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SOME STUDIES IN THE CHEMISTRY OF REACTIVE INTERMEDIATES

by

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Department of Chemistry

SUMMARY

A number of reactions of tetrahalogenobenzynes have been investigated. The reactions of tetrafluorobenzyne with 2-methyl- and 2,5-dimethylfuran gave the expected Diels-Alder adducts (dihydro-tetrafluoroepoxynaphthalene derivatives) which on treatment with butadiene afforded 9-methyl- and 9,10-dimethyltetrahydrotetrafluoroanthracenes. Further reactions with tetrafluorobenzyne followed by dehydrogenation gave 9-methyl- and 9,10-dimethyloctafluorotriptycenes which were used to study new examples of long-range $^{19}F—^{1}H$ spin-spin coupling ^{1}H n.m.r. spectroscopy.

Reactions of tetrahalogenobenzynes with 6,6-dimethyl- and 6,6-diphenylfulvene afforded dihydromethanonaphthalene derivatives which on selective hydrogenation at low temperature gave tetrahydromethanonaphthalene derivatives. Flash Vacuum Pyrolysis (F.V.P.) of these compounds at 600°C resulted in the formation of tetrahydrocyclopentindene derivatives and isopropenylindene derivatives. However, the pyrolysis of higher temperatures produced a complex mixture of products.

Improvements in the preparation of 3,6-dimethoxyanthranilic acid allowed the use of this precursor in reactions of dimethoxybenzyne, particularly with methoxyarenes. The reaction with veratrole allowed the preparation of 1,5,8-trimethoxybenzobarrelenone (1,5,8-trimethoxy--3,4-dihydro-1,4-ethenonaphthalen-2(1H)-one) which was used in the synthesis of 1,4-dimethoxy-5,9-dihydro-5,9-methanobenzocyclohepten-6-one, a model compound which was used in an investigation of the abnormal ultraviolet spectrum of flavothebaone trimethyl ether. The acid-catalysed rearrangements of 1,5,8-trimethoxybenzobarrelene gave 2,4',5-trimethoxybiphenyl as well as the expected 5,8-dimethoxybenzobarrelenone.

ACKNOWLEDGEMENTS

I should like to express my sincere gratitude to Dr.H.Heaney for his considerable help and encouragement in the pursuit of this work.

I am also indebted to Loughborough University of Technology for a research demonstratorship, for laboratory and other facilities, and the Science Research Council (through the P.C.M.U.) for high resolution mass spectra and high field ^{1}H n.m.r. spectra.

I thank my friends and colleagues including academic and technical staff as well as other research workers in the laboratories at Loughborough for many helpful discussions.

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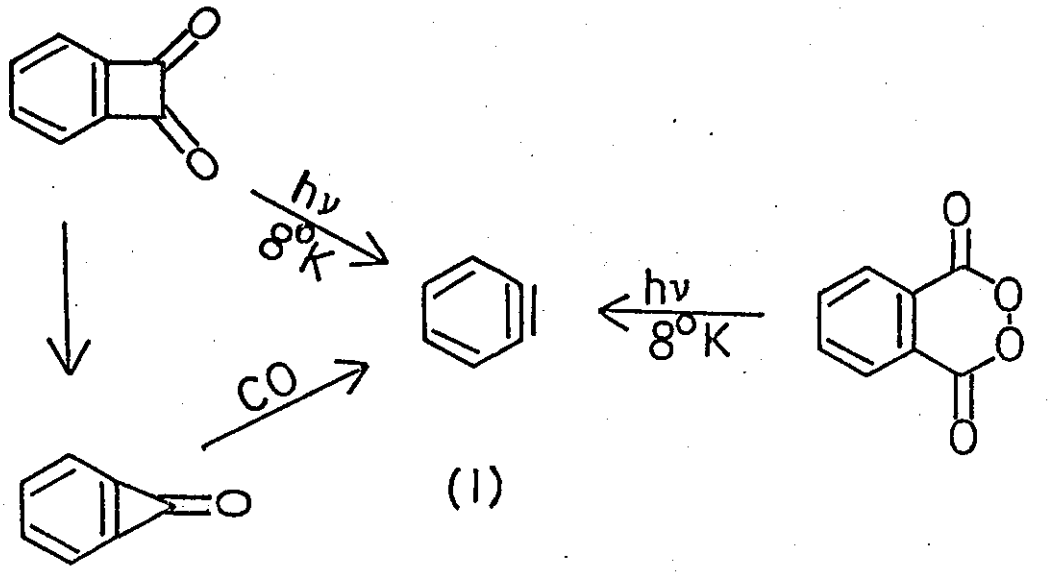
INTRODUCTION

INTRODUCTION

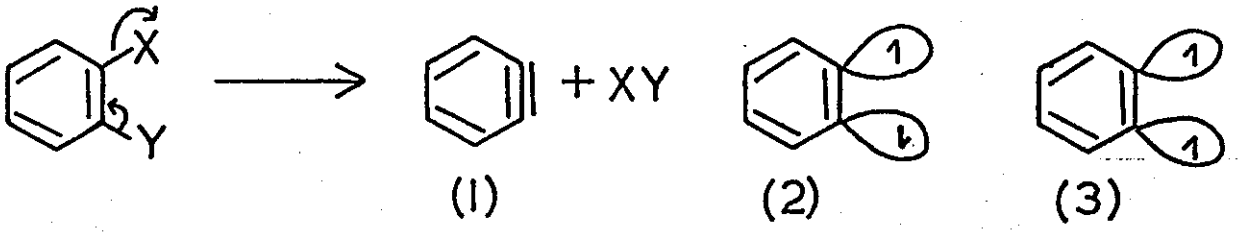
Although the chemistry of arynes[1] and their derivatives has grown enormously during the past two decades, the intermediacy of a 'C_6H_4' species was postulated[2] as early as a hundred years ago. The species 'C_6H_4' the parent of the family of arynes has never been isolated at normal temperatures but its existence in gas phase has been demonstrated by time-resolved mass spectroscopy[3] and has been shown to possess a half-life period of ca. 10^{-4} sec..

Other evidence for the existence of benzyne has been obtained recently by Chapman and his collaborators.[4] They have successfully recorded the first-ever infra-red spectrum of benzyne which they generated by the photolysis of phthaloyl peroxide and benzocyclobuten-1,2-dione at 8°K. The various bands observed in the spectrum of benzyne are at 1627, 1607, 1451, 1053, 1038, 849, 736 and 469 cm^{-1} and favour the structure (1) for the intermediate.

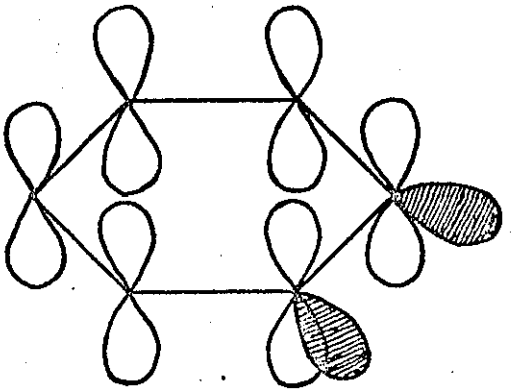


(1)

Benzyne is now generally accepted to be represented by the formula (1) and is produced by the elimination of two ortho substituents from the aromatic system leaving thereby two sp^2 hybridised orbitals orthogonal to the π-system of the ring with two extra electrons distributed between them (4). Benzyne exists in a singlet ground state (2) and the



(1) (2) (3)



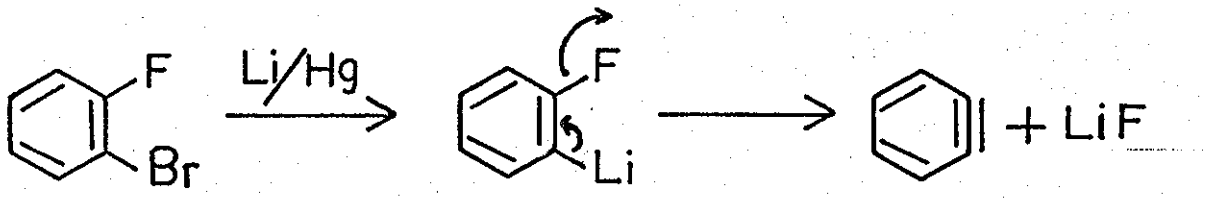
(4)

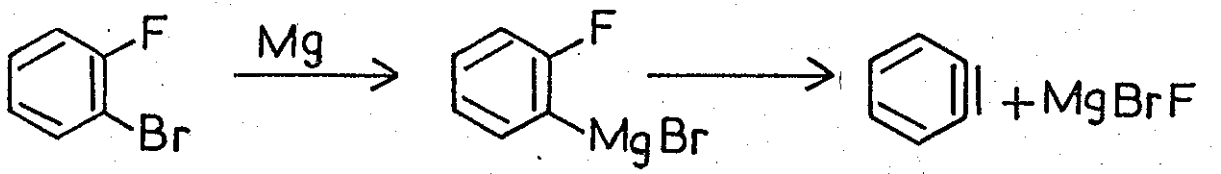
bond order is ca. 2.5. It behaves as a strained olefine, the aromatic character is undisturbed and the high reactivity of the intermediate is attributed to the ring strain. There is very little known about the benzyne reactions in triplet state (3).[5] An alternative name for benzyne is dehydrobenzene and both are common in the literature.

Over the years arynes have been generated in a variety of ways. In earlier methods arynes were usually produced by the action of very strong bases such as potassium amide and sodamide in liquid ammonia or lithium alkyls and lithium aryls in ether on aryl halides. The main

disadvantage of all of these methods is that the scope for the reaction becomes very much limited because some or most of the aryne formed is trapped by the base which itself is a strong nucleophile.

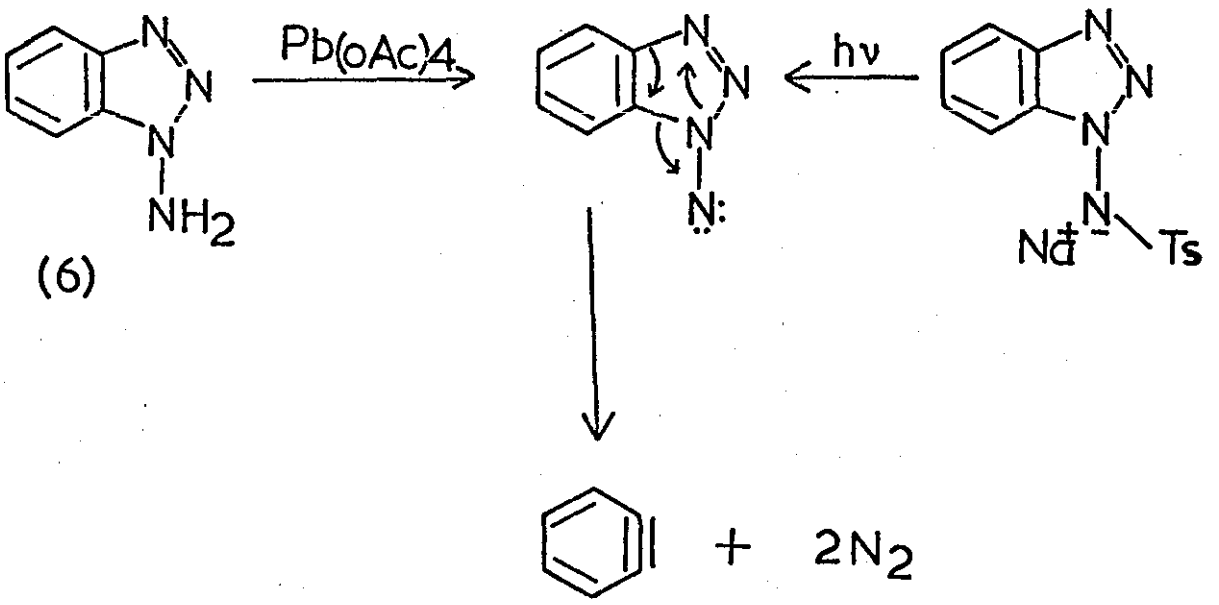
The procedure in which benzyne was successfully trapped by dienes in a Diels-Alder type reaction was first introduced by Wittig[6] starting from 1,2-dihalogenobenzenes and lithium amalgam or magnesium.





Other routes to benzyne include the pyrolysis of phthalic anhydride, indanetrione and various other substrates;[7] the photolysis of phthaloyl peroxide, o-diiodobenzene and many other compounds[8] and flash photolysis of benzenediazonium-2-carboxylate (5) also gives rise to benzyne.[3] The yields of benzyne in all these cases is rather low.

Oxidation of 1-aminobenzotriazole (6) with lead tetra-acetate or nickel peroxide is another good source of producing benzyne in high yield[9] and under mild conditions.

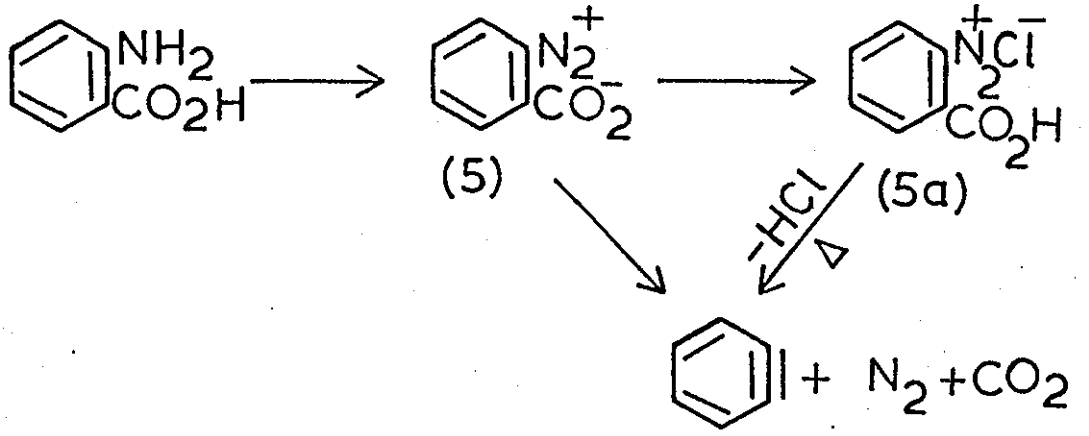


Recently, Cadogan[10] has reported the formation of benzyne from aniline.

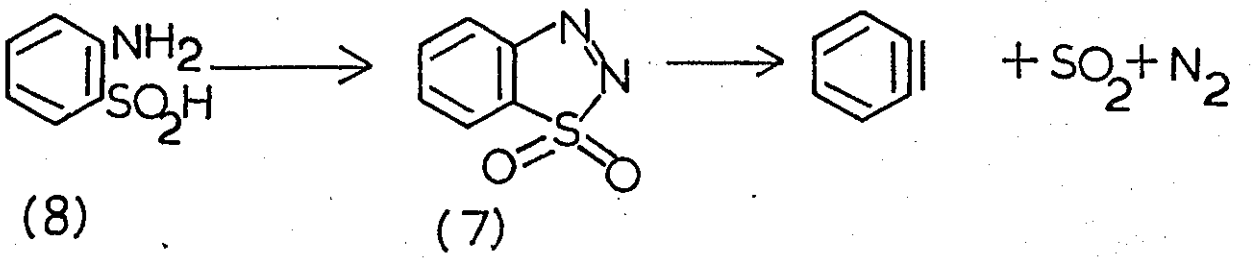
Most of the aforesaid methods of generation of arynes suffer from either a limited availability of aryne precursors or the low yields of the desired products and even more due to the inconvenience in preparing and in handling the starting materials.

