	1.96	39	302.04	0.43
5	93.04	4.28	40	321.03	2.50
6	97.05	0.54	41	371.06	1.32
7	99.93	22.27	42	421.05	2.96
8	101.00	0.61	43	422.10	0.36
9	108.99	4.39	44	440.07	0.68
10	112.03	5.53			
11	118.99	1.89			
12	124.08	0.71			
13	131.00	100.00			
14	132.04	3.32			
15	143.05	6.53			
16	149.98	0.50			
17	155.08	0.82			
18	159.00	2.32			
19	162.03	2.82			
20	169.02	0.46			
21	171.03	0.96			
22	174.07	0.57			
23	181.00	2.36			
24	189.97	0.68			
25	193.03	4.25			
26	205.09	1.21			
27	209.03	0.79			
28	212.03	3.00			
29	221.03	1.36			
30	224.07	0.39			
31	231.03	2.50			
32	240.00	0.54			
33	243.02	1.78			
34	252.02	1.03			
35	255.09	0.82			

AB19X 4 A.BRYLIFF NEG I-BU 10 22-JAN-85
CAL:CALN22 STA: 0:43



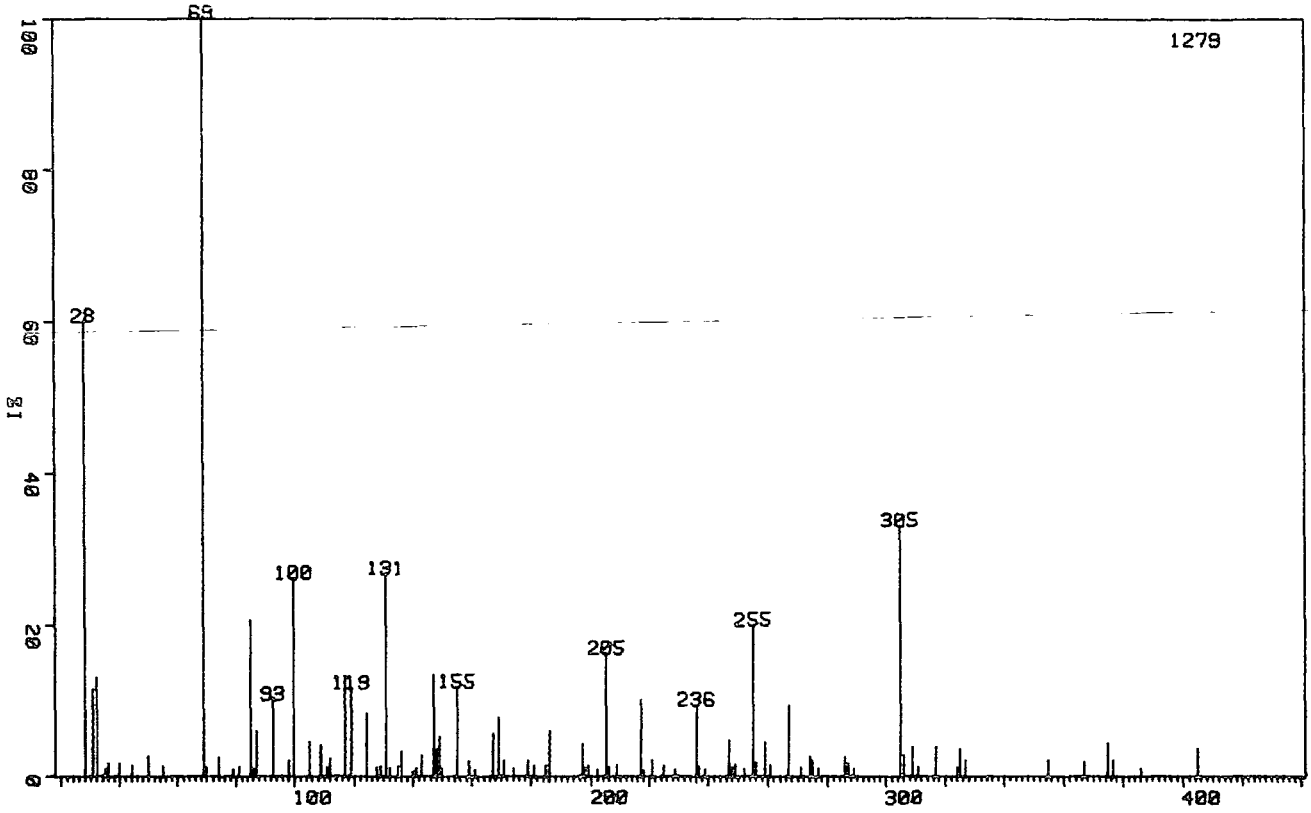
MASS	%HT. BASE
112.07	0.91
127.03	1.98
128.10	5.62
174.13	0.41
178.12	3.55
186.11	0.66
190.02	5.49
191.05	0.35
209.07	8.88
210.07	0.53
212.08	0.60
224.12	2.35
236.09	0.78
252.07	1.29
255.09	0.60
262.08	23.56
263.13	1.60
267.05	1.04
271.04	3.14
274.06	19.20
275.07	1.54
286.07	6.90
287.06	0.63
293.05	40.13
294.07	2.95
298.04	2.79
305.07	12.96
306.07	1.22
312.06	10.32
313.08	0.72
317.07	1.10
324.10	2.64
336.10	15.00
337.09	1.44
343.06	2.48
355.06	6.71
356.05	0.69
374.06	100.00
375.11	9.16
376.09	0.41
386.04	0.69
393.05	0.66
412.02	19.17
413.06	1.85
440.04	6.12
441.06	0.72

AB18X 81 A.BAYLIFF EI CAP.COL 11 27-FEB-85
CAL:CALP17 STA: 5:10

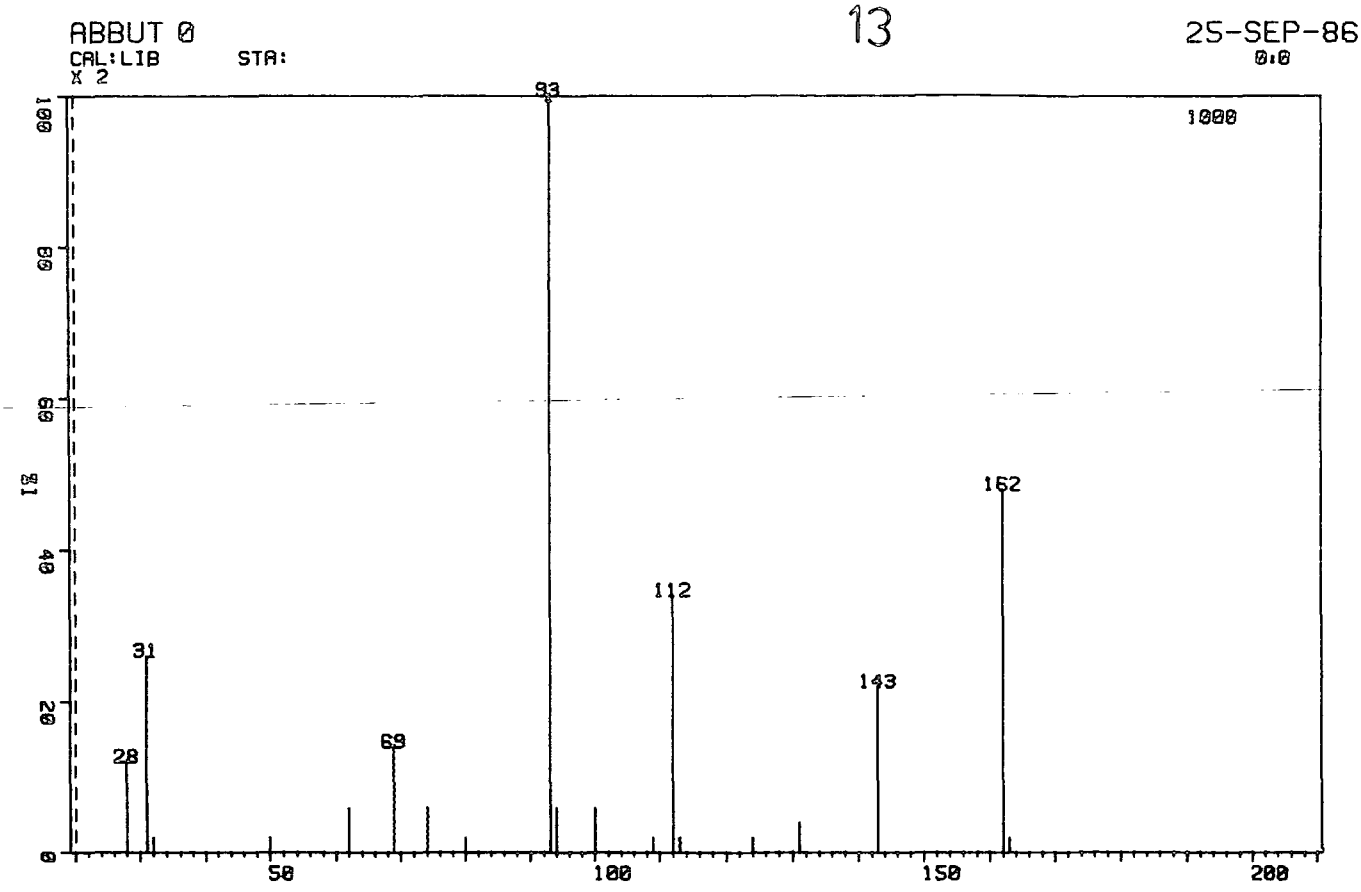


MASS	%HT. BASE	MASS	%HT. BASE
28.11	32.31	180.90	4.92
30.87	7.31	182.94	0.55
31.98	6.94	185.94	5.10
39.80	0.92	192.90	2.07
44.08	1.06	199.85	0.97
47.06	0.87	201.89	1.24
49.85	3.26	204.97	9.56
55.07	0.64	208.93	2.07
68.93	18.75	213.93	0.64
70.92	0.97	216.94	3.63
74.02	1.84	217.91	0.55
77.96	9.05	220.89	9.60
80.91	3.17	221.91	0.64
86.00	0.74	223.95	2.67
89.85	0.78	232.92	0.51
92.99	7.12	235.91	3.12
97.97	0.87	251.84	0.92
99.89	100.00	254.91	17.74
100.95	2.71	255.92	1.24
101.98	1.70	266.89	4.09
105.03	2.44	273.91	1.24
108.94	12.09	282.87	8.04
111.96	3.12	285.92	1.33
116.98	6.07	301.87	1.06
118.94	1.52	304.92	2.25
123.97	10.16	332.80	0.60
124.99	0.51	354.83	4.09
128.91	0.78	363.84	0.97
130.89	68.01	382.84	1.79
131.95	2.34	401.87	0.60
132.97	0.97	479.62	2.02
135.98	2.21	510.48	8.46
142.94	3.54	511.52	1.52
147.94	1.19		
149.88	0.78		
154.98	12.82		
155.99	0.83		
161.93	0.78		
166.94	3.08		
170.88	0.97		
173.96	3.91		
178.92	0.87		

AB18X 106 A.BAYLIFF EI CAP.COL 12 27-FEB-85
CAL:CRLP17 STA: 6:45

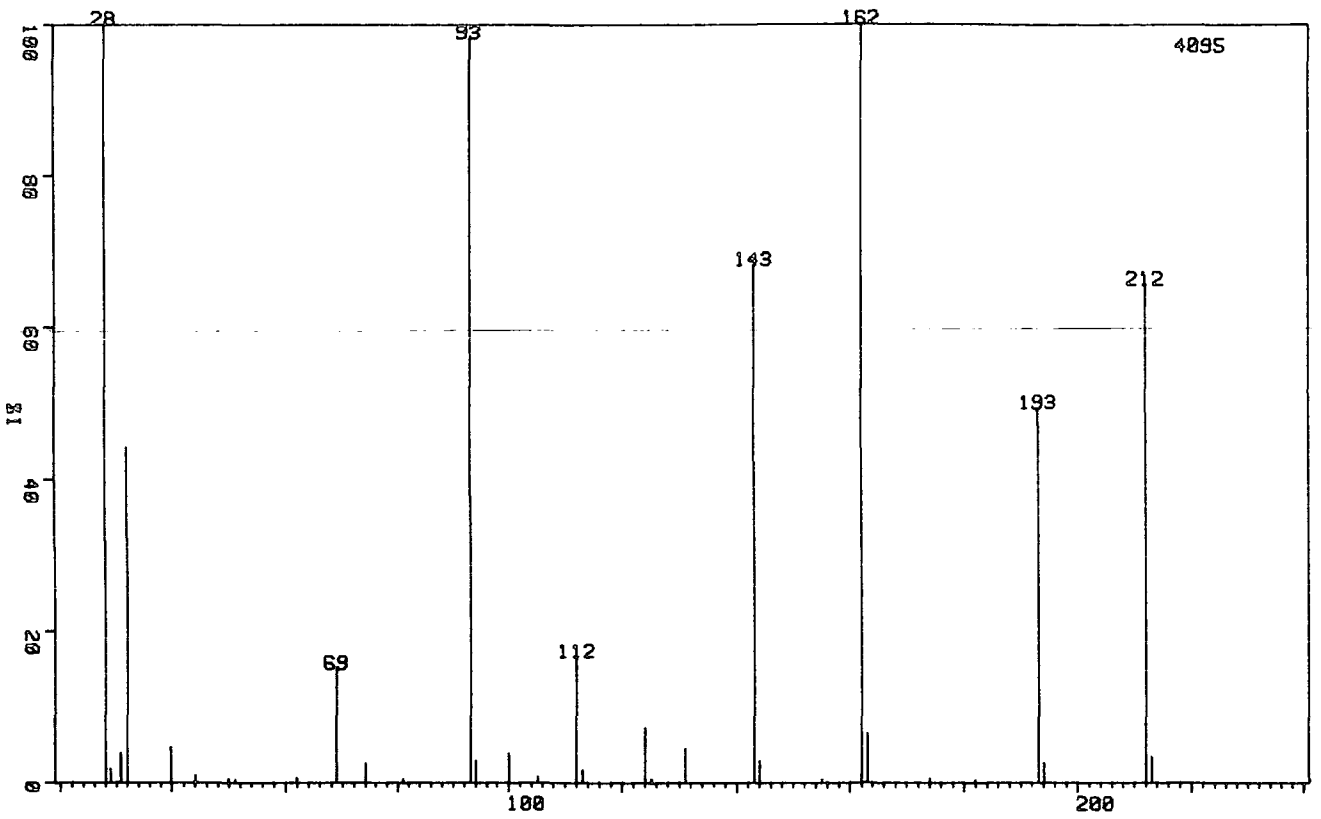


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
28.11	60.05	160.89	0.94	308.88	3.99
30.86	11.57	166.99	5.79	310.89	1.41
31.97	13.14	168.95	7.74	316.98	3.99
35.10	1.02	170.91	2.11	323.96	1.17
36.10	1.80	173.99	1.09	324.90	3.75
39.80	1.80	178.95	2.19	326.89	2.27
44.07	1.56	180.91	1.49	354.91	2.27
49.85	2.74	184.93	1.49	366.90	1.95
55.07	1.49	185.95	6.10	374.83	4.46
68.93	100.00	196.89	4.30	376.89	2.27
69.87	1.41	197.93	1.17	385.97	1.09
74.05	2.58	198.89	1.49	404.92	3.83
78.96	1.02	201.92	1.02		
80.93	1.41	204.95	16.26		
84.99	20.72	205.94	1.33		
86.02	1.02	208.89	1.64		
86.97	6.02	216.96	10.24		
92.99	10.16	217.94	0.86		
97.96	2.11	220.89	2.27		
99.88	26.19	224.93	1.56		
105.01	4.61	228.95	1.02		
108.91	4.14	235.96	9.46		
110.90	1.41	236.91	1.33		
111.98	2.42	238.89	0.94		
117.01	13.37	246.92	4.93		
118.95	11.65	247.94	1.33		
124.00	8.37	248.90	1.72		
127.47	1.33	251.90	1.02		
128.92	1.49	254.95	20.02		
130.91	26.82	255.96	1.88		
131.94	1.17	258.92	4.61		
134.94	1.49	260.91	1.56		
135.96	3.36	266.95	9.46		
139.85	0.78	270.87	1.25		
140.94	1.09	273.95	2.74		
142.97	2.81	274.90	2.19		
146.95	13.45	276.88	1.17		
147.96	3.60	285.96	2.66		
148.90	5.24	286.92	1.80		
149.91	1.09	288.90	1.09		
154.97	11.81	304.95	33.07		
158.88	2.03	305.95	2.89		



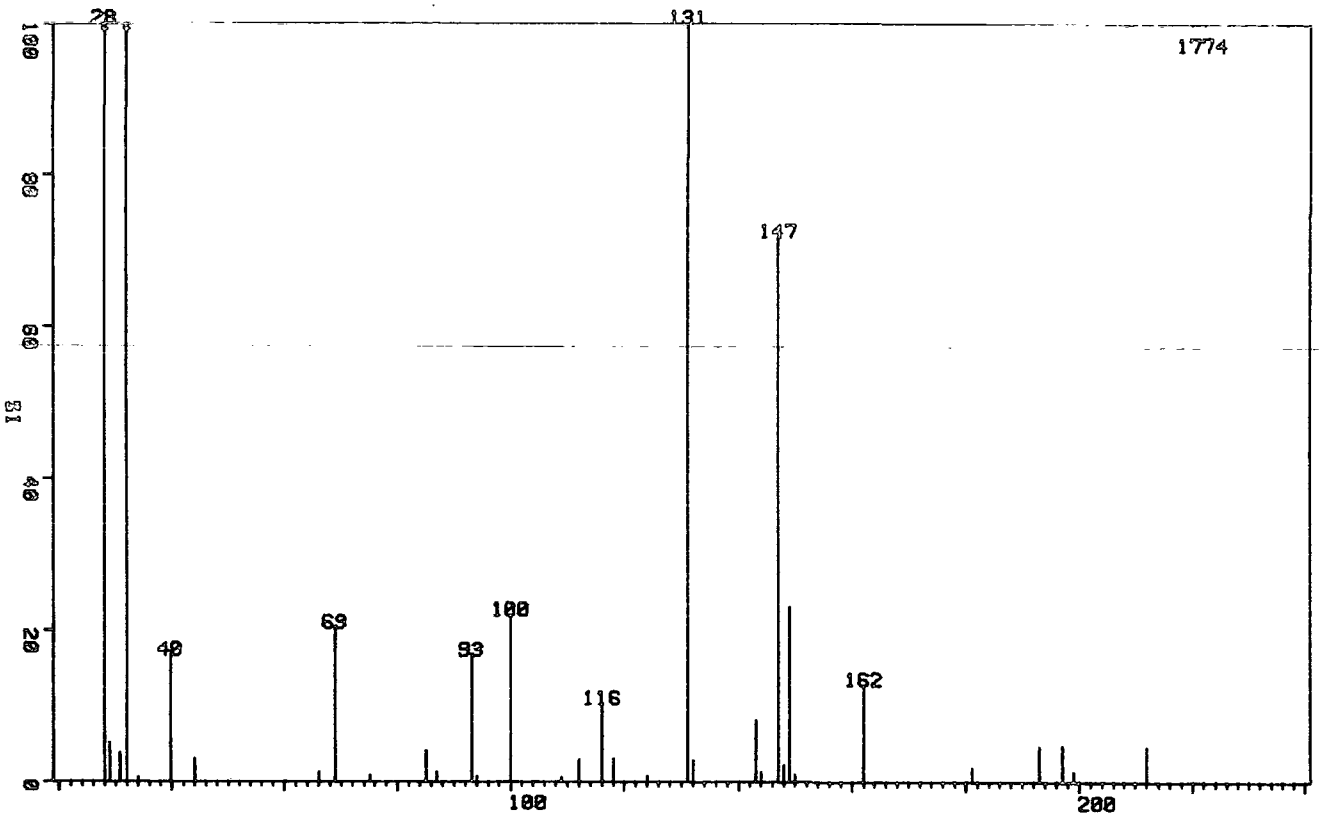
28.06	5.92
30.83	13.12
31.95	1.10
49.88	0.92*
62.04	2.50*
69.01	6.82
74.10	3.15*
80.96	0.54*
93.06	100.00
94.08	3.39
99.97	3.18
109.04	0.62
112.07	17.38
113.11	0.57
124.11	0.98
131.03	1.87
143.07	11.16
144.10	0.45
159.11	0.36*
162.09	23.87
163.12	1.04

ABEPX 8 A.BAYLIFF 14 08-AUG-84
CAL:CALM30 STA: 1:30

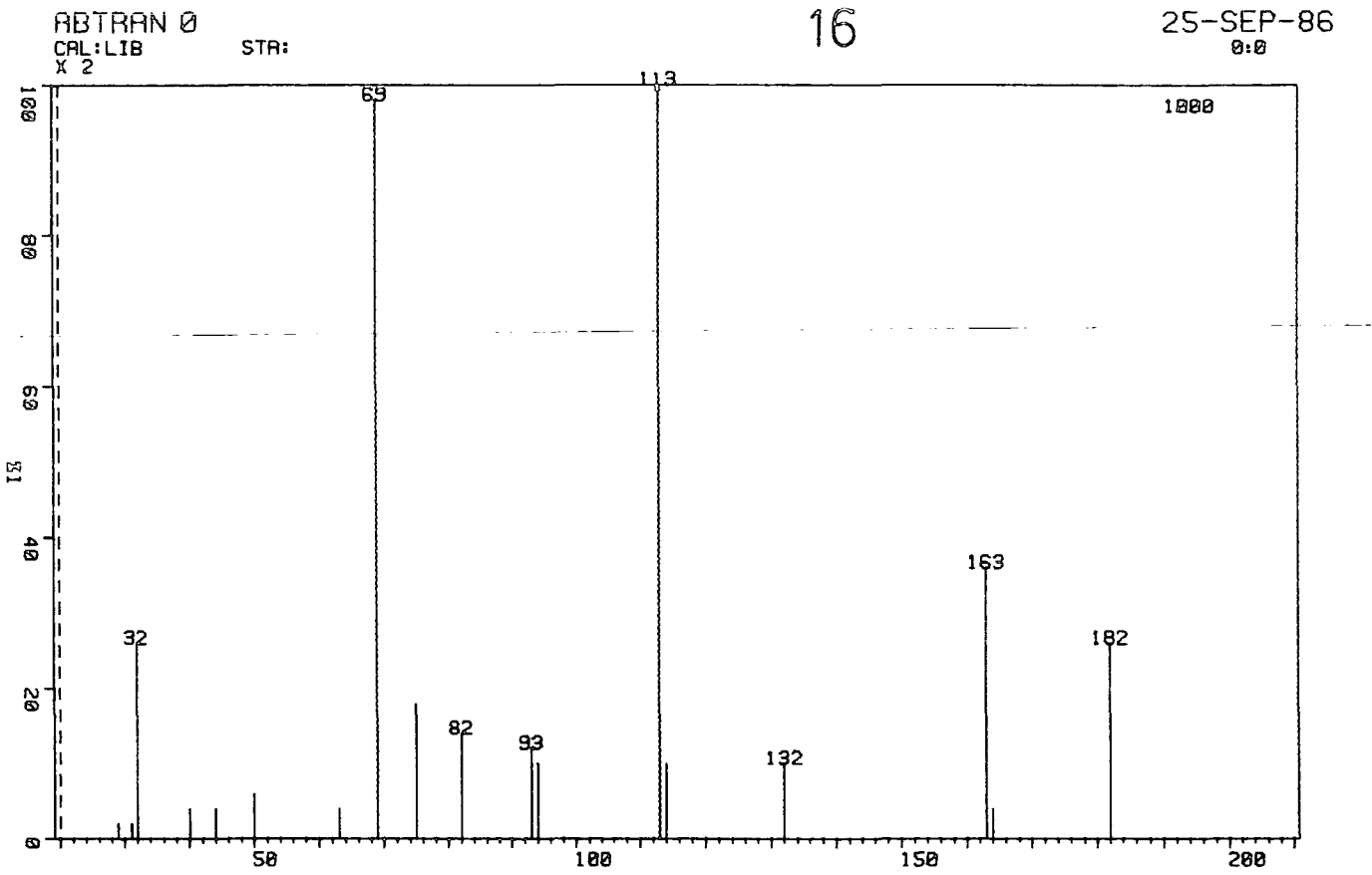


MASS	%HT. BASE
28.00	100.00
28.93	1.81
30.83	3.91
31.94	44.22
39.81	4.69
44.09	1.06
49.97	0.44
50.95	0.34
62.06	0.68
68.99	15.13
74.08	2.64
80.95	0.42
93.05	98.12
94.07	2.91
99.97	3.80
105.10	0.83
112.05	16.20
113.08	1.78
124.10	7.30
125.11	0.37
131.04	4.52
143.08	68.25
144.08	2.98
155.10	0.44
162.06	100.00
163.09	6.59
174.10	0.61
182.07	0.34
193.08	47.43
194.11	2.66
212.06	65.62
213.09	3.49

ABEPX 10 A.BAYLIFF 15 08-AUG-84
CAL:CALM30 STA: 1:51

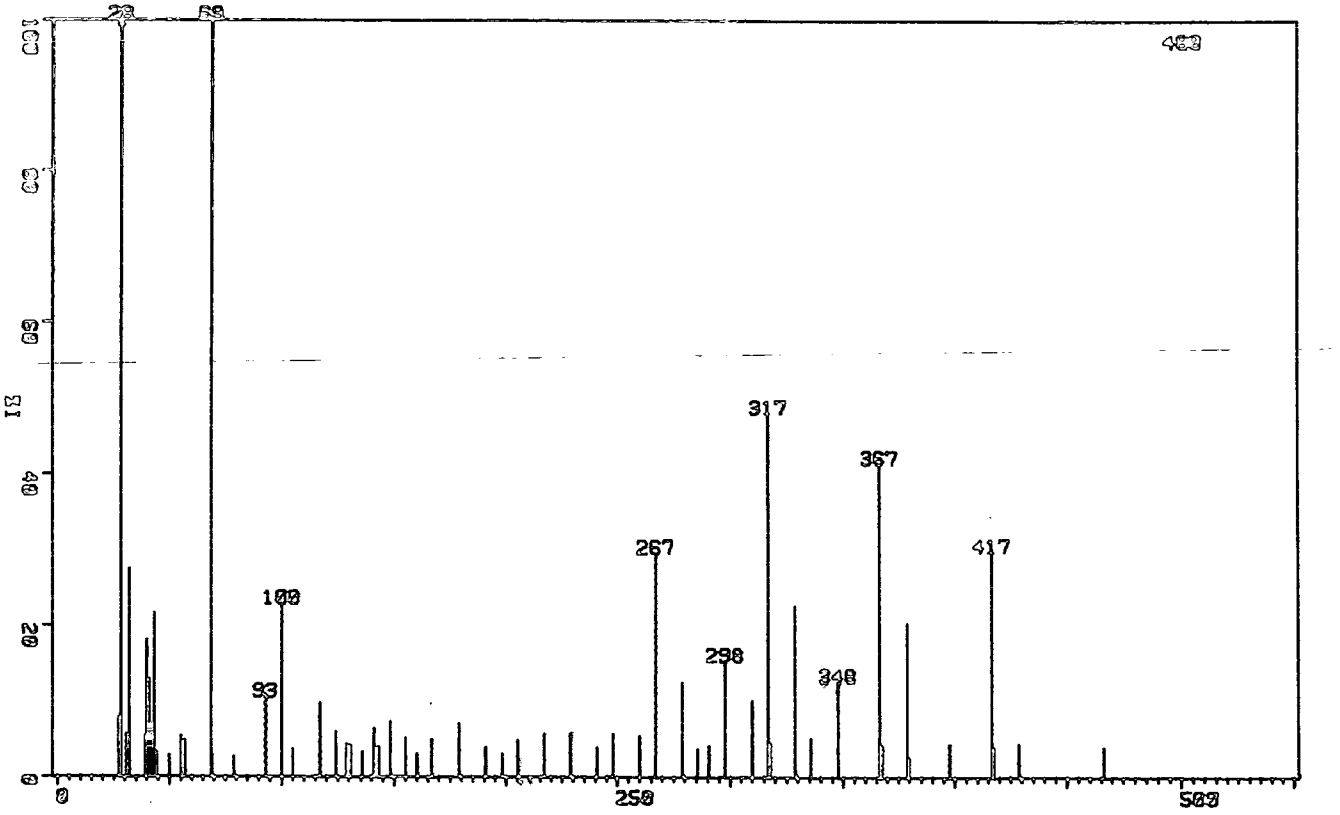


MASS	%HT. BASE
28.06	100.00
28.93	2.25
30.83	1.66
31.94	66.89
34.10	0.27
39.80	7.25
44.09	1.34
66.06	0.56
68.99	8.82
75.09	0.39
85.02	1.81
87.00	0.56
93.03	7.23
94.07	0.32
99.95	9.55
108.99	0.27
112.03	1.29
116.04	4.47
118.02	1.34
124.10	0.37
131.02	43.32
132.07	1.25
143.08	3.54
144.11	0.59
147.01	31.11
148.02	0.98
148.97	10.04
149.97	0.46
162.06	5.57
181.04	0.85
193.07	2.03
197.07	2.10
199.05	0.61
212.07	2.03



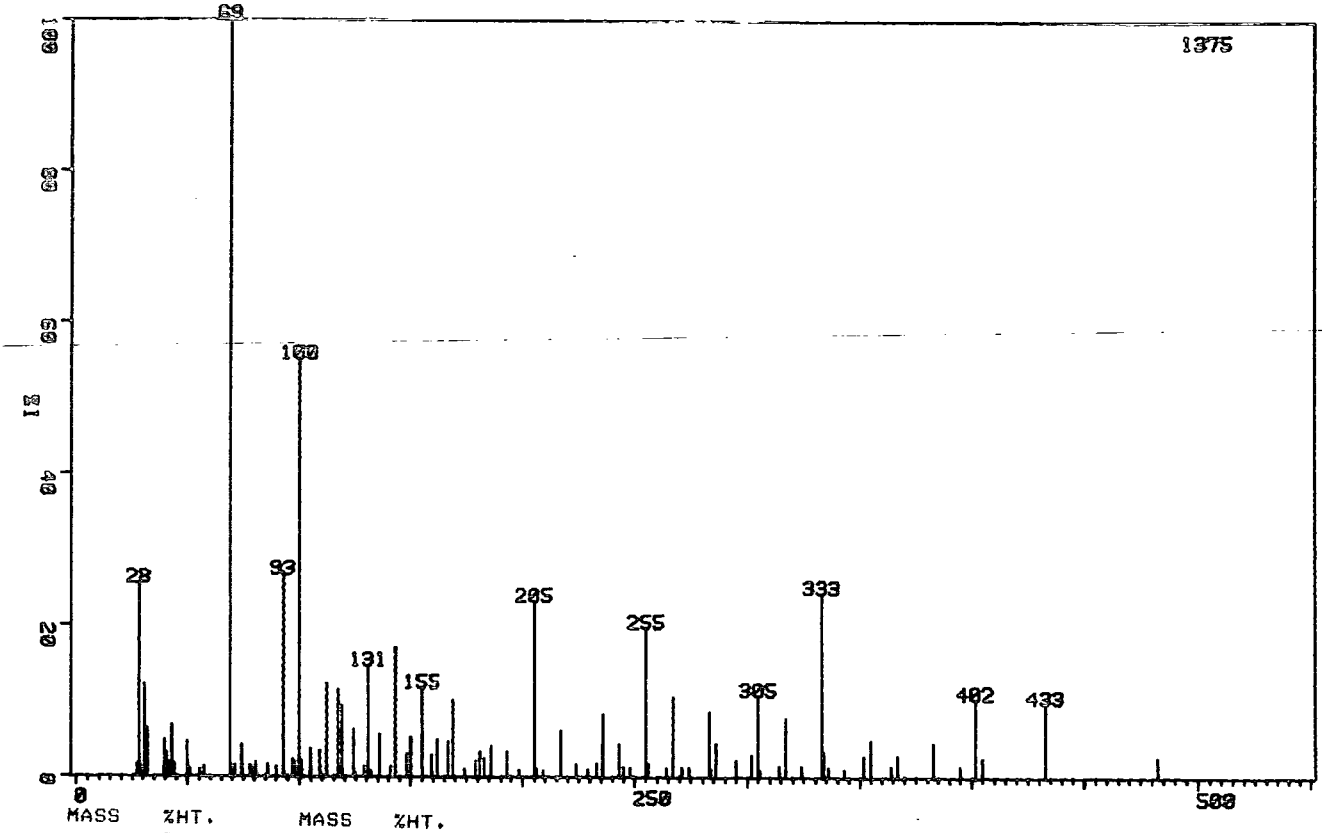
MASS	RINT. BASE
182.08	13.12
164.11	1.58
163.12	18.35
132.08	4.50
114.09	5.35
113.07	100.00
94.10	4.86
93.07	9.50
82.01	6.93
75.10	9.23
69.99	49.21
63.11	1.58
50.97	2.55
44.14	2.31
39.86	1.70
32.02	13.12
30.92	4.01
29.00	1.22