The most widely used method these days eliminates the use of metal cations, halide ions and strong bases. This involves the diazotisation of anthranilic acid to give benzenediazonium-2-carboxylate (5), which can be isolated but when dry it detonates.[11] On mild pyrolysis (ca. 40-60°C) it decomposes to benzyne, carbon dioxide and nitrogen. The procedure is very simple, the reaction conditions are extremely mild and the yields of benzyne-adducts are usually high. Diazotisation can also be carried out in situ, which is very convenient and safe. The exact mechanism of the decomposition of (5) is not yet clear. The method has been extended

to other arynes.

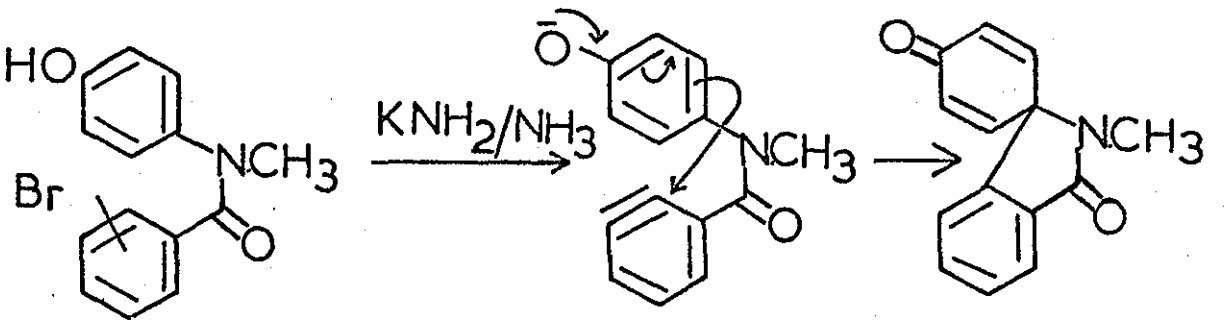


Likewise, 1,2,3-benzothiadiazole-1,1-dioxide (7),which is formed from 2-aminobenzenesulphinic acid (8) fragments readily in organic solvents at ca. 20°C to give benzyne in good yield, together with sulphur dioxide and nitrogen.[12]



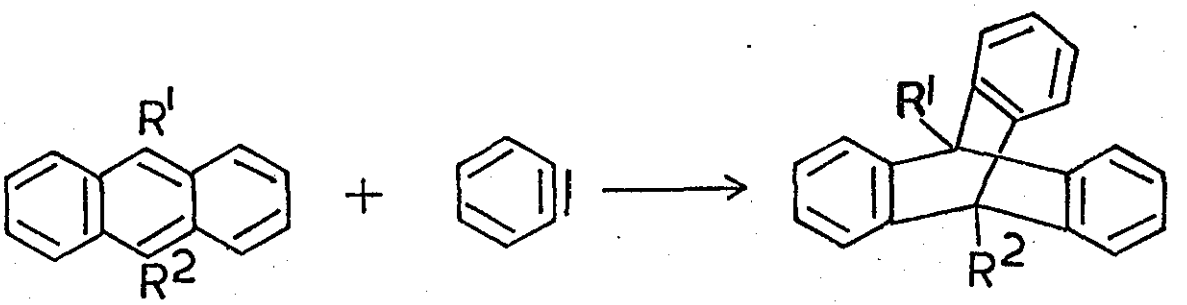
Arynes are highly electrophilic species and react with a large number of compounds. Of these nucleophilic additions and cycloaddition reactions have been extensively studied. These reactions are synthetically very important because they often produce compounds which are otherwise inaccessible. A good example in this case is the preparation of the

spiro compound (9).[13]



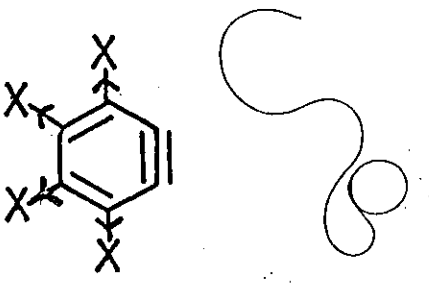
(9)

A great number of 1,2-cycloaddition and 1,3-dipolar cycloaddition reactions of benzynes have been investigated during the past few years.[1] The most useful of all the cycloaddition reactions of benzynes is the Diels-Alder reaction with dienes. Benzyne acts as a powerful dienophile and even adds to systems not normally considered to be dienes, for instance, benzene. The addition of benzyne to aromatic hydrocarbons affords bridged ring systems[1] which are otherwise inaccessible; Diels-Alder addition of benzyne to anthracene derivatives is the best-known method for preparing various substituted triptycenes (10).



(10)

In recent years, much attention has been devoted in these laboratories to the chemistry of highly halogenated arynes.[14,23] The presence of four electron withdrawing substituents on benzyne (11) makes the intermediate much more electrophilic than benzyne itself. It has been shown that aromatic hydrocarbons form charge-transfer complexes with highly

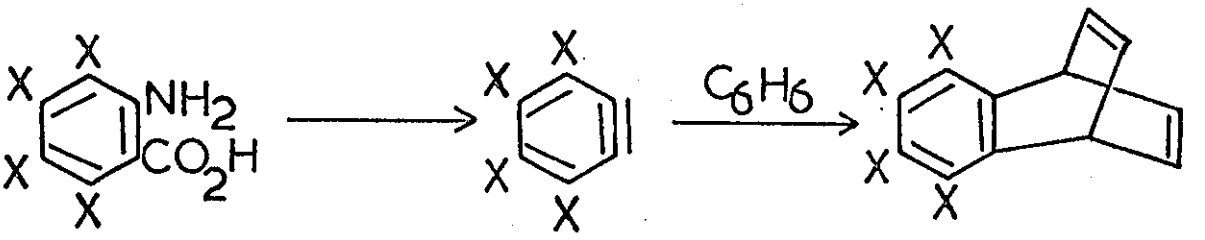


(11)

fluorinated aromatic compounds[15] and such a charge-transfer in the case of tetrahalogenobenzyne precursors could be partially responsible for the high reactivity of halogenated arynes towards the aromatic compounds. Pentafluorophenyl Grignard and lithium reagents[16] are more stable than the corresponding o-fluorophenyl Grignard and lithium reagents would indicate a higher activation energy for the formation of tetrafluorobenzyne which might account for its higher reactivity.

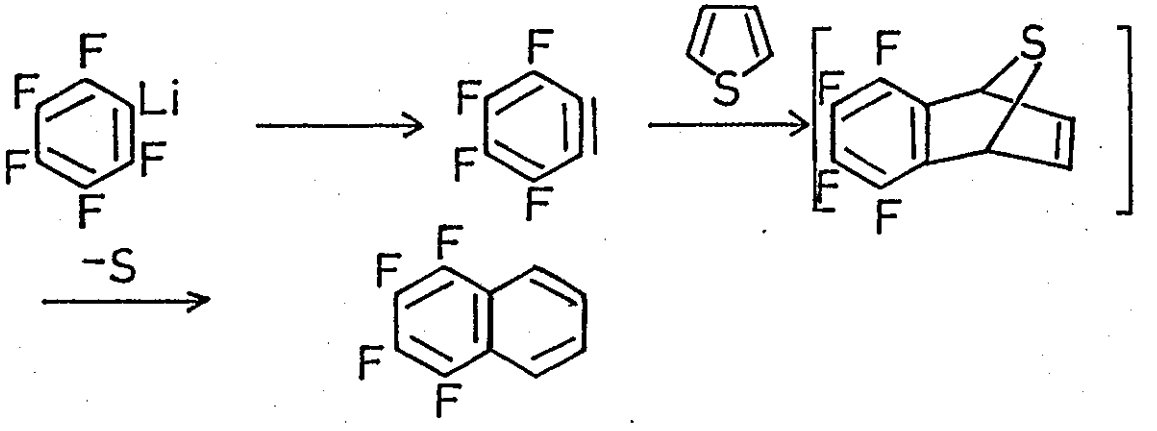
The methods commonly employed for the generation of tetrahalogenobenzynes are on parallel lines to those already described in the case of benzyne. Pentafluorophenylmagnesium halides,[17] pentachlorophenylmagnesium chloride,[18] pentafluorophenyl-lithium[16b] and pentachlorophenyllithium[19] are all good precursors of tetrafluoro- and tetrachlorobenzynes.

Again, tetrahalogenobenzynes have been generated in high yields by the aprotic diazotisation of their corresponding anthranilic acids.



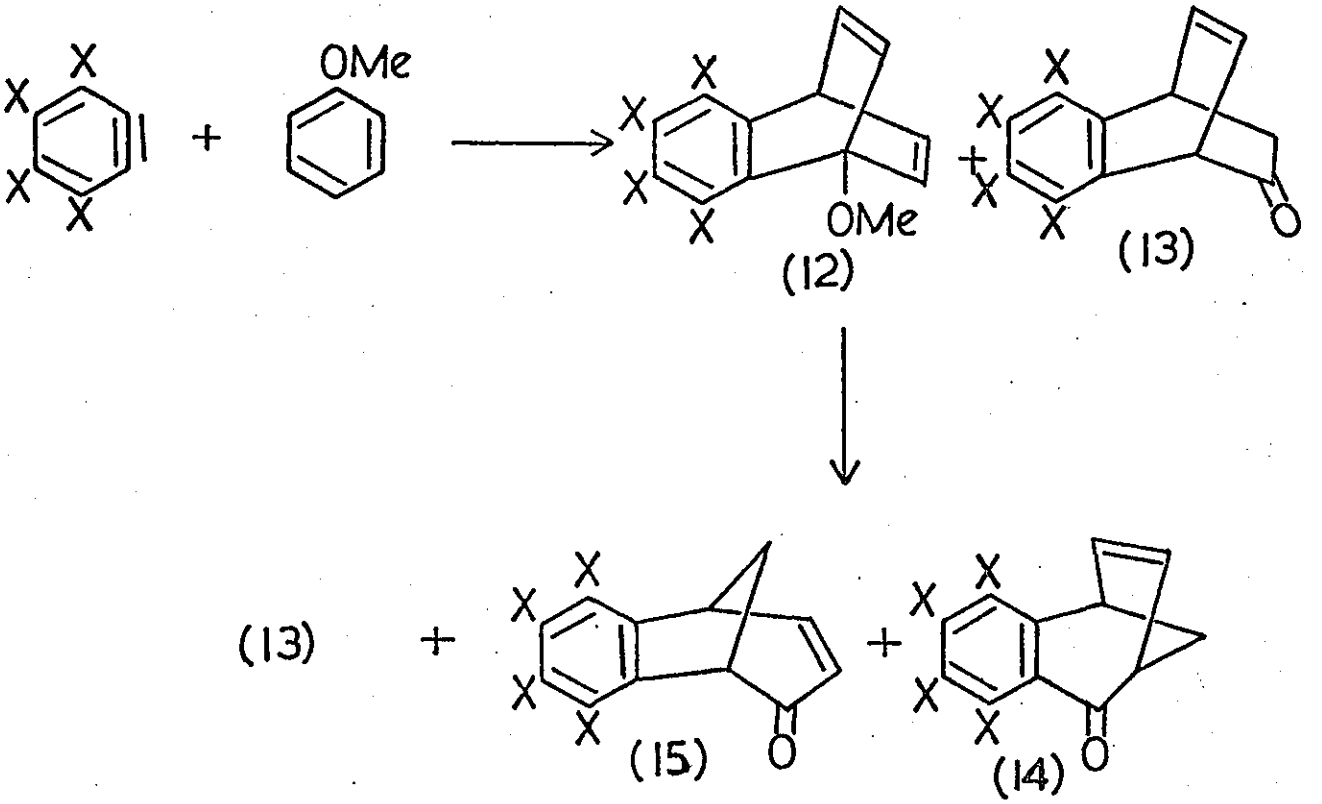
X =	F,[20]	35%
X =	Cl,[21]	55%
X =	Br,[22]	67%
X =	I,[23]	25%

Like benzynes, tetrahalogenoarynes undergo all kinds of nucleophilic additions and cycloaddition reactions but in much higher yields.[23] Tetrafluorobenzyne generated from pentafluorophenyl-lithium has been added to thiophen in the first observed Diels-Alder reaction of thiophen.[24]

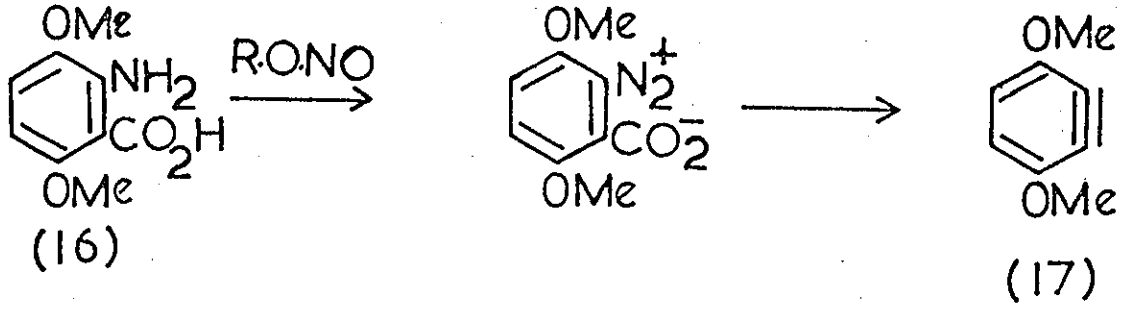


Furthermore, the high reactivity of tetrahalogenobenzynes has also been shown in their ability to cleave aliphatic ethers in good yield,[22,25] and to undergo addition reactions with a variety of carbonyl compounds.[26]

Nevertheless, the Diels-Alder adducts of tetrahalogenobenzynes with alkoxyaromatic compounds are of great interest. For instance, tetrahalogenobenzynes react with anisole to give the benzobarrelene derivative (12) and the benzobarrelenone (13). The compound (12) on treatment with acid rearranges readily to ketones (13), (14) and (15).[27] The mechanism of formation of these products is intriguing and is being investigated in these laboratories.



Very recently, 2-amino-3,6-dimethoxybenzoic acid (16) has been prepared[28] and like other anthranilic acids has been shown to be an efficient precursor for 3,6-dimethoxybenzyne (17).



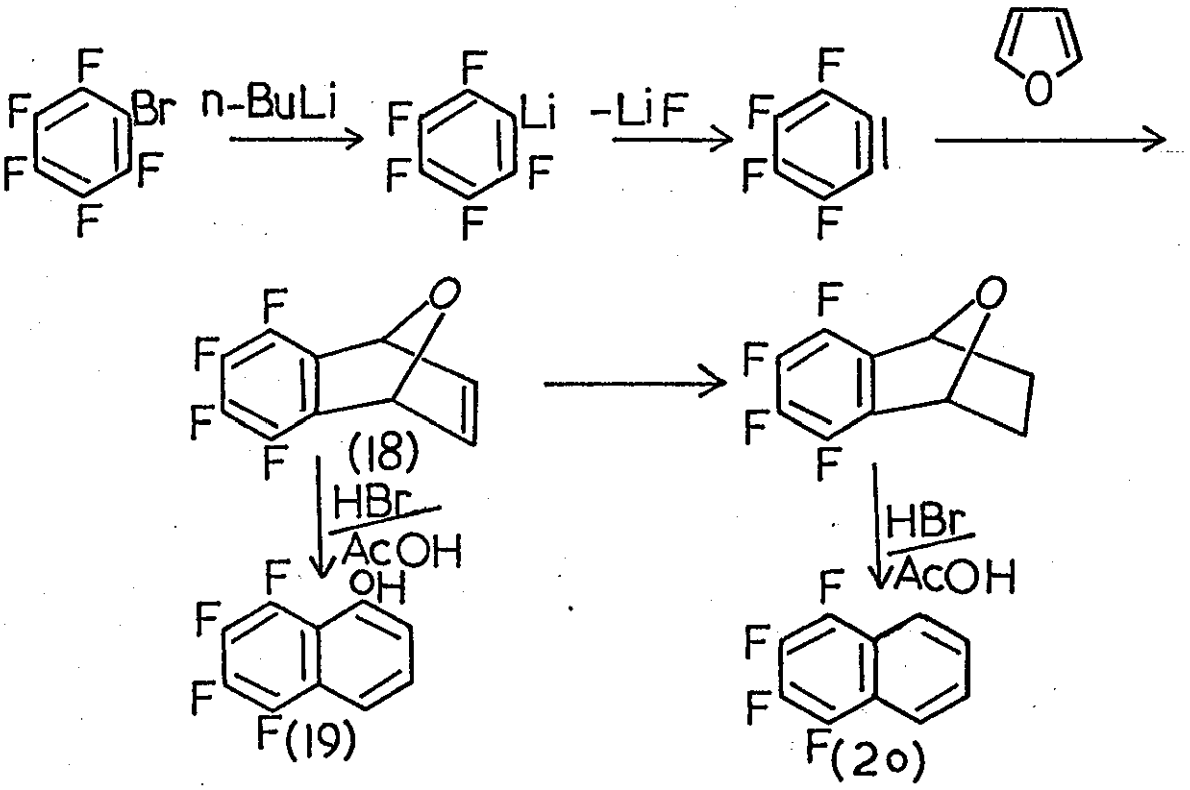
The work described in this thesis deals mainly with the generation of tetrafluoro- and tetrachloro- and 3,6-dimethoxy-benzyne and the utilisation of these highly reactive species in the synthesis of various compounds.

CHAPTER 1

SYNTHESIS OF 9-METHYL- AND 9,10-DIMETHYL-1,2,3,4,5,6,7,8-OCTAFLUORO-9,10-DIHYDRO-9,10,o-BENZENO-ANTHRACENES (9-METHYL- AND 9,10-DIMETHYL-1,2,3,4,5,6,7,8-OCTAFLUOROTRIPTYCENES)

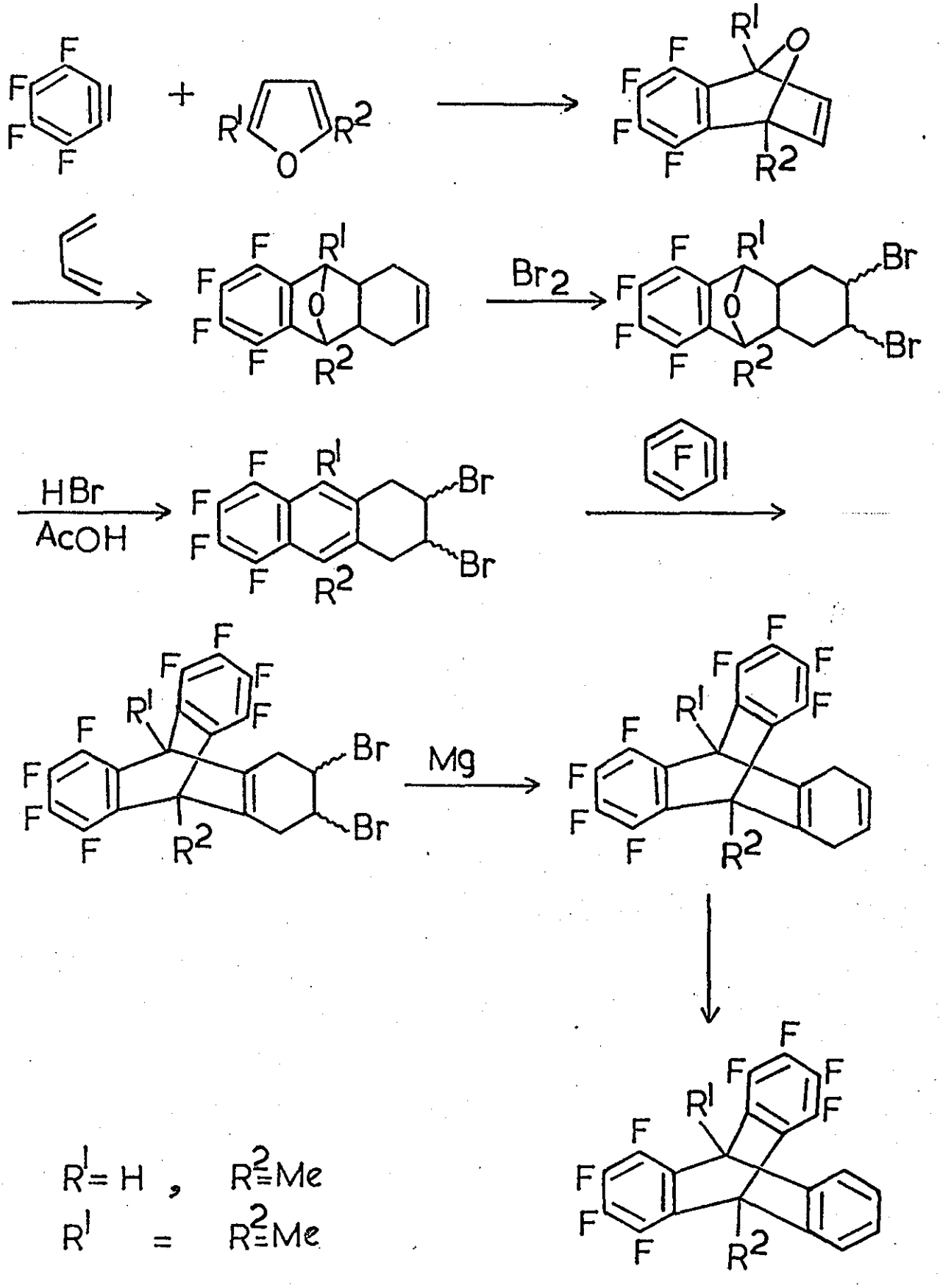
INTRODUCTION

Abundant data are now available on the cycloaddition reactions of tetrahalogenobenzynes with conjugated dienes.[14,23] However, the first Diels-Alder addition of tetrafluorobenzyne with furan to give 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydronaphthalene (18) was accomplished in 1962.[16b] The compound (18) can be readily converted into tetrafluoro-1-naphthol (19) and tetrafluoronaphthalene (20) in high yield.



The present work was undertaken with the view to extend the scope of tetrafluorobenzyne reactions to substituted furans and to investigate a good synthetic route to 9-alkyl- and 9,10-dialkyl-1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9,10-o-benzenoanthracenes[29] (octafluorotriptycenes) as outlined in Scheme 1.

Long range $^{19}F\text{---}^{1}H$ spin-spin coupling in the ^{1}H n.m.r. spectra has been observed in a variety of tetrafluorobenzyne-arene adducts[30,38] prepared in these laboratories in the past few years. The furan adduct



$R^1 = H$, $R^2 = Me$

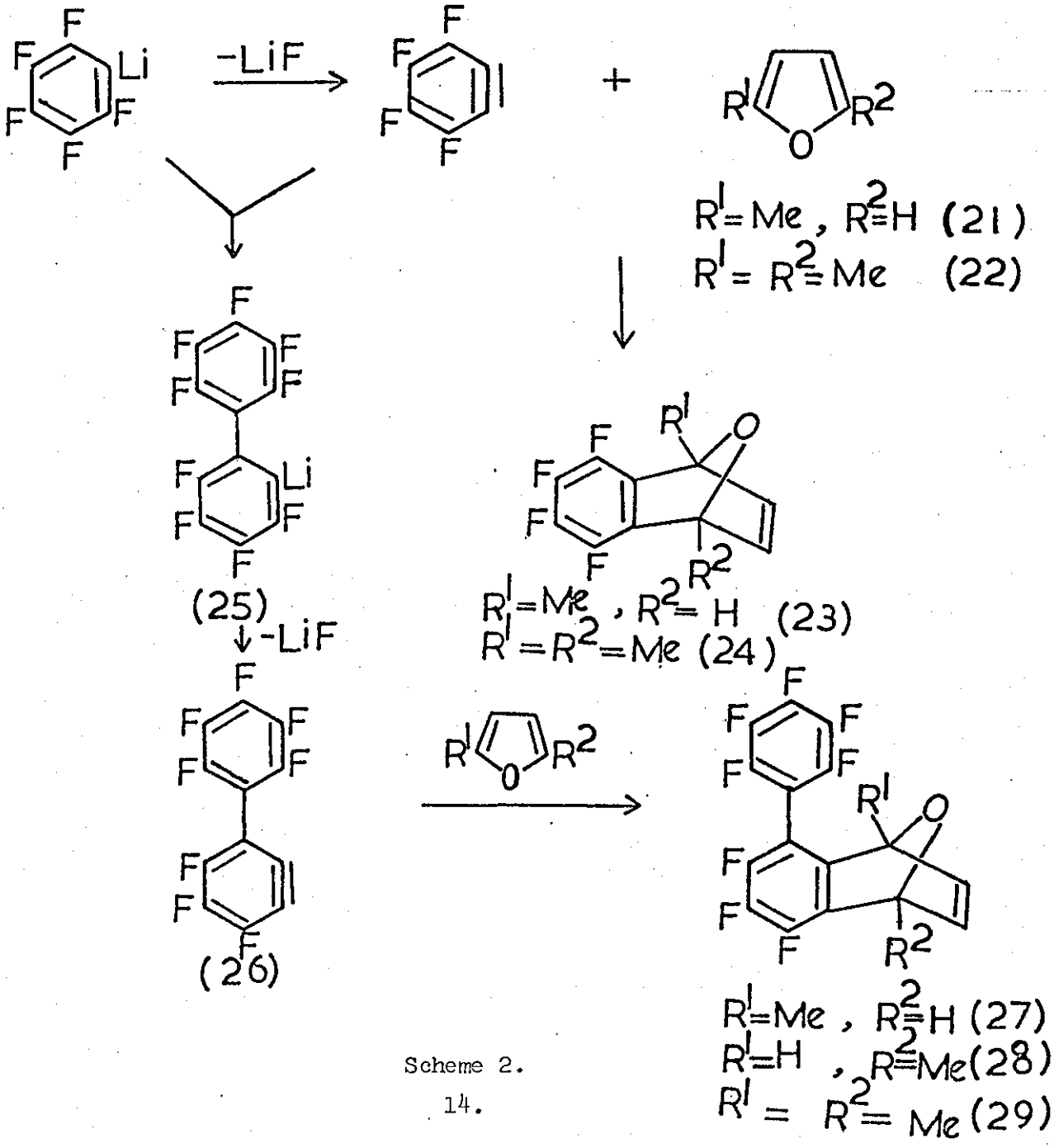
$R^1 = R^2 = Me$

Scheme 1

(18) also shows long range spin-spin coupling between the fluorine atoms at positions 5 and 8 and the hydrogen atoms at positions 1 and 4.[31] It was, therefore, of interest to examine this effect in the ^{1}H n.m.r. spectra of substituted furan-tetrafluorobenzyne adducts and in various other compounds involved in the synthesis of octafluoro-triptycenes.

DISCUSSION

The reactions of tetrafluorobenzyne generated from pentafluorophenyllithium[16b] with 2-methylfuran (21) and 2,5-dimethylfuran[32] (22) produced the expected cycloadducts 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1--methylnaphthalene (23) and 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro--1,4-dimethylnaphthalene (24) in high yield (Scheme 2). The structures of the adducts (23) and (24) were confirmed from their elemental analysis and spectral data.



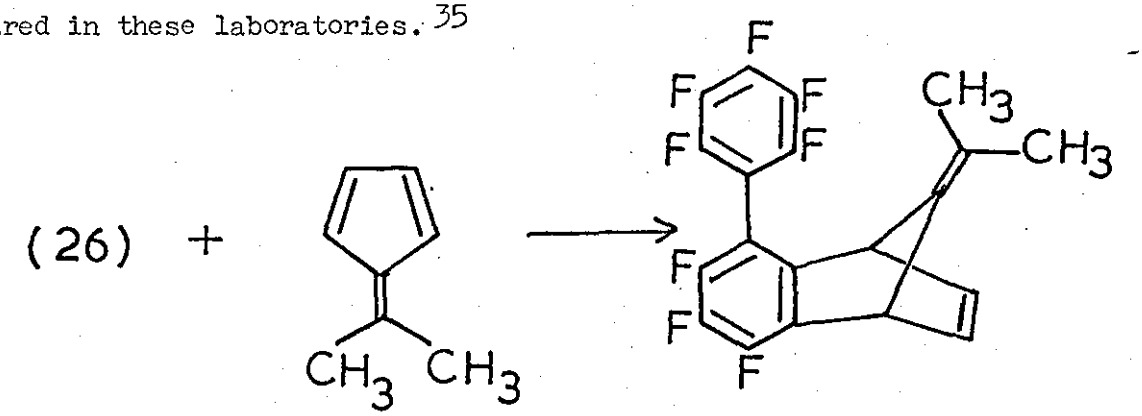
Scheme 2.

Massey and his co-workers have shown that the decomposition of pentafluorophenyl-lithium in a large excess of furan leads only to tetrafluorobenzyne-furan adduct (18).[33] They have also reported the formation of 2-lithiononafluorobiphenyl[34] (25) from tetrafluorobenzyne and pentafluorophenyl-lithium which then loses lithium fluoride to give rise to 3-pentafluorophenyltrifluorobenzyne (26). However, the intermediate formation of the aryne (26) was also indicated in tetrafluorobenzyne reactions with 2-methyl- and 2,5-dimethylfuran in which only a 3 molar equivalent of the furans was present. Thus, in the case of 2-methylfuran a mixture of two possible isomeric products was obtained which was separated by preparative layer chromatography over silica-gel. Elution with ether-light petroleum (1:4,v/v) gave 1,4-epoxy-6,7,8--trifluoro-1,4-dihydro-1-methyl-5-pentafluorophenylnaphthalene (28) in 5% yield and 1,4-epoxy-5,6,7-trifluoro-1,4-dihydro-1-methyl-8-pentafluorophenylnaphthalene (27) in 2.5% yield (Scheme 2). The structures of the isomers were deduced from their ^{1}H n.m.r. spectral data. In compound (28), for instance, the olefinic protons showed a multiplet at τ 2.8-3.15, the bridgehead proton was observed as a multiplet at τ 4.65, and the methyl resonance was observed as a singlet at τ 7.95 which was identical with the chemical shift of the methyl group in the compound (23). On the other hand, the n.m.r. spectrum of the compound (27) showed a multiplet at τ 2.7-3.2 for olefinic protons, a multiplet at τ 4.05 ascribed to a bridgehead proton and the methyl resonance was observed as a singlet at τ 8.52. This suggests that the biphenyl system in compound (27) is twisted; the upfield shift of ca. 0.6 p.p.m. in the methyl group is attributed to the diamagnetic anisotropy of the C_6F_5 residue in the molecule as compared with the compound (28) in which

the bridgehead methine proton is shielded and exhibits an upfield shift of 0.6 p.p.m. Furthermore, the structures of the adducts (27) and (28) were compatible with their analytical and other spectral data.

Likewise, 3-pentafluorophenyltrifluorobenzyne (26) was trapped by 2,5-dimethylfuran and afforded the Diels-Alder adduct 1,4-epoxy-5,6,7--trifluoro-1,4-dihydro-1,4-dimethyl-8-pentafluorophenylnaphthalene (29) in 10% yield (Scheme 2) as the only product. Its structure was supported by its elemental analysis and spectral data. In the ^{1}H n.m.r. spectrum the methyl group at position 1 was observed as a singlet at τ 8.55 and the methyl group at position 4 also showed a singlet at τ 7.95 which was consistent with the chemical shift of the methyl group in compound (24).