RB191X 4S A.BRAYLIFF CRP.COL EI 17 29-JAN-85
CRL:CRLP17 STR: 2:53



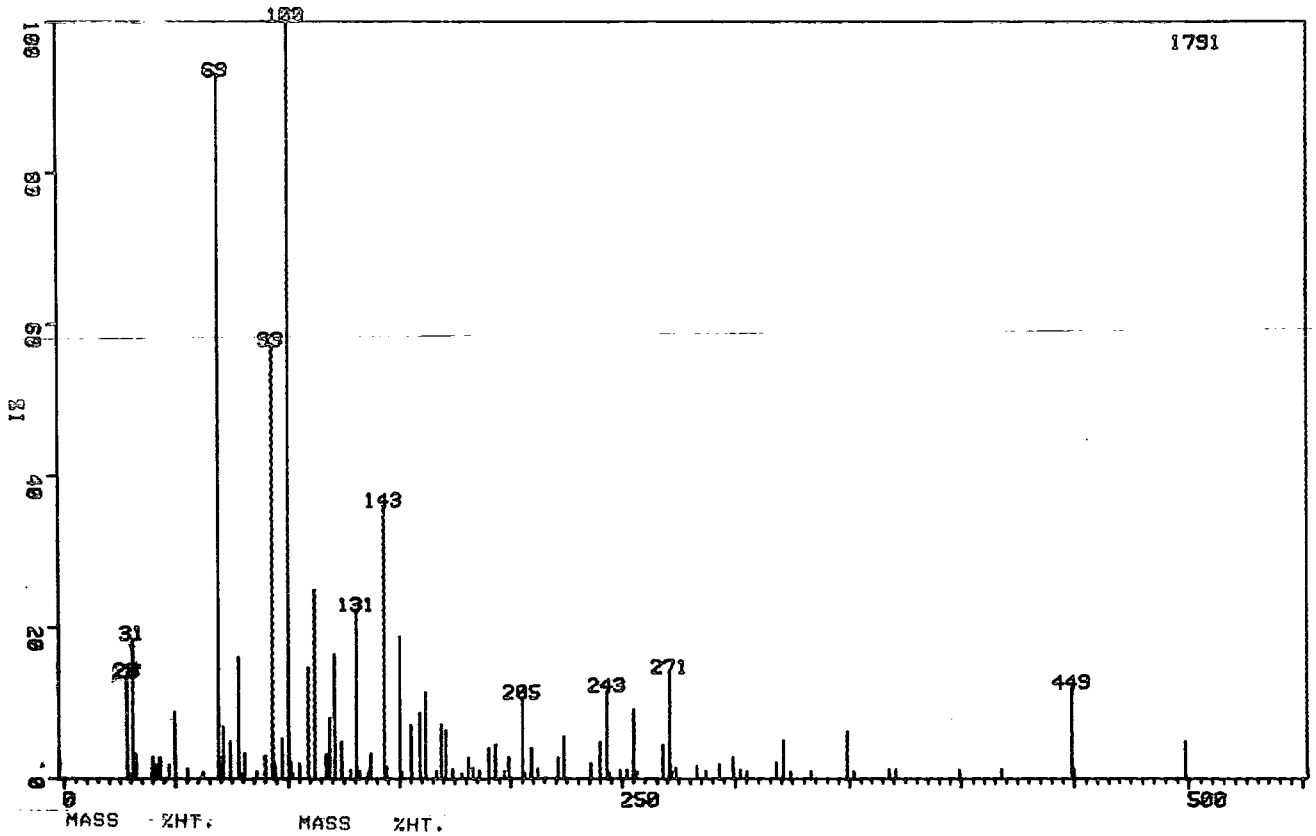
MASS	%HT. BASE	MASS	%HT. BASE
27.23	7.44	278.81	11.74
28.11	100.00	285.85	3.52
30.86	5.28	290.82	3.91
31.97	25.83	297.83	14.48
38.96	5.09	309.78	9.59
39.80	17.03	316.80	45.21
40.94	12.13	317.81	4.31
42.03	6.46	328.76	21.33
43.11	20.35	335.79	4.89
44.07	3.13	347.72	11.94
49.84	2.74	366.70	38.94
55.12	5.09	367.75	3.91
57.10	4.50	378.68	19.18
68.92	93.93	379.69	2.54
69.00	2.74	397.68	4.11
78.92	2.54	416.63	27.98
92.95	9.98	417.62	3.72
99.84	21.53	428.57	4.11
104.99	3.52	466.48	3.72
116.95	9.20		
123.94	5.68		
128.88	4.11		
130.88	3.91		
135.98	3.13		
140.90	6.07		
142.97	3.72		
147.95	6.85		
154.95	4.89		
159.88	2.94		
166.96	4.70		
178.90	6.65		
190.85	3.72		
197.91	2.94		
204.90	4.50		
216.87	5.48		
228.84	5.48		
240.85	3.72		
247.89	5.48		
259.88	5.09		
266.88	27.79		

AB191X 55 A.BAYLIFF CAP.COL EI 18 29-JAN-85
CAL:CALP17 STA: 3:31



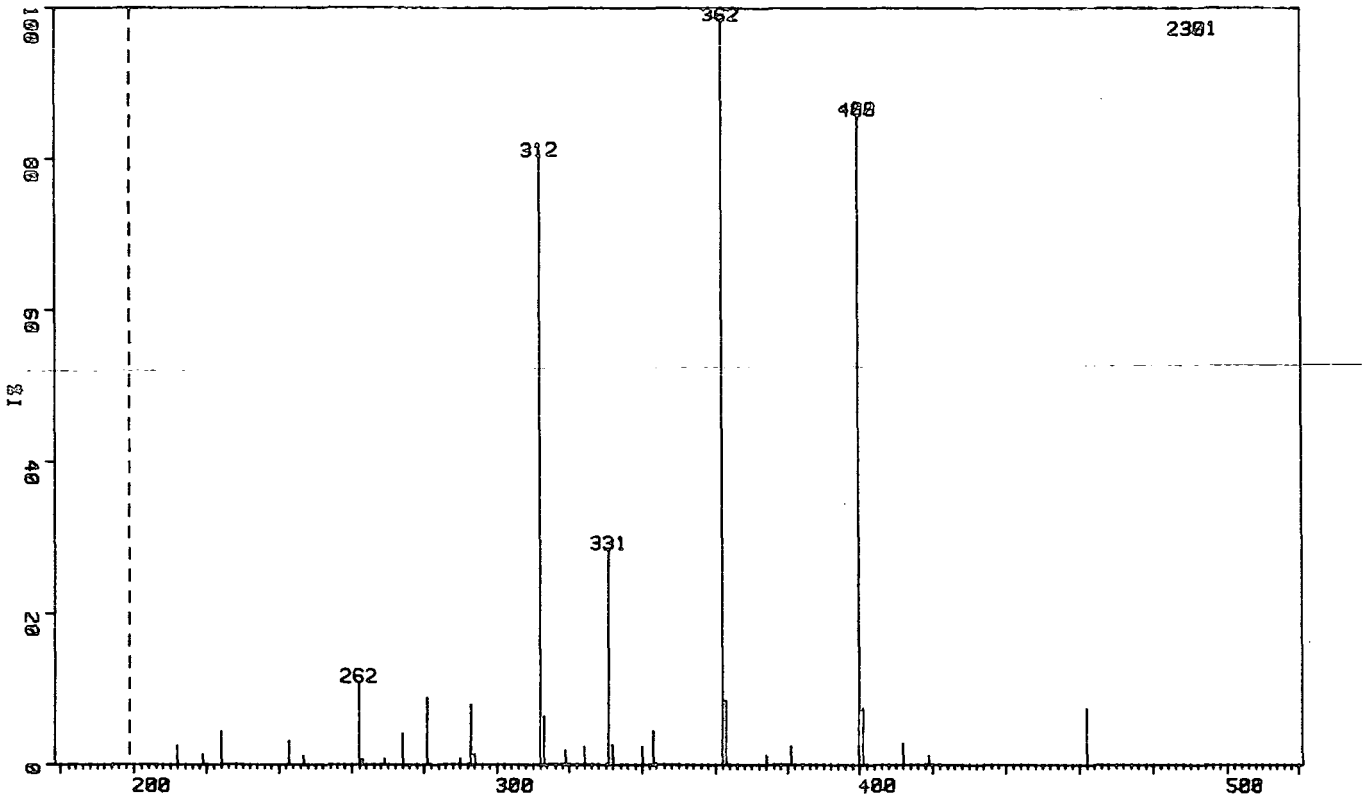
MASS	%HT. BASE	MASS	%HT. BASE
27.23	1.67	178.92	2.11
28.11	25.60	180.90	3.42
29.00	1.38	182.92	2.55
30.86	12.15	185.94	4.07
31.97	6.40	192.90	3.42
38.96	1.16	197.89	1.02
39.80	4.87	204.91	23.27
40.94	3.13	205.90	1.09
42.03	1.96	208.90	0.87
43.11	6.91	216.93	6.18
44.08	1.67	223.91	1.82
49.84	4.65	228.88	1.09
50.92	1.09	232.91	1.89
55.12	0.95	235.90	8.29
57.10	1.38	242.87	4.44
68.93	100.00	244.93	1.38
69.87	1.16	247.90	1.24
70.94	1.53	254.89	19.78
74.04	4.22	255.93	1.82
77.99	1.53	263.91	1.24
78.95	1.09	266.92	10.69
80.92	1.96	270.87	1.31
86.01	1.67	273.94	1.31
89.87	1.38	282.87	8.73
93.00	26.76	283.92	1.09
97.00	2.33	285.92	4.51
97.98	1.96	294.92	2.25
99.90	55.20	301.87	2.98
100.94	2.11	304.92	10.84
105.01	3.78	305.92	0.87
108.93	3.49	313.89	1.53
111.95	12.29	316.89	7.93
116.97	11.64	323.90	1.53
118.92	9.31	332.90	24.36
123.96	6.33	333.90	3.42
128.90	1.38	335.94	1.38
130.90	14.76	342.90	1.09
131.96	0.80	351.85	2.84
135.98	5.67	354.89	4.87
140.91	1.45	363.88	1.53
142.95	17.16	366.89	2.91
147.94	3.13	382.90	4.58
149.87	5.24	394.89	1.53
154.97	11.85	401.83	10.40
158.91	2.98	404.88	2.62
161.92	5.02	432.78	9.89
166.93	4.65	482.67	2.69
168.90	10.18		

AB191X 68 A.BAYLIFF CAP.COL EI 19 29-JAN-85
CAL:CALP17 STA: 4:21



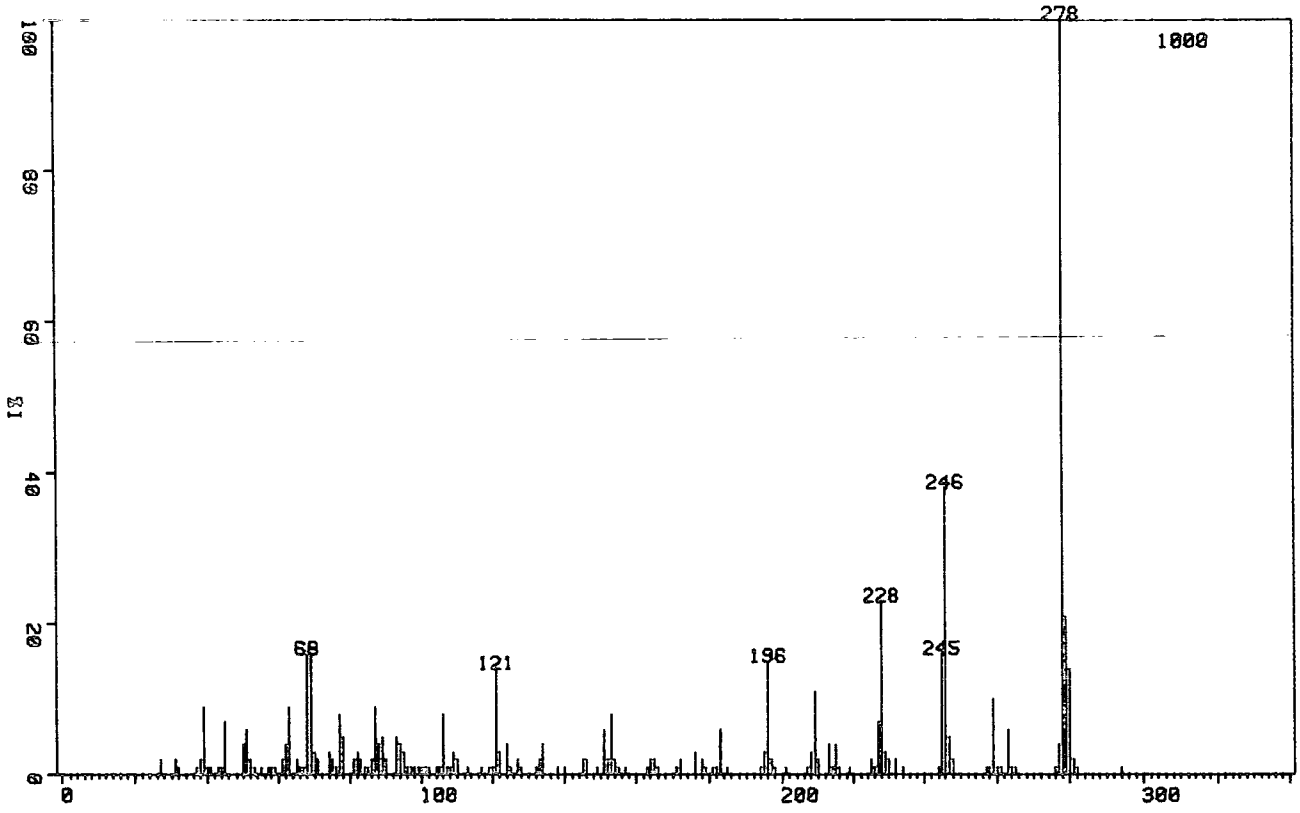
MASS	%HT. BASE	MASS	%HT. BASE
28.11	13.51	168.88	7.15
29.00	0.78	170.90	6.42
30.86	18.48	173.95	1.23
31.97	3.24	177.91	0.78
38.96	0.78	180.89	2.74
39.80	2.79	182.94	1.40
40.94	1.84	185.95	1.12
42.03	1.28	189.87	3.96
43.11	2.79	192.95	4.47
47.05	1.79	196.94	0.95
49.85	8.88	198.90	2.85
55.07	1.34	204.93	10.66
61.97	0.89	205.94	0.78
68.92	92.85	208.89	4.02
69.87	0.95	211.93	1.23
70.94	6.87	220.88	2.85
74.04	4.91	223.94	5.64
77.98	16.08	235.90	2.01
78.95	0.67	239.85	4.91
80.92	3.41	242.91	11.61
86.02	0.95	243.93	0.84
89.87	3.02	248.88	1.17
93.00	57.17	251.90	1.17
94.03	1.84	254.95	9.16
97.00	5.25	255.96	0.95
99.91	100.00	267.92	4.47
100.94	2.18	270.90	14.01
101.97	0.67	271.93	0.95
105.01	1.95	273.92	1.56
108.93	14.68	282.87	1.68
111.95	24.96	286.94	1.12
116.97	3.18	292.91	1.95
118.91	8.04	298.87	2.90
120.90	16.47	301.90	1.17
123.96	4.86	304.92	1.06
127.92	1.17	317.86	2.18
130.88	22.28	320.88	5.08
131.94	1.06	323.94	0.95
135.97	1.06	332.89	1.01
136.94	3.29	348.84	6.25
142.93	36.07	351.90	1.06
143.94	1.62	367.87	1.28
149.86	18.76	370.86	1.28
150.93	0.89	398.89	1.17
154.96	7.15	417.84	1.23
158.90	8.65	448.78	12.06
161.90	11.39	449.83	1.28
166.94	1.01	498.69	5.03

ABS04 5 A.BAYLIFF NEG.(ARGON) 20 26-SEP-86
CRL:CRLNEG STR: 0:52
X 2



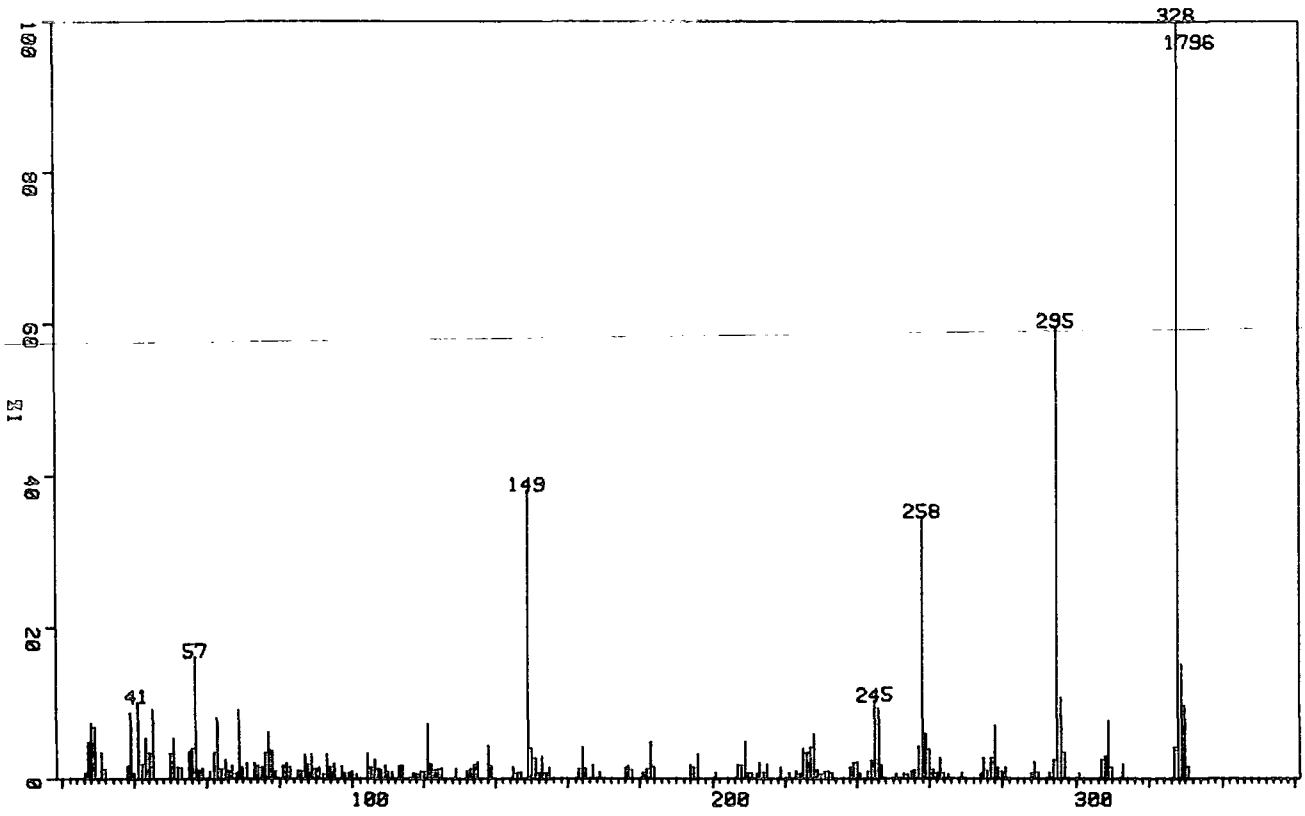
MASS	%HT. BASE
174.02	1.43
180.97	1.13
192.01	1.09
193.01	100.00
194.03	8.17
195.03	0.56
211.99	1.43
218.98	0.83
223.99	2.48
243.00	1.78
247.02	0.65
261.99	6.21
262.98	0.39
268.98	0.48
274.02	2.35
280.96	5.08
289.97	0.48
293.03	4.52
294.05	0.74
312.03	45.55
313.03	3.61
319.03	1.09
324.05	1.39
331.00	16.17
332.02	1.48
339.97	1.35
343.01	2.56
362.03	55.76
363.05	4.78
374.05	0.74
381.00	1.43
400.04	48.63
401.04	4.22
412.06	1.61
419.01	0.70
462.09	4.22

AB102 0 A.BAYLIFF EI 21 21-AUG-86
CAL:LIB STA: 0:0



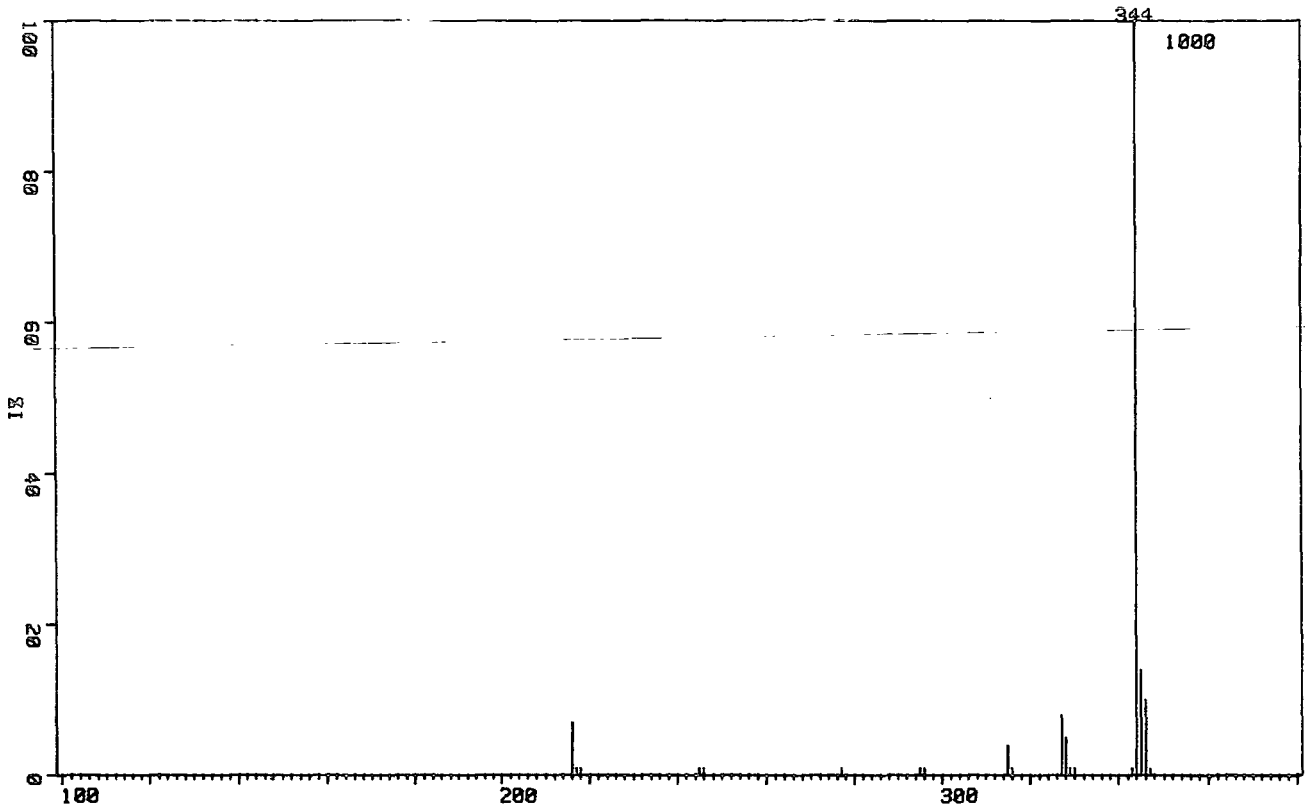
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.37	0.47	69.88	2.62	104.01	1.43	146.95	0.41	197.88	0.79	260.76	0.93
27.30	2.01	70.93	2.18	105.02	0.67	148.93	1.34	199.85	0.47	262.74	5.65
29.05	0.38	73.03	0.47	105.99	7.92	149.90	0.47	200.85	0.87	263.75	0.61
30.93	2.42	74.05	2.74	107.00	0.90	150.93	5.71	206.86	0.87	264.75	0.55
32.01	0.55	75.07	1.66	107.98	1.43	151.95	2.01	207.82	2.91	275.75	0.73
37.13	0.73	76.00	0.44	108.96	2.82	152.92	8.09	208.83	10.92	276.75	3.67
38.07	2.27	76.08	0.87	109.92	1.83	153.93	2.01	209.80	1.57	277.73	100.00
38.99	8.59	77.07	7.83	110.93	0.38	154.93	0.99	210.83	1.19	278.73	21.05
39.89	0.55	78.05	4.66	111.97	0.32	155.92	0.32	212.83	4.37	279.71	14.10
40.97	0.99	79.01	0.38	112.98	0.76	156.93	0.87	213.86	0.93	280.71	1.89
43.13	0.67	80.93	2.15	114.00	0.55	162.93	1.43	214.88	4.02	281.72	0.55
44.08	1.05	81.98	2.91	116.96	0.67	163.96	1.66	215.84	1.48	293.70	0.84
45.10	6.81	83.02	1.72	117.92	0.49	164.95	2.42	216.86	0.38		
49.88	3.58	84.04	0.96	118.92	0.90	165.92	0.84	218.80	1.34		
50.95	6.35	85.06	1.05	119.90	0.84	168.88	0.55	224.85	2.42		
52.03	1.69	86.06	1.51	120.92	14.21	169.86	0.52	225.82	1.34		
53.09	1.43	87.01	8.68	121.95	3.23	170.88	0.84	226.82	6.72		
55.09	0.67	87.95	3.99	122.96	1.11	171.91	2.45	227.81	22.79		
55.14	0.44	88.02	0.41	123.97	4.10	174.91	0.35	228.79	3.41		
56.05	0.41	88.98	4.63	124.95	1.37	175.91	2.50	229.78	2.07		
57.04	0.70	89.86	0.38	126.99	1.60	176.89	3.32	230.79	0.44		
57.12	0.79	89.96	2.45	127.98	0.79	177.87	2.42	231.80	0.73		
58.00	1.34	92.00	0.35	128.91	0.52	178.85	0.55	232.82	2.04		
58.95	0.87	93.00	5.27	130.92	0.32	179.85	0.35	233.84	1.31		
60.94	1.69	94.01	3.67	131.96	0.70	180.86	1.08	238.78	0.52		
62.01	4.28	95.04	3.26	132.98	1.98	181.89	1.02	242.80	0.38		
63.01	1.75	96.04	0.79	133.98	4.05	182.89	5.94	243.79	1.14		
63.06	9.14	97.03	0.90	134.99	0.44	183.91	4.34	244.82	15.81		
64.00	0.52	98.01	0.61	136.92	0.58	184.91	0.76	245.81	37.96		
64.09	1.54	98.97	0.67	137.92	1.48	186.91	0.41	246.82	5.09		
65.10	1.78	99.87	0.61	138.90	1.14	188.84	0.32	247.81	2.01		
66.11	1.28	99.91	1.16	139.92	0.73	193.88	1.40	256.79	0.90		
67.98	0.64	100.91	0.55	142.96	0.32	194.89	2.94	257.77	0.79		
68.93	16.04	100.99	0.76	144.97	2.07	195.89	15.37	258.77	9.69		
69.02	0.38	102.04	1.16	145.97	2.01	196.88	2.13	259.75	1.69		

AB72X 5 A.BAYLIFF 22 03-JUN-85
CAL:CALT1 STA: 0:51



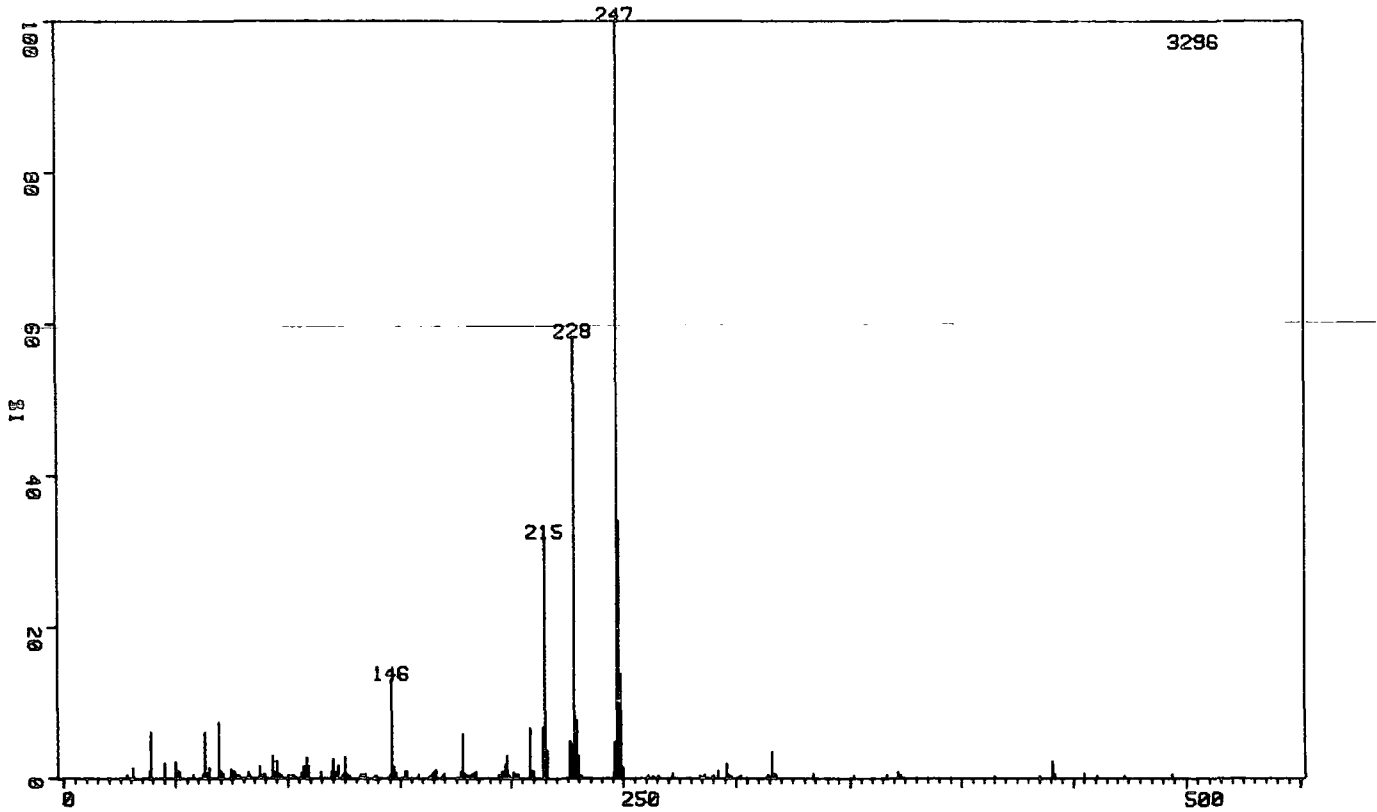
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.37	0.78	63.98	0.56	92.99	3.23	137.93	4.40	212.93	2.12	261.93	0.72
27.30	4.84	64.06	1.34	93.97	1.50	138.91	1.67	213.94	0.84	262.91	2.78
28.17	7.35	65.08	2.56	94.04	0.84	144.98	1.50	214.97	1.89	263.93	0.78
28.19	1.45	66.08	1.00	95.00	2.06	145.98	0.84	218.90	1.50	265.05	0.50
29.02	1.78	67.06	1.73	95.08	1.39	147.02	0.89	220.98	0.72	268.91	0.84
29.05	6.79	68.03	0.67	97.07	1.67	148.92	38.14	223.04	1.06	273.91	0.56
30.93	1.06	68.91	9.08	97.96	0.72	149.91	4.01	223.95	0.61	274.92	2.73
30.95	3.51	69.00	2.73	98.93	0.84	150.93	2.73	224.94	3.95	275.92	1.06
32.03	1.28	69.85	1.56	99.87	1.00	151.95	0.84	225.96	3.45	276.92	2.78
38.07	1.67	69.98	1.00	100.96	0.56	152.92	3.06	226.93	4.18	277.90	7.13
38.98	8.74	70.94	1.45	104.02	3.40	153.93	0.84	227.93	5.96	278.90	1.45
39.88	0.78	71.04	2.12	105.02	1.50	154.93	1.50	228.90	1.17	279.88	1.06
40.96	10.08	73.07	2.12	105.97	2.56	162.91	1.34	229.88	0.61	280.93	1.50
42.05	1.89	74.07	1.73	107.00	1.34	163.91	4.23	230.93	0.95	287.90	0.72
43.08	1.73	75.09	1.50	107.96	1.11	164.41	0.89	231.95	1.06	288.93	2.28
43.12	5.40	76.09	3.45	108.94	1.78	164.93	1.34	232.96	0.84	289.92	0.89
44.09	3.45	77.08	6.18	109.90	0.95	166.94	1.84	237.90	1.50	292.95	0.84
44.12	0.95	78.05	3.73	111.03	0.89	168.86	0.89	238.90	2.12	293.97	2.51
45.09	9.19	79.02	1.06	112.94	1.67	175.94	1.39	239.92	2.28	294.96	59.63
45.14	1.67	80.93	1.61	113.45	1.61	176.92	1.73	240.91	0.72	295.97	10.75
49.88	3.40	81.02	1.78	113.96	1.84	177.89	1.17	242.94	1.00	296.96	3.45
50.94	5.46	81.98	2.06	116.94	0.78	180.90	0.84	243.95	2.45	300.87	0.72
52.02	1.61	82.07	0.95	117.90	0.61	181.94	1.28	244.96	10.30	306.94	2.56
53.07	1.50	83.02	0.95	118.90	0.95	182.94	4.90	245.97	9.41	307.93	3.01
55.12	3.62	83.12	1.61	119.88	0.95	183.94	1.61	246.96	1.73	308.92	7.74
56.13	4.01	85.02	1.00	120.95	7.35	193.90	1.84	250.89	0.61	309.88	1.56
57.11	16.15	85.12	1.11	121.98	1.95	194.92	1.50	252.95	0.61	312.91	1.95
57.98	0.67	86.01	1.06	122.99	1.11	195.91	3.29	253.95	0.50	326.93	4.18
58.06	1.11	86.96	3.17	123.99	1.28	200.86	0.84	254.98	0.95	327.92	100.00
58.93	1.39	87.89	1.89	124.97	1.39	206.92	1.84	255.96	1.11	328.91	15.14
58.97	0.50	87.98	0.72	128.92	1.34	207.89	1.78	256.95	4.23	329.87	9.74
60.93	1.00	88.95	3.29	131.96	1.00	208.91	4.96	257.95	34.52	330.91	1.67
61.98	3.51	89.92	1.34	133.00	1.22	209.88	0.84	258.93	5.96		
62.98	1.17	90.98	1.50	133.99	1.84	210.90	0.72	259.91	3.90		
63.04	8.13	91.96	0.61	135.06	2.23	211.96	0.61	260.91	1.17		

AB81B 0 A.BAYLIFF CI 23 21-AUG-86
CRL:L1B STA: 0:0



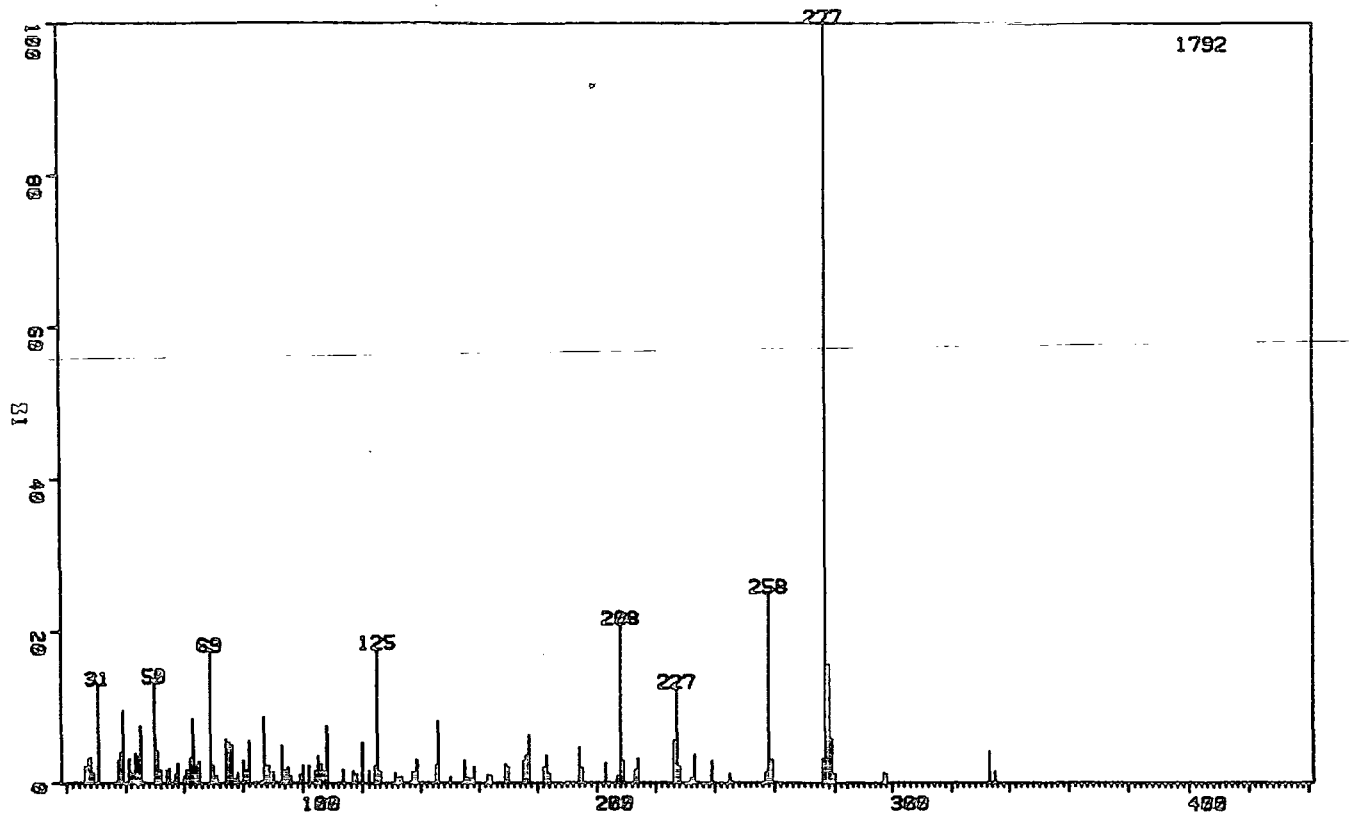
MASS	%HT. BASE	MASS	%HT. BASE
60.89	0.26	373.30	0.43
62.97	0.26	384.30	3.08
67.01	0.40	385.25	0.58
68.93	0.63	386.18	0.49
70.93	0.32		
85.05	0.32		
120.79	0.37		
215.66	6.54		
216.65	0.89		
217.62	0.60		
244.61	0.29		
245.62	0.89		
276.57	0.60		
294.52	0.66		
295.51	1.47		
296.52	0.37		
308.45	0.40		
315.44	4.44		
316.43	0.72		
317.43	0.43		
324.44	0.37		
327.42	7.72		
328.42	4.87		
329.38	1.30		
330.38	0.49		
342.38	0.43		
343.40	0.95		
344.39	100.00		
345.38	14.17		
346.37	9.68		
347.36	1.35		
348.38	0.37		
368.36	0.37		
370.36	0.58		
372.33	0.26		

AB171X 9 R.BAYLIFF EI 24 01-NOV-85
CAL:CALP1S STR: 1:25



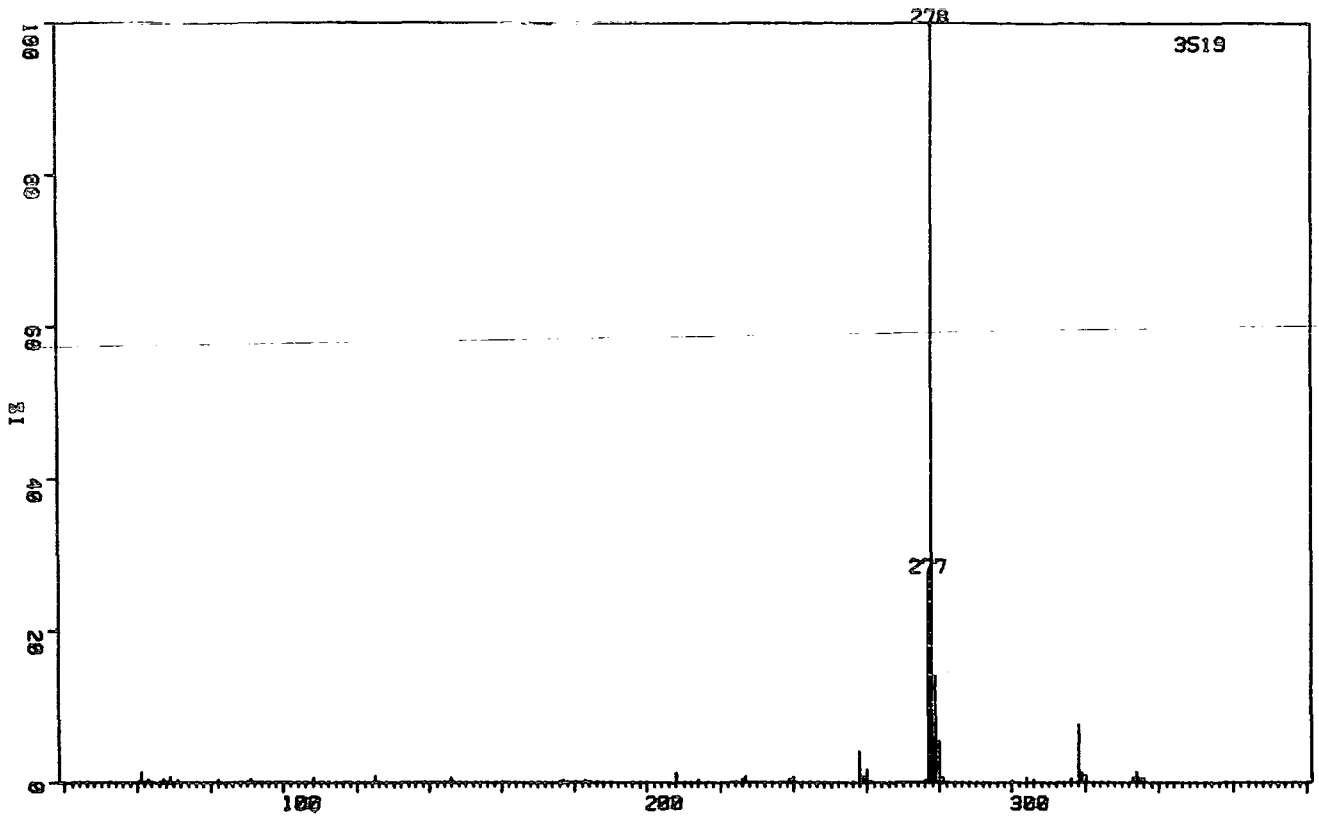
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
28.10	0.42	121.97	1.76	225.93	4.95
30.83	1.43	123.99	0.52	226.93	4.55
38.02	0.94	124.98	2.88	227.92	58.31
38.94	6.16	126.03	0.58	228.91	7.68
45.06	2.03	127.02	0.39	229.89	3.06
49.86	2.21	131.98	0.46	230.94	0.33
50.93	1.09	134.01	0.58	245.93	4.82
51.99	0.94	137.98	0.33	246.94	100.00
57.98	0.46	138.95	0.42	247.95	34.01
61.98	0.52	145.01	0.36	248.91	13.87
62.98	0.55	145.97	13.14	249.89	1.46
63.03	6.13	146.97	1.52	260.97	0.39
64.06	0.82	147.95	0.70	262.95	0.27
65.08	1.43	151.96	0.94	265.97	0.42
68.91	7.46	152.98	1.06	271.92	0.70
69.86	1.00	157.94	0.46	283.92	0.30
70.93	0.70	162.94	0.33	285.97	0.46
74.06	1.24	163.98	0.39	289.91	0.39
75.07	1.12	164.98	0.88	291.90	1.00
76.07	0.97	165.99	1.21	295.91	1.97
77.07	0.42	168.92	0.39	296.93	0.42
78.04	0.49	169.87	0.70	297.92	0.33
81.97	0.91	176.96	0.88	301.96	0.39
83.01	0.39	177.95	5.92	313.88	0.55
86.99	1.67	178.93	0.70	315.90	3.55
88.01	0.33	179.91	0.39	316.93	0.64
88.97	0.58	180.90	0.30	317.92	0.46
89.94	0.52	181.93	0.49	333.88	0.73
92.98	3.06	182.96	0.70	351.90	0.39
94.00	0.79	183.98	0.91	366.93	0.52
95.02	2.34	193.96	0.49	371.85	0.79
96.01	0.64	195.95	0.97	372.96	0.39
97.01	0.39	196.94	1.85	415.00	0.30
99.90	0.49	197.94	3.00	434.92	0.30
102.00	0.46	198.91	0.42	440.91	2.34
103.03	0.33	200.88	0.82	441.93	0.61
105.98	0.73	201.96	0.58	454.86	0.70
107.00	1.61	202.98	0.58	460.93	0.39
107.97	2.73	207.93	6.71	472.89	0.33
108.94	1.67	208.92	1.12	493.89	0.64
114.02	0.91	209.91	1.06		
118.92	0.97	213.97	6.86		
119.89	2.58	214.98	31.86		
120.95	0.79	215.99	3.73		

AB194X 4 R.BAYLIFF EI 25 29-JAN-85
CRL:CRLT31 STR: 0:43

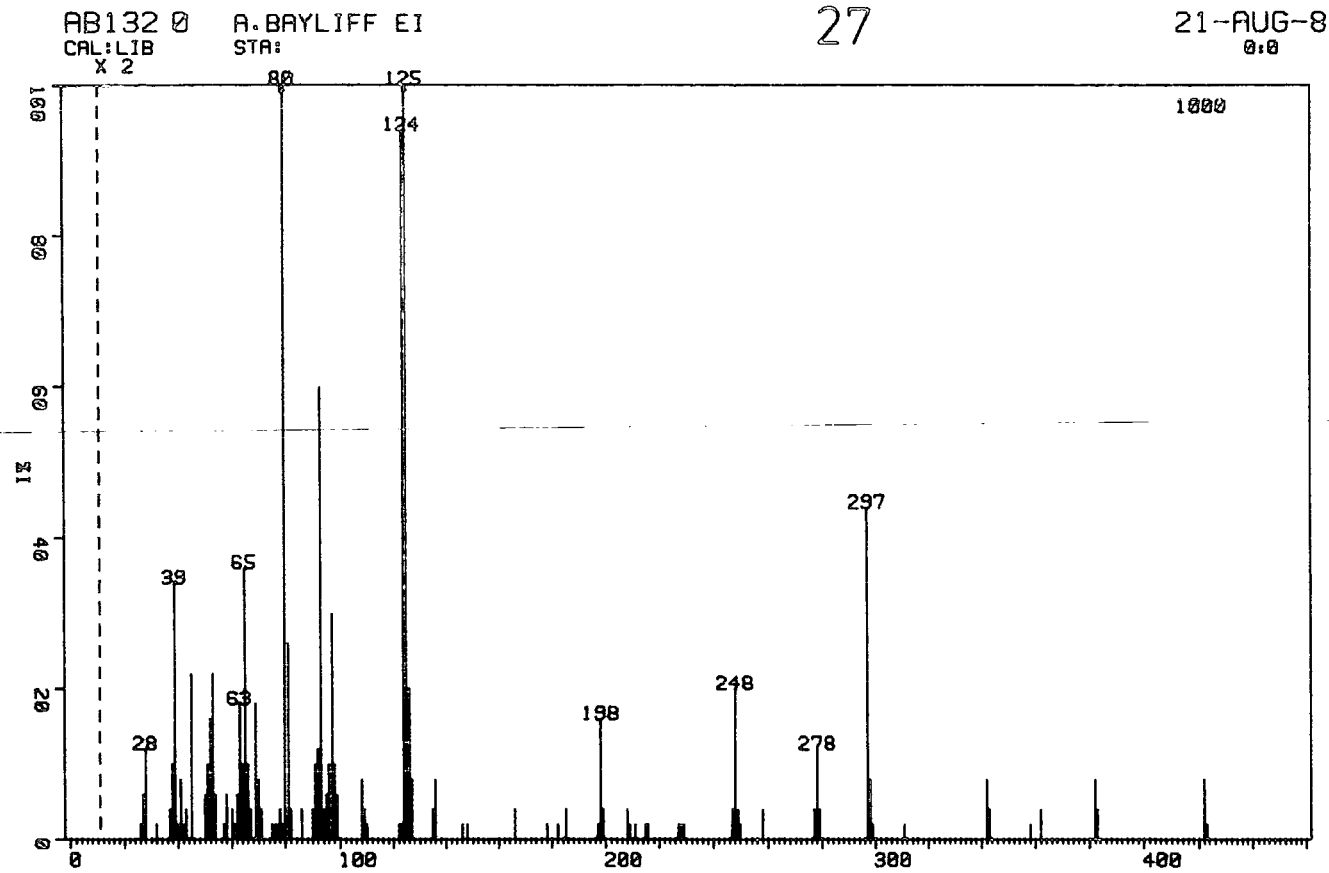


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.30	2.12	88.49	2.23	194.05	4.69
27.23	3.18	89.95	1.45	195.04	1.95
28.10	2.40	93.01	4.97	203.01	2.62
28.11	3.35	94.02	1.67	207.02	0.89
28.97	1.34	95.04	2.01	208.00	20.93
30.86	12.95	96.04	0.89	208.99	2.85
37.09	2.96	98.98	1.17	213.02	1.67
38.04	3.96	99.93	2.34	214.06	3.18
38.96	9.54	102.04	2.29	226.02	5.64
40.94	3.18	104.04	1.62	227.02	12.56
42.04	1.23	105.04	3.63	228.01	2.12
43.07	1.79	106.03	2.57	232.03	0.67
43.11	3.91	107.04	1.56	233.04	3.74
44.08	3.46	108.02	7.53	238.99	2.96
44.11	1.00	113.55	1.84	245.03	1.17
45.09	7.53	117.04	1.62	257.02	1.40
45.14	3.40	117.99	1.17	258.00	25.00
49.88	13.34	119.96	5.30	259.00	3.07
50.95	4.19	122.03	1.67	276.01	3.12
52.03	1.73	124.07	2.18	277.01	100.00
54.09	1.67	125.02	17.75	278.01	15.62
55.09	1.95	126.09	1.51	278.98	5.80
57.05	1.17	131.00	1.40	279.98	1.12
58.02	2.62	132.03	0.78	297.02	1.40
59.93	0.84	133.07	0.84	298.01	1.17
60.97	1.84	137.01	1.40	333.06	4.19
62.03	3.24	138.05	1.17	335.04	1.56
63.03	3.24	138.52	3.07		
63.08	8.48	145.10	2.29		
64.11	2.29	146.04	8.15		
65.10	2.90	149.97	0.84		
68.92	17.41	155.03	2.96		
69.86	2.29	156.02	0.67		
70.94	1.06	157.02	0.45		
74.08	5.92	158.01	2.12		
75.04	2.12	163.03	1.06		
75.08	5.36	164.06	0.95		
76.08	5.08	169.00	2.57		
77.07	0.61	169.96	2.01		
78.04	1.34	175.00	2.85		
79.95	2.96	176.04	3.63		
80.94	1.73	177.02	6.25		
81.98	5.52	181.99	2.06		
87.00	8.82	183.04	3.63		
88.02	0.95	184.04	1.28		

AB194X 10 A.BAYLIFF CI I-BU 26 29-JAN-85
CAL:CALT31 STA: 1:34



MASS	%HT. BASE
60.95	1.39
63.04	0.37
67.07	0.37
68.92	0.71
69.00	0.57
71.01	0.31
81.93	0.31
90.94	0.40
107.95	0.54
124.94	0.91
145.97	0.43
175.95	0.23
176.91	0.34
182.94	0.28
207.87	1.34
213.97	0.31
225.93	0.37
226.92	0.77
238.86	0.40
239.85	0.77
257.91	4.09
258.89	0.91
259.92	1.76
260.93	0.28
275.91	0.26
276.91	27.71
277.91	100.00
278.91	14.21
279.88	5.43
280.92	0.65
299.98	0.28
303.98	0.68
306.00	0.31
316.00	0.40
317.99	7.62
318.98	1.28
319.97	0.97
332.94	0.65
333.96	1.39
334.95	0.43
335.94	0.48



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.36	1.41	79.03	0.94	196.92	1.41
27.29	3.36	79.97	51.98	197.91	8.34
28.17	6.46	80.95	1.01	198.89	1.55
32.00	0.67	81.03	13.52	207.91	1.68
37.12	2.08	82.00	2.49	208.91	0.87
38.06	5.45	82.08	0.74	210.91	1.14
38.98	17.28	84.06	1.61	214.96	0.74
39.87	1.41	89.97	2.35	215.97	1.34
40.95	3.56	91.02	5.51	226.90	1.41
42.04	1.34	92.06	5.72	227.90	1.48
43.12	1.55	93.02	1.55	228.90	0.81
45.09	11.43	93.10	29.79	246.94	1.75
49.87	3.16	94.10	2.08	247.95	9.89
50.94	5.18	95.03	2.82	248.94	1.82
52.01	7.80	96.03	4.84	249.92	1.01
53.07	10.56	97.03	14.59	257.91	1.95
54.10	2.89	98.01	5.11	276.89	1.75
57.02	1.41	98.97	2.56	277.92	5.58
57.99	2.56	107.98	3.77	278.90	1.55
59.86	1.75	108.96	1.75	296.89	22.39
60.93	1.41	109.92	0.74	297.91	4.24
62.00	3.03	121.94	1.21	298.90	1.41
62.52	1.82	122.97	1.41	310.92	0.87
63.04	8.54	123.99	47.34	341.88	4.44
64.07	4.84	125.00	100.00	342.93	1.55
65.09	18.09	125.99	10.15	361.86	1.68
66.09	5.18	126.99	4.30	381.88	3.70
67.07	2.15	134.97	1.68	382.94	1.48
68.92	9.21	135.98	3.90	421.88	3.97
69.87	3.77	145.96	1.21	422.92	1.14
70.95	2.42	147.94	1.21		
75.10	1.08	165.96	1.55		
76.09	0.87	177.90	0.74		
77.09	1.01	182.00	1.34		
78.06	2.15	184.94	2.02		

ABS71X S A.BAYLIFF 28 15-NOV-84
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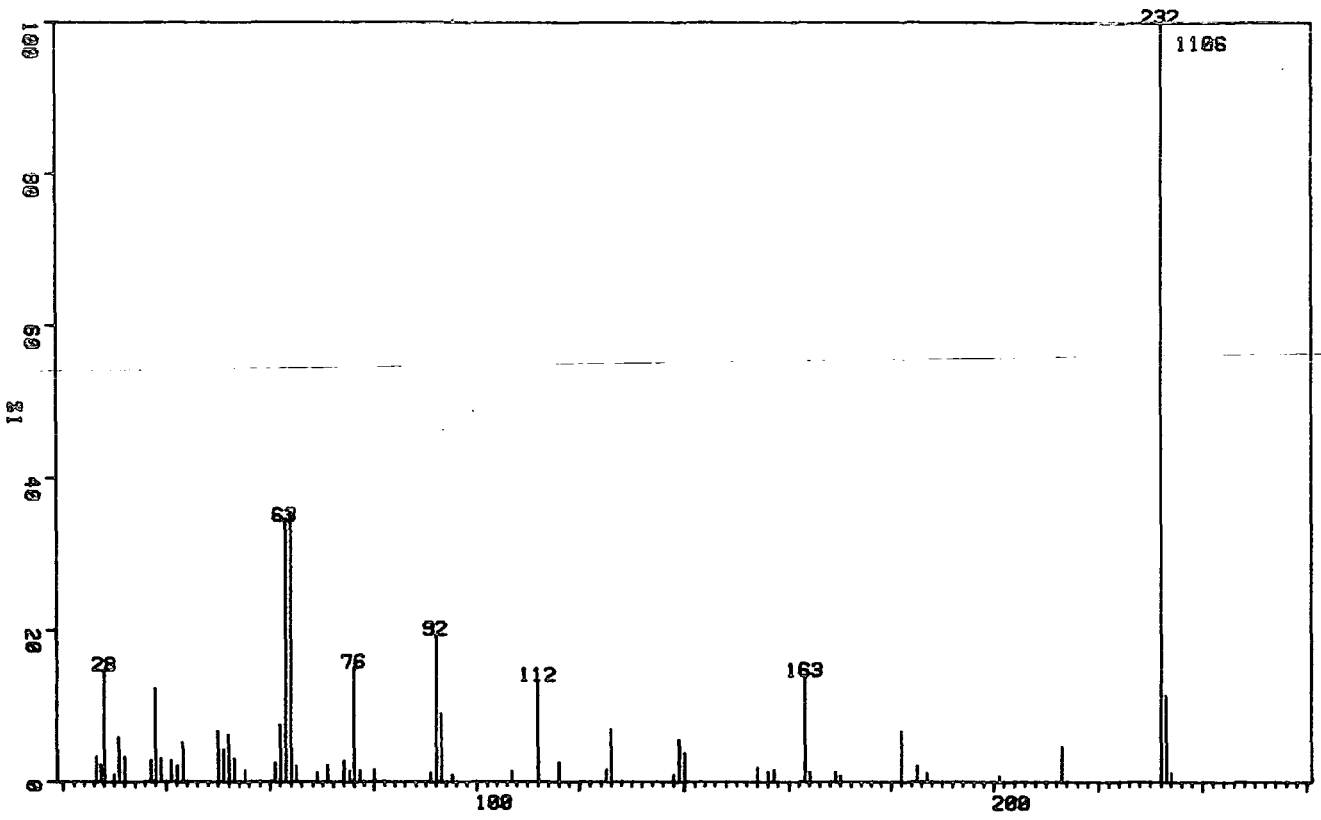

MASS	%HT. BASE	MASS	%HT. BASE
26.37	3.35	116.04	2.62
27.30	2.26	125.06	1.54
28.17	14.74	126.07	6.96
29.89	0.99	138.02	0.99
30.93	5.97	139.02	5.61
32.03	3.35	139.95	3.80
37.13	2.80	154.07	1.90
38.08	12.30	156.07	1.36
39.00	3.07	157.07	1.63
40.98	2.80	163.08	14.01
42.07	2.08	164.08	1.36
43.14	5.15	169.01	1.36
49.90	6.78	169.99	0.81
50.98	4.34	182.05	6.78
52.06	6.24	185.10	2.17
53.08	3.07	187.09	1.18
55.13	1.54	201.01	0.81
60.97	2.53	213.08	4.70
62.05	7.50	232.09	100.00
63.10	34.36	233.11	11.48
64.10	35.53	234.10	1.27
65.09	2.08		
68.95	1.36		
70.93	2.26		
74.06	2.80		
75.08	1.45		
76.09	15.10		
77.08	1.45		
79.93	1.63		
91.00	1.27		
92.05	19.44		
93.05	9.04		
95.10	0.99		
107.06	1.45		
112.00	13.38		

AB31 0 A.BAYLIFF EI 29 21-AUG-86
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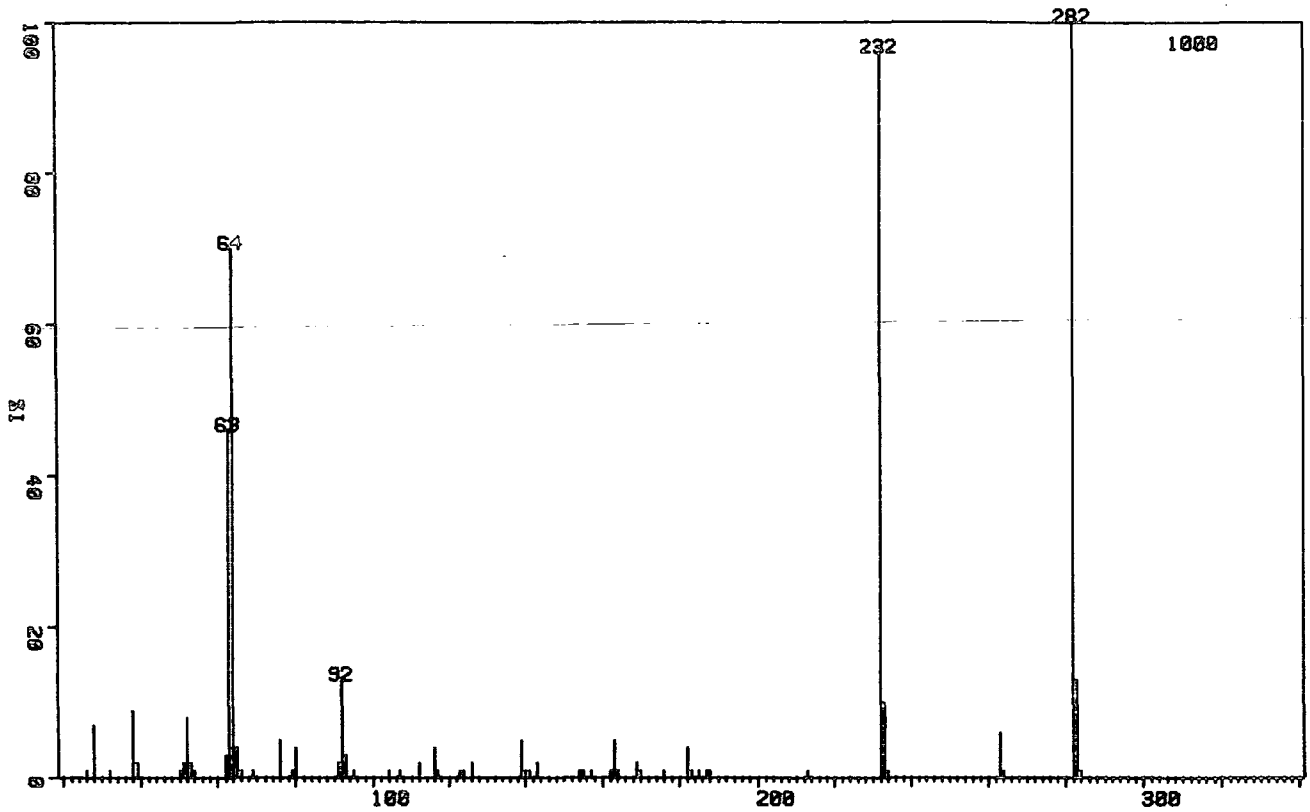
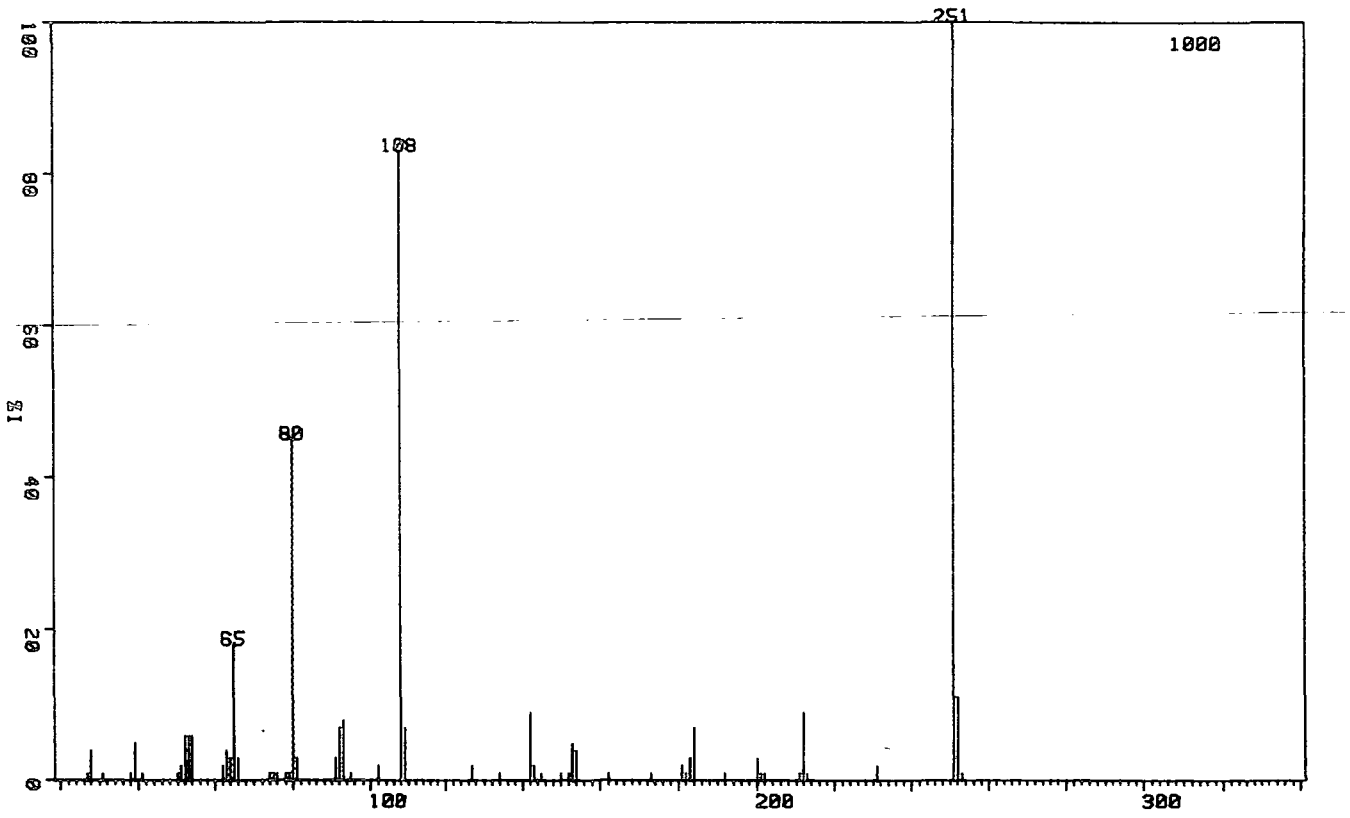