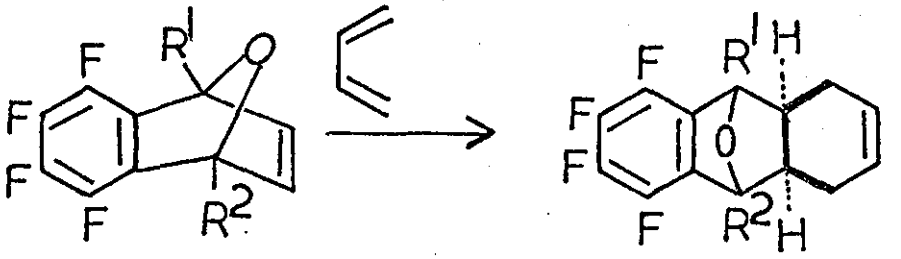
Incidentally, when this work was in progress, an analogous compound (30) derived from the aryne (26) and 6,6-dimethylfulvene was also prepared in these laboratories.[35]



(30)

Earlier studies have revealed that benzyne-furan adduct behaves as an excellent dienophile which on further Diels-Alder addition followed by dehydration leads to higher anellated aromatic hydrocarbons.[36] Wolthuis[37] has synthesised various substituted anthracenes in this manner. Thus, making use of the same approach, the reactions of the

compounds (23) and (24) with excess of buta-1,3-diene at 70°C for 14 days resulted in the formation of 1,4-cyclo-adducts, 9,10-epoxy-5,6,7,8--tetrafluoro-1,4,4a,9,9a,10-hexahydro-9-methylanthracene (31) and 9,10--epoxy-5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9,10-dimethylanthracene (32) in quantitative yield (Scheme 3). The structures (31) and (32) were

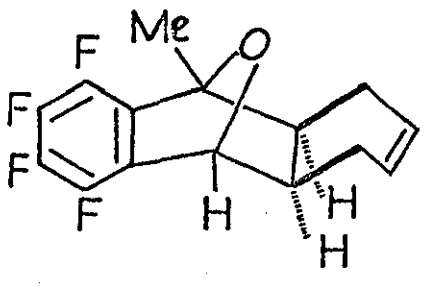


R^1=Me , R^2=H (23) R^1= Me , R^2= H (31)

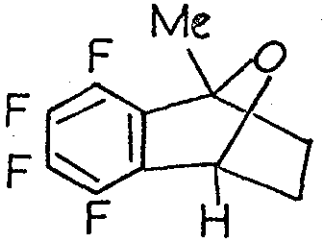
R^1 = R^2= Me (24) R^1 = R^2= Me (32)

Scheme 3

consistent with their elemental analysis and spectral data. The stereochemistry of (31) was assigned on the basis of a comparison of the ^1H n.m.r. spectra of the adducts (31) and (33).[29] In the case of (31) the bridgehead methine proton was observed as a doublet at τ 4.94 $/J/_{H,H}$ (endo) = 1.7 Hz. whereas the methine proton in compound (33) gave rise to a doublet of doublets at 4.45 $/J/_{H,H}$ (endo) = 1.7 Hz. and $/J/_{H,H}$ (exo) = 6.2 Hz. These observations lead to the conclusion that H_{4a} and H_{9a} are endo in the compound (31).



(31)



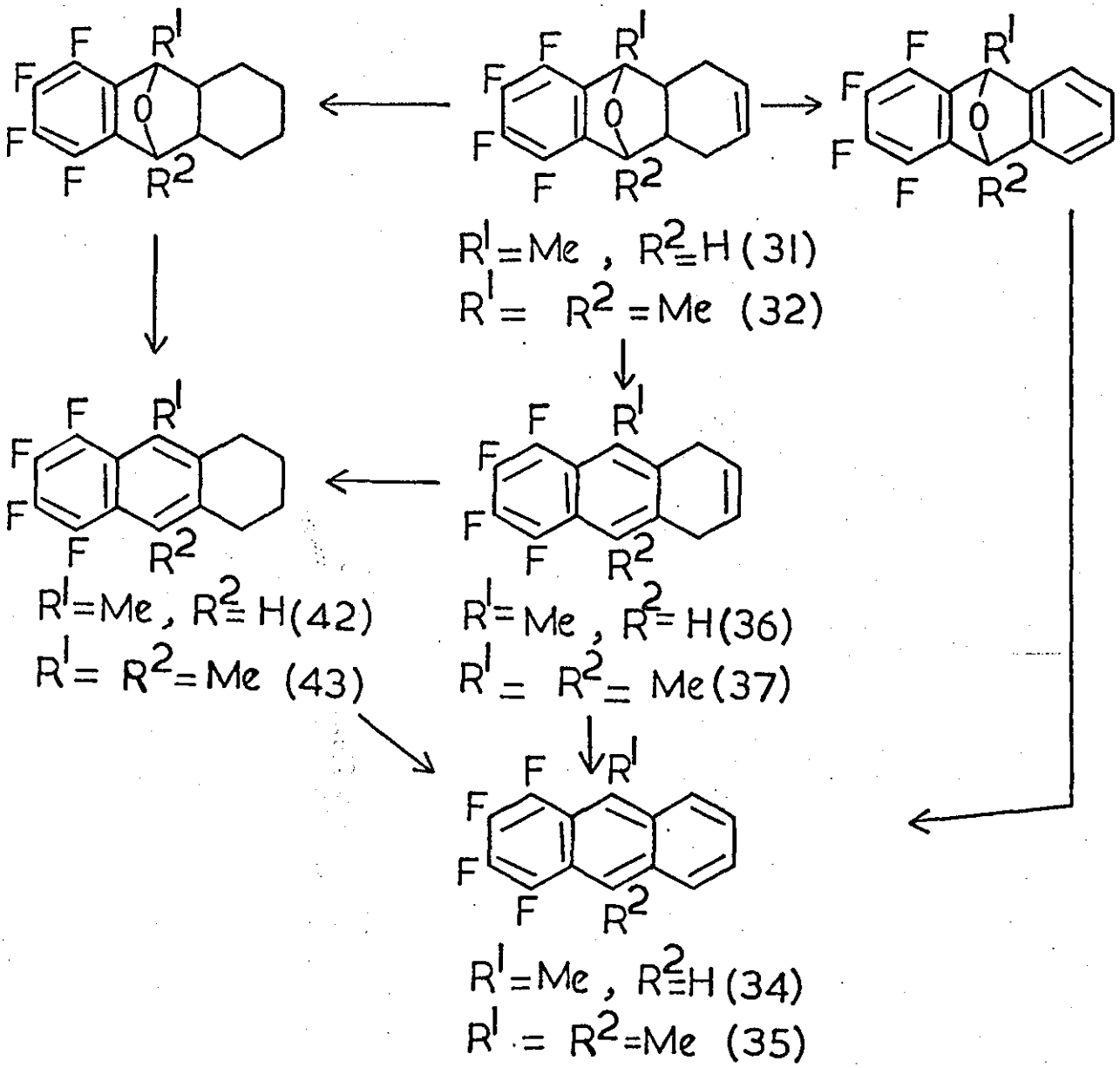
(33)

After having obtained the adducts (31) and (32) the next step was to convert them to their corresponding anthracene derivatives. A number of suitable routes seemed possible to obtain the required compounds (34) and (35) (Scheme 4). However, previous work[38] had either failed or had led to products which were not characterised adequately. For example, all attempts to dehydrogenate the addducts (31) and (32) with chloranil, dichlorodicyano-p-benzoquinone, or palladium-carbon to their anthracene derivatives were unsuccessful.

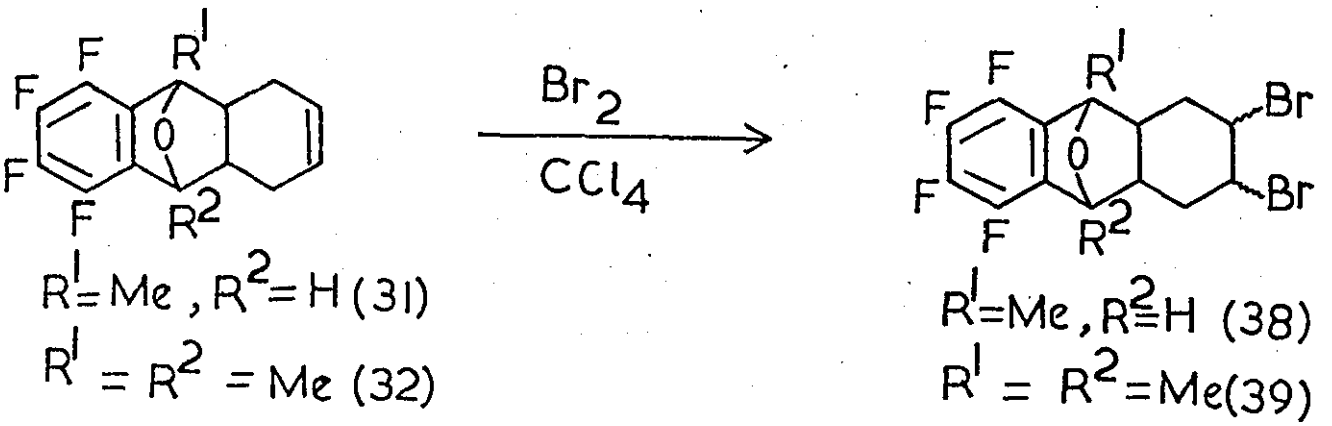
The compounds (31) and (32) apparently gave (36) and (37) when heated under reflux with acetic anhydride containing a small quantity of hydrobromic acid.[38] However, the purification of the products in these reactions was a problem and the yields were also not good. The compounds (36) and (37) were hydrogenated to (42) and (43) respectively.

In a different approach however, the adducts (31) and (32) were reacted with bromine in carbontetrachloride at room temperature and after the work-up gave the isomeric dibromides, 2,3-dibromo-9,10-epoxy--5,6,7,8-tetrafluoro-1,2,3,4,4a,9,9a,10-octahydro-9-methylanthracene (38) and 2,3-dibromo-9,10-epoxy-5,6,7,8-tetrafluoro-1,2,3,4,4a,9,9a,10--octahydro-9,10-dimethylanthracene (39) in quantitative yield (Scheme 5). The assigned structures, (38) and (39) were compatible with the spectral data.

When the compound (38) was heated under reflux in acetic acid containing hydrobromic acid for 12 hours, a mixture of two compounds was obtained which were separated by column chromatography on silica-gel. Elution with light petroleum afforded 1,2,3,4-tetrafluoro-9-methylanthracene (34) in 33% yield and further elution with benzene gave the expected

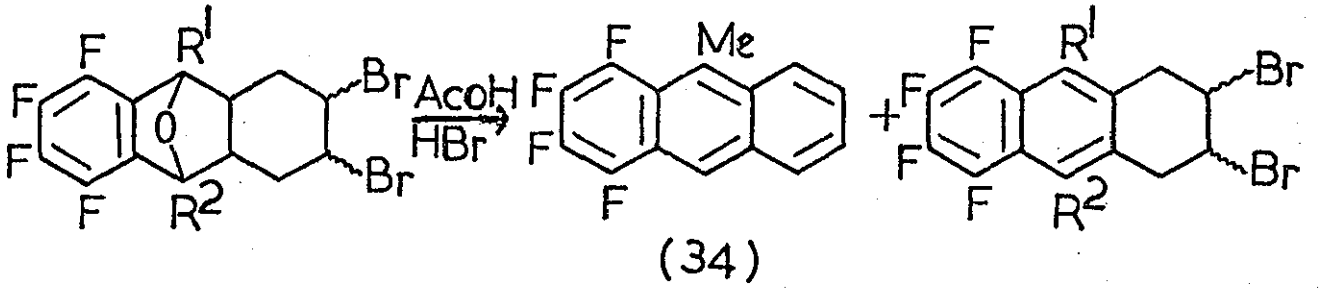


Scheme 4



Scheme 5

2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-methylanthracene (40) in 65% yield (Scheme 6). The formation of anthracene (34) is unusual but quite interesting as dehydration and dehydrobromination have occurred in this reaction. The structures of the compounds (34) and (40) were



$R^1 = Me$, $R^2 = H$ (38)

$R^1 = R^2 = Me$ (39)

$R^1 = Me$, $R^2 = H$ (41)

$R^1 = R^2 = Me$ (42)

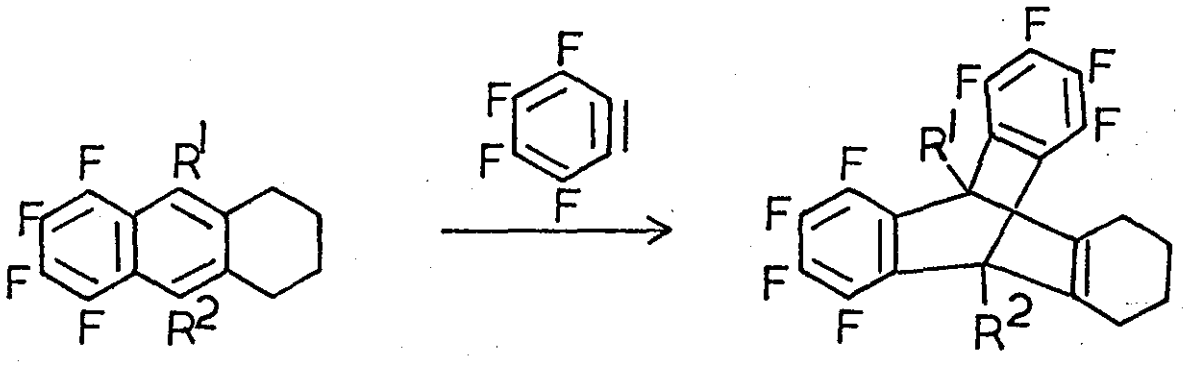
Scheme 6

confirmed from their spectral data. The compound (34) had also been prepared in these laboratories by other workers[38] and the new material was found to be identical with the authentic sample.

Similarly, the compound (39) under identical conditions formed the anticipated 2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9,10--dimethylanthracene (41) in 84% yield (Scheme 6). The structure of this compound was characterised by its mass spectrum. The ^1H n.m.r. could not be obtained because of its very low solubility in various solvents.

The compounds (42) and (43) were then reacted with tetrafluorobenzyne generated from pentafluorophenylmagnesium chloride and after the usual

work-up gave rise to the expected cyclo-adducts, 1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9-methyl-triptycene (44) in 50% yield and 1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9,10-dimethyl-triptycene (45) in 58% yield (Scheme 7). The structures of these compounds were established from their elemental analytical and spectral data.

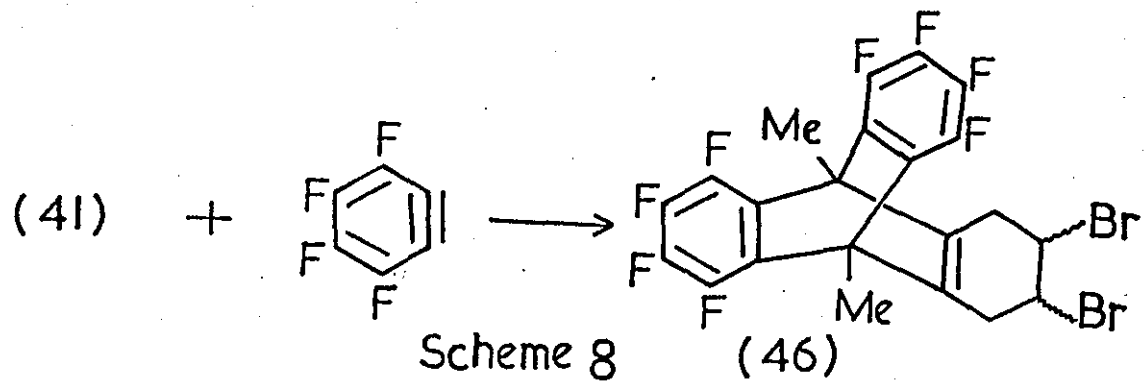


$R^1 = Me, R^2 = H$ (42)
$R^1 = R^2 = Me$ (43)

$R^1 = Me, R^2 = H$ (44)
$R^1 = R^2 = Me$ (45)

Scheme 7

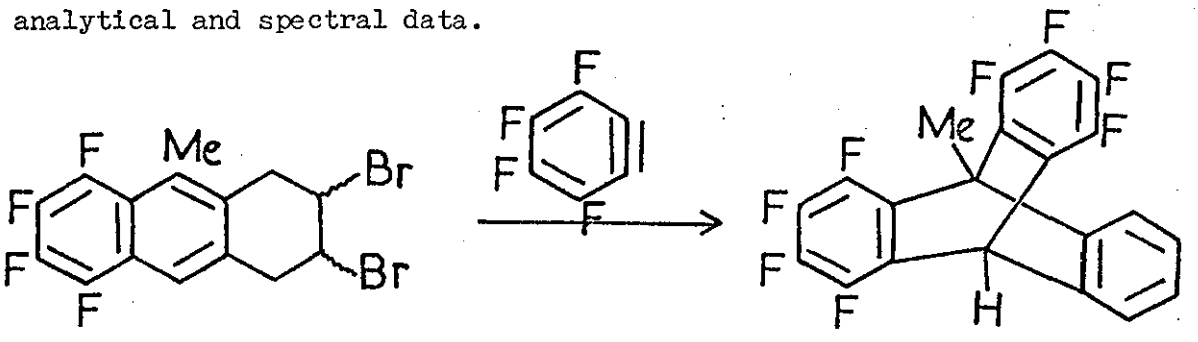
Likewise, compound (41) upon reaction with tetrafluorobenzyne from pentafluorophenylmagnesium chloride gave the expected 14,15-dibromo-1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9,10-dimethyltriptycene (46) in 60% yield (Scheme 8). The structure (46) was consistent with its ^1H n.m.r. and mass spectra.



Scheme 8 (46)

However, when compound (40) was allowed to react with an excess of tetrafluorobenzyne generated from pentafluorophenylmagnesium chloride,

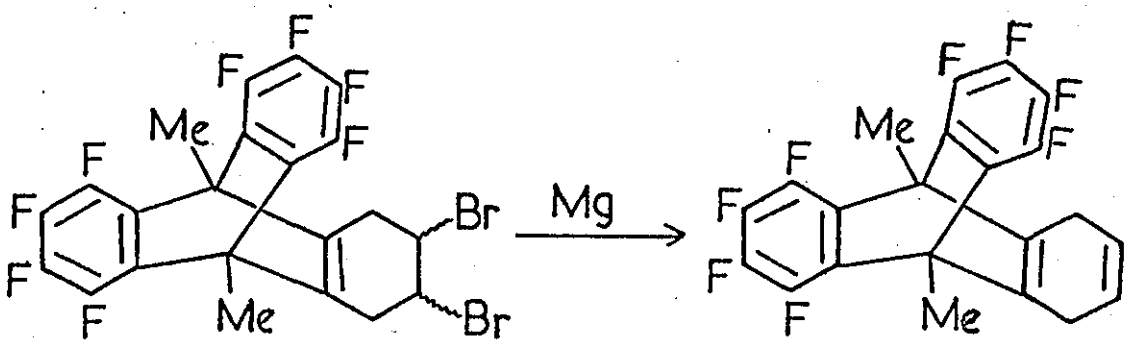
1,2,3,4,5,6,7,8-octafluoro-9-methyltriptycene (47) was the only product isolated in 55% yield (Scheme 9). Benzyne in its reactions has been found to dehydrogenate various substrates.[1a] In this particular reaction formal dehydrobromination has occurred. It is possible that the initial adduct was debrominated by the excess of magnesium present in the reaction mixture and the dihydrotriptycene thus produced gave rise to the product isolated. The structure of the compound (47) was compatible with its analytical and spectral data.



(40) (47)

Scheme 9

The compound (46) was debrominated very cleanly with magnesium in ether and after the standard work-up gave 1,2,3,4,5,6,7,8-octafluoro--13,16-dihydro-9,10-dimethyltriptycene (48) in 85% yield (Scheme 10).



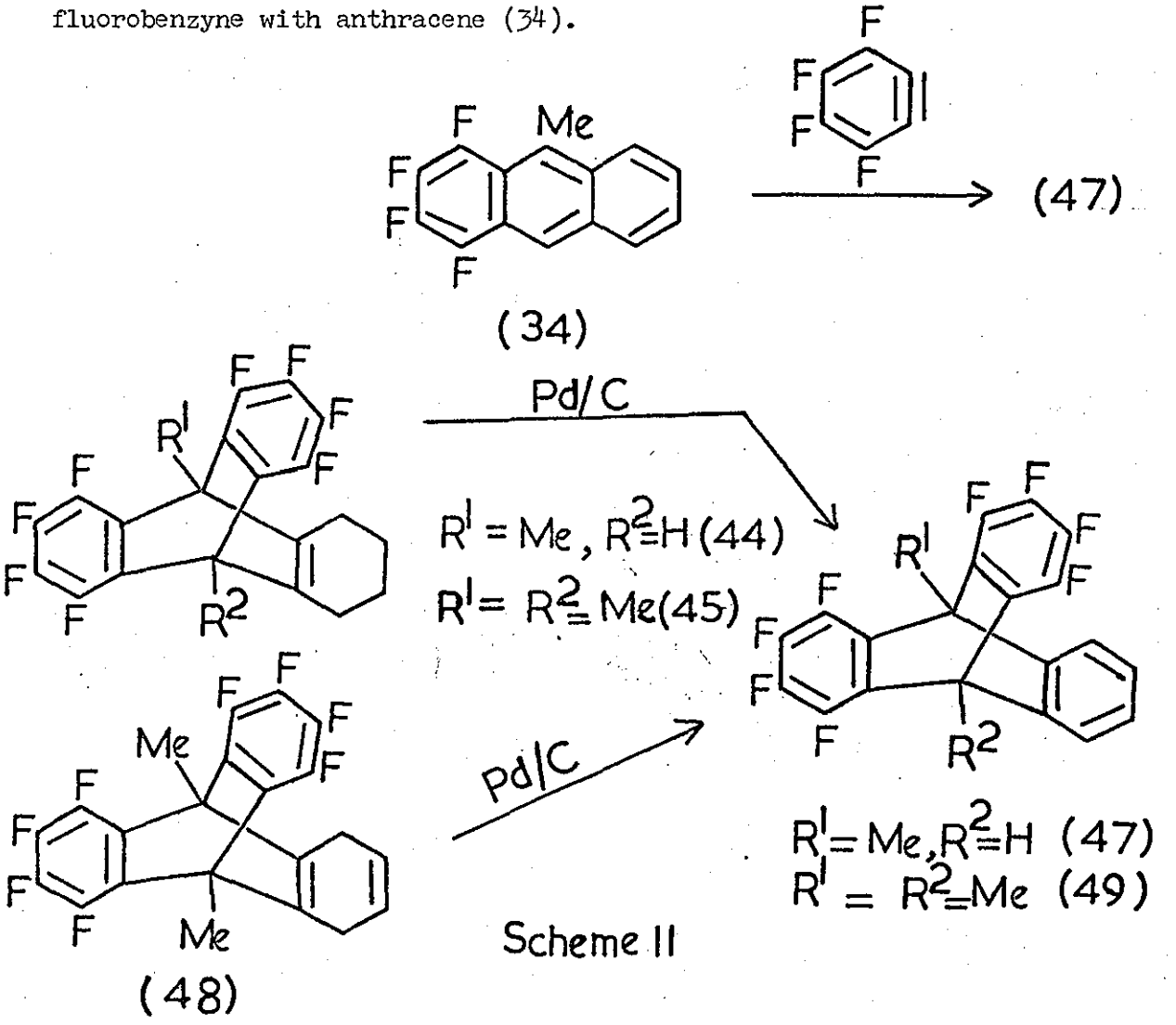
(46) (48)

Scheme 10

The compound (48) was characterised by ^{1}H n.m.r. and mass spectrometry.

The final step in the synthesis of dihydrobenzenoanthracene derivatives, therefore, is to dehydrogenate the adducts (44), (45) and (48)

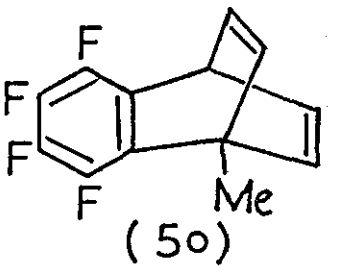
to the required products. Thus, (44), (45) and (48) on heating with palladium-carbon at 240-270°C under an atmosphere of nitrogen resulted in the formation of (47) and 1,2,3,4,5,6,7,8-octafluoro-9,10-dimethyl-triptycene (49) in high yield (Scheme 11). The structure of the compound (49) was established from its elemental analysis and spectral data. The compound (47) was also obtained in high yield from the reaction of tetrafluorobenzyne with anthracene (34).



Scheme 11

Long-range ^{19}F——^{1}H spin-spin coupling was studied from the ^{1}H n.m.r. spectra of the various compounds described above. It was noteworthy that all those compounds containing an oxygen bridge showed very small ^{19}F——^{1}H spin-spin coupling. The methyl resonances in the

compounds (23) and (24) in which a methyl group is in a peri-relationship to a fluorine atom are slightly broadened. They do not show the pronounced long-range $^{19}F—^{1}H$ spin-spin coupling which has been observed in the benzobarrelene derivatives, for example, in the compound (50) $|^{5}J_{HF}|$ is 5.1 Hz.[30]



(50)

The absence of appreciable $^{19}F—^{1}H$ spin-spin coupling in the compounds (23), (24), (27), (28), (29), (31), (32), (38) and (39) may be associated with the presence of the electronegative bridging group in these molecules. On the other hand, the compounds without the oxygen bridge gave rise to pronounced long-range $^{19}F—^{1}H$ spin-spin coupling. In the compounds (44-49) for instance, the methyl resonances were observed as triplets $|^{5}J_{HF}|$ *ca.* 6 Hz. All these results are given in Table 1.

Table 1

Compound	R_1	R_2	$J_{^1H\text{---}^{19}F}$ R_1	$J_{^1H\text{---}^{19}F}$ R_2
23	Me	H	Peak broadening only	2Hz.
24	Me	Me	" " "	
27	Me	H	" " "	2Hz.
28	H	Me	" " "	
29	Me	Me	" " "	
31	Me	H	" " "	
32	Me	Me	" " "	
34	Me	H	6 Hz.	-
36	Me	H	6 Hz.	-
38	Me	H	Peak broadening only	
39	Me	Me	" " "	
40	Me	H	5.1 Hz.	
41	Me	Me	^1H n.m.r. spectrum was not recorded.	
44	Me	H	6 Hz.	1.6 Hz.
46	Me	Me	6.35 Hz.	-
47	Me	H	5.95 Hz.	1.6 Hz.
48	Me	Me	6 Hz.	-
49	Me	Me	6 Hz.	-

Experimental

General :-

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. All compounds were colourless solids unless otherwise stated.

All reactions involving organolithium or Grignard reagents were carried out in a glassware dried overnight at 120°C and under an atmosphere of oxygen free nitrogen. Anhydrous magnesium sulphate was used as a drying agent for organic solutions unless otherwise stated. The solvents were dried and purified by standard procedures. Light petroleum refers to the fraction b.p. 60-80°C unless otherwise stated.

Thin layer chromatography was carried out using silica-gel (Merck PF_{254}). Column chromatography was carried out with silica-gel (Fisons) and 'CAMAG' alumina (Brockmann activity 1).

Analytical g.l.c. was carried out using a Pye 104 series chromatograph on 5ft. columns of (a) 20% S.E. 30 on chromosorb W and (b) 10% APIEZON L on chromosorb W, using a hydrogen flame ionisation detector.

Infra-red spectra were determined for potassium bromide discs in the case of solids or as thin films in the case of liquids unless otherwise stated, on a Perkin-Elmer 257 spectrometer. Ultra-violet spectra were determined with a Unicam SP 8000 spectrophotometer. ^1H N.m.r. spectra were determined using Perkin-Elmer 60 MHz. R10 and 90 MHz. R32 instruments using tetramethylsilane as an internal standard. ^1H n.m.r. spectra at 220 MHz. and 100 MHz. were recorded at the P.C.M.U. (Harwell). Mass spectra were recorded on an A.E.I. MS12 spectrometer and high resolution mass measurements were carried out at the P.C.M.U. Molecular weights of bromo- and chloro-compounds as determined by mass spectrometry correspond to the major molecular ions in the isotopic clusters.

1. Preparation of 2,5-dimethylfuran.[32]

Hexane-2,5-dione (114 g.), acetic anhydride (112 g.), and zinc chloride (1 g.) were placed in a round bottom flask and after the exothermic reaction had subsided the mixture was heated under reflux for 3 hours. On cooling the reaction mixture was made alkaline with sodium hydroxide (6N) and steam distilled. The organic phase was separated, dried (Na_2SO_4) and distillation of the crude product gave 2,5-dimethylfuran (22), (49g., 52%), b.p. 94-96°C (lit.[32] b.p. 93-94°C).

2. Reaction of tetrafluorobenzyne with 2-methylfuran.

A solution of n-butyl-lithium (25 ml., 0.06 mole) was added dropwise to a stirred solution of bromopentafluorobenzene (12.4 g., 0.05 mole) in ether (100 ml.) at -70°C. After a further period of 30 minutes at -70°C 2-methylfuran (12.3 g., 0.15 mole) in ether (30 ml.) was slowly introduced into the reaction flask. The reaction mixture was then allowed to warm to room temperature and after about 12 hours was washed with dilute hydrochloric acid, water, and dried. The solvent was removed and distillation under reduced pressure afforded 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1-methylnaphthalene (23) (7 g., 61%), b.p. 50-52°C at 0.3 mm Hg., m.p. 26-28°C (from methanol).

Preparative t.l.c. of the residue left after the distillation of (23) gave three products.

(a) More of compound (23), (1.1 g., 10%), thus increasing the overall yield to 71%.

^{1}H n.m.r. ($CDCl_3$) τ 2.8-3.15 (m., 2 olefinic protons), 4.1 (t., bridgehead proton), and 7.95 (s., 3 methyl protons).

$\nu_{max.}$ 3000, 2960, 1500, 1400, 1310, 1280, 1200, 1150, 1120, 1040, 1000, 940, 860, 835, 725 cm.$^{-1}$

$\lambda_{max.}$(ethanol) 265 (logϵ 2.78) nm.

Found: C, 57.55; H, 2.85%; M (mass spectrometry), 230. $C_{11}H_6F_4O$ requires C, 57.4; H, 2.65%; M, 230.

(b) 1,4-epoxy-6,7,8-trifluoro-1,4-dihydro-1-methyl-5-pentafluorophenyl-naphthalene (28), (1 g., 5%), m.p. 130°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 2.8-3.15 (m., 2 olefimic protons), 4.65 (m., bridgehead proton), and 7.95 (s., 3 methyl protons).

$\nu_{max.}$ 3000, 2955, 1660, 1645, 1530, 1500, 1420, 1395, 1365, 1300, 1280, 1220, 1200, 1140, 1130, 1080, 1050, 980, 900, 840, 750, 730 and 715 cm.$^{-1}$

Found: C, 53.95; H, 2.0%; M (mass spectrometry), 378. $C_{17}H_6F_8O$ requires C, 53.9; H, 1.6%; M, 378; m/e 378, 362, 352 and 335; and

(c) 1,4-epoxy-5,6,7-trifluoro-1,4-dihydro-1-methyl-8-pentafluorophenyl-naphthalene (27), (0.5 g., 2.5%), m.p. 148-150°C (from hexane). ^{1}H n.m.r. ($CDCl_3$) τ 2.7-3.2 (m., 2 olefinic protons), 4.05 (m., bridgehead proton) and 8.52 (s., 3 methyl protons).