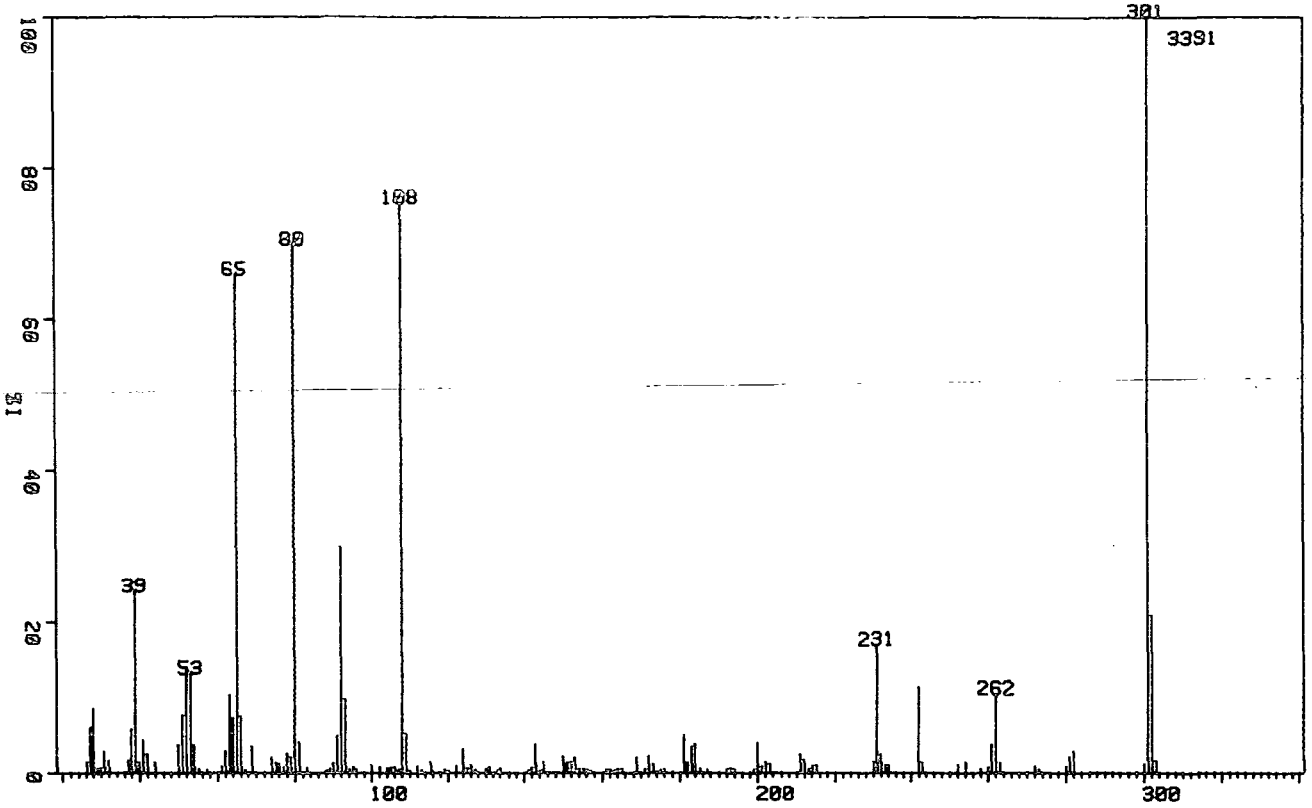
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.32	0.72	36	154.05	0.68
2	28.13	7.48	37	155.05	0.50
3	32.02	0.95	38	157.06	0.99
4	38.09	9.42	39	162.00	0.77
5	39.00	2.30	40	163.06	4.60
6	49.90	1.22	41	164.06	0.50
7	50.98	2.16	42	169.02	2.43
8	52.07	7.62	43	170.00	0.50
9	53.09	1.76	44	176.08	0.59
10	54.13	0.59	45	182.03	4.06
11	62.07	2.70	46	183.07	0.45
12	63.12	46.06	47	185.07	1.22
13	64.11	69.76	48	187.03	0.95
14	65.09	4.01	49	188.04	0.54
15	66.08	0.77	50	213.06	1.13
16	68.96	0.99	51	232.04	96.12
17	76.08	5.36	52	232.91	10.37
18	78.97	0.63	53	234.05	0.99
19	79.90	4.01	54	263.07	5.99
20	90.96	2.12	55	264.09	0.81
21	92.02	13.47	56	282.06	100.00
22	93.02	3.06	57	282.97	12.57
23	95.08	1.22	58	284.08	1.08
24	104.07	0.72			
25	107.05	0.68			
26	112.01	1.98			
27	116.04	4.24			
28	116.54	0.50			
29	123.06	0.50			
30	124.02	0.99			
31	126.05	2.48			
32	139.01	4.60			
33	139.96	0.86			
34	140.99	0.63			
35	143.01	2.25			

AB500 0 A.BAYLIFF E.I. 30 18-APR-85
CAL:LIB STA: 0:0



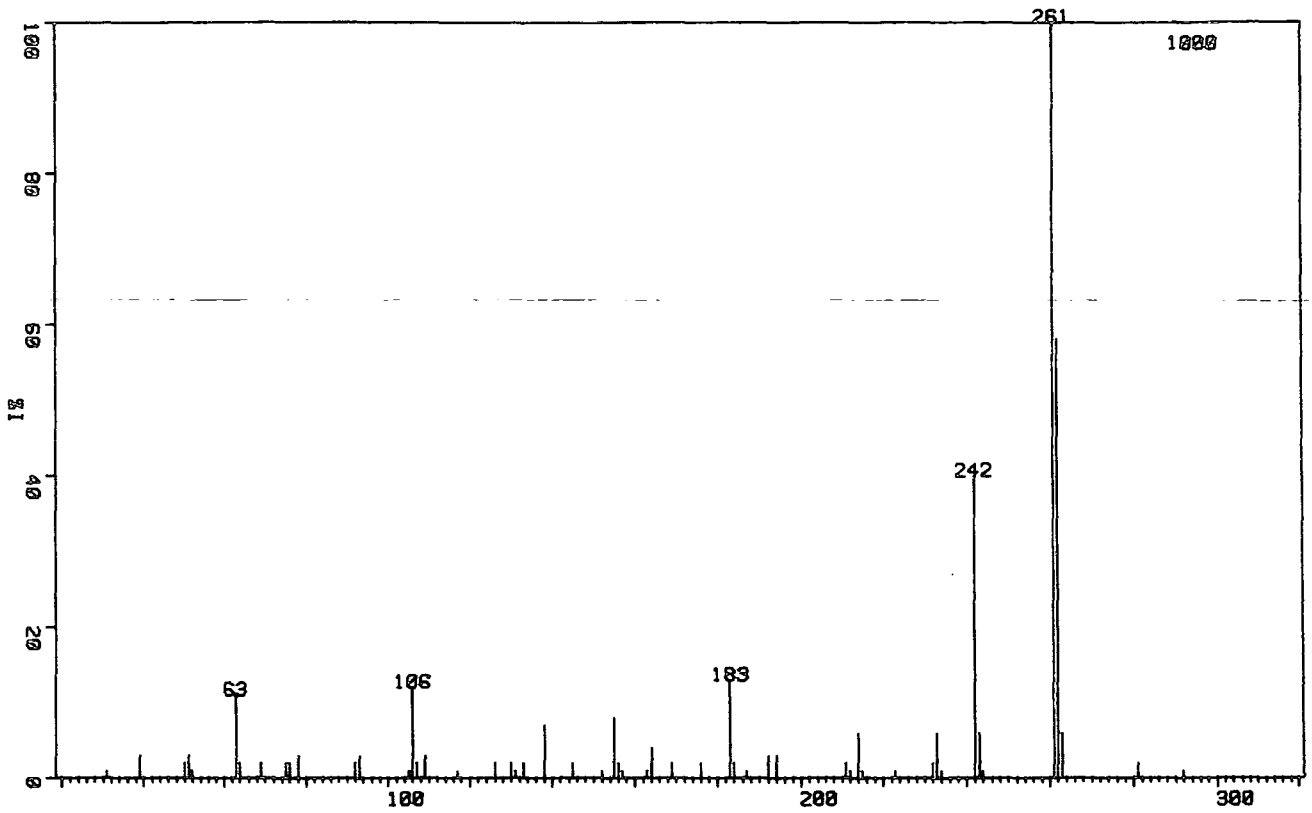
MASS	%HT. BASE	MASS	%HT. BASE
27.21	0.86	181.91	1.11
28.09	4.46	182.93	3.00
30.84	1.46	183.95	7.03
38.03	1.46	191.90	1.29
38.95	5.40	199.85	2.83
40.91	1.37	200.89	1.11
49.86	1.20	201.97	1.37
50.93	1.63	210.89	1.29
51.99	5.57	211.96	8.83
53.06	5.83	212.95	1.11
54.09	1.37	230.89	1.63
61.98	1.29	250.88	100.00
63.03	3.51	251.92	10.71
64.06	2.91	252.95	0.86
65.09	17.31		
66.07	2.66		
74.02	1.20		
75.04	1.20		
76.04	1.11		
77.99	1.29		
78.96	1.03		
79.91	44.56		
80.95	3.17		
90.93	2.49		
91.98	6.60		
92.96	7.54		
95.00	1.29		
101.95	1.54		
107.96	82.60		
108.92	6.60		
126.93	1.97		
133.93	1.46		
141.91	8.91		
142.89	1.80		
144.96	0.94		
149.84	0.86		
151.93	1.46		
152.96	4.97		
153.97	3.51		
161.90	0.94		
172.92	1.37		
180.87	2.40		

ABS10X 0 A.BAYLIFF CAP.COL 31 24-SEP-86
CAL:CALP4 STA: 13:43



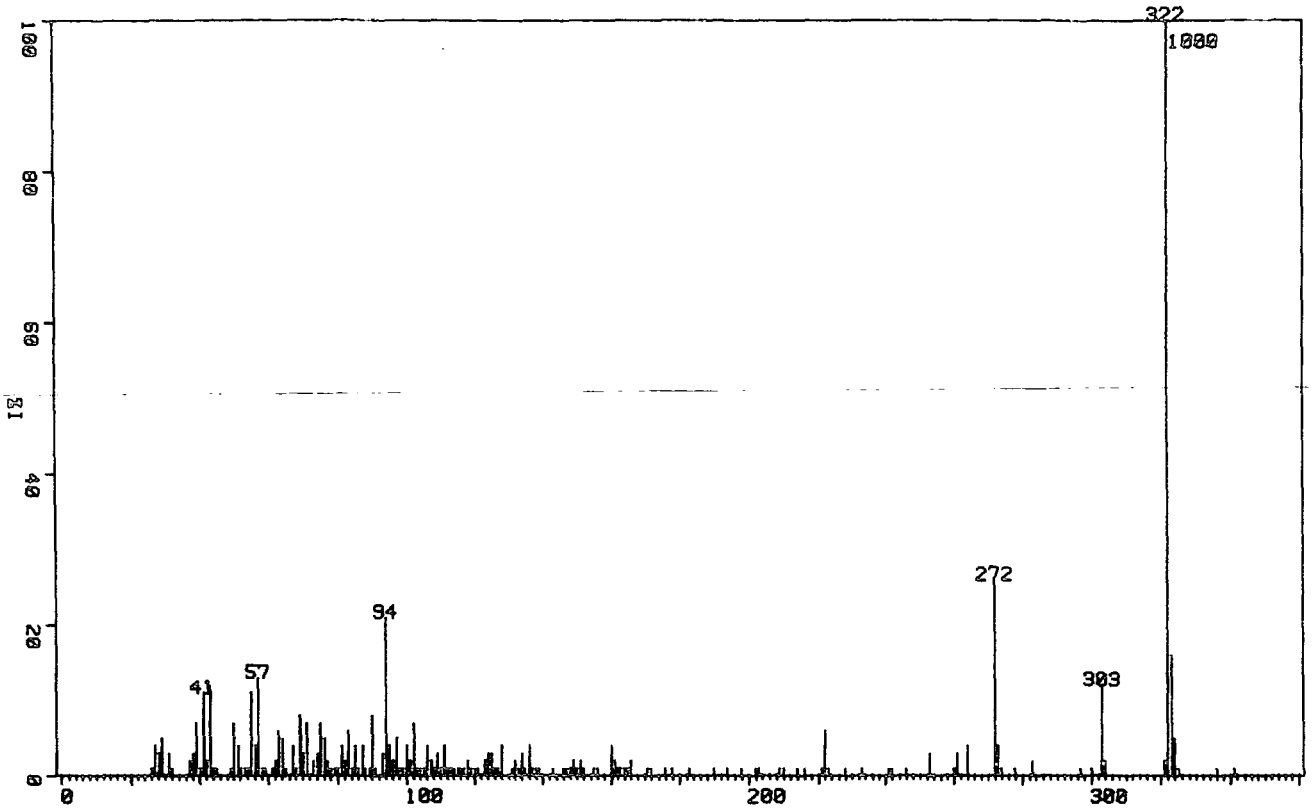
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.28	1.53	90.99	4.87	157.06	0.32
27.22	6.07	92.03	29.93	161.05	0.44
28.10	8.61	93.02	9.82	162.06	0.44
28.98	0.56	94.03	0.47	163.06	0.35
29.81	0.77	95.07	0.86	164.08	0.56
30.86	2.95	96.07	0.44	165.11	0.59
31.97	1.71	99.92	1.09	169.03	2.03
37.10	1.65	102.04	0.83	171.03	0.50
38.04	5.81	104.07	0.62	172.04	2.24
38.96	24.06	105.04	0.71	173.08	1.15
39.80	0.53	106.07	0.80	175.04	0.35
39.86	1.42	107.06	0.38	200.03	4.07
40.94	4.36	108.04	75.35	201.06	0.91
42.04	2.57	109.01	5.19	202.07	1.47
44.11	1.45	109.99	0.32	203.10	1.18
49.89	3.77	112.01	0.97	211.05	2.51
50.96	7.70	113.04	0.38	212.06	1.80
52.03	14.13	115.56	1.45	213.08	0.50
53.10	13.18	119.02	0.44	214.08	1.03
54.12	3.77	119.99	0.27	215.09	1.09
55.10	0.56	122.06	0.88	230.02	1.47
57.09	0.44	124.03	3.16	231.04	16.99
60.98	0.80	125.07	0.62	232.06	2.48
62.04	2.83	126.08	1.09	233.11	1.00
63.09	10.35	127.08	0.38	234.08	1.03
64.13	7.25	129.99	0.50	242.06	11.38
65.10	65.82	131.00	0.86	243.06	1.45
66.08	7.49	133.07	0.32	252.07	1.12
67.06	0.38	134.10	0.68	254.11	1.45
68.93	3.57	141.00	0.35	258.06	0.56
74.04	2.03	142.04	0.80	260.01	0.65
75.06	1.42	143.01	3.83	261.04	3.75
76.05	1.27	144.05	0.35	262.06	10.50
77.05	0.74	145.06	1.45	263.08	1.33
78.02	2.62	149.99	2.18	272.09	1.03
78.98	2.06	150.50	0.94	273.10	0.44
79.93	69.83	151.04	1.24	280.06	0.91
80.98	4.04	152.04	1.47	281.07	2.12
83.05	0.77	153.06	2.03	282.09	2.89
88.00	0.32	154.08	0.56	300.10	1.18
88.97	0.44	155.04	0.53	301.07	100.00
89.93	1.30	156.07	0.47	302.10	21.00
				303.10	1.65

AB192A 0 32 25-SEP-86
CRL:LIB STA: 0:0



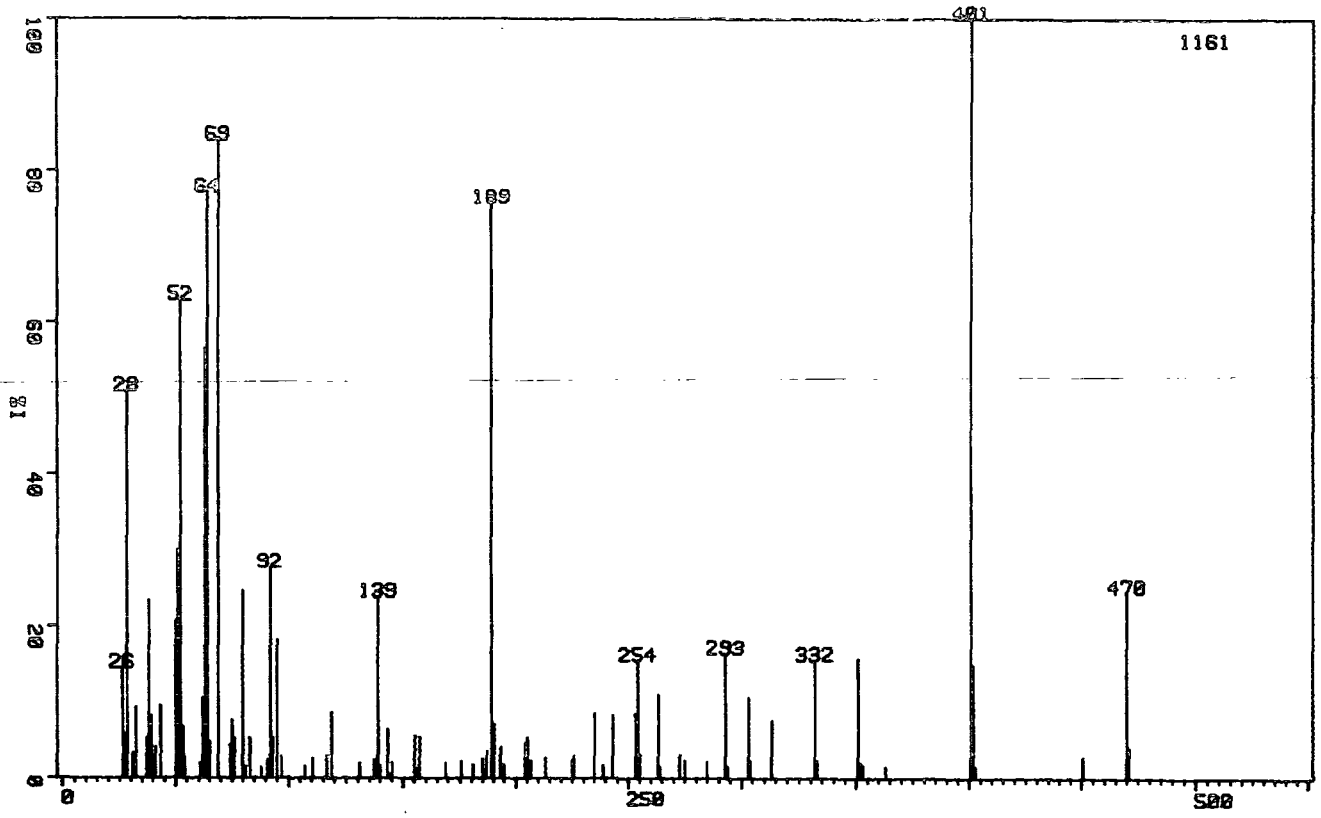
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.35	0.31	104.99	1.34	163.90	4.03	233.79	1.03	297.77	0.31	354.64	1.00
27.28	0.77	106.01	11.96	164.92	0.49	238.76	0.43	298.73	0.63	355.66	0.40
30.91	1.11	106.99	2.31	166.89	0.29	240.75	0.46	299.72	0.83	358.68	0.60
37.11	0.26	107.98	0.29	167.87	0.71	241.76	39.28	300.76	0.31	359.63	0.49
38.05	0.74	108.91	3.03	168.85	1.51	242.78	5.91	303.73	0.51	360.62	0.40
38.97	3.23	111.93	0.46	169.84	0.29	243.79	0.94	307.75	0.29	362.65	0.60
49.86	1.80	113.99	0.94	170.84	0.31	244.82	0.34	308.75	0.29	364.67	0.51
50.93	3.25	115.04	0.63	175.88	1.57	246.77	0.31	311.69	2.08	365.61	0.66
52.00	1.34	116.04	0.31	176.89	0.26	251.76	0.31	312.72	0.83	366.65	0.43
53.02	0.43	116.92	1.23	180.84	0.31	257.82	0.26	313.72	0.46	367.66	0.34
55.06	0.29	117.92	0.31	181.84	0.69	258.80	0.29	314.71	1.71	369.55	3.34
60.93	0.26	122.92	0.43	182.86	13.05	259.73	0.57	315.71	0.60	370.61	0.60
61.98	0.71	123.93	0.29	183.87	1.83	260.73	100.00	317.73	0.43	377.56	1.28
63.02	10.59	124.95	0.97	184.89	0.26	261.77	57.66	321.71	0.46	378.60	0.34
64.05	2.26	125.94	1.91	186.86	1.11	262.79	6.48	322.70	1.28	384.63	0.26
68.92	1.51	129.85	2.20	187.86	0.54	263.81	0.77	323.69	2.28	385.62	0.40
70.90	0.26	130.85	1.23	191.84	2.85	269.79	0.26	324.72	1.54	386.58	1.46
74.03	0.77	131.90	0.69	192.85	0.46	270.79	0.26	325.71	0.60	387.61	0.37
75.04	2.43	132.93	2.28	193.85	3.14	271.82	0.26	326.74	0.31	391.55	1.43
76.04	2.14	133.95	0.29	194.86	0.88	272.80	0.23	329.63	1.63	392.60	0.34
77.02	0.40	135.93	0.26	204.84	0.29	275.80	0.31	330.67	0.37	393.58	0.69
78.01	2.97	136.92	0.71	205.83	0.40	276.78	0.43	331.66	0.51	397.58	0.60
78.96	0.46	137.91	6.71	206.84	0.29	278.76	0.26	334.71	0.46	398.60	0.34
80.92	0.80	138.89	0.66	209.78	0.31	279.73	0.80	335.67	1.86	403.56	0.71
87.02	0.54	142.89	0.49	210.78	2.03	280.74	2.23	336.70	1.23	404.57	0.63
87.99	0.49	143.93	0.54	211.80	1.06	281.77	0.40	337.69	0.57	415.53	2.91
89.91	0.26	144.93	1.54	212.81	0.88	283.82	0.26	338.68	2.34	416.52	0.66
91.97	2.00	151.90	1.11	213.82	5.62	286.80	0.43	339.68	0.57	419.52	0.26
92.97	2.94	154.89	7.74	214.83	1.00	287.76	0.86	340.69	0.29	424.55	1.23
94.00	0.51	155.91	1.66	220.80	0.29	288.77	0.26	341.68	0.40	425.61	0.29
95.04	0.23	156.91	1.00	222.79	1.06	291.72	1.28	342.70	0.31	428.58	0.29
98.93	0.51	158.83	0.77	223.81	0.34	292.77	0.37	346.70	0.26	443.52	0.74
99.89	0.60	160.86	0.31	224.85	0.29	294.77	0.31	347.69	0.40	454.52	0.40
101.98	0.57	161.88	0.29	231.76	2.11	295.79	0.26	348.68	0.29	474.48	0.34
104.01	0.46	162.90	1.28	232.78	5.68	296.78	0.43	353.63	4.97	483.47	0.51

AB91 0 A.BAYLIFF EI 33 21-AUG-86
CAL:LIB STA: 0:0



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.36	0.93	72.10	0.42	108.93	0.37	140.05	0.39	191.09	0.48	301.94	0.54
27.29	4.28	73.08	1.52	109.04	2.51	141.09	0.48	193.12	0.45	302.93	11.69
28.17	3.46	74.08	2.93	110.01	1.04	141.95	0.31	193.96	1.04	303.92	2.00
29.02	0.34	75.09	6.76	110.93	3.80	142.96	0.56	194.95	0.54	320.88	1.86
29.05	5.27	76.09	5.04	111.06	3.72	143.96	0.45	196.96	0.42	321.93	100.00
30.92	2.79	77.08	1.86	111.46	0.48	145.01	0.45	197.92	0.70	322.96	15.77
30.95	0.54	78.06	0.62	111.96	0.99	145.98	0.59	201.92	0.99	323.95	5.29
32.02	0.93	79.03	1.32	112.09	0.87	146.99	1.41	202.93	1.04	324.95	0.76
37.13	1.91	79.99	0.59	112.98	0.39	147.96	0.73	207.93	0.45	334.94	0.48
38.07	2.73	80.97	0.56	113.12	1.07	148.94	2.39	208.91	1.10	335.93	0.87
38.99	7.35	81.05	4.53	113.99	0.37	149.05	0.54	209.88	0.76	340.89	0.73
39.82	0.37	82.00	0.99	115.00	0.34	149.91	0.56	213.98	2.34	359.89	8.93
39.88	0.76	82.09	2.20	116.00	0.62	150.03	0.37	214.97	0.37	360.92	1.41
40.97	11.72	83.03	0.70	116.95	0.65	150.91	1.55	215.98	0.39	361.93	0.51
42.06	2.00	83.13	6.31	117.89	1.55	151.08	0.87	220.94	0.54	463.87	0.65
43.09	0.59	84.02	0.39	118.91	0.34	151.43	0.54	221.92	6.05	527.74	0.54
43.13	12.25	84.12	1.91	118.99	0.25	151.97	1.10	222.93	0.82		
44.08	1.07	85.11	4.42	119.87	0.68	153.13	0.51	223.95	0.45		
44.17	0.45	85.98	1.21	120.42	0.34	154.10	0.37	225.94	0.54		
45.10	1.21	86.08	0.34	120.95	0.42	154.94	1.27	226.96	0.34		
45.15	0.65	86.94	3.91	121.05	0.62	155.12	0.31	227.95	1.46		
48.97	0.48	87.95	1.49	121.98	0.37	155.92	0.65	232.92	1.21		
49.88	6.96	88.87	0.28	122.08	0.45	158.91	0.34	233.94	0.45		
50.95	4.25	88.91	0.87	123.11	1.63	159.87	4.20	239.90	0.54		
52.02	1.44	89.88	7.69	123.97	2.76	160.92	2.22	240.93	0.87		
53.09	1.35	90.97	1.27	124.09	0.82	161.94	0.59	241.97	0.65		
54.13	0.96	92.02	0.28	124.95	3.41	162.97	0.45	243.97	0.31		
55.09	0.45	92.98	3.01	125.11	2.11	163.10	0.56	244.98	0.48		
55.14	11.04	93.05	0.99	125.97	0.82	163.97	0.54	245.94	0.65		
56.14	3.66	93.97	20.92	126.08	0.79	165.10	0.59	251.93	0.42		
57.12	13.32	95.07	4.08	127.08	0.70	165.96	2.00	252.95	2.84		
58.00	0.31	95.98	1.07	127.96	4.20	166.10	0.28	253.96	0.56		
58.08	0.73	96.09	1.86	128.93	0.48	166.95	0.31	258.96	0.48		
59.00	0.37	97.09	5.15	130.88	1.27	167.10	0.28	259.91	0.96		
60.95	1.13	98.07	1.10	131.92	2.17	168.90	0.42	260.92	2.51		
62.01	2.00	98.94	0.70	132.96	1.21	169.88	0.25	261.94	0.39		
63.05	6.20	99.04	1.44	133.99	3.13	170.90	0.82	263.97	3.89		
64.08	4.70	99.89	3.60	134.98	0.42	171.91	0.73	264.96	0.56		
65.10	0.76	100.98	1.77	135.08	0.62	174.89	0.51	270.91	0.82		
66.08	0.42	101.48	0.82	135.98	3.60	175.98	0.70	271.91	26.33		
67.07	3.86	102.02	6.73	136.09	0.39	176.96	0.51	272.91	3.83		
68.04	1.49	103.05	0.93	136.47	0.54	177.09	0.42	273.92	1.41		
68.93	4.59	104.06	0.76	136.96	0.68	177.96	0.99	277.93	1.32		
69.00	8.14	105.05	1.46	137.09	1.04	179.09	0.51	282.91	1.52		
69.85	3.29	105.99	4.36	137.95	1.35	182.97	1.24	283.92	0.37		
69.98	2.90	107.00	1.63	138.08	0.51	183.95	0.65	284.90	0.31		
70.94	0.37	107.09	0.65	138.95	0.42	188.93	0.37	295.91	0.42		
71.05	7.01	107.97	0.93	139.06	0.96	189.93	1.91	296.93	0.68		
71.99	0.28	108.07	0.48	139.93	0.51	190.92	0.42	299.87	0.90		