$\nu_{max.}$ 1640, 1500, 1465, 1390, 1300, 1135, 1065, 980, 860, 830 and 722 cm.$^{-1}$

Found: C, 54.1; H, 1.65%; M (mass spectrometry), 378. $C_{17}H_6F_8O$ requires C, 53.9; H, 1.6%; M, 378; m/e 378, 362, 352, 335.

3. Reaction of tetrafluorobenzyne with 2,5-dimethylfuran.

The reaction was carried out as described in the case of 2-methylfuran and the usual work-up afforded 1,4-epoxy-5,6,7,8-tetrafluoro--1,4-dihydro-1,4-dimethylnaphthalene (24), (8.1 g., 66%), b.p. 56-58°C at 0.3 mm Hg., m.p. 52-54°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.1 (m., 2 olefinic protons), 8.0 (s., 6 methyl protons).

$\nu_{max.}$ 2990, 2960, 2930, 2860, 1500, 1405, 1390, 1310, 1270, 1160, 1140, 1030, 890, 830, 722 cm.$^{-1}$

$\lambda_{max.}$ (ethanol) 264 (log ϵ 3.01) nm.

Found: C, 58.85; H, 3.45%; M (mass spectrometry), 244.

$C_{12}H_8F_4O$ requires C, 59.0; H, 3.3%; M, 244; m/e 244, 229, 218 and 203.

The residue left after the distillation of (24) was placed on a column of neutral alumina. Elution with light petroleum gave 1,4-epoxy-5,6,7-trifluoro-1,4-dihydro-1,4-dimethyl-8-pentafluorophenylnaphthalene (29), (1.8 g., 10%), m.p. 140-141°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 3.1 (s., 2 olefinic protons),
7.95 (s., 3 methyl protons) and
8.55 (s., 3 methyl protons).

$\nu_{max.}$ 2960, 2930, 2860, 1650, 1505, 1465, 1375, 1160, 1140, 1060, 990, 890, 860, 830, 735 and 725 cm.$^{-1}$

Found: C, 55.0; H, 2.1%; M (mass spectrometry), 392.

$C_{18}H_8F_8O$ require C, 55.1; H, 2.05%; M, 392; m/e 392, 376, 365, 349, 329, 310, 279 and 273.

4. Reaction of 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1-methyl-naphthalene (23) with buta-1,3-diene.

A mixture of compound (23), (2g., 0.01 mole), hydroquinone (ca. 10 mg.) and buta-1,3-diene (1.1 g., large excess) was heated in a sealed tube for 14 days at 70°C and the work-up gave 9,10-epoxy-5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9-methylanthracene (31), (98%), m.p. 62-63°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 4.01-4.13 (m., 2 olefinic protons, 4.94 (d., bridgehead proton, $|J|$ = 1.7 Hz.), 7.37-8.20 (m., 6 protons), and 8.22 (s., 3 methyl protons).

$\nu_{max.}$ 3050, 3035, 3015, 2965, 2910, 2855, 1640, 1500, 1455, 1400, 1290, 1150, 1030, 855 and 712 cm.$^{-1}$

$\lambda_{max.}$ (ethanol) 280 (log ϵ 2.09) and 261 (2.51) nm.

Found: C, 63.1; H, 4.3%; M (mass spectrometry), 284. $C_{15}H_{12}F_4O$ requires C, 63.4; H, 4.25%; M, 284.

5. Reaction of 1,4-epoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-dimethyl-naphthalene (24) with buta-1,3-diene.

A mixture of compound (24), (2.44 g., 0.011 mole), hydroquinone (ca. 10 mg.) and buta-1,3-diene (1.1 g.) was heated in a sealed tube as described in the previous experiment and the usual work-up yielded 9,10-epoxy-5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9,10-dimethylanthracene (32), (2.98 g., 100%), m.p. 84-85°C (from methanol).

^{1}H n.m.r.($CDCl_3$) τ 3.97-4.1 (m., 2 olefinic protons), 7.55-8.20 (m., 6 protons) and 8.25 (s., 6 methyl protons).

$\nu_{max.}$ 3055, 2920, 2860, 1495, 1460, 1410, 1390, 1380, 1290, 1235, 1160, 1100, 1070, 1030, 900, 860 and 710 cm.$^{-1}$

$\lambda_{max.}$ (ethanol) 280 (log ϵ 2.02) and 260 (2.44) nm.

Found: C, 64.65; H, 4.75%; M (mass spectrometry) 298. $C_{16}H_{14}F_4O$ requires C, 64.45; H, 4.75%; M, 298.

6. Reaction of 9,10-epoxy-5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro--9-methylanthracene (31) with bromine.

Bromine (3.0 g., 0.018 mole) was added dropwise at room temperature to a stirred solution of (31), (5.0 g., 0.019 mole) in carbon tetrachloride (100 ml.). After the addition of bromine the reaction mixture was kept at room temperature for a further period of 4 hours. The solvent was removed under reduced pressure to give an isomeric mixture of the dibromides, 2,3-dibromo-9,10-epoxy-5,6,7,8-tetrafluoro-1,2,3,4,4a,9,9a, 10-octahydro-9-methylanthracene,(38), (7.7 g., 97%), m.p. 116-121°C (from benzene).

^{1}H n.m.r. ($CDCl_3$) τ 4.82 (m., one proton), 5.17 (m., one proton, 5.65 (m., one proton), 7.85 (m., 6 protons), and 8.18 (s., 3 protons).

$\nu_{max.}$ 3100, 2980, 2930, 1500, 1405, 1295, 1155, 1110, 1050, 1010, 975, 935, 835 and 700 cm.$^{-1}$

M.W. M (mass spectrometry), 444; m/e 446, 444 and 442. $C_{15}H_{12}Br_2F_4O$ requires M, 444.

7. Reaction of 9,10-epoxy-5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9,10-dimethylanthracene (32) with bromine.

Bromine (1.1 g., 0.007 mole) was added dropwise at room temperature to a well-stirred solution of (32), (2.0 g., 0.07 mole) in carbon tetrachloride (50 ml.). The usual work-up afforded 2,3-dibromo--9,10-epoxy-5,6,7,8-tetrafluoro-1,2,3,4,4a,9,9a,10-octahydro-9,10--dimethylanthracene (39), (3.0 g., 99.5%), m.p. 120-122°C (from benzene).

^{1}H n.m.r. ($CDCl_3$) τ 5.2 (m., one proton), 5.75 (m., one proton), 7.8-8.1 (m., 6 protons) and 8.2 (s., 6 protons).

$\nu_{max.}$ 1500, 1460, 1410, 1390, 1380, 1300, 1290, 1240, 1150, 1105, 1030, 910, 860 and 710 cm.$^{-1}$

M.W. M (mass spectrometry), 458; m/e 460, 458, and 456. $C_{16}H_{14}Br_2F_4O$ requires M, 458.

8. Action of acid on 2,3-dibromo-9,10-epoxy-5,6,7,8-tetrafluoro--1,2,3,4,4a,9,9a,10-octahydro-9-methylanthracene (38).

A mixture of compound (38), (5.2 g., 0.011 mole), acetic acid (70 ml.) and hydrobromic acid (11 ml.) was heated under reflux for 12 hours. The standard work-up gave a mixture of two compounds which were separated by column chromatography (silica-gel) and yielded :

(a) 1,2,3,4-tetrafluoro-9-methylanthracene (34), (1.0 g., 33%), m.p. 239°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 1.6-3.5 (m., 5 protons), 7.35 (d., 3 protons), $|J|_{HF}$ = 6.0 Hz.)

$\lambda_{max.}$ (cyclohexane) 386 (log ϵ 4.01), 366 (4.10) and 347 (3.93) nm.

M.W. M (mass spectrometry), 264. $C_{15}H_8F_4$ requires M, 264; and

(b) 2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-methylanthracene (40), (3.2 g., 65%), m.p. 150-151°C (from benzene).

^{1}H n.m.r. ($CDCl_3$) τ 2.28 (br.s., 1 proton), 5.12 (m., 2 protons), 5.5-6.8 (m., 4 protons), and 7.28 (d., 3 protons, $|J|_{H-F}$ = 5.1 Hz.).

$\nu_{max.}$ 3000, 2960, 1680, 1615, 1590, 1515, 1490, 1455, 1400, 1360, 1270, 1180, 1155, 995, 930, 890, 870, 815 and 735 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 302 (log ϵ 3.64), 291(3.77), 282 (3.75) and 281 (3.75) nm.

M.W. M (mass spectrometry), 426; m/e 428, 426 and 424. $C_{15}H_{10}Br_2F_4$ requires M, 426.

9. Action of acid on 2,3-dibromo-9,10-epoxy-5,6,7,8-tetrafluoro-1,2,3,4,4a,9,9a,10-octahydro-9,10-dimethylanthracene (39).

A mixture of compound (39), (2.0 g., 0.004 mole), acetic acid (50 ml.) and hydrobromic acid (4 ml.) was heated under reflux for 11 hours. The usual work-up gave 2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9,10-dimethylanthracene (41), (1.6 g., 84%), m.p. 226-227°C, needles (from benzene).

$\nu_{max.}$ 2960, 2925, 2860, 1670, 1575, 1525, 1460, 1375, 1175, 1150, 1080, 1010, 930, 900, 880 and 722 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 297 (log ϵ 3.75) and 286 (3.72) nm.

M.W. M (mass spectrometry), 440; m/e 442, 440 and 438.

$C_{16}H_{12}Br_2F_4$ requires M, 440.

10. Reaction of tetrafluorobenzyne with 5,6,7,8-tetrafluoro-1,2,3,4--tetrahydro-9-methylanthracene (42).

A solution of chloropentafluorobenzene (0.5 g., 0.0025 mole) in ether (15 ml.) and 1,2-dibromoethane (0.2 g., 0.0012 mole), were added dropwise to a suspension of magnesium (0.1 g., 0.004 mole) in ether (10 ml.) during 30 minutes at room temperature. After the additions were complete the reaction mixture was stirred at this temperature for a further period of 1 hour. A solution of compound (42), (0.4 g., 0.0015 mole) in cyclohexane (30 ml.) was then added to this, and the ether was replaced with cyclohexane by distillation until the temperature of the distillate reached 80°C. The reaction mixture was then heated under reflux for 5 hours and after a further period of 12 hours at room temperature was acidified with hydrochloric acid (2N). The organic layer was separated and the aqueous phase was extracted with ether (2 x 50 ml.). The combined organic layers were washed with water, dried, and the solvent was removed under reduced pressure. The residue on column chromatography over silica-gel and elution with light petroleum gave 1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9-methyltriptycene (44), (0.3 g., 50%) m.p. 238-240°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 4.57 (t., one proton, $|J_{H-F}|$ = 1.6 Hz.),
7.62 (t., 3 protons, $|J_{H-F}|$ = 6.0 Hz.),
7.75 (m., 4 protons), and 8.5 (m., 4 protons).

$\nu_{max.}$ 2950, 2900, 2875, 1500, 1480, 1060, 1000, 975, 815 and 765 $cm.^{-1}$

$\lambda_{max.}$ (ethanol) 258 (log ϵ 3.09) nm.

Found: C, 60.3; H, 2.95%; M (mass spectrometry) 416. $C_{21}H_{12}F_8$ requires C, 60.6, H, 2.9%; M, 416.

11. Dehydrogenation of 1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9-methyltriptycene (44).

Compound (44), (88 mg.) was heated with palladium (10% on carbon; 60 mg.) at 250°C under nitrogen for 4 hours. The cold residue was extracted with ether and afforded 1,2,3,4,5,6,7,8-octafluoro-9-methyltriptycene (47), (48 mg., 56%), m.p. 204-205°C, needles (from light petroleum). ^{1}H n.m.r. ($CDCl_3$) τ 2.3-2.9 (m., 4 protons, 3.8 (t., 1 proton, $|J|_{H-F}$ = 1.6 Hz.), and 7.25 (t., 3 protons, $|J|_{H-F}$ = 5.95 Hz.). $\nu_{max.}$ 3040, 2965, 1500, 1290, 1110, 1060, 1000, 975, 890, 815 and 765 cm.$^{-1}$

Found: C, 61.25; H, 2.0%; M (mass spectrometry), 412.

$C_{21}H_8F_8$ requires C, 61.15; H, 1.95%; M, 412; m/e 412, 397, 378, 347.

12. Reaction of tetrafluorobenzyne with 2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-methylanthracene (40).

Chloropentafluorobenzene (2.0 g., 0.01 mole) in ether (30 ml.) and 1,2-dibromoethane (0.94 g., 0.005 mole) were added dropwise to a suspension of magnesium (0.36 g., 0.015 mole) in ether (30 ml.) during 30 minutes at room temperature. The reaction mixture was then stirred at this temperature for a further period of one hour. The compound (40), (0.8 g., 0.0019 mole) in cyclohexane (30 ml.) was added and the ether was replaced by cyclohexane by distillation until the temperature of the distillate reached 80°C. The reaction mixture was then heated under reflux for 6 hours and after a further period of 12 hours at room temperature was acidified with hydrochloric acid (2N). The usual work-up followed by column chromatography over silica-gel and elution with light petroleum gave 1,2,3,4,5,6,7,8-octafluoro-9-methyltriptycene (47), (55%), m.p. and mixed m.p. 204-205°C; i.r. spectra identical.

13. Reaction of tetrafluorobenzyne with 1,2,3,4-tetrafluoro-9-methylanthracene (34).

A solution of compound (34), (0.8 g., 0.003 mole) in cyclohexane (30 ml.) was added to a solution of pentafluorophenylmagnesium chloride [from chloropentafluorobenzene (2.0 g., 0.010 mole), magnesium (0.36 g., 0.015 mole) and 1,2-dibromoethane (0.94 g., 0.005 mole)] in ether and the ether was then replaced with cyclohexane by distillation. The reaction mixture was heated under reflux for 6 hours and allowed to stand at room temperature for a further period of 12 hours. It was then acidified with hydrochloric acid (2N). The standard work-up and column chromatography over silica-gel yielded 1,2,3,4,5,6,7,8-octafluoro-9-methyltriptycene (47), (60%), m.p. and mixed m.p. 204-205°C; i.r. spectra identical.

14. Reaction of tetrafluorobenzyne with 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9,10-dimethylanthracene (43).

A solution of the compound (43), (0.28 g., 0.001 mole) in cyclohexane (20 ml.) was added to a solution of pentafluorophenylmagnesium chloride [from chloropentafluorobenzene (0.2 g., 0.001 mole), magnesium (0.036 g., 0.0015 mole) and 1,2-dibromoethane (0.0005 mole)] in ether (10 ml.) and the reaction was repeated in the same fashion as described under experiment Number 10. The usual work-up followed by column chromatography over silica-gel gave 1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9,10-dimethyltriptycene (45), (58%), m.p. 262-265°C (sublimes) (from hexane).

^{1}H n.m.r. ($CDCl_3$) τ 7.55-7.90 (m., 10 protons) and 8.40-8.60 (m., 4 protons).

$\nu_{max.}$ 3020, 2950, 2870, 1635, 1615, 1490, 1294, 1110, 1057, 890, 830 and 730 cm.$^{-1}$

Found: C, 61.3; H, 3.4%; M (mass spectrometry), 430. $C_{22}H_{14}F_8$ requires C, 61.4; H, 3.3%; M, 430.

15. Dehydrogenation of 1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9,10-dimethyltriptycene (45).

A mixture of compound (45), (100 mg.) and palladium (10% on carbon; 70 mg.) was heated at 260°C for five hours under an atmosphere of N_2. The cold residue was extracted with ether and work-up then gave 1,2,3,4,-5,6,7,8-octafluoro-9,10-dimethyltriptycene (49), (72%), m.p. 225-227°C, colourless needles (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 2.38-2.95 (m., 4 protons), and 7.30 (m., 6 protons, $|J|_{H-F}$ = 6 Hz.).