AB8X 3 A.BAYLIFF EI 34 22-JAN-85
CRL:CRLT31 STA: 0:34



MASS	%HT. BASE	MASS	%HT. BASE
26.30	14.56	156.99	5.43
27.23	5.86	168.93	2.07
28.11	50.99	175.99	2.24
30.86	3.27	180.89	1.81
31.97	9.30	184.98	2.58
37.09	5.25	185.95	0.78
38.03	23.43	186.98	3.53
38.96	8.27	188.94	75.71
39.80	2.76	189.92	7.15
40.94	4.05	192.94	4.05
43.10	9.56	193.97	0.95
49.87	20.76	194.96	1.81
50.94	29.89	203.95	4.65
52.02	62.96	204.94	5.43
53.04	6.80	205.94	2.33
53.07	3.19	206.95	2.33
54.08	2.93	212.95	2.76
60.95	1.98	224.95	2.41
62.01	10.59	225.94	3.01
63.06	56.50	234.94	8.53
64.09	77.17	238.88	1.81
65.10	4.91	242.90	8.35
68.93	84.07	252.93	8.44
74.03	4.39	253.96	15.50
75.05	7.58	254.94	3.10
76.05	5.25	262.95	11.02
79.89	24.72	263.94	1.46
80.96	1.55	272.93	3.10
83.04	5.25	274.93	2.33
88.00	1.46	284.92	2.15
90.95	2.41	292.88	16.45
91.99	27.73	293.93	1.64
92.99	5.25	302.92	10.77
95.05	18.17	303.94	2.33
96.99	2.84	312.94	7.58
107.03	1.64	331.93	15.59
110.97	2.67	332.92	2.33
116.99	2.93	350.89	15.85
118.94	8.70	351.94	2.07
130.94	2.07	352.92	1.81
136.99	2.41	362.94	1.55
138.00	2.33	400.87	100.00
138.95	23.86	401.91	14.99
139.94	1.72	402.95	1.64
142.97	6.46	450.86	2.84
145.02	2.07	469.85	24.55
154.97	5.60	470.88	4.05
156.00	1.38		

AB41X S A.BRAYLIFF EI 35 22-JAN-85
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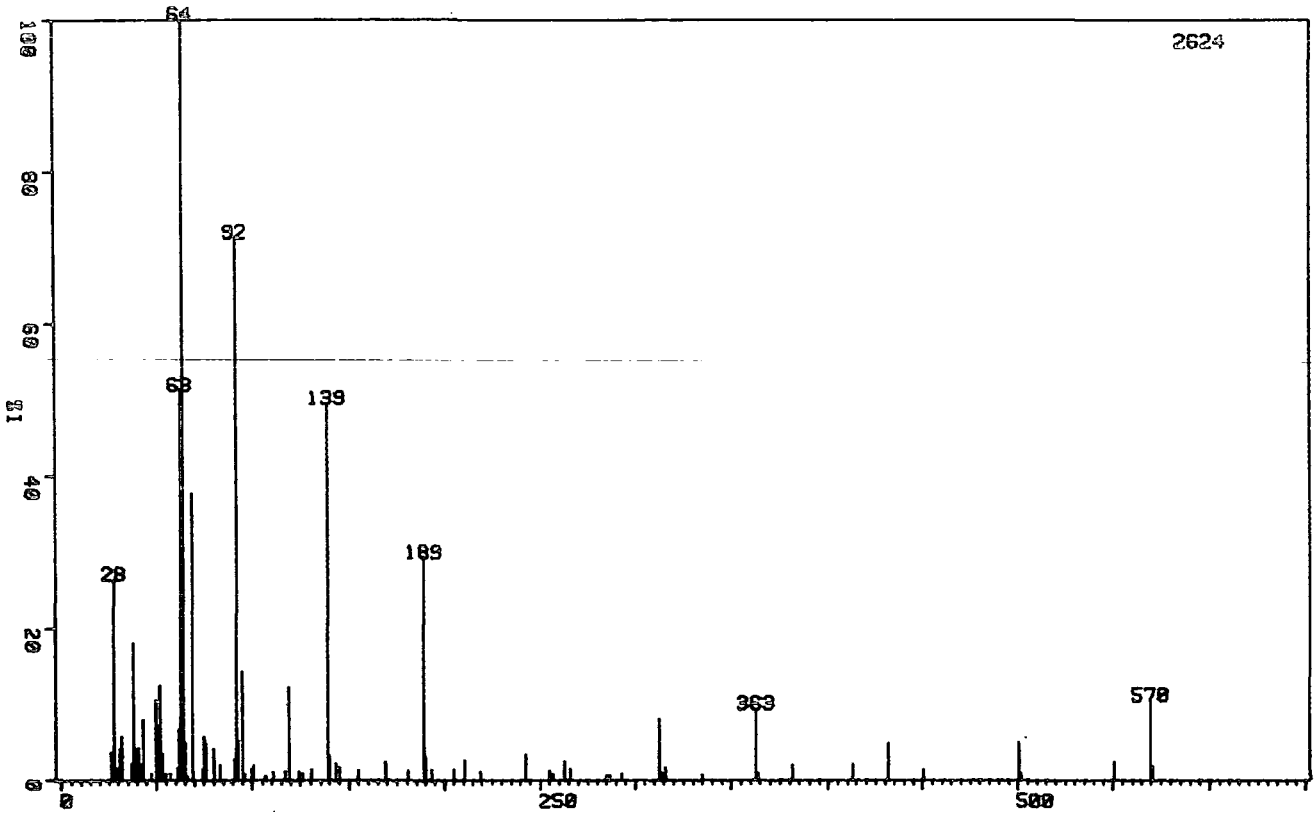
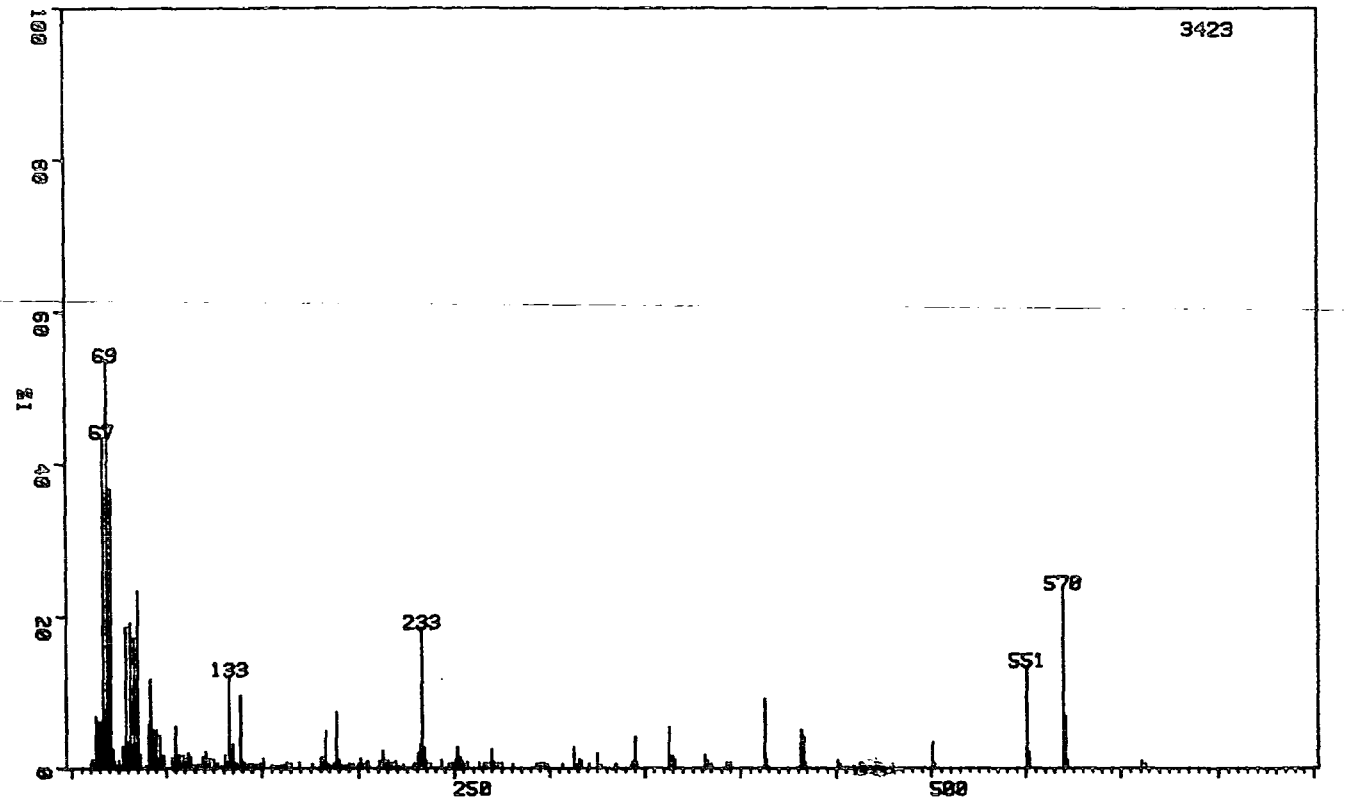


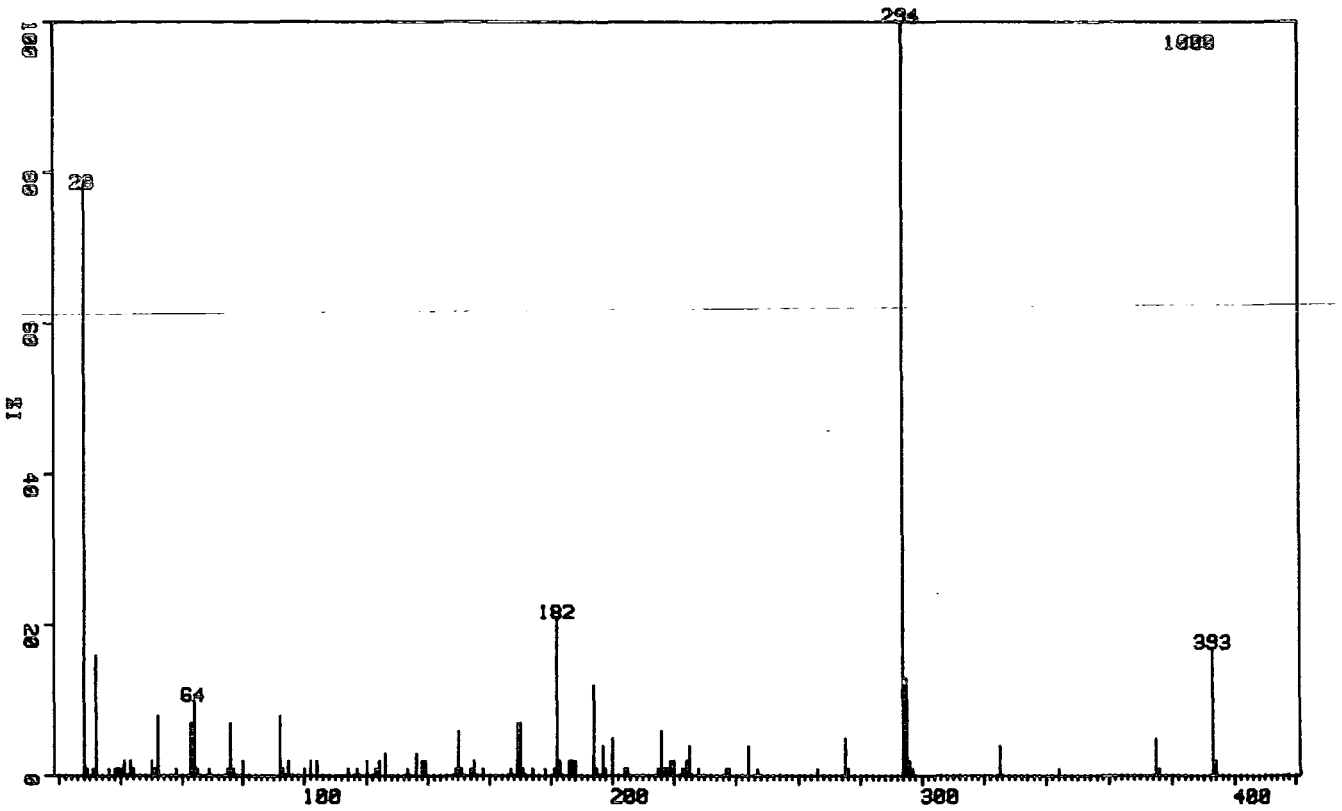
MASS	%HT. BASE	MASS	%HT. BASE
26.30	3.70	118.97	12.35
27.23	2.93	124.02	1.18
28.11	26.37	126.07	0.88
28.13	0.84	130.98	1.45
29.00	1.68	138.99	49.54
30.86	4.12	139.97	3.16
31.97	5.87	143.01	2.21
37.09	2.21	145.06	1.75
38.04	18.14	155.01	1.41
38.96	4.12	168.97	2.48
39.80	2.59	180.93	1.30
40.94	4.31	188.95	29.23
42.03	2.17	189.94	3.01
43.10	8.04	192.95	1.45
47.06	0.99	204.95	1.52
49.87	10.59	210.94	2.71
50.94	6.97	218.95	1.14
52.03	12.50	242.89	3.43
53.04	3.51	254.93	1.26
53.08	0.84	256.96	0.80
54.08	0.84	262.95	2.52
55.14	0.91	265.94	1.60
57.07	0.95	284.92	0.57
60.96	1.71	286.91	0.69
62.01	6.71	292.88	0.91
63.07	51.22	312.95	8.08
64.10	100.00	313.94	0.95
65.08	4.99	315.93	1.75
66.06	0.46	334.91	0.84
68.94	37.80	362.92	9.41
74.04	1.49	363.93	1.03
75.06	5.79	381.88	2.06
76.05	4.88	412.89	2.21
79.90	4.19	431.92	4.88
83.04	2.02	450.88	1.49
90.95	2.78	500.80	5.07
92.00	71.30	501.86	0.95
93.02	5.18	550.84	2.40
95.05	14.29	569.87	10.56
96.05	0.91	570.90	1.87
99.90	1.52		
100.97	1.98		
107.06	0.46		
111.00	1.11		

AB41X 10 A.BAYLIFF CI I-BU 36 22-JAN-85
CAL:CALT31 STA: 1:35



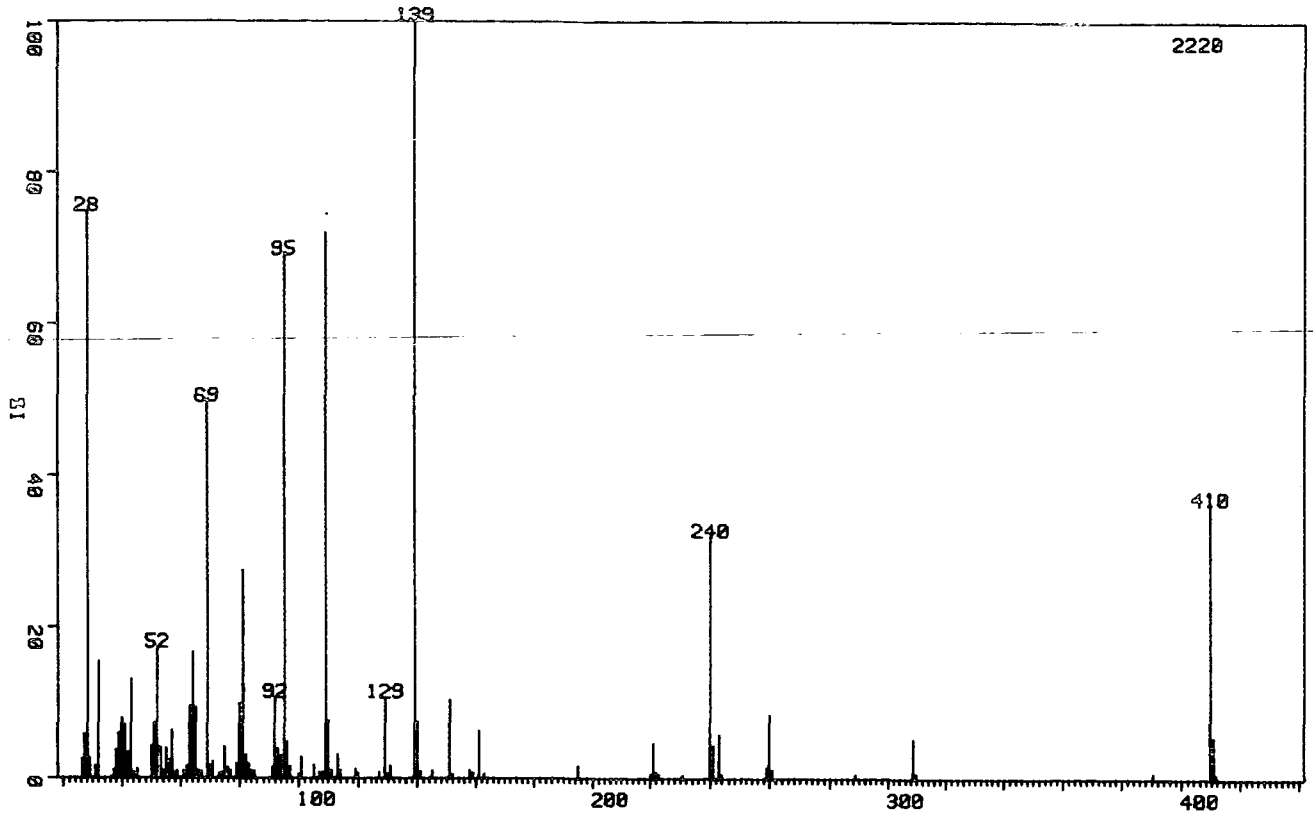
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE		
60.94	1.14	107.98	0.70	163.05	0.38	250.91	1.20	412.88	9.11
61.96	0.53	108.97	1.72	164.97	0.70	251.92	2.83	413.90	1.14
63.01	6.75	109.91	0.85	168.91	0.82	252.95	1.43	431.88	5.11
64.05	6.13	110.95	1.40	175.93	0.58	253.95	0.99	432.94	4.09
65.06	6.11	111.97	2.04	180.83	1.49	254.93	0.56	433.93	0.79
66.06	5.61	112.96	1.55	181.91	0.99	256.94	0.88	450.89	1.08
67.05	43.44	113.07	0.61	182.94	4.91	262.92	0.73	451.87	0.44
68.02	6.43	115.01	0.50	183.96	0.44	265.94	0.53	458.88	0.26
68.98	53.55	117.01	0.44	184.94	0.38	266.92	0.67	462.87	0.76
69.92	16.39	118.92	1.55	186.95	0.50	268.93	0.64	472.91	0.38
70.89	0.35	119.89	0.47	188.90	7.45	269.90	2.54	500.79	3.39
70.98	36.75	119.94	0.35	189.90	1.17	270.91	0.79	501.91	0.56
72.03	2.48	120.94	2.19	190.96	0.38	272.96	0.58	550.71	13.41
73.03	1.02	121.99	0.41	192.91	0.38	274.93	0.85	551.79	2.10
74.04	0.47	123.01	1.31	194.95	0.64	280.88	0.56	569.81	23.61
75.04	1.08	124.97	1.20	196.94	0.50	292.93	0.50	570.88	6.89
76.03	0.38	125.08	0.32	199.89	0.58	294.94	0.67	571.95	1.14
77.00	2.95	125.99	0.44	200.93	1.26	296.94	0.58	610.86	0.99
77.98	1.72	126.97	0.56	201.96	0.38	298.89	0.47	612.94	0.58
78.94	18.58	128.96	0.35	203.95	0.73	306.91	0.56		
79.89	3.51	130.92	1.81	204.95	1.02	312.89	2.83		
80.96	19.19	131.95	0.96	210.90	0.96	313.94	0.50		
82.02	3.01	132.97	12.27	212.91	2.31	315.93	1.17		
83.05	17.09	133.99	1.78	213.93	0.44	316.93	1.05		
84.08	3.18	135.01	3.21	214.96	1.14	320.89	0.70		
85.09	23.37	135.99	0.85	215.96	0.32	324.97	1.96		
86.09	1.90	136.94	0.35	216.95	0.73	327.02	0.35		
88.94	0.35	137.02	0.67	218.92	0.96	334.96	0.67		
90.93	5.87	138.89	9.64	220.89	0.29	342.93	0.41		
91.95	11.71	139.88	0.99	222.94	0.38	343.92	0.79		
92.99	5.11	140.95	0.73	227.93	0.29	344.91	4.18		
94.03	1.26	142.97	0.56	228.91	0.53	345.93	0.91		
95.05	5.02	145.01	0.64	230.85	1.99	362.87	5.40		
96.05	1.31	146.06	0.32	231.90	3.21	363.92	0.88		
97.04	4.41	147.00	0.41	232.92	18.46	364.93	1.64		
98.03	1.11	148.98	0.56	233.93	2.72	365.94	1.17		
99.00	1.67	150.94	1.23	234.95	0.99	381.85	1.81		
102.99	1.49	154.93	0.29	236.93	0.58	382.92	1.02		
103.98	0.41	156.98	0.29	242.89	1.14	384.94	0.50		
105.03	5.64	158.99	0.35	246.91	0.53	392.91	0.82		
106.04	0.85	160.93	0.41	248.90	0.73	393.89	0.38		
107.01	1.84	162.93	0.82	249.87	0.56	394.91	0.85		

ABCPDS 0 A.BAYLIFF EI 37 21-AUG-86
CAL:LIB STA: 0:0



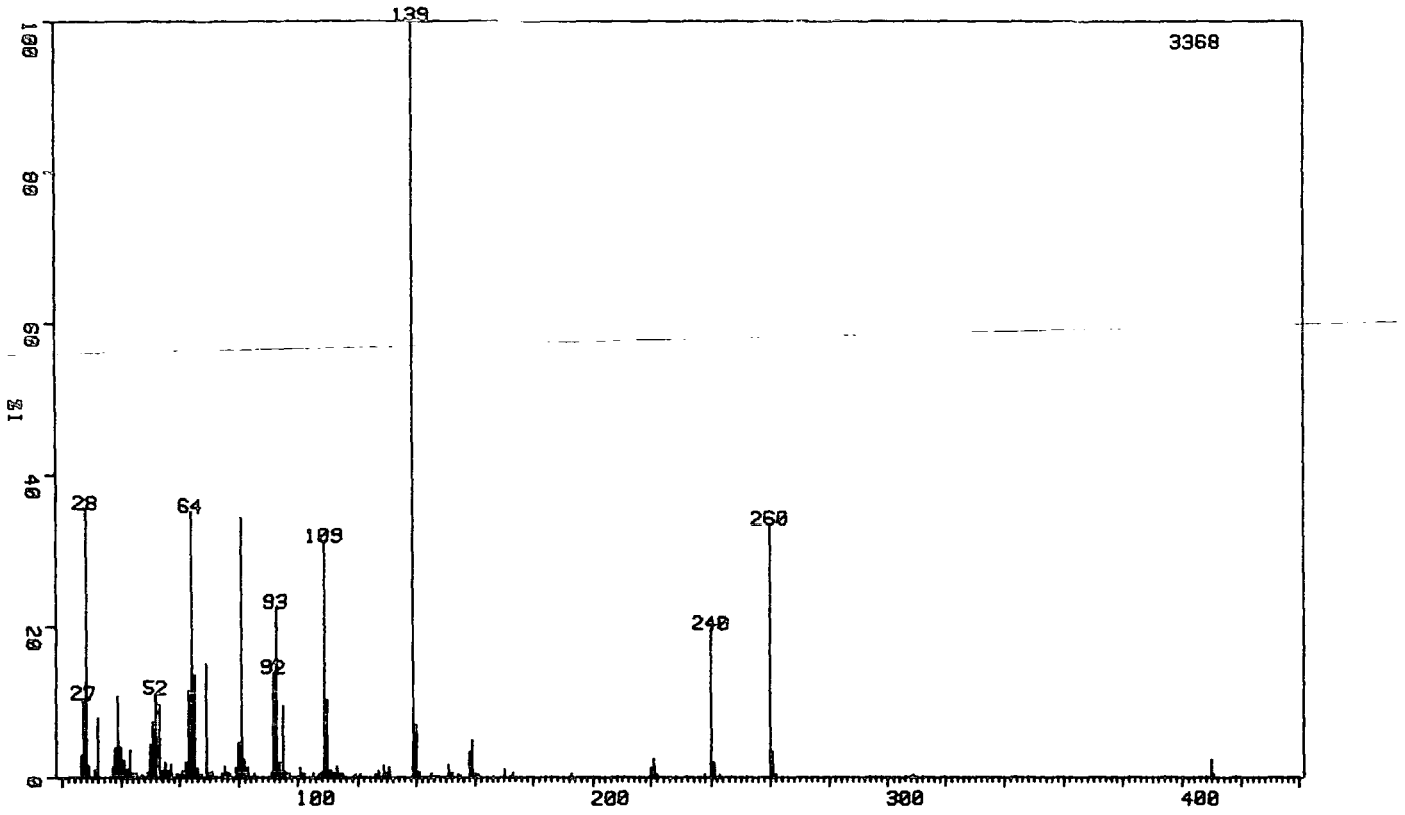
PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	26.24	0.46	36	126.00	2.90	71	227.90	0.86
2	28.06	78.13	37	132.92	0.56	72	236.91	0.66
3	28.94	1.02	38	135.91	3.41	73	237.86	0.61
4	30.84	1.17	39	137.90	2.24	74	243.90	4.53
5	31.94	16.48	40	138.88	2.14	75	246.88	1.17
6	36.09	0.71	41	148.86	0.66	76	265.81	0.97
7	38.03	1.27	42	149.85	5.65	77	274.85	5.34
8	38.95	1.32	43	150.93	0.92	78	275.86	0.66
9	39.82	1.17	44	153.94	0.86	79	293.78	100.00
10	40.92	2.34	45	154.94	1.98	80	294.75	13.73
11	43.06	1.58	46	157.95	0.86	81	295.85	1.63
12	44.07	0.76	47	166.89	0.97	82	296.84	0.76
13	49.86	1.78	48	168.89	7.63	83	324.73	3.51
14	50.92	1.37	49	169.89	6.92	84	343.71	1.27
15	52.00	8.19	50	170.95	0.76	85	374.54	5.14
16	58.03	0.51	51	173.94	0.61	86	375.54	0.61
17	63.01	7.07	52	177.97	0.86	87	393.48	16.94
18	64.05	10.17	53	180.96	0.66	88	394.46	2.70
19	65.06	0.76	54	181.92	20.65			
20	68.91	0.97	55	182.95	2.19			
21	74.99	1.12	56	185.91	1.98			
22	75.98	6.92	57	186.94	1.73			
23	76.96	0.61	58	187.90	1.68			
24	79.80	2.39	59	193.87	11.95			
25	91.93	8.39	60	194.92	1.37			
26	92.95	0.71	61	196.89	4.17			
27	94.98	1.63	62	197.90	0.66			
28	99.84	0.81	63	199.87	4.53			
29	101.93	1.07	64	203.92	0.76			
30	103.99	1.73	65	204.89	1.32			
31	113.94	1.27	66	215.91	6.36			
32	116.90	1.17	67	216.93	1.42			
33	119.86	2.03	68	217.91	1.12			
34	122.97	0.92	69	218.89	1.78			
35	123.96	2.29	70	224.91	3.76			

AB762X 3 A.BAYLIFF 38 04-JUN-85
CAL:CALT1 STA: 0:33



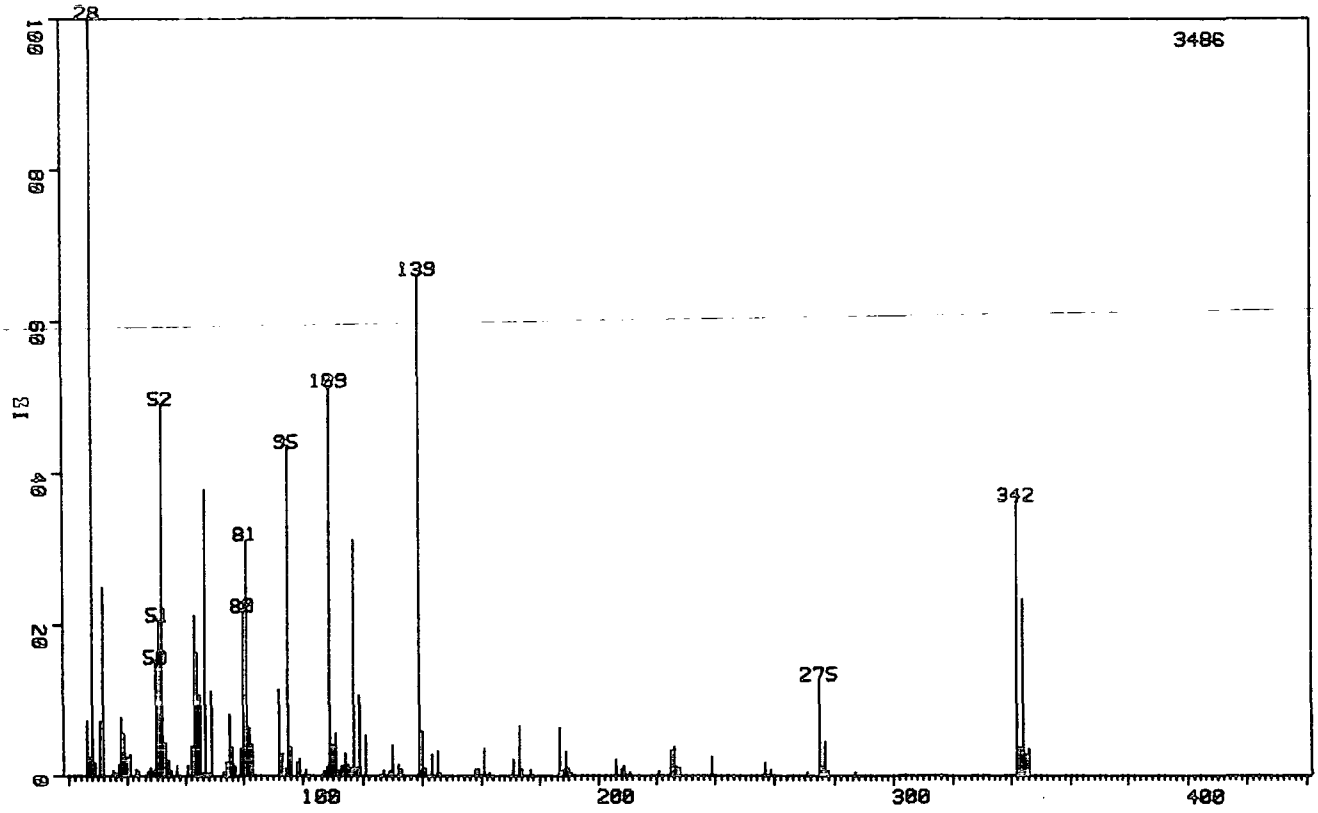
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.37	2.57	61.98	1.53	105.06	1.80	258.84	1.44
27.30	5.81	63.02	9.50	106.98	0.86	259.83	8.47
28.17	74.91	64.06	16.71	107.97	0.81	260.84	1.17
28.19	0.68	65.07	9.37	108.93	72.03	288.76	0.50
29.02	1.26	66.07	0.95	109.89	7.70	308.72	5.27
29.05	2.66	67.06	0.90	110.94	1.04	309.75	0.72
30.94	1.62	68.91	49.73	112.97	3.20	390.55	0.81
32.02	15.45	68.98	3.29	113.99	1.08	409.54	36.40
37.12	1.13	69.86	0.50	118.97	1.26	410.51	5.54
38.06	3.74	69.93	1.67	119.94	0.72	411.54	0.63
38.98	5.99	70.98	2.21	126.96	0.81		
39.81	7.97	73.01	0.59	128.87	10.72		
39.87	0.86	73.03	0.45	129.88	0.59		
40.96	7.07	74.02	0.72	130.91	1.71		
42.01	0.59	75.04	4.14	138.94	100.00		
42.05	3.42	76.04	1.40	139.92	7.43		
43.08	1.40	77.03	0.99	140.93	0.95		
43.12	13.11	78.93	1.94	144.99	1.04		
44.08	0.72	79.89	9.86	150.89	10.50		
44.15	0.72	80.97	27.52	151.96	0.50		
45.14	1.26	82.00	3.11	157.95	1.08		
49.87	4.23	83.03	1.22	158.94	0.77		
50.93	7.34	83.09	1.94	160.92	6.31		
52.01	17.30	84.11	1.04	162.96	0.63		
53.05	4.01	85.10	0.95	194.89	1.71		
54.06	0.95	90.94	1.53	219.82	0.54		
54.10	0.63	91.96	10.77	220.86	4.73		
55.09	1.13	92.99	3.96	221.63	0.41		
55.12	3.96	94.01	3.06	221.89	0.86		
56.12	2.43	95.01	69.14	222.94	0.50		
57.04	0.54	96.01	4.86	230.88	0.41		
57.10	6.31	96.07	0.59	239.87	32.03		
58.02	0.72	97.06	1.58	240.87	4.37		
58.97	0.95	99.85	0.50	242.88	5.86		
60.92	0.95	100.90	2.93	243.89	0.63		