$\nu_{max.}$ 1620, 1480, 1385, 1330, 1105, 1055, 1040, 895, 865, 810 and 752 cm.$^{-1}$

Found: C, 62.1; H, 2.45%; M (mass spectrometry), 426. $C_{22}H_{10}F_8$ requires C, 61.95; H, 2.35%; M, 426.

16. Reaction of tetrafluorobenzyne with 2,3-dibromo-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9,10-dimethylanthracene (41).

A solution of pentafluorophenylmagnesium chloride [from chloropentafluorobenzene (1.0 g., 0.005 mole), magnesium (0.18 g., 0.0075 mole) and 1,2-dibromoethane (0.47 g., 0.0025 mole)] in ether was prepared in the usual manner and to this was then added a solution of compound (41), (0.85 g., 0.002 mole) in cyclohexane (40 ml.). The reaction was repeated in a manner described under the experiment Number 10. The standard work-up and column chromatography over silica-gel afforded 14,15-dibromo-1,2,3,4,-5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9,10-dimethyltriptycene (46), (0.67 g., 60%), m.p. 201-204°C, colourless rods (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 5.5 (br. s., 2 protons), 6.45-7.35 (m., 4 protons) and 7.65 (t., 6 protons, $|J|_{H-F}$ = 6.35 Hz.).

$\nu_{max.}$ 3060, 3000, 2900, 1610, 1500, 1405, 1330, 1280, 1210, 1110, 1050, 990, 890, 860 and 710 cm.$^{-1}$

M.W. M (mass spectrometry), 588; m/e 590, 588 and 586. $C_{22}H_{12}Br_2F_8$ requires M, 588.

17. Reaction of 14,15-dibromo-1,2,3,4,5,6,7,8-octafluoro-13,14,15,16-tetrahydro-9,10-dimethyltriptycene (46) with magnesium.

A suspension of magnesium (0.1 g., 0.004 mole) in ether (10 ml.) was activated by the addition of 1,2-dibromoethane (a trace) and a solution of the dibromo-compound (46), (0.105 g., 0.00017 mole) in ether (5 ml.) was added to it. The reaction mixture was stirred at room temperature for 4 hours and then the ether was replaced with cyclohexane (20 ml.) by distillation as usual and the reaction was carried out for a further period of 4 hours at 80°C. The standard work-up gave 1,2,3,4,5,-6,7,8-octafluoro-13,16-dihydro-9,10-dimethyltriptycene (48), (0.065 g., 85%), m.p. 240-243°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 4.32 (s., 2 protons), 7.05 (s., 4 protons) and 7.62 (t., 6 protons, $|J|_{H-F}$ = 6 Hz.).

M.W. M (mass spectrometry), 428; m/e 428, 413, 398, 374 and 351.

$C_{22}H_{12}F_8$ requires M, 428.

18. Dehydrogenation of 1,2,3,4,5,6,7,8-octafluoro-13,16-dihydro-9,10-dimethyltriptycene (48).

A mixture of compound (48), (60 mg.) and palladium (10% on carbon; 50 mg.) was heated at 240-270°C for 4 hours. The cold residue was extracted with ether and after the work-up gave 1,2,3,4,5,6,7,8-octafluoro-9,10-dimethyltriptycene (49), (40 mg. 66%), m.p. and mixed m.p. 225-228°C; i.r. spectra identical.

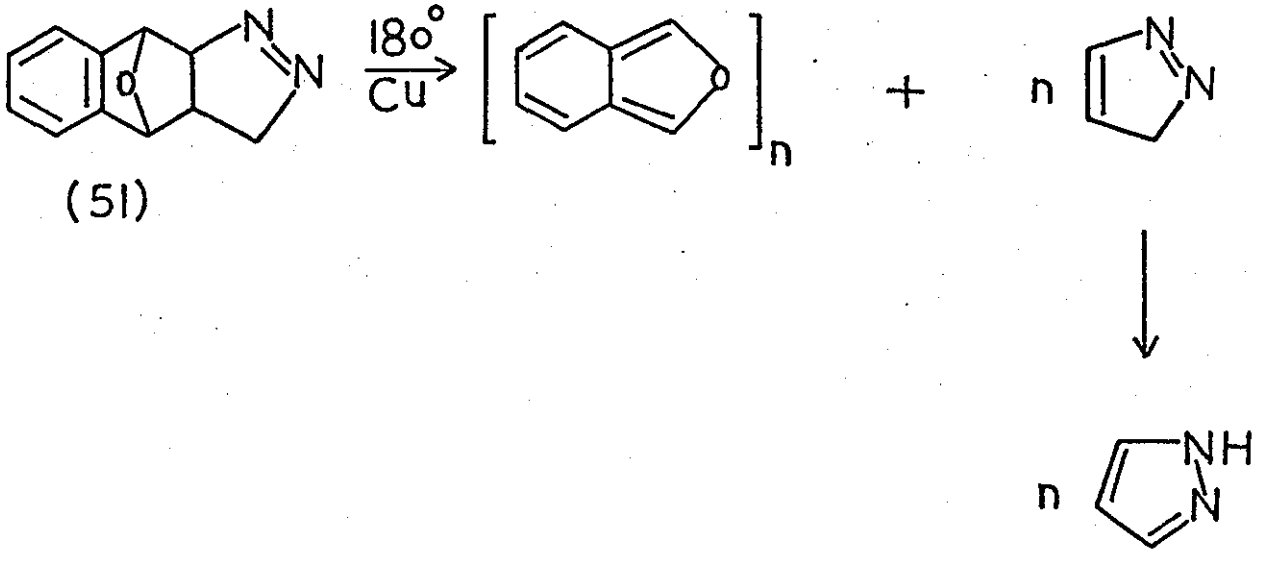
CHAPTER 2

FLASH VACUUM PYROLYSIS OF SOME 1,4-BRIDGED-1,2,3,4-TETRAHYDRONAPHTHALENE DERIVATIVES

INTRODUCTION

The technique of Flash Vacuum Pyrolysis[39] (F.V.P.) has intrigued a number of organic chemists during the past few years. This new technique has enabled new compounds to be prepared which have fascinated organic chemists for years both from a theoretical and synthetic standpoint. Many have previously been considered as transient species or were unknown.

Pyrolysis played a significant role in the early development of organic chemistry because it was one of the main routes of obtaining new organic compounds. The majority of the earlier work on pyrolytic reactions was collated in 1929.[40] Interestingly, apart from a few thermal reactions of synthetic use, this area of chemistry was not much exploited. This was because many of the pyrolysis products under prolonged exposure times at high temperatures underwent uncontrolled secondary reactions, resulting in the formation of complex mixtures of products. Wittig and Pohmer[6], for instance, ended up with a polymeric isobenzofuran when they heated the compound (51) with copper powder at 180°C. Another interesting example is the pyrolysis of the related compound (52) which gave even more complex results.[41]



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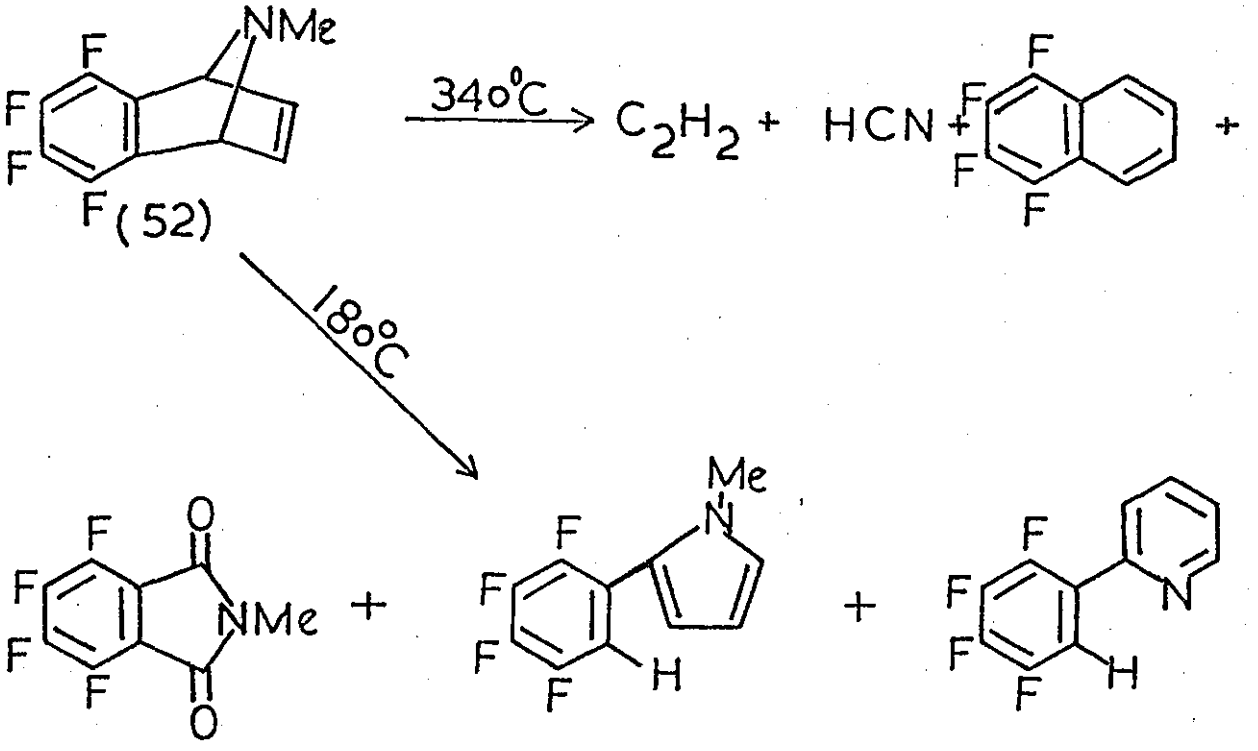
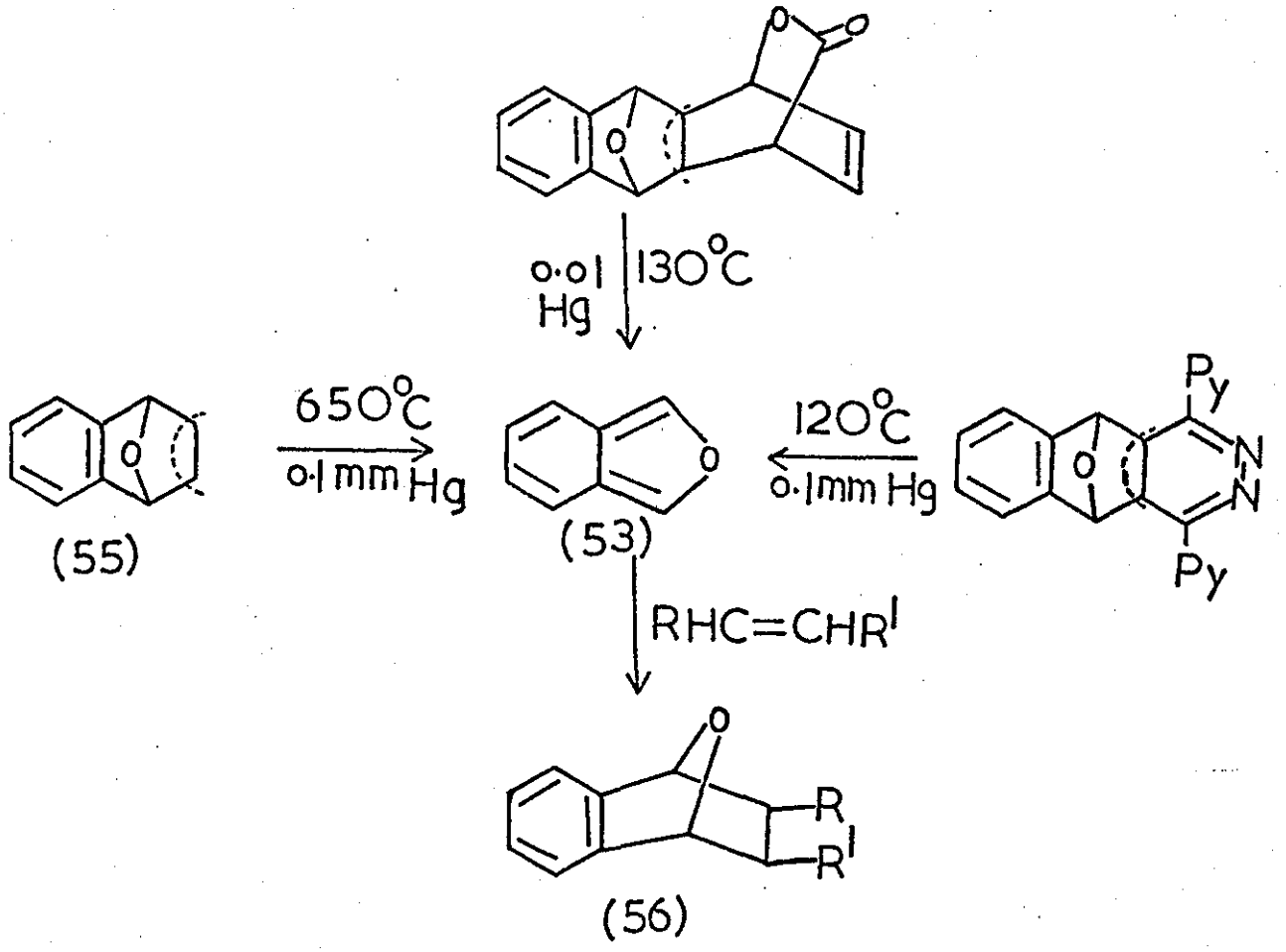
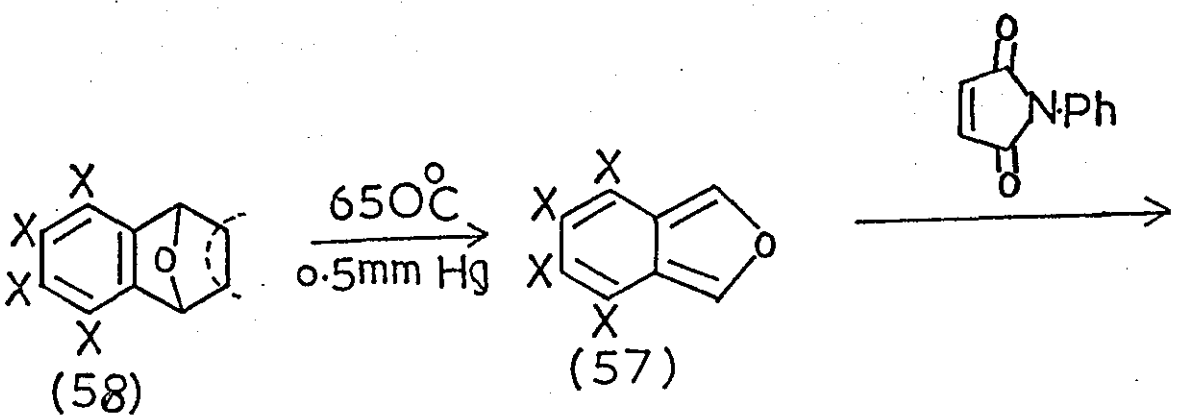


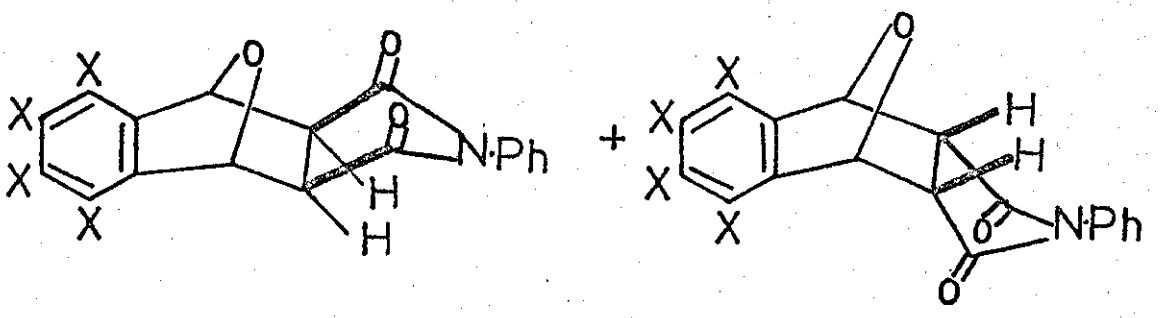
However, using (F.V.P.), in which the organic substrate is only exposed to high temperatures for a very short period of time, many of the more complicated side reactions are avoided. The procedure is quite straightforward and the pyrolysis products are frequently obtained in high yield.

Although certain substituted isobenzofuran and isoindole derivatives are stable and have been described in the literature for many years, the parent systems were, until recently, only shown to exist as transient reaction intermediates.[42,43] It is only within the past two years that isobenzofuran (53)[44] and isoindole (54)[45] have been isolated and some light has been thrown on their high reactivity and low stability. Thus, the compound (55) on passing through a quartz tube at 650°C has been found to give a quantitative yield of isobenzofuran (53)[44] which readily forms adducts (56) with various dienophiles.

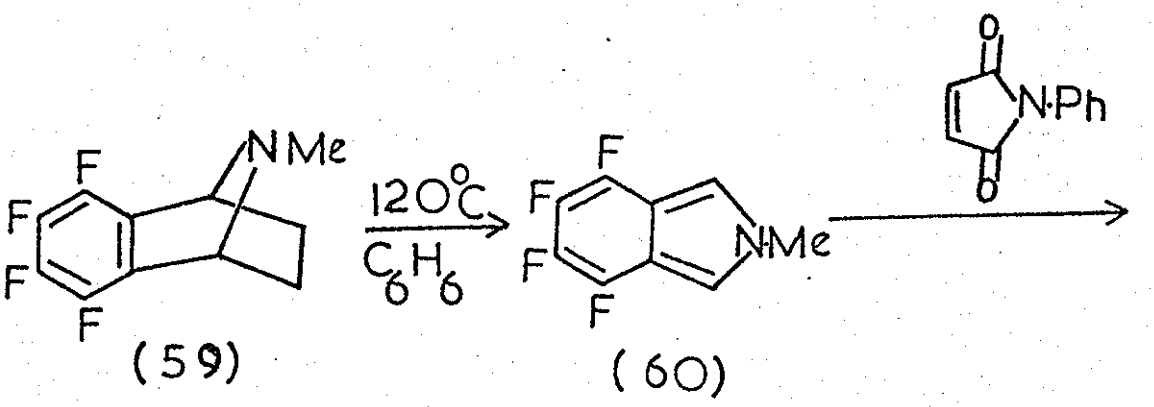


Workers in these laboratories have obtained the tetrahalogenoisobenzofurans (57; X = F or Cl) quantitatively by F.V.P. of the compounds (58; X = F or Cl) at 600°C.[45] Spectral and other available data indicate that the presence of four electron withdrawing substituents in the homocyclic ring of isobenzofuran have a pronounced effect on the stability of these compounds. The stability decreases in the order tetrafluoroisobenzofuran > tetrachloroisobenzofuran > isobenzofuran.[27b, 46] The compounds (57) form endo- and exo-cycloadducts with N-phenylmaleimide.

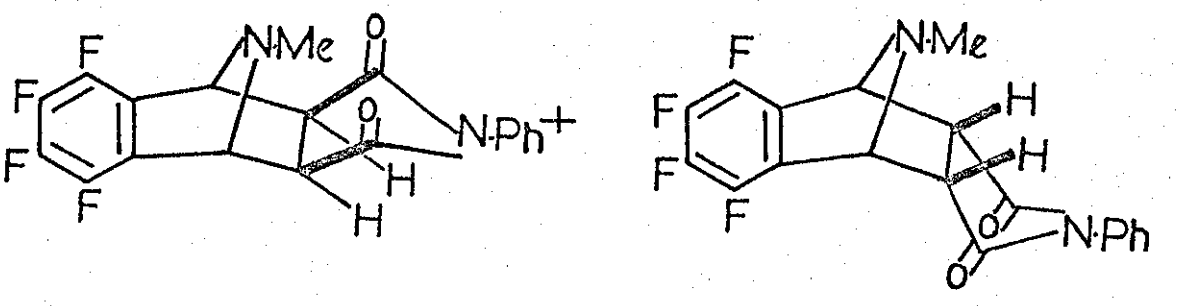




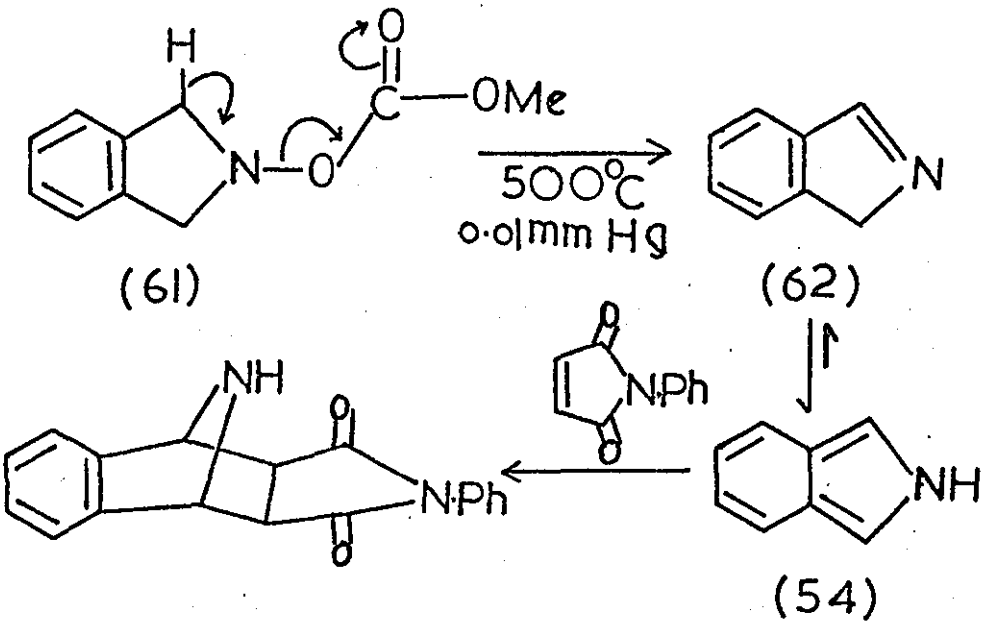
Interestingly, the compound (59) on heating at 120°C for one week in degassed ethanol or benzene loses ethylene and produces tetrafluoro-N-methylisoindole (60) in a quantitative yield.[46] This compound was found to have a much greater stability than N-methylisoindole. It reacts with N-phenylmaleimide at 120°C to give a 1:1 mixture of endo- and exo-cycloadducts. The remarkable stability of this system is ascribed to the fact that the N-substituted isoindoles exist only in the o-quinonoid form.[47] Furthermore, more recent observations of Bornstein and his co-workers[48] indicate that the greater stability of tetrafluoroisoindole than that of the parent compound is attributed to the presence of fluorine substituents in the system. Isoindole (54),[45] an exceedingly reactive



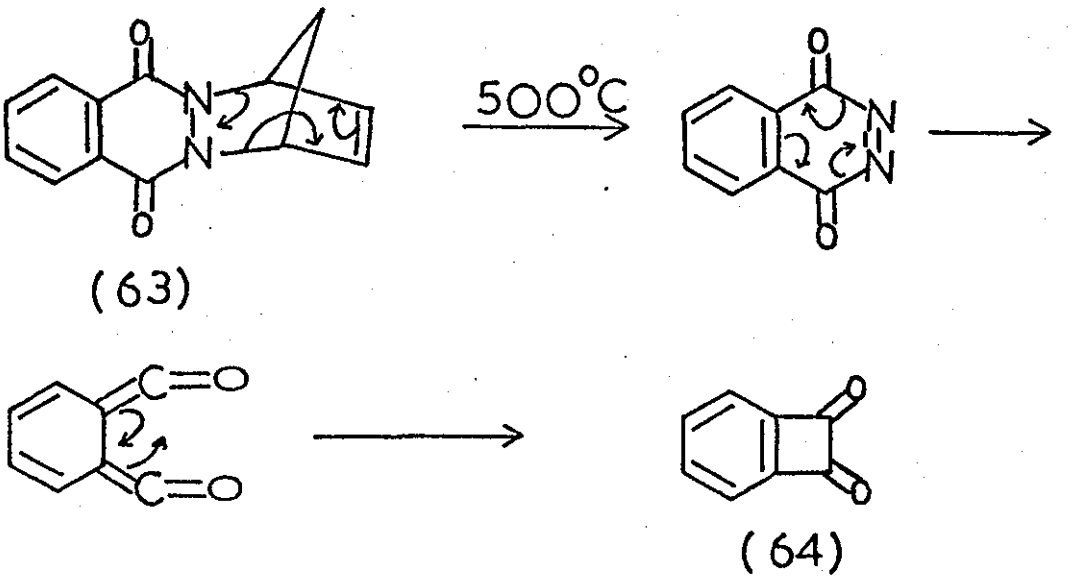
(59) (60)



compound, was elegantly obtained by the pyrolysis of compound (61) at 500°C and has been shown to exist in both the o-quinonoid (54) and isoindolenine (62) structures.[45,48]

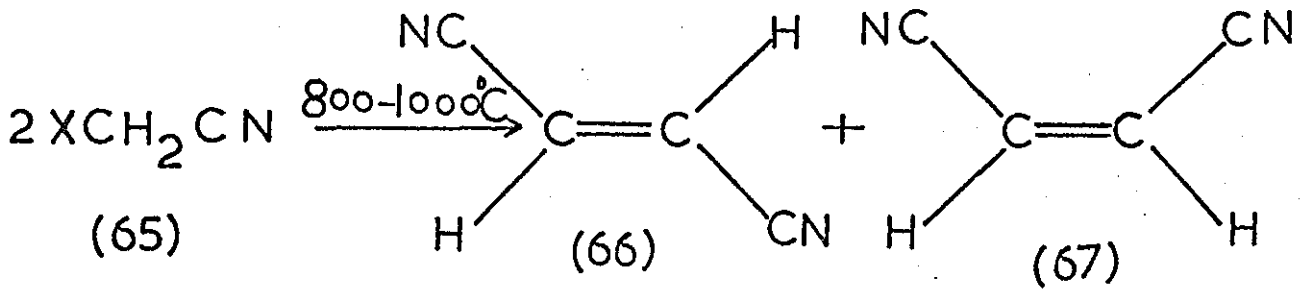


Likewise, various other retro-Diels-Alder reactions have been carried out by flash vacuum pyrolysis and their chemistry explored.[39,49] The compound (63) suffers retrogression at 500°C to give rise to benzocyclobutenedione (64) in a high yield.[50]



Another useful synthetic potential of F.V.P. is illustrated in the

coupling reactions. Hashimoto and his co-workers have found[51] that monchalogenonitriles (65) at 800-1000°C lead to the formation of compounds (66) and (67) in good yields.

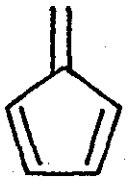


Furthermore, the F.V.P. technique has not only been applied to synthesise compounds, but its utility has also been realised in studies of highly reactive short-lived species such as benzynes,[7,50] carbenes,[52] and nitrenes.[53]

Work was therefore initiated to investigate the reactions of the compounds [(79)-(82)] under flash vacuum pyrolysis conditions.

DISCUSSION

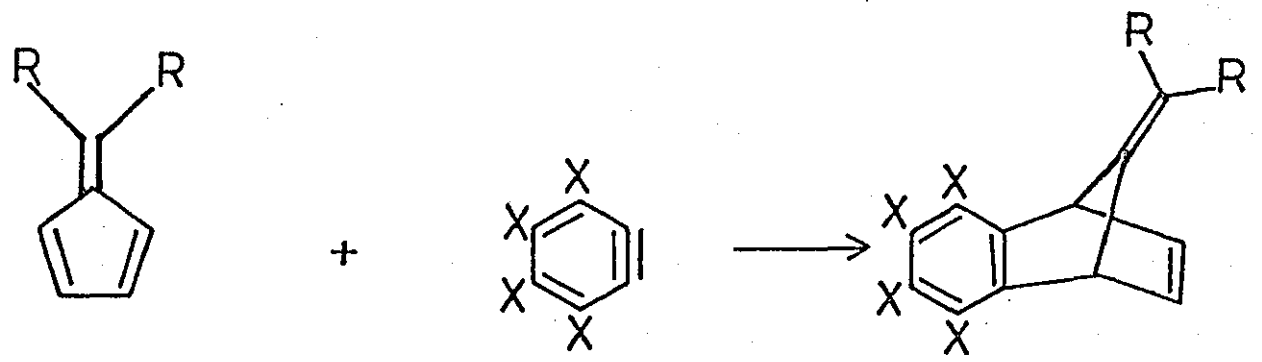
The fulvenes, compounds containing the structural moiety (68) have been known for a long time. These compounds behave both as dienes[54] and as dienophiles[55] in Diels-Alder reactions although the former type of reactivity is more common.



(68)

6,6-Dimethylfulvene (69) undergoes 1,4-cycloaddition reactions with benzyne[56] and with tetrahalogenobenzynes.[35,57] In the present investigation, 6,6-dimethylfulvene (69)[58] and 6,6-diphenylfulvene (70)[59] were prepared by the standard literature procedures. Following Muneyuki and Tanida's[56] method the reaction of fulvene (69) with benzyne afforded 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (71) in an improved yield of 42% (Scheme 14). Similarly, fulvene (70) was reacted with benzyne generated by the aprotic diazotisation of anthranilic acid and after the work-up gave the adduct 1,4-dihydro-9-(diphenylmethylene)--1,4-methanonaphthalene (72) in a high yield (88%) (Scheme 14). The structure (72) was compatible with its analytical and spectral data. The reactions of 6,6-dimethylfulvene (69) with tetrafluorobenzyne generated from pentafluorophenyl-lithium and with tetrachlorobenzyne formed by the aprotic diazotisation of tetrachloroanthranilic acid[60] each produced the expected cycloadducts 5,6,7,8-tetrafluoro-1,4-dihydro--9-isopropylidene-1,4-methanonaphthalene (73) in 35% yield and 5,6,7,8--tetrachloro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (74) in 21% yield (Scheme 14). The structures of the compounds (73) and (74) were consistent with their spectral data. Interestingly, in the reaction

of the fulvene (69) with tetrafluorobenzyne using a 1:1 ratio of the diene

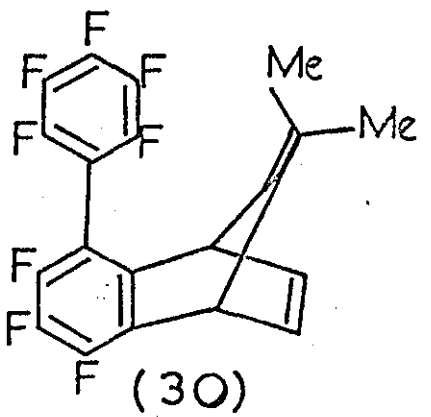


R=Me (69)
R=Ph (70)

R=Me, X=H (71)
R=Ph, X=H (72)
R=Me, X=F (73)
R=Me, X=Cl (74)

Scheme 14

and pentafluorophenyl-lithium, two additional compounds (30) and (75) were also isolated.[35,57]



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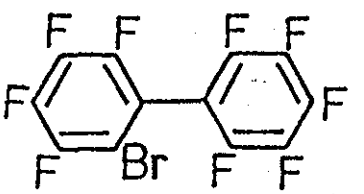