AB761X 3 A.BAYLIFF 39 04-JUN-85
CAL:CALT1 STA: 0:33



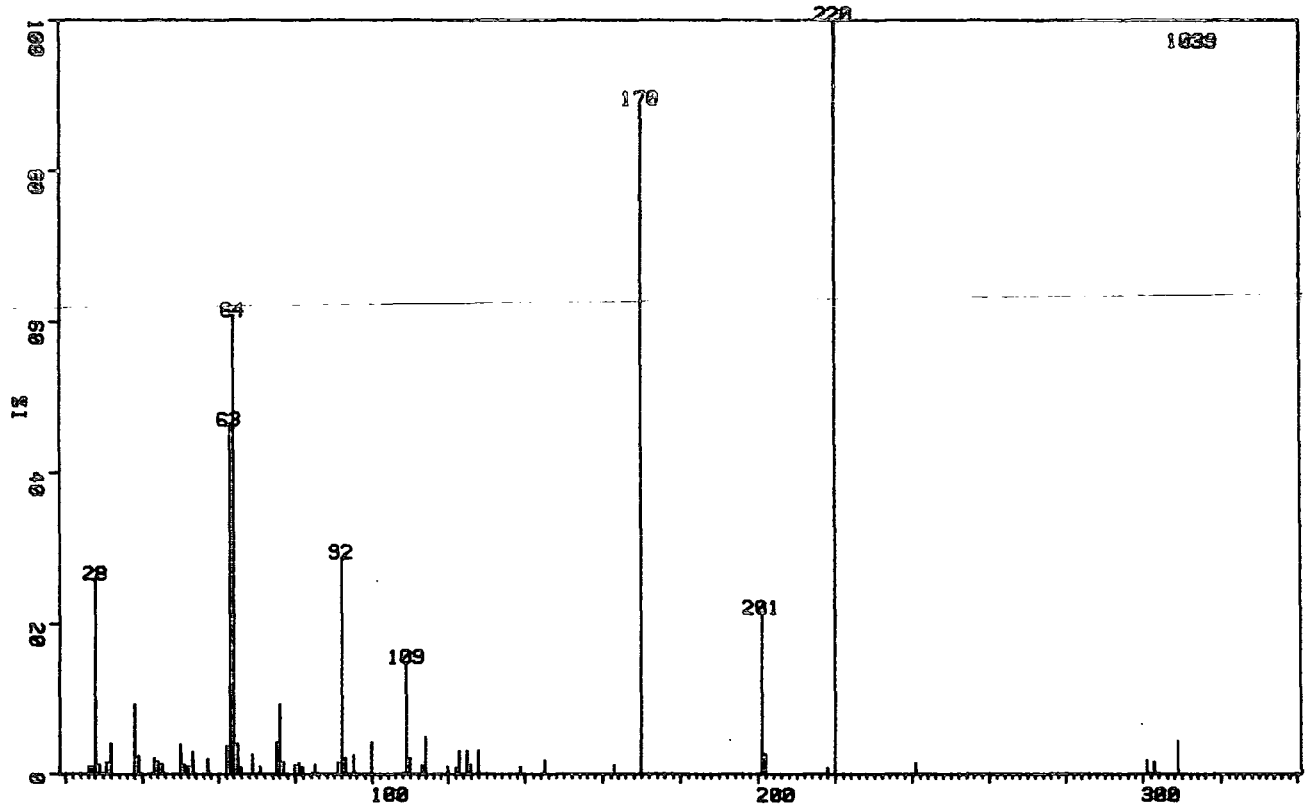
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.37	2.97	63.04	11.49	108.94	31.24	239.89	19.69
27.30	10.48	64.07	35.15	109.91	10.27	240.91	2.05
28.17	35.60	65.09	13.54	110.93	0.98	242.94	0.45
28.19	0.45	66.07	1.22	111.96	0.45	259.89	33.52
29.02	1.57	67.08	0.33	112.95	1.48	260.92	3.47
29.05	1.04	68.93	15.17	113.98	0.39	261.94	0.33
30.93	1.07	69.00	1.19	114.99	0.50	308.81	0.33
32.03	7.96	69.95	0.62	118.96	0.42	409.61	2.38
37.13	1.43	71.01	0.80	120.88	0.45	410.59	0.39
38.07	3.95	74.04	0.56	125.96	0.45		
38.98	10.87	75.06	1.51	126.95	0.89		
39.82	4.07	76.06	0.68	128.87	1.63		
39.87	0.92	77.02	0.27	129.89	0.68		
40.96	2.32	77.05	0.50	130.91	1.40		
42.02	0.56	78.96	1.31	138.93	100.00		
42.06	1.10	79.43	0.36	139.92	7.01		
43.08	0.59	79.91	4.60	140.93	0.74		
43.12	3.65	80.96	34.41	144.99	0.50		
44.09	0.68	81.99	2.43	150.90	1.69		
45.15	0.68	83.03	1.37	151.97	0.53		
47.06	0.36	83.09	0.80	154.00	0.42		
48.96	0.65	85.12	0.42	155.00	0.33		
49.88	4.42	90.94	0.56	157.97	3.36		
50.94	7.33	91.99	13.93	158.95	4.99		
52.02	11.16	93.02	22.57	159.94	0.45		
53.06	9.65	94.04	2.05	160.93	0.39		
54.09	0.98	95.04	9.50	169.89	1.10		
55.11	2.11	95.10	0.30	172.98	0.56		
56.13	1.04	96.04	0.77	192.95	0.50		
57.06	0.98	97.10	0.50	219.84	1.25		
57.11	1.84	100.93	1.31	220.89	2.46		
58.99	0.39	101.99	0.45	221.28	0.27		
59.87	0.33	105.06	0.56	221.39	0.27		
60.93	0.89	107.00	0.42	221.95	0.33		
61.99	2.05	107.98	0.68	237.92	0.45		

AB172X 6 A.BAYLIFF EI 40 01-NOV-85
CAL:CRLP1S STR: 1:1



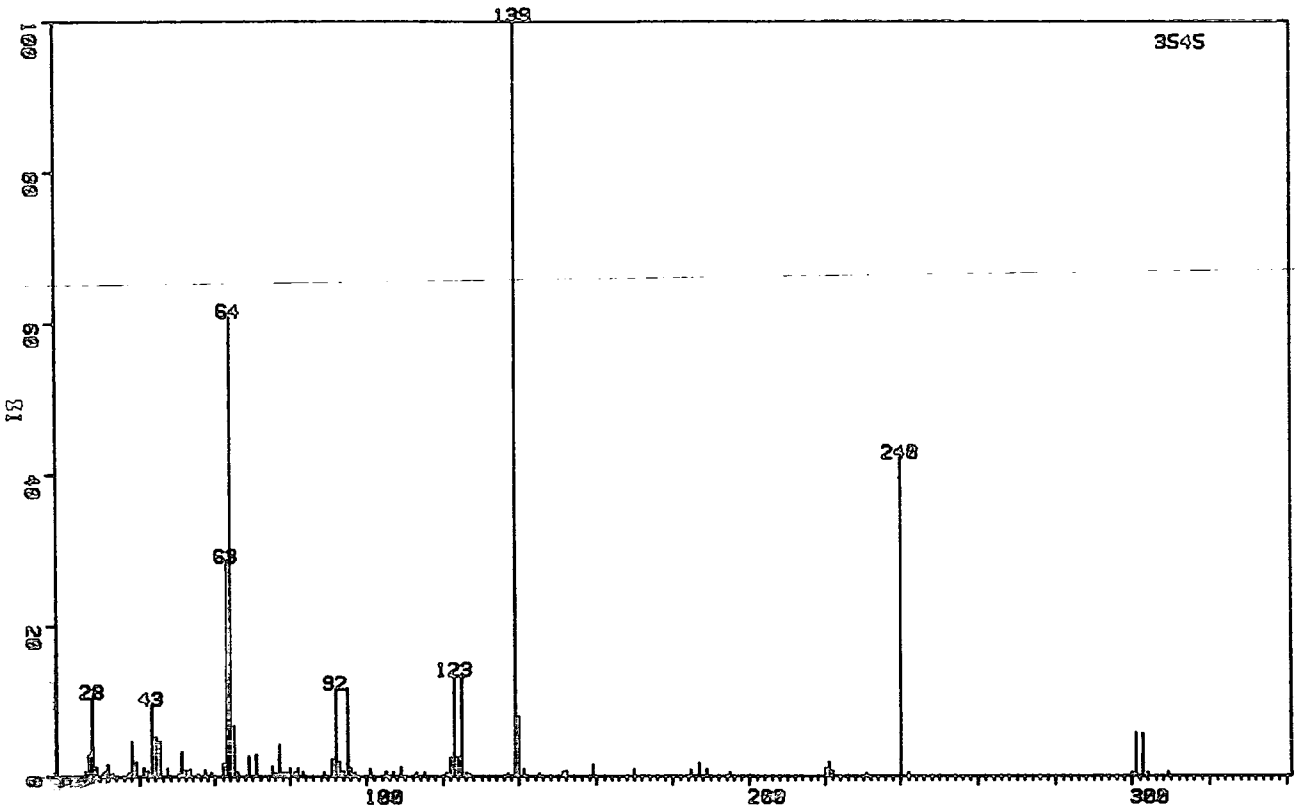
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.28.	7.31	76.07	3.82	162.96	0.40
27.22	2.50	77.06	1.41	170.93	2.21
28.10	100.00	78.96	3.70	172.96	6.63
28.95	1.72	79.92	21.72	173.99	0.95
30.85	7.26	80.97	31.18	176.96	0.80
31.96	25.04	81.99	6.31	186.92	6.45
35.09	0.77	83.04	4.19	187.92	0.72
36.09	0.32	91.99	11.47	188.90	3.30
37.08	1.55	93.03	2.75	189.90	1.06
38.03	7.77	94.05	0.95	190.93	0.32
38.96	5.62	95.04	43.34	205.95	2.15
39.79	2.50	96.04	3.82	207.94	0.86
39.85	1.69	97.95	1.75	208.93	1.29
40.93	2.81	98.94	2.35	210.92	0.43
43.10	0.86	100.92	0.89	220.94	0.66
44.08	0.66	107.01	0.66	224.93	3.38
47.03	0.63	107.99	1.20	225.95	3.79
47.06	0.57	108.97	51.41	226.92	1.23
47.99	1.09	109.93	4.07	227.91	1.12
48.95	0.66	110.95	5.65	238.92	2.55
49.84	0.49	111.98	0.75	256.90	1.75
49.88	14.95	112.99	1.32	258.90	0.80
50.94	20.51	114.01	2.95	270.92	0.46
52.02	49.02	115.03	1.43	274.89	12.68
53.04	4.25	115.95	1.06	275.92	1.18
53.08	4.36	116.94	31.18	276.92	4.53
54.08	2.12	117.92	1.09	277.92	0.72
55.10	0.75	118.89	10.67	286.93	0.49
57.06	1.41	120.97	5.39	341.82	36.32
57.11	0.55	127.01	0.75	342.89	3.73
60.94	1.46	128.95	0.60	343.91	23.38
62.00	4.02	129.92	4.13	344.93	2.81
63.05	21.31	131.96	1.52	345.92	3.61
64.08	16.29	133.01	0.89		
65.07	0.49	138.97	66.09		
65.10	10.76	139.93	5.88		
66.10	0.40	140.96	1.03		
67.01	37.87	143.01	2.84		
67.98	0.40	145.01	3.30		
68.92	11.24	146.01	0.29		
73.02	0.40	157.96	0.92		
74.06	1.86	158.93	0.95		
75.07	8.23	160.93	3.59		

AB130 110 A.BAYLIFF EX130 41 18-JUN-85
CAL:CALH30 STA: 18:3



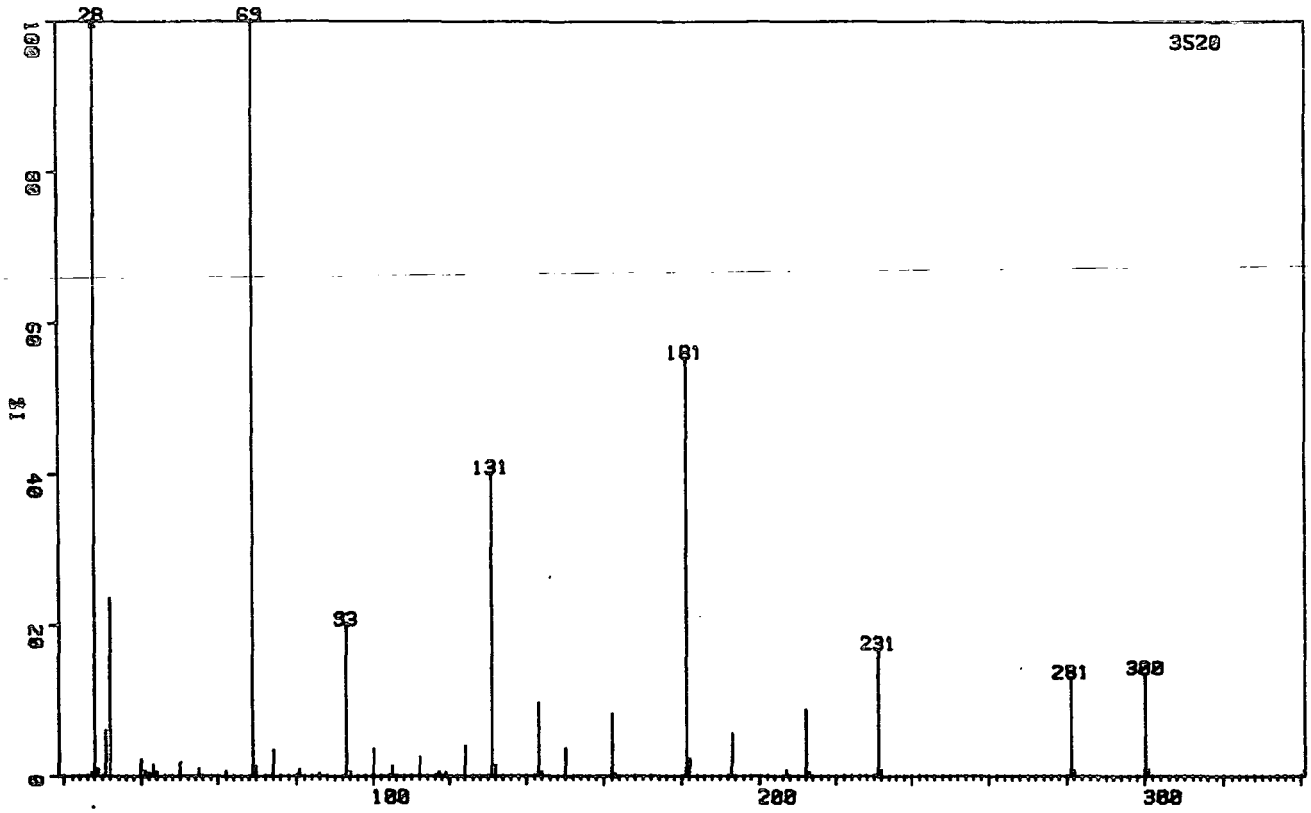
MASS	%HT. BASE	MASS	%HT. BASE
26.31	1.06	99.90	4.23
27.25	0.96	108.95	14.82
28.13	25.89	109.92	2.12
29.02	1.25	113.03	1.15
30.92	1.54	114.06	5.00
32.02	4.14	119.91	1.06
38.09	9.34	121.95	0.87
39.01	2.41	122.98	3.18
43.13	2.21	125.00	3.18
44.15	1.64	126.07	1.35
45.19	1.35	127.99	3.18
49.90	3.95	138.97	0.96
50.99	1.25	145.08	1.92
52.06	1.06	163.03	1.25
53.08	2.98	170.03	88.84
57.15	2.02	200.97	21.37
62.06	3.85	201.98	2.69
63.10	46.29	217.97	0.87
63.29	0.77	220.08	100.00
64.05	60.83	241.00	1.54
65.07	4.04	300.99	1.83
66.05	0.87	303.03	1.64
68.93	2.60	309.00	4.43
70.99	1.06		
75.06	4.23		
76.06	9.34		
77.04	1.64		
79.82	1.25		
80.96	1.54		
81.94	0.96		
85.10	1.25		
90.99	1.54		
92.04	28.78		
93.05	2.21		
95.07	2.60		

AB130 74 A.BAYLIFF EX130 42 18-JUN-85
CRL:CRLM30 STA: 12:12



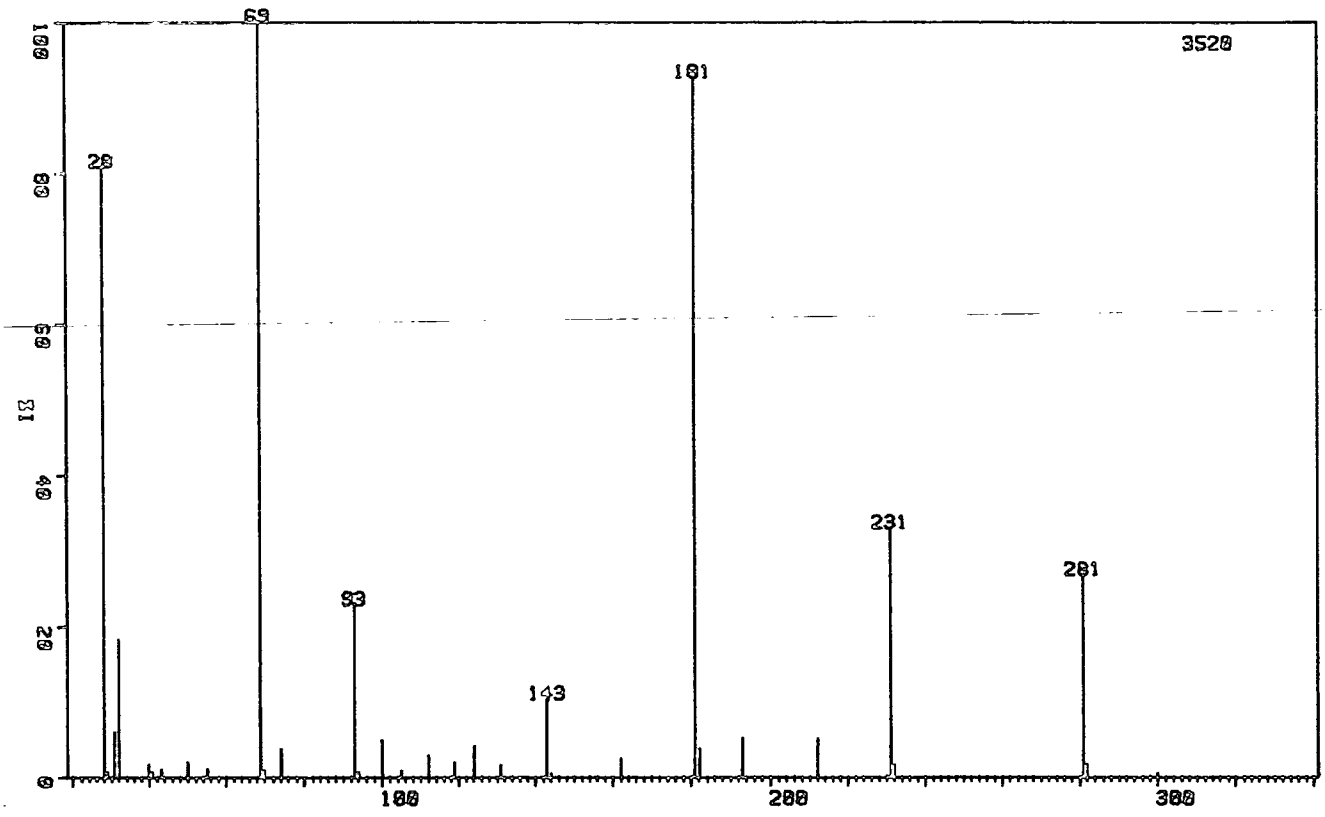
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.31	0.56	79.83	1.07	186.91	1.75
27.25	2.79	80.92	0.39	188.91	0.99
28.13	10.49	81.96	1.10	195.06	0.37
29.00	1.21	83.10	0.62	219.99	1.04
30.92	0.39	89.00	0.54	221.06	1.89
32.01	1.61	90.99	2.28	222.08	0.76
33.11	0.31	92.02	11.59	230.98	0.34
37.13	0.42	93.05	1.86	240.07	42.17
38.08	4.71	94.01	0.68	242.01	0.48
39.00	1.86	95.07	11.76	300.03	0.48
40.99	1.16	96.04	1.10	301.00	5.78
42.04	0.65	97.04	0.48	302.89	5.70
43.11	9.51	100.96	1.02	304.09	0.39
44.15	5.25	104.96	0.65	309.09	0.59
45.17	4.68	106.95	0.62		
47.12	1.10	108.96	1.24		
49.90	0.28	112.99	0.48		
50.95	3.24	115.04	0.54		
52.05	0.79	120.93	0.37		
53.08	0.96	121.92	2.48		
55.16	0.28	122.95	13.37		
57.14	0.87	123.96	2.51		
59.01	0.42	124.95	13.00		
62.04	1.69	125.98	0.42		
63.09	28.43	127.02	0.28		
64.13	60.90	137.05	0.31		
65.10	6.69	138.98	100.00		
66.06	0.56	139.82	7.90		
68.93	2.68	141.03	0.96		
70.97	2.99	145.09	0.34		
75.07	1.38	151.02	0.54		
76.06	0.34	152.07	0.76		
77.04	4.23	159.04	1.55		
78.02	0.48	170.00	0.93		
78.88	0.39	184.92	0.87		

AB501X 4 A.BAYLIFF E.I. 43 16-JUL-78
CAL:CALT9 STA: 0:36

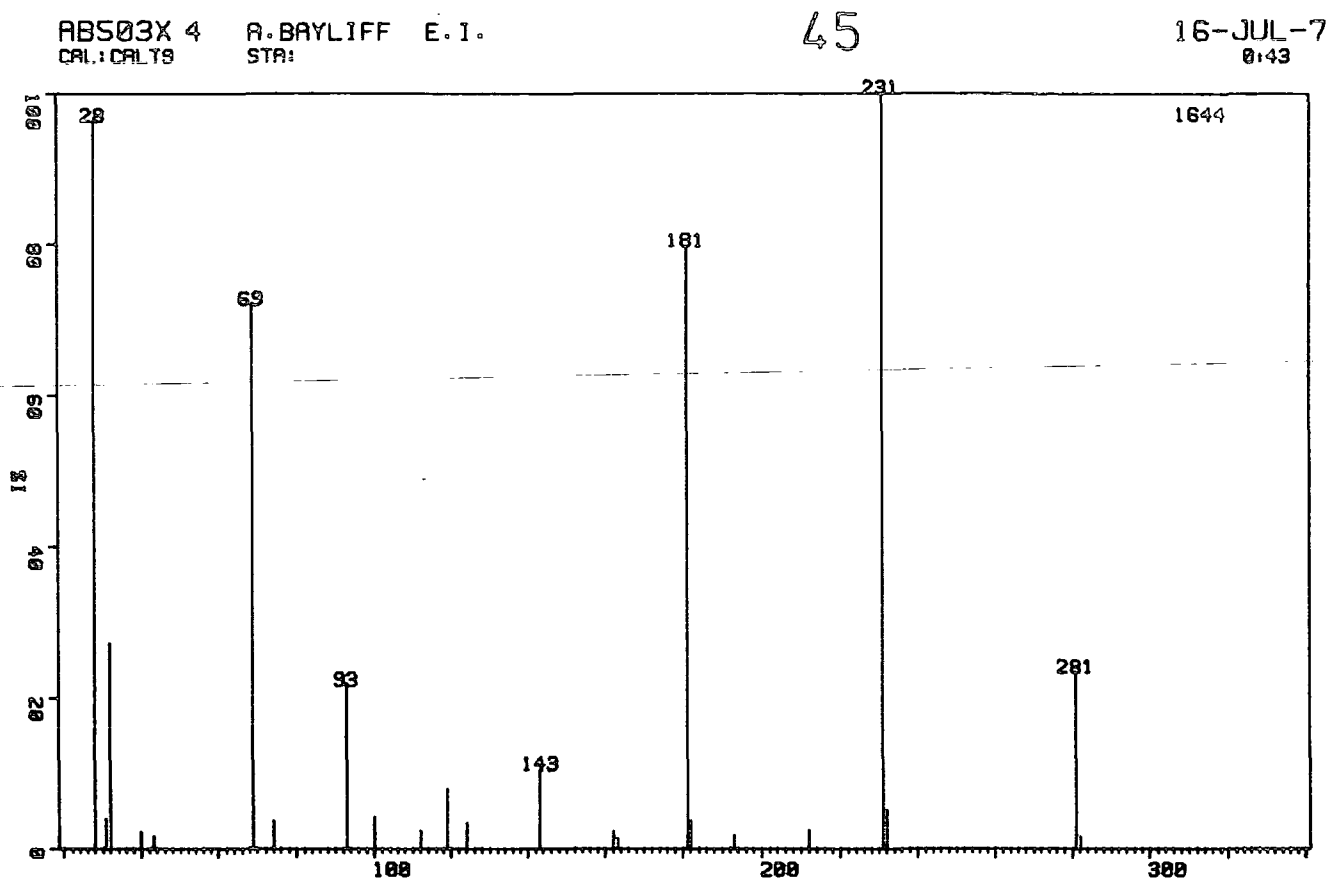


MASS	%HT. BASE	MASS	%HT. BASE
27.23	0.42	181.05	54.71
28.10	100.00	182.09	2.30
28.96	0.93	193.08	5.65
30.86	6.04	207.14	0.81
31.97	23.35	212.04	8.65
39.80	2.22	213.06	0.56
40.95	0.67	231.04	16.63
42.04	0.42	232.06	0.87
43.11	1.49	281.09	12.87
44.08	0.51	282.10	0.76
49.87	1.77	300.09	13.46
55.11	1.04	301.11	0.81
62.03	0.70		
69.00	98.90		
69.95	1.26		
74.11	3.46		
80.99	0.98		
86.10	0.42		
93.07	19.92		
94.10	0.65		
99.95	3.57		
105.07	1.32		
112.03	2.47		
117.04	0.45		
119.00	0.53		
124.06	3.99		
131.01	39.67		
132.04	1.32		
143.07	9.64		
144.08	0.37		
150.01	3.65		
162.06	8.15		
163.08	0.34		

AB502X 3 A.BAYLIFF E.I. 44 16-JUL-78
CRL:CRLT9 STR: 0:35

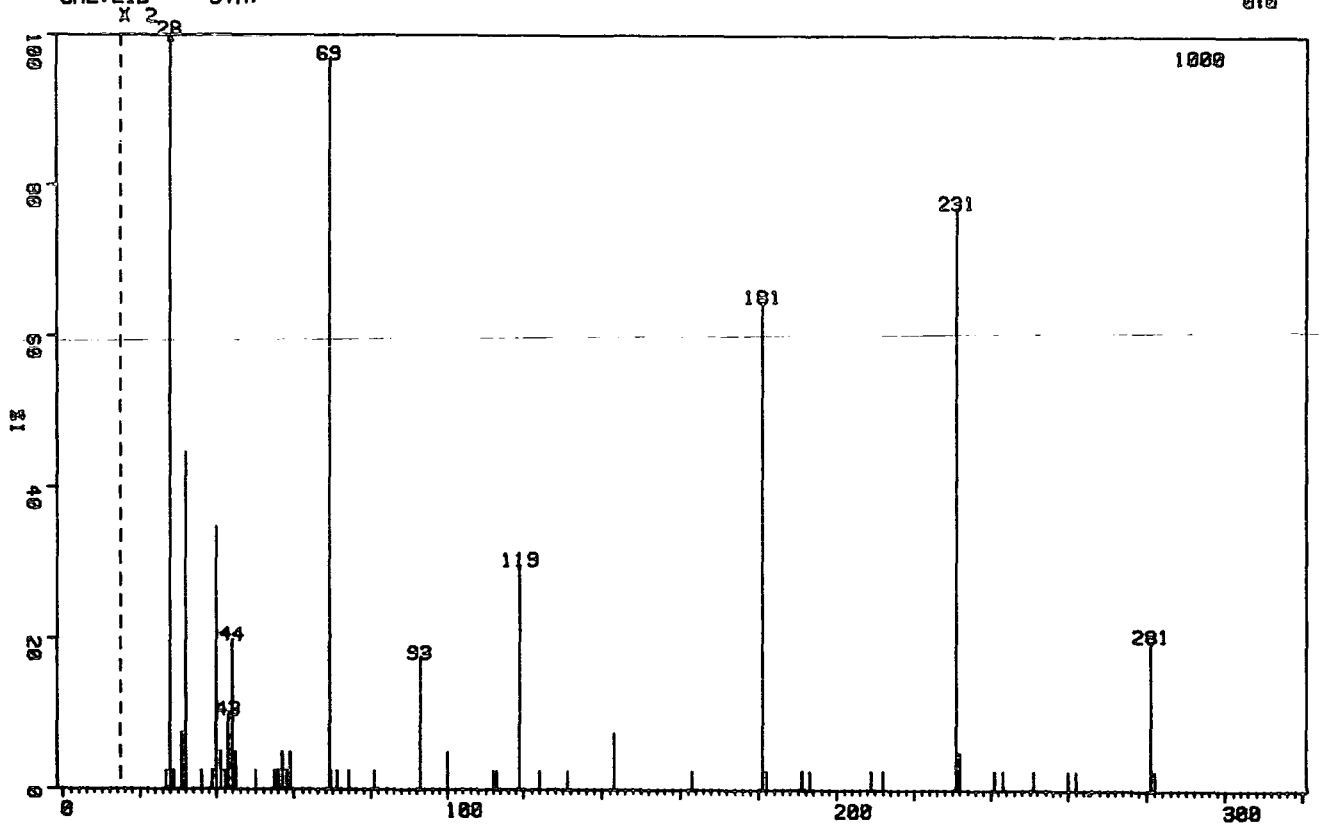


MASS	%HT. BASE
28.10	80.91
28.96	0.65
30.86	6.11
31.97	18.38
39.80	1.73
40.94	0.65
43.11	1.14
49.87	2.05
55.10	1.16
68.99	100.00
69.93	0.97
74.09	3.84
93.08	22.98
94.10	0.77
99.96	5.00
105.07	0.94
112.03	2.93
118.99	2.02
124.05	4.15
131.00	1.68
143.05	10.43
144.07	0.45
162.04	2.44
181.02	92.70
182.04	3.81
193.04	5.26
212.04	5.20
231.01	33.04
232.03	1.65
281.04	26.79
282.05	1.76
300.06	0.54



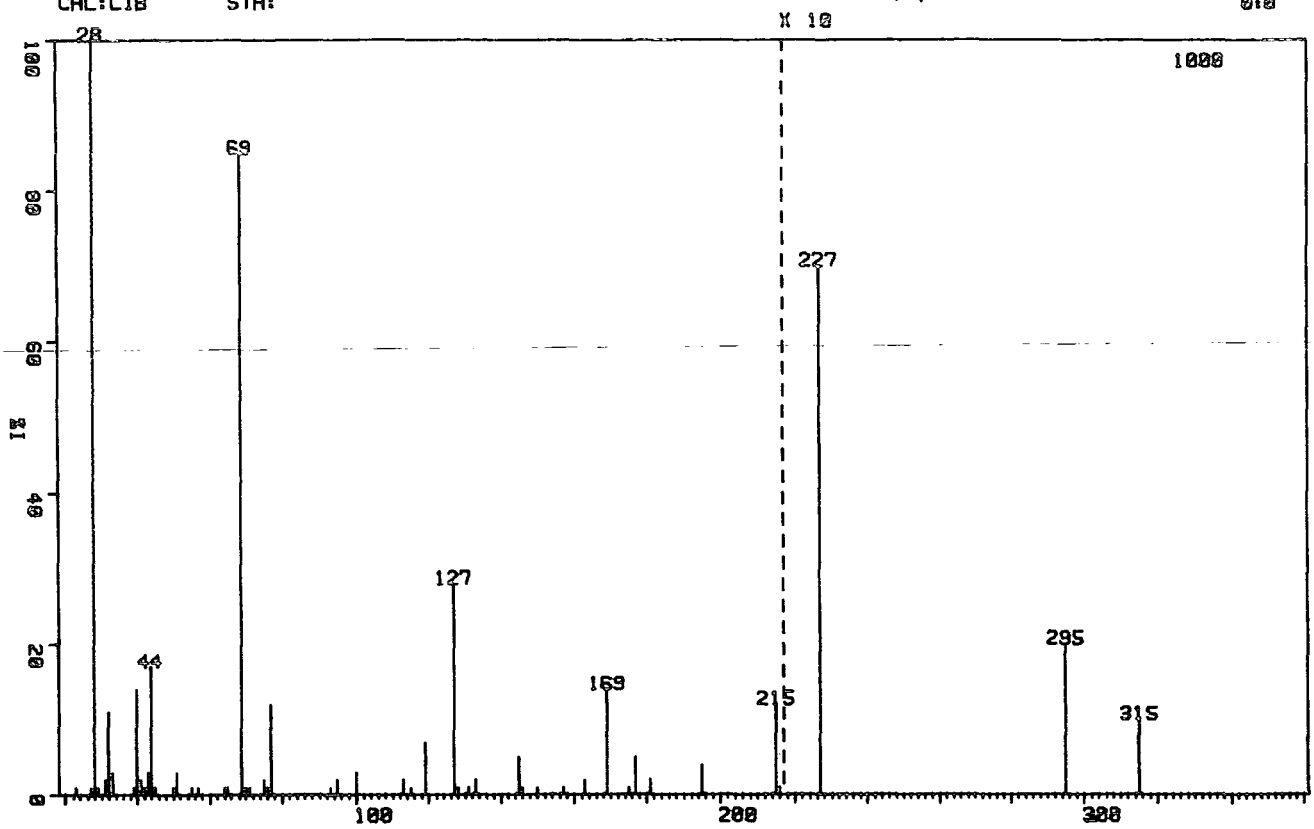
MASS	%HT. BASE
28.10	96.29
30.86	3.95
31.97	27.25
39.80	2.25
43.11	1.58
68.99	72.02
74.09	3.77
93.09	21.65
99.98	4.26
112.06	2.37
119.03	7.97
124.09	3.41
143.09	10.52
162.08	2.31
163.10	1.40
181.04	79.74
182.06	3.65
193.07	1.82
212.06	2.43
231.04	100.00
232.05	5.17
281.07	23.30
282.08	1.64

AB78 0 A.BAYLIFF EI 46 21-AUG-86
CAL:LIB STA: 0:0



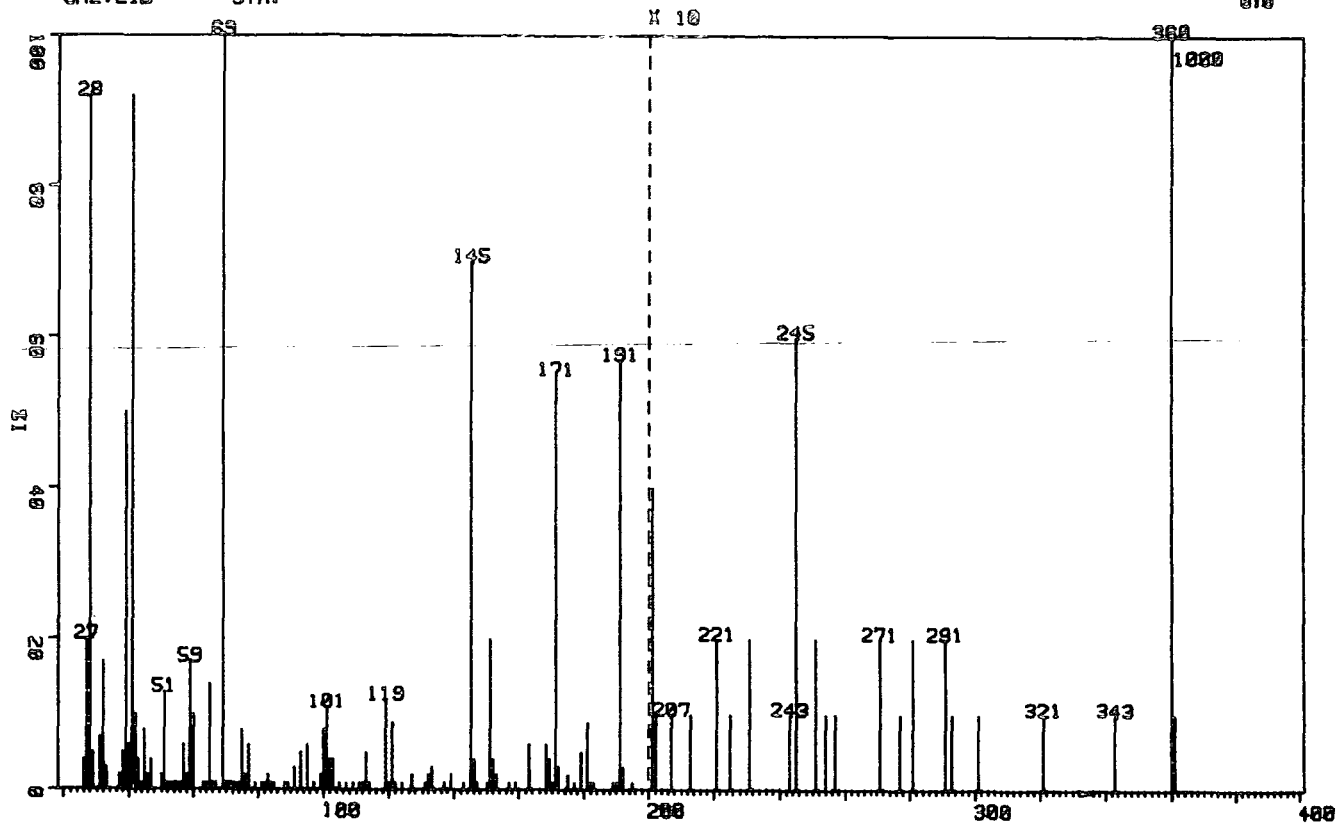
MASS	%HT. BASE	MASS	%HT. BASE
27.30	1.24	119.00	12.18
28.17	100.00	124.05	1.07
28.19	0.54	130.99	0.54
29.02	1.24	143.05	2.76
29.06	1.41	162.04	0.73
30.93	2.82	163.07	0.96
30.95	1.38	181.02	25.68
32.03	18.27	182.03	1.27
36.15	0.65	190.95	1.35
39.00	0.68	192.98	1.38
39.83	13.96	193.06	0.65
40.98	1.83	209.03	0.59
42.07	0.93	212.04	0.54
43.10	0.73	231.04	31.41
43.14	4.06	232.05	1.75
44.11	7.58	240.94	0.59
45.17	2.09	242.99	0.54
49.88	0.73	251.05	0.37
55.11	0.42	259.95	1.18
55.16	0.99	261.98	1.18
56.16	0.68	281.04	7.64
57.14	1.78	282.08	0.51
58.08	0.70		
59.02	1.95		
68.98	38.77		
69.05	0.76		
71.06	0.82		
74.08	1.27		
81.00	0.65		
83.16	0.45		
85.20	0.45		
93.08	7.41		
99.98	1.55		
112.04	1.18		
113.06	1.04		

AB115 0 A.BAYLIFF EI 47 21-AUG-86
CAL:LIB STA: 0:0



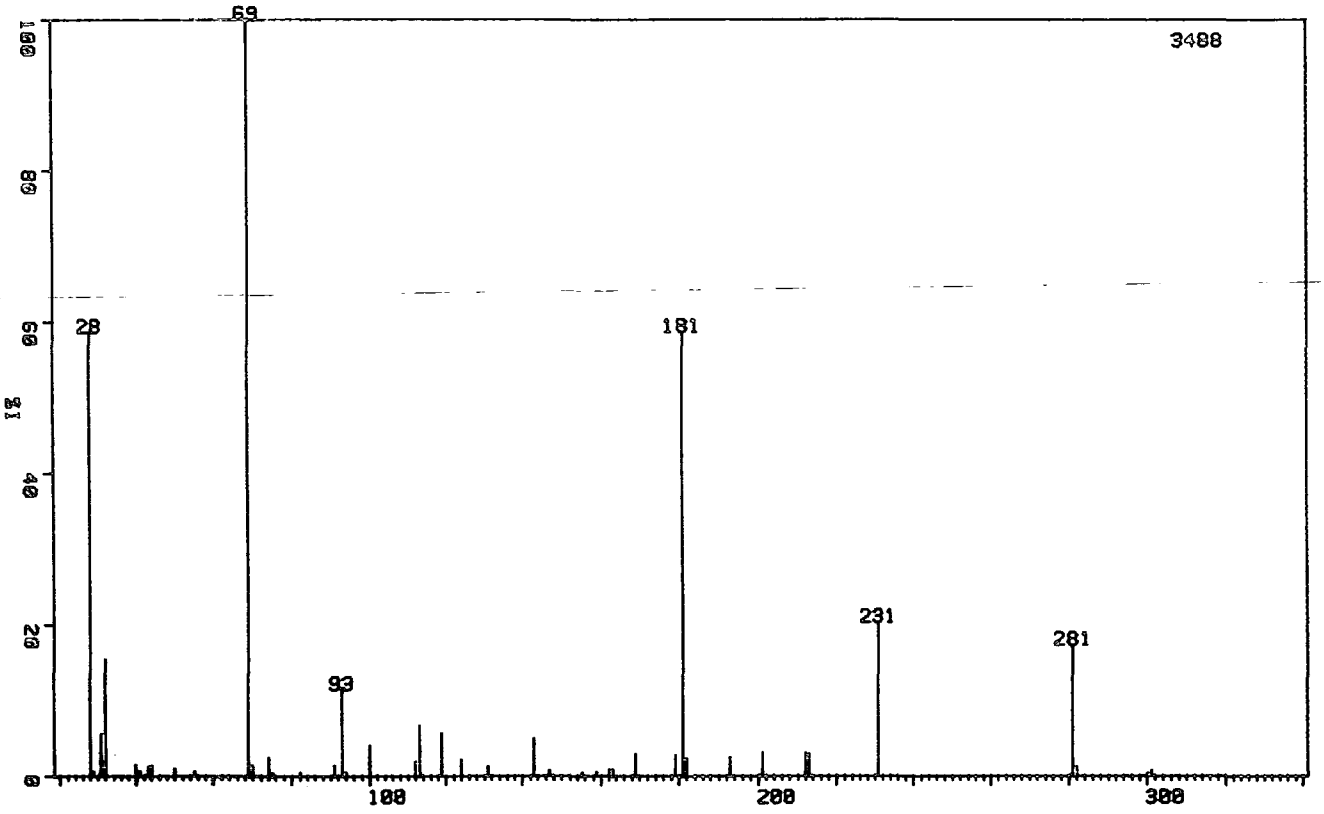
MASS	%HT. BASE	MASS	%HT. BASE
27.29	1.33	115.07	0.41
28.17	100.00	118.97	6.80
29.02	1.11	127.05	28.32
29.05	0.80	128.02	1.22
30.93	2.10	130.98	0.86
30.95	0.64	133.04	1.96
32.03	11.12	145.07	5.23
33.13	2.68	146.08	1.47
39.00	0.94	147.04	0.47
39.83	14.08	149.99	0.58
40.98	1.55	157.06	0.64
42.08	0.88	163.06	2.30
43.10	1.05	169.02	13.72
43.14	3.37	175.08	0.88
44.11	16.84	177.07	4.65
45.17	1.08	181.03	1.80
49.88	0.64	195.10	3.84
50.96	3.35	197.05	0.53
55.17	0.77	207.07	0.47
56.17	0.44	215.08	11.97
57.09	1.30	216.07	0.58
57.15	1.47	227.08	7.49
64.11	0.41	245.09	0.47
65.12	1.30	263.11	0.47
68.96	84.96	295.14	1.60
69.03	0.53	315.14	1.33
69.90	0.91		
71.07	0.64		
75.10	2.24		
76.08	0.69		
77.07	11.97		
93.06	1.00		
95.10	2.41		
99.94	3.43		
113.04	1.96		

AB123 0 A.BAYLIFF E.I. 48 21-AUG-86
CAL:LIB STA: 0:0



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.37	3.60	69.00	1.38	120.95	8.88	202.95	0.30
27.29	20.22	69.88	1.02	121.98	1.19	206.94	1.41
28.17	92.48	69.97	1.11	123.97	0.91	212.93	0.83
28.19	2.60	70.99	0.50	124.99	0.44	220.88	2.05
29.02	2.21	71.04	1.30	126.87	1.36	224.93	0.66
29.05	5.06	72.04	0.41	127.01	2.16	230.89	2.10
30.92	5.12	73.08	0.50	130.93	1.60	242.70	1.44
30.95	7.08	74.05	0.53	131.98	2.05	244.93	5.59
32.02	17.23	74.13	1.38	133.00	2.90	250.91	2.21
33.12	3.07	75.03	7.96	136.99	1.27	256.91	1.36
37.13	2.16	76.04	1.74	138.97	1.52	270.86	1.74
38.07	4.65	77.03	5.59	142.96	1.19	276.94	0.83
38.98	50.41	78.98	0.58	145.00	69.88	280.86	1.63
39.32	4.89	80.93	1.13	145.99	3.51	290.92	1.58
39.88	6.31	81.00	0.58	146.96	1.47	292.90	0.83
40.96	91.70	82.01	0.64	149.91	1.00	300.91	1.13
42.05	10.29	83.03	2.41	150.94	19.58	320.88	0.86
43.08	1.94	83.09	0.91	151.97	4.26	342.86	0.58
43.12	4.29	84.05	0.77	152.99	1.91	359.88	10.40
44.09	1.11	85.12	0.58	153.05	0.25	360.91	1.22
45.12	0.39	87.96	1.16	156.98	1.44		
45.14	7.72	88.93	0.91	158.91	1.19		
46.12	1.66	89.87	0.50	162.95	6.31		
47.06	0.61	90.89	2.85	163.97	0.36		
47.09	4.23	90.97	0.50	167.87	5.72		
49.87	1.74	92.98	4.84	168.94	4.09		
50.93	13.27	94.01	0.53	169.92	0.77		
52.02	0.83	95.02	5.61	170.94	54.62		
53.08	1.05	97.08	0.66	171.97	3.29		
54.11	1.62	98.93	1.77	174.96	1.96		
55.13	1.77	99.88	7.52	176.97	1.19		
56.13	1.19	100.96	10.67	178.91	5.28		
57.05	5.84	102.00	4.09	180.90	0.82		
57.11	3.26	103.04	3.62	181.96	0.64		
58.03	2.35	105.08	0.94	183.00	0.86		
58.97	17.23	107.00	1.22	188.96	1.30		
58.99	9.35	108.96	0.53	189.94	0.61		
59.90	9.71	110.92	0.50	190.97	56.64		
63.04	0.86	111.94	1.47	191.98	3.26		
64.05	1.33	112.98	4.78	192.94	0.44		
65.07	14.21	114.01	0.58	194.98	0.75		
67.08	1.44	118.90	11.81	200.91	3.93		
68.93	100.00	119.90	0.61	201.94	0.75		

A236BX 5 A.BAYLIFF E.I. 49 22-MAY-78
CRL:CRLT9 STR: 0:51



PEAK NO.	MASS	%HT. BASE
3	28.10	58.69
4	28.96	0.60
5	30.85	5.62
6	31.97	15.45
7	39.80	1.46
8	40.94	0.57
9	43.11	1.20
10	44.08	1.35
11	49.86	1.06
12	55.09	0.60
13	68.97	100.00
14	69.92	1.49
15	74.08	2.47
16	75.10	0.37
17	82.04	0.37
18	91.00	1.49
19	93.05	11.44
20	94.08	0.43
21	99.95	4.04
22	112.02	1.86
23	113.06	6.71
24	118.98	5.71
25	124.04	2.15
26	130.98	1.26
27	143.03	4.99
28	147.04	0.77
29	155.05	0.37
30	158.99	0.52
31	162.00	0.97
32	163.04	0.97
33	168.98	2.95
34	179.00	2.72
35	181.00	58.72
36	182.01	2.35
37	193.01	2.52
38	200.99	3.10
39	212.01	3.12
40	213.02	2.98
41	230.97	20.41
42	280.95	17.40
43	281.97	1.26
44	299.94	0.34
45	300.99	0.72

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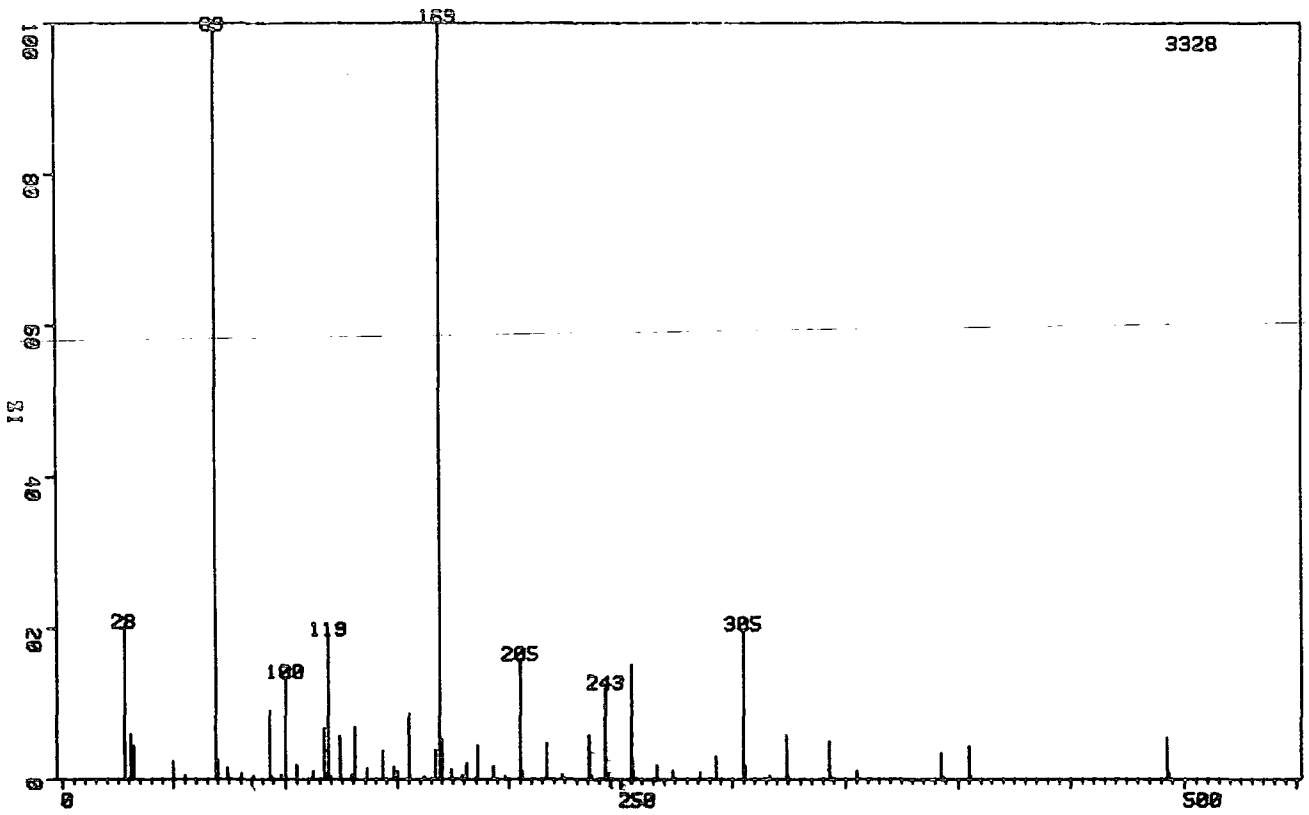
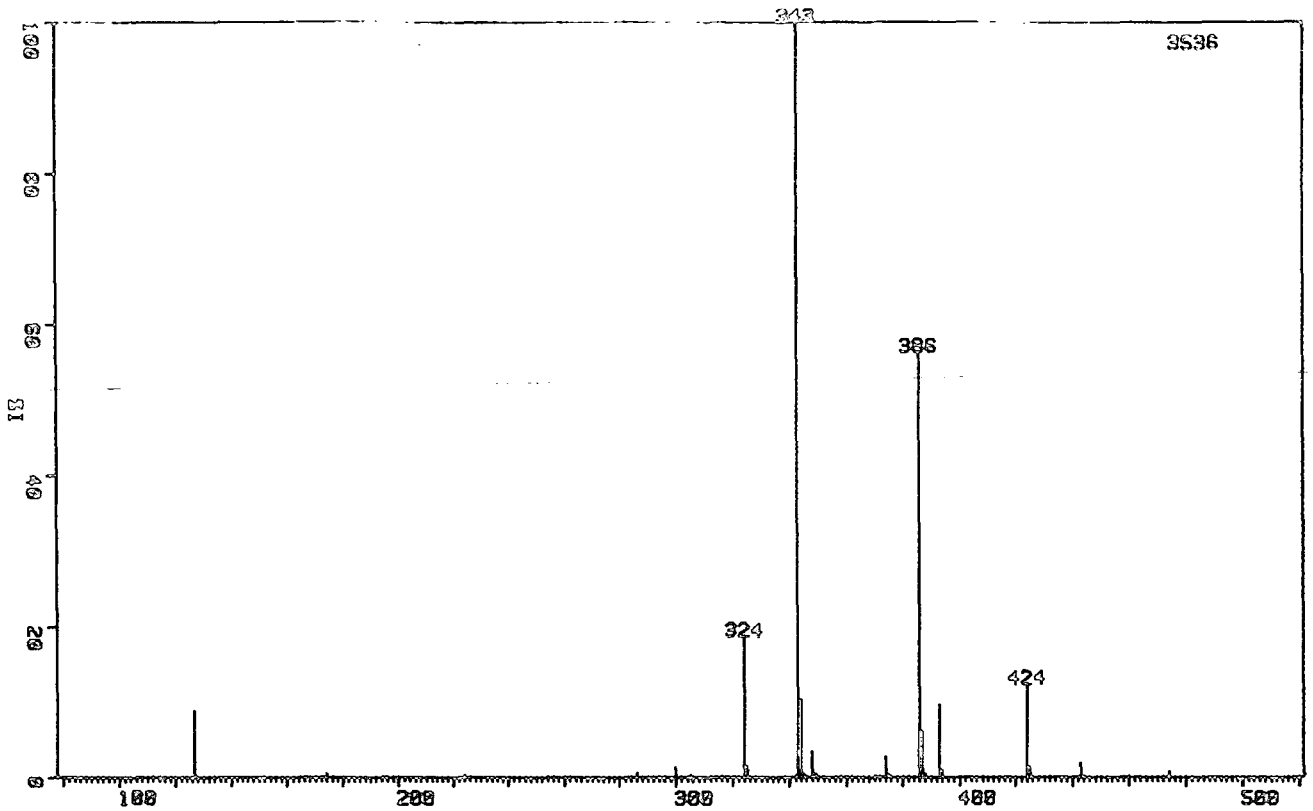


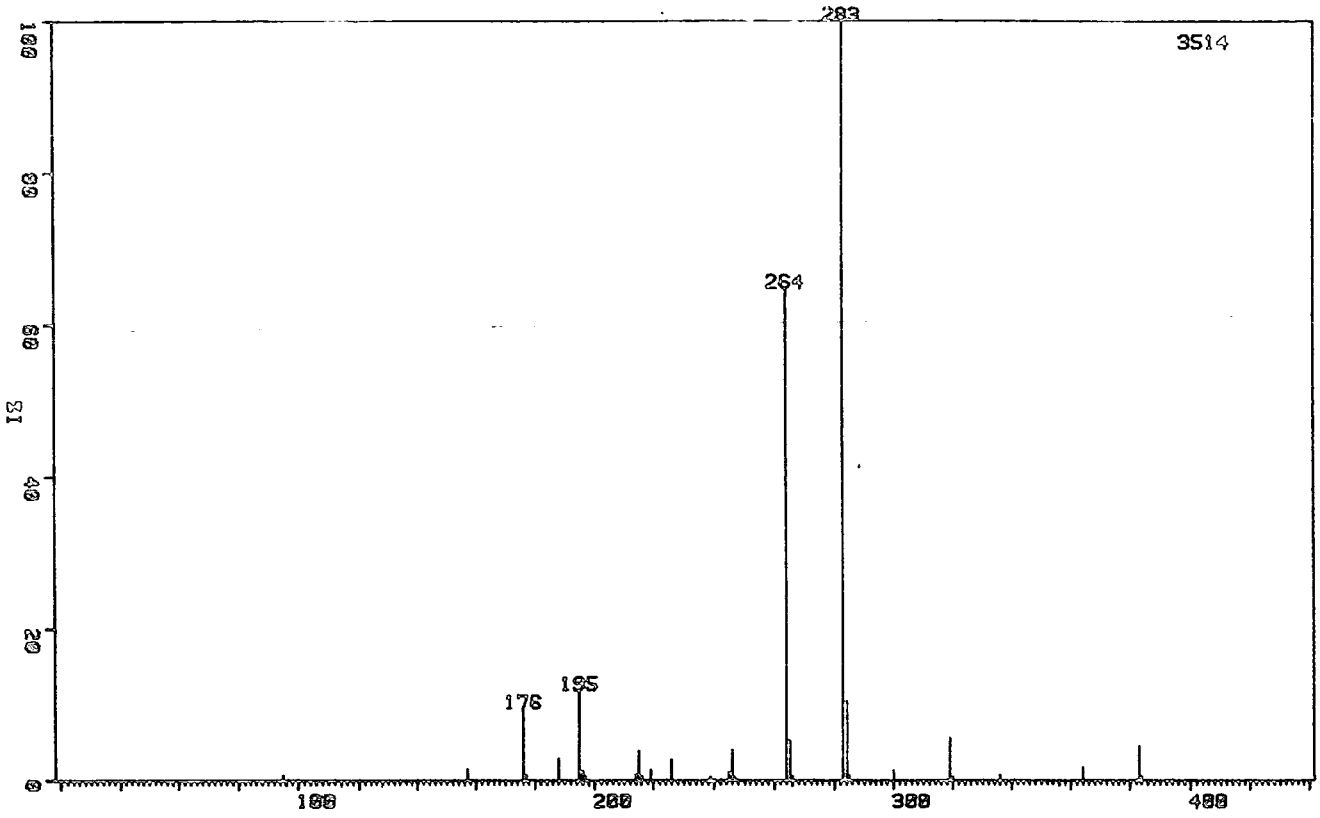
MASS	%HT. BASE	MASS	%HT. BASE
28.09	20.16	205.93	1.11
30.85	6.13	216.90	4.78
31.96	4.48	223.90	0.60
49.85	2.34	235.88	5.92
55.07	0.51	236.91	0.45
68.94	99.01	242.89	12.02
69.89	2.52	243.94	0.72
74.06	1.56	254.89	15.17
80.93	0.81	255.93	1.17
86.03	0.48	266.90	1.89
93.00	9.10	273.91	1.20
94.02	0.39	285.88	0.99
97.98	0.63	292.89	3.09
99.89	13.46	304.91	19.83
105.02	1.89	305.91	1.86
111.97	1.11	316.87	0.51
116.99	6.73	323.90	5.77
117.97	0.33	324.90	0.63
118.94	19.20	342.86	5.02
119.91	0.42	343.89	0.33
123.98	5.74	354.88	1.08
128.92	0.63	392.80	3.55
130.91	6.94	393.87	0.33
135.97	1.47	404.85	4.48
142.93	3.79	405.90	0.39
147.92	1.65	492.68	5.53
149.86	1.14	493.68	0.75
154.97	8.77		
161.93	0.33		
166.93	3.91		
168.89	100.00		
169.89	5.23		
173.97	1.32		
178.92	0.57		
180.91	2.19		
185.97	4.57		
192.95	1.74		
197.92	0.48		
204.92	15.84		

A214CN 66 A.BAYLIFF 214C NEG.(I-BU) 51 28-AUG-86
CAL:CALNEG STA: 9:29



MASS	%HT. BASE
127.0214	8.88
174.0404	0.51
224.1039	0.25
286.1596	0.59
300.0773	1.27
305.1505	0.31
324.1422	18.75
325.1127	1.47
343.1288	100.00
344.0951	10.32
345.0961	0.42
348.0966	3.37
349.0951	0.40
374.1390	2.77
375.1175	0.31
386.1112	56.31
387.0868	6.19
388.0902	0.37
393.0828	9.64
394.0740	0.99
424.1619	12.44
425.1102	1.44
443.1221	1.98
474.1048	0.82

AB179X 0 A.BAYLIFF NEG I-BU 52 20-JAN-85
CRL:CRLN21 STA: 0:35



MASS	%HT. BASE
95.06	0.71
157.07	1.51
176.02	9.56
177.00	0.65
188.00	2.99
195.02	11.95
196.02	1.34
197.04	0.60
214.02	0.80
215.02	3.93
216.04	0.60
218.98	1.45
226.03	2.73
239.00	0.48
245.00	1.14
246.01	4.07
247.03	0.40
264.00	64.88
265.02	5.26
266.02	0.54
283.01	100.00
284.03	10.44
285.04	0.51
299.97	1.37
318.97	5.69
319.97	0.40
336.01	0.74
364.02	1.74
382.99	4.52
383.98	0.54

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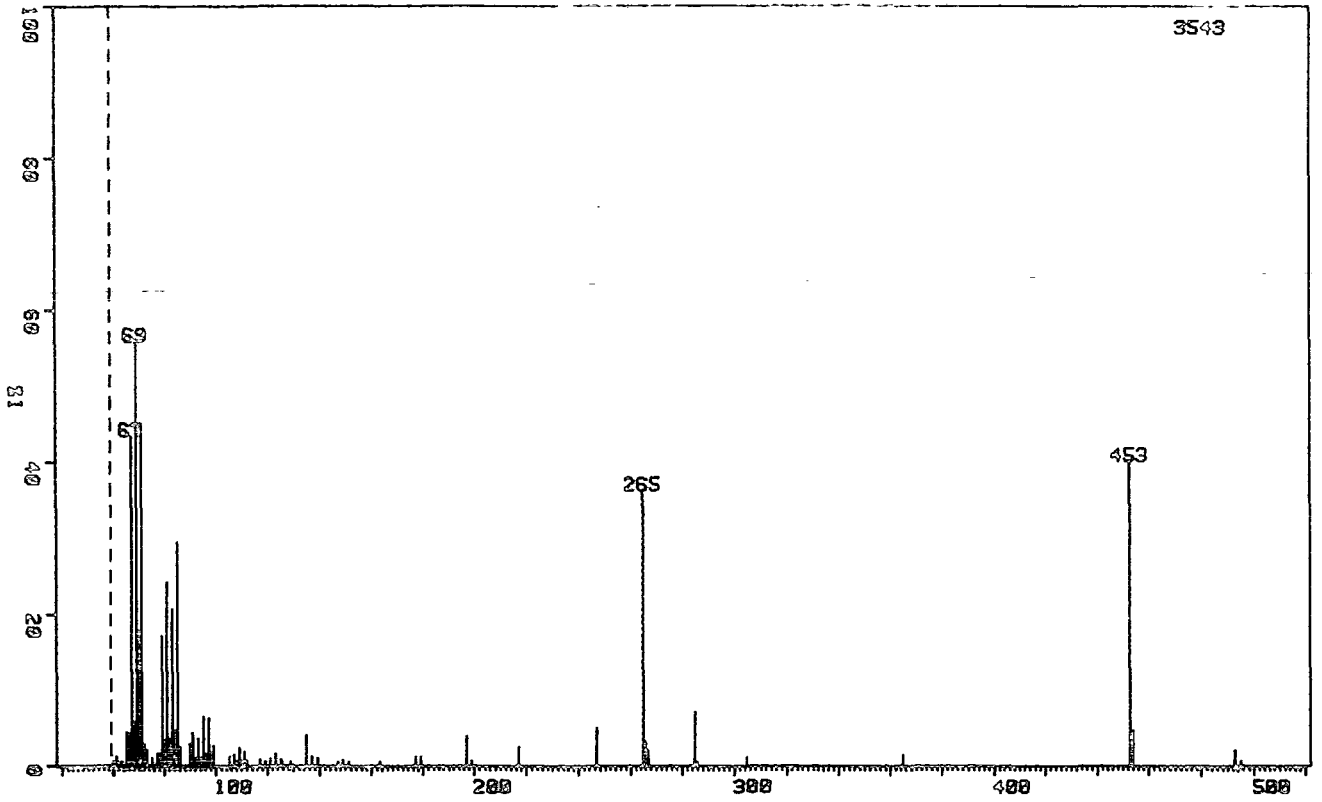
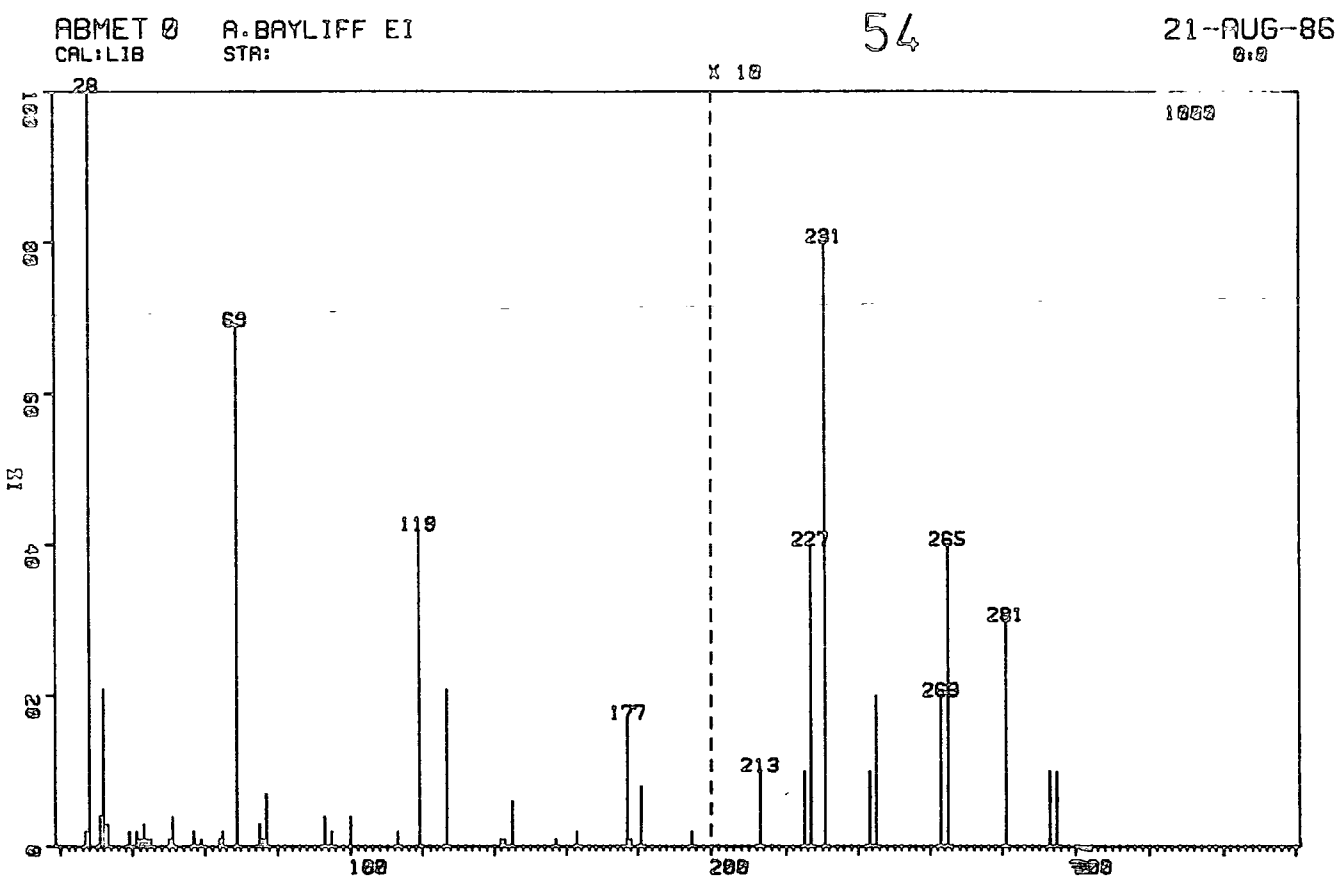
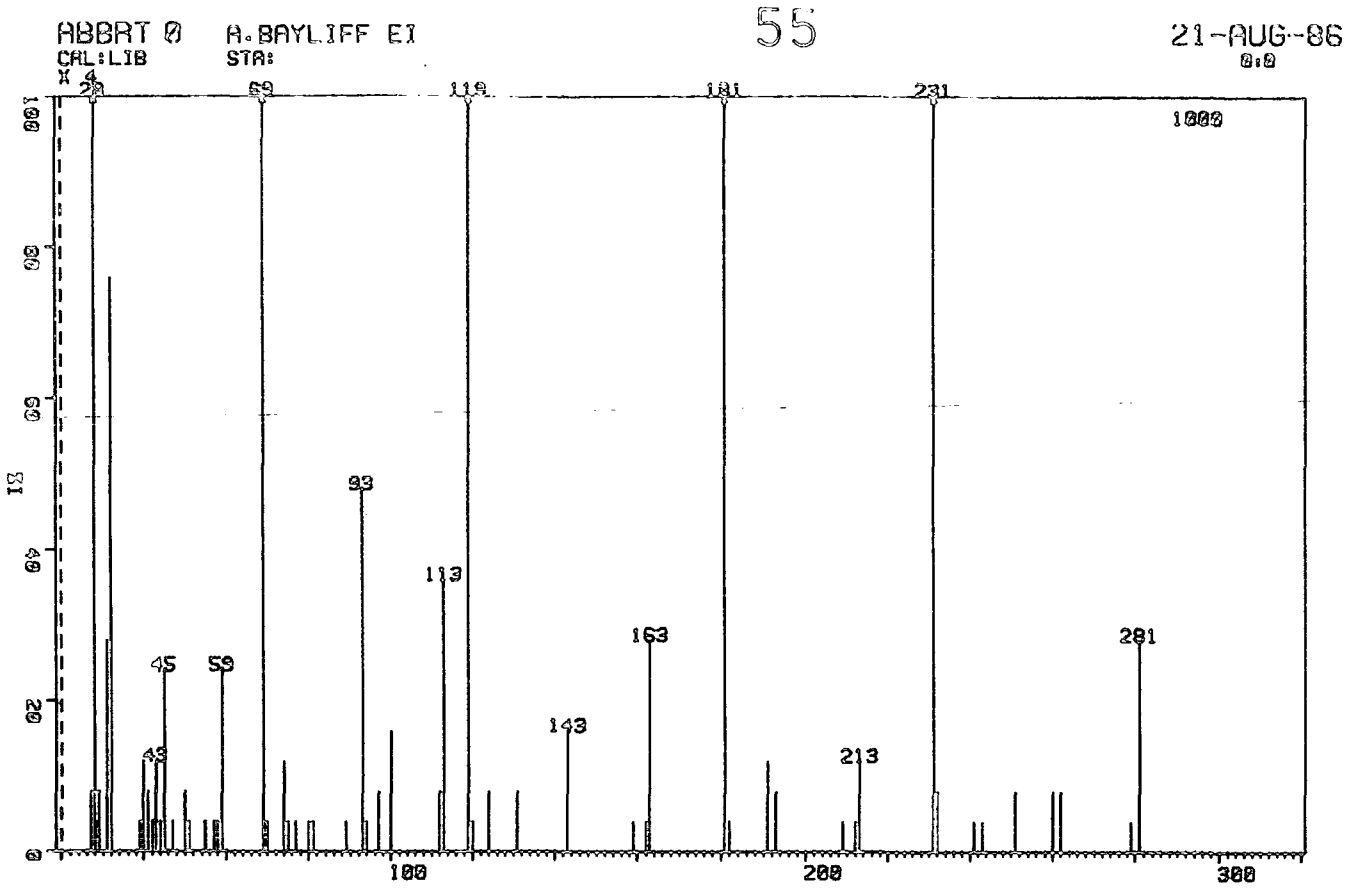
CAL:CALT31 STA: 0:35
X 2



MASS	%HT. BASE	MASS	%HT. BASE
60.97	0.59	135.00	2.00
63.04	0.31	137.09	0.65
65.08	2.23	139.03	0.54
66.08	2.12	147.09	0.25
67.07	21.73	149.01	0.40
68.04	2.96	151.02	0.51
69.00	27.97	163.06	0.31
69.94	8.95	176.91	0.68
71.00	22.47	178.89	0.68
72.06	1.44	196.89	1.95
73.04	1.04	198.94	0.37
75.10	0.54	216.90	1.30
77.01	0.85	246.83	2.51
77.98	0.87	264.85	18.15
78.94	8.61	265.91	1.64
79.89	1.72	266.89	1.02
80.97	12.14	284.89	3.58
82.02	1.81	285.93	0.25
83.06	10.41	304.93	0.65
84.08	2.34	364.84	0.76
85.09	14.76	452.73	20.10
86.09	1.27	453.79	2.34
89.87	1.50	492.79	1.04
90.97	2.20	494.87	0.31
92.02	0.56		
93.05	1.83		
94.07	0.54		
95.09	3.27		
96.09	0.87		
97.08	3.16		
98.06	0.90		
99.03	1.33		
105.06	0.68		
107.07	0.76		
108.06	0.37		
109.03	1.21		
110.00	0.37		
111.04	0.99		
112.08	0.37		
116.98	0.40		
119.03	0.28		
121.02	0.51		
123.08	0.85		
125.11	0.45		
128.94	0.28		



MASS	%HT. BASE		
27.23	1.60	177.91	0.96
28.11	100.00	180.85	8.26
30.86	3.91	194.93	2.05
31.97	20.61	212.88	0.83
33.07	3.46	224.91	1.02
38.95	1.66	226.90	4.48
40.94	1.73	230.86	8.39
42.03	0.96	242.87	0.83
43.10	3.01	244.92	2.24
44.06	1.22	262.89	1.60
45.12	1.22	264.92	3.78
49.85	1.22	280.83	2.75
50.92	4.29	292.90	1.15
57.06	2.50	294.93	1.34
59.00	0.77		
64.06	1.34		
65.08	1.66		
68.95	69.08		
75.04	2.69		
76.04	0.77		
77.03	6.72		
92.96	3.65		
95.00	2.30		
99.86	3.39		
112.98	2.43		
118.93	42.00		
126.99	21.45		
141.86	0.83		
142.97	1.28		
144.99	5.51		
156.97	0.90		
162.94	1.86		
176.92	16.77		



MASS	%HT. BASE	MASS	%HT. BASE
27.23	1.79	97.04	1.90
28.11	87.75	99.95	3.61
28.13	1.08	103.11	0.37
28.97	2.10	105.06	0.54
29.00	1.62	112.01	2.36
30.86	6.68	113.04	9.18
30.89	2.07	118.98	39.07
31.97	18.76	119.95	0.88
38.96	1.14	124.04	1.59
39.80	2.53	128.91	0.48
40.94	2.42	130.90	0.71
42.03	1.11	131.00	1.51
43.06	1.59	143.03	4.12
43.10	2.70	147.03	0.37
44.07	1.51	158.98	1.22
44.11	0.48	162.00	0.99
45.13	6.45	163.02	6.65
47.09	1.34	164.03	0.48
49.86	2.07	168.98	0.48
50.93	0.91	180.95	31.15
55.09	0.71	181.97	1.45
55.14	0.60	190.85	2.98
57.13	0.88	192.95	2.42
58.06	1.51	197.00	0.48
59.01	5.57	208.96	1.19
63.05	0.43	209.88	0.37
68.96	100.00	211.94	0.85
69.04	0.51	212.98	2.53
69.90	0.82	228.96	0.48
71.05	0.37	230.93	33.53
73.08	0.34	231.95	1.90
74.05	2.67	238.77	0.31
75.07	1.22	240.80	0.97
77.06	0.65	242.92	1.17
79.82	0.48	250.96	2.30
80.85	0.60	259.88	1.59
80.97	0.80	261.90	1.76
81.94	0.34	278.89	0.71
82.03	0.48	280.97	7.02
89.04	0.77	282.01	0.45
90.97	0.37	292.97	0.45
93.04	12.56		
94.05	0.65		

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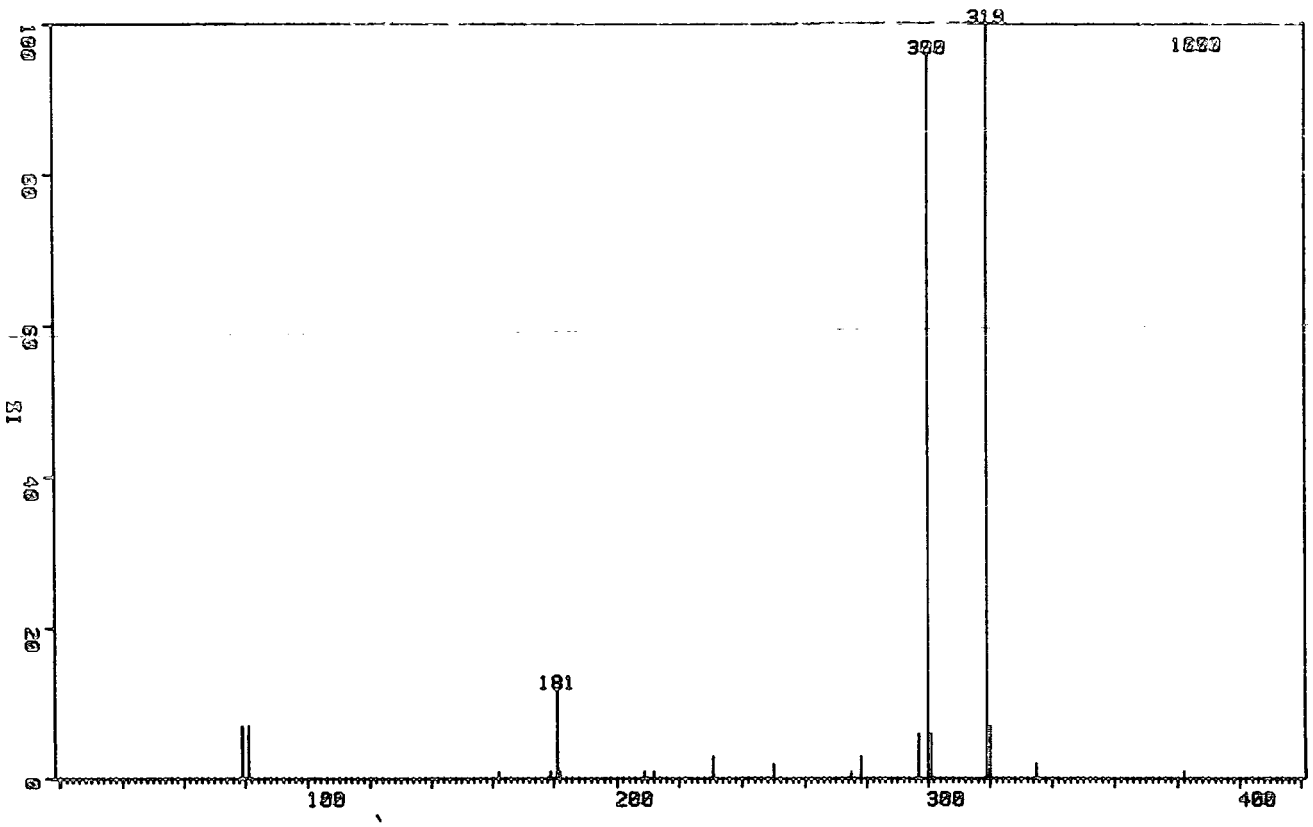

MASS	%HT. BASE
78.90	7.12
80.88	7.34
162.12	0.61
179.08	0.89
181.09	12.34
182.11	0.61
209.11	1.28
212.13	0.78
231.15	3.11
250.12	2.00
275.18	0.61
278.17	2.95
297.19	6.11
300.15	96.33
301.17	6.50
319.18	100.00
320.19	6.84
335.24	1.56
381.25	1.28

APPENDIX 4

The Board of studies in Chemistry requires that each postgraduate thesis contains an appendix listing;

a) all research colloquia, seminars, and lectures arranged by the Department of Chemistry during the period of the authors residence as a postgraduate student,

b) all research conferences attended and papers presented by the author during the period in which the research for the thesis was carried out;

c) details of the postgraduate induction course.

a) Research Colloquia, Seminars and Lectures.

1983

5 October — Prof. J. P. Maier (University of Basel,Switzerland), "*Recent approaches to spectroscopic characterisation of cations*".

12 October — Dr C. W. M^{c}Leland (University of Port Elizabeth, Australia), "*Cyclisation of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations*".

19 October — Dr. N. W. Alcock (University of Warwick), "*Aryl Tellurium(IV) compounds, patterns of primary and secondary bonding*".

20 October * Prof. R. B. Cundall (University of Salford), *Explosives*".

26 October * Dr. R. H. Friend (Cavendish Laboratory, University of Cambridge), "*Electronic properties of conjugated polymers*".

3 November — Dr. G. Richards (University of Oxford), "*Quantum*

pharmacology".

10 November * Dr. G. Thorpe (Sterling Organics), "*Applied chemistry and the pharmaceutical industry*".

24 November * Prof. D. A. King (University Of Liverpool), "*Chemistry in two dimensions*".

30 November Prof. I. Cowie (University of Stirling),"*Molecular interpretation of non-relaxation processes in polymer glasses*".

1 December * Dr. J. D. Coyle (The Open University),"*The problem with sunshine*".

14 December Prof. R. J. Donovan (University Of Edinburgh),"*Chemical and physical processes involving ion pair states of the halogen molecules*".

1984

10 January Prof. R. Hester (university of York),"*Nano second laser spectroscopy of reaction intermediates*".

18 January * Prof. R. K. Harris (University of East Anglia), "*Multi-nuclear solid state magnetic resonance*".

26 January Prof. T. L. Blundell (Birbeck College, London) "*Biological recognition: interactions of macromolecular surfaces*".

2 February * N. B. H. Jonathon (University of Southampton), "*Photoelectron spectroscopy – a radical approach*".

8 February Dr. B. T. Heaton (University of Kent), "*Multi-nuclear n.m.r. studies*".

15 February * Dr. R. M. Paton (University of Edinburgh), "*Heterocyclic synthesis using nitrile sulphides*".

16 February * Prof. D. Phillips (The Royal Institution), "*Luminescence and the photochemistry– a light entertainment*".

23 February Prof. F. G. A. Stone (University of Bristol), "*The use of the carbene and carbyne groups to synthesise metal clusters*".

1 March * Prof. A. J. Leadbetter (Rutherford Appleton Laboratories), "*Liquid crystals*".

7 March * Dr. R. T. Walker (University of Birmingham), "*Synthesis and biological properties of some 5-substituted uracil derivatives; yet another example of serendipity in antiviral chemistry*".

8 March Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "*Phospholipids and biomembranes: basic structure and future techniques*".

21 March * Dr. P. Sherwood (University of Newcastle), "*X-Ray photoelectron spectroscopic studies of electrode and other surfaces*".

23 March Dr. A. Ceulemans (Catholic University of Leuven), "*The development of field type models of bonding in molecular clusters*";

28 March * R. S. C. Centenary Lecture. Prof. H. Schmidbaur (Technical University of Munich F.R.G.), "*Ylides in the coordination sphere of metals; synthetic, structural, and theoretical aspects*".

2 April * Prof. K. O'Driscoll (University of Waterloo), "*Chain ending reactions in free radical polymerisations*".

3 April Prof. C. H. Rochester (University of Dundee), "*Infrared studies of adsorption at the solid–liquid interface*".

25 April * Dr. R. M. Acheson (Department of Biochemistry, University of Oxford), "*Some heterocyclic detective stories*".

27 April Dr. T. Albright (University of Houston), "*Sigmatrophic rearrangements in organometallic chemistry*".

14 May * Prof. W. R. Dolbier Jr. (University of Florida), "*Cycloaddition reactions of fluorinated allenes*".

16 May * Dr. P. J. Garrett (University College, London), "*Syntheses with dilithiated vicinal diesters and carboximides*".

31 May Dr. A. Haaland (University of Oslo), "*Electron diffraction studies of some organometallic compounds*".

11 June Dr. J. B. Street (I.B.M. San Jose), "*Conducting polymers derived from pyrolles*".

19 September Dr. C. Brown (I.B.M. San Jose), "*New superbase reactions—organic compounds*".

21 September Dr. H. W. Gibson (Signal UOP Research Centre, Des Plaines, Illinois), "*Isomerisation of polyacetylene*".

18 October * Dr. N. Logan (University of Nottingham), "N_2O_4 *and rocket fuels*".

19 October * Dr. A. Germain (Univeriste du Languedoc, Montpelier), "*Anodic oxidation of the perfluoro organic compounds in perfluoro sulphonic acids*".

24 October Prof. R. K. Harris (University of Durham), "*N.m.r. of solid polymers*".

1 November * Prof. B. J. Aylett (Queen Mary College, University of London), "*Silicon-dead common or refined*".

7 November Dr. H. S. Munro (University of Durham), "*New information from E.S.C.A. data*".

7 November Prof. W. W. Porterfield (Hampden Sidney College, U.S.A.), "*There is no borane chemistry, only geometry*".

15 November * Prof. B. T. Golding (University of

Newcastle-upon-Tyne), "*The vitamin B_{12} mystery*".

21 November * Dr. W. J. Feast (University of Durham), "*A plain man's guide to polymeric organic metals*".

22 November * Prof. D. T. Clark (I.C.I. New Science Group), "*Structure, bonding, reactivity and synthesis as revealed by E.S.C.A.*".

28 November Dr. T. A. Stephenson (University of Edinburgh), "*Some recent studies in platinium metal chemistry*".

29 November * Prof. C. J. M. Sterling (University College of North Wales), "*Molecules taking the strain*".

6 December * Prof. R. D. Chambers (University of Durham), "*The unusual world of fluorine chemistry*".

1985

24 January * Dr. A. K. Covington (University of Newcastle-upon-Tyne), "*Chemistry with chips*'.

31 January * Dr. M. L. H. Green (University of Oxford), "*Naked atoms and negligee ligands*'.

7 February Prof. A. Ledwith (Pilkington Brothers),"*Glass as a high technology material*'.

13 February Dr. G. W. J Fleet (University of Oxford), "*Synthesis of some alkaloids from carbohydrates*".

14 February * Dr. J. A. Salthouse (University of Manchester),"*Sun et Lumiere*, (a chemical energy show.".

19 February Dr. D. J. Mincher (University of Durham), "*Stereoselective syntheses of some novel anthracyclinones related to the anti-cancer drug adriamycin and to the steffimycin antibiotics*".

21 February Prof. P. M. Maitlis F.R.S. (University of Sheffield), "*What use is rhodium*".

27 February * Dr. R. E. Mulvey (University of Durham), "*Some unusual*

lithium complexes".

7 March — Dr. P. J. Rodgers (I.C.I. plc Agricultural Division, Billingham), "*Industrial polymers from bacteria*".

7 March — ¤ Dr. P. W. Atkins (University of Oxford), "*Magnetic reactions*".

12 March — Prof. K. J. Packer (BP Research Centre), "*N.m.r. investigations of the structure of solid polymers*".

14 March — ¤ Prof. A. R. Katritzky FRS (University of Florida), "*Some adventures in heterocyclic chemistry*".

21 March — Dr. M. Poliakoff (University of Nottingham), "*New methods for detecting organometallic intermediates in solution*".

28 March — ¤ Prof. H. Ringsdorf (Organic Chemistry Institute, University of Mainz), "*Polymeric liposomes as models for biomembranes and cells*".

24 April — Dr. M. C. Grosel (Bedford College, University of London), "*Hydroxypyridone dyes— bleachable one dimensional metals*".

1 May — ¤ Dr. D. Parker (I.C.I. plc Petrochemicals and Plastics Division, Wilton), "*Applications of radioisotopes in industrial research*".

7 May — Prof G. E. Coates (formerly of the University of Wyoming, U.S.A.), "*Chemical education in Britain and America: successes and deficiencies*".

8 May — Prof. D. Tuck (University of Windsor, Ontario), "*Lower oxidation state chemistry of indium*".

8 May — Prof. G. Williams (University College of Wales, Aberystwyth), "*Liquid crystalline polymers*".

9 May — ¤ Prof. R. K. Harris (University of Durham), "*Chemistry in a spin*".

14 May — Prof. J. Passmore (University of New Brunswick), "*The synthesis and characterisation of some novel selenium-iodine cations, aided by* ^{77}*Se n.m.r. spectroscopy*".

15 May — * Dr. J. E. Packer (University of Auckland, New Zealand), "*Studies of free radical reactions in aqueous solution using ionising radiation*".

17 May — Prof. I. D. Brown (Institute for Materials Research, M^{c}Master University, Canada), "*Bond valence as a model for inorganic chemistry*".

21 May — Dr. D. L. H. Williams (University of Durham), "*Chemistry in colour*".

22 May — * Dr. R. Grimmett (University of Otago, Dunedin, New Zealand), "*Some aspects of nucleophilic substitution in imidazoles*".

22 May — * Dr. M. Hudlicky (Virginia State University, Blacksburg), "*Preferential elimination of hydrogen fluoride from vicinal bromofluorocarbons*".

13 June — Dr. D. Woollins (Imperial College, University of London), "*Metal-sulphur-nitrogen complexes*".

14 June — * Prof. Z. Rappoport (The Hebrew University, Jerusalem), "*The rich mechanistic world of nucleophilic vinylic substitution*".

19 June — Dr. T. N. Mitchell (University of Dortmund), "*Some synthetic and n.m.r.-spectroscopic studies of organotin compounds*".

26 June — * Prof. G. Shaw (University of Bradford), "*Some synthetic studies in imidazole nucleosides and the antibiotic coformycin*".

12 July — Dr. K. Laali (Hydrocarbon Research Institute, University of Southern California), "*Recent*

developments in superacid chemistry and mechanistic considerations in electrophilic aromatic substitutions; a progress report".

13 September* Dr. V. S. Palmer (University of Delhi), "*Enzyme Assisted ERC Synthesis*".

17 October * Dr. C. J. Ludman (University of Durham), "*Some Thermochemical Aspects of Explosions*".

24 October * Dr. J. Dewing (U. M. I. S. T.), "*Zeolites - Small Holes, Big Opportunities*".

30 October Dr. S. N. Whittleton (University of Durham), "*An Investigation of a Reaction Window*".

31 October * Dr. P. Timms (University of Bristol), "*Some Chemistry of Fireworks*".

5 November * Prof. M. J. O'Donnell (Indiana-Perdue University), "*New Methodology for the Synthesis of Amino Acids*".

7 November Prof. G. Ertl (University of Munich), "*Heterogeneous Catalysis*".

14 November * Dr. S. G. Davies (University of Oxford), "*Chirality Control and Molecular Recognition*".

20 November * Dr. J. A. H. Macbride (Sunderland Polytechnic), "*A Heterocyclic Tour on a Distorted Tricycle - Biphenylene*".

21 November Prof. K. H. Smith (University of Newcastle), "*Chemistry of Si-Al-O-N Engineering Ceramics*".

28 November Dr. B. A. G. Clark (Kodak Ltd.), "*Chemistry and Principles of Colour Photography*".

28 November Prof. D. J. Waddington (University of York), "*Resources for the Chemistry Teacher*".

<u>1986</u>

15 January Prof. N. Sheppard (University of East Angla),

"*Vibrational and Spectroscopic Determinations of the Structures of Molecules Chemisorbed on Metal Surfaces*".

23 January Prof. Sir Jack Lewis (University of Cambridge), "*Some more Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls*".

29 January * Dr. J. H. Clark (University of York), "*Novel Fluoride Ion Reagents*".

30 January Dr. N. J. Phillips (University of Tec gy, Loughborough), "*Laser Holography*".

12 February Dr. J. Yarwood (University of Durham), tructure *of Water in Liquid Crystals*".

12 February * Prof. O. S. Tee (Concordia University, M al), "*Bromination of Phenols*".

13 February * Prof. R. Grigg (Queens University, Belfas *Generation of 1,3-Dipoles*".

19 February * Prof. G. Procter (University of Salford), " proaches *to the Synthesis of some Natural Products*".

20 February Dr. C. J. F. Barnard (Johnson Matthey Group) "*Platinum Anti-Cancer Drug Development*".

26 February Miss C. Tull (University of Durham),"*ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics*".

27 February * Prof. R. K. Harris (University of Durham), "*The Magic of Solid State NMR*".

5 March * Dr. D. Hathaway (University of Durham), "*Herbicide Selectivity*".

5 March Dr. D. M. Schroder (University of Edinburgh), "*Studies on Macrocycle Complexes*".

6 March * Dr. B. Iddon (University of Salford), "*The Magic of*

Chemistry".

12 March Dr. J. M. Brown (University of Oxford), "*Chelate Control in Homogeneous Catalysis*".

14 May Dr. P. R. R. Langridge-Smith (University of Cambridge), "*Naked Metal Clusters - Synthesis, Characterisation and Chemistry*".

9 June Prof. R. Schmutzler (University of Braunschweig), "*Mixed Valence Diphosphorous Compounds*".

23 June Prof. R. E. Wilde (Texas Technical University), "*Molecular Dynamic Processes from Vibrational Bandshapes*".

Lectures starred were attended.

b) **Research conferences attended**

17th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, December, 1983.

Graduate Symposium, Durham, April, 1984.

International Symposium on "Chemistry of Carbanions", Durham, July, 1984.

18th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, December, 1984.

Graduate Symposium, Durham, April, 1985.

General Poster Meeting, Newcastle-upon-Tyne, December, 1985.

Graduate Symposium, Durham, April, 1986.

Postgraduate Heterocyclic Symposium, Birmingham, July, 1986.

International Symposium to celebrate the "Centenary of the discovery of fluorine", Paris, August, 1986.

c) **Postgraduate Induction Course**

In each part of the course, the uses and limitations

of the various services available were explained.

Departmental Organisation: - Dr. E. J. F. Ross.

Safety Matters: - Dr. M. R. Crampton.

Electrical Appliances and Infrared Spectroscopy: - (the late) Mr. R. N. Brown.

Chromatography and Micro Analysis: - Mr. T. F. Holmes.

Atomic Absorption Spectrometry and Inorganic Analysis: - Mr. R. Coult.

Library Facilities: - Mr. R. B. Woodward.

Mass Spectrometry: - Dr. M. Jones.

Nuclear Magnetic Resonance Spectroscopy: - Dr. R. S. Mathews.

Glassblowing Techniques: - Mr. R. Hart and Mr. G. Haswell.

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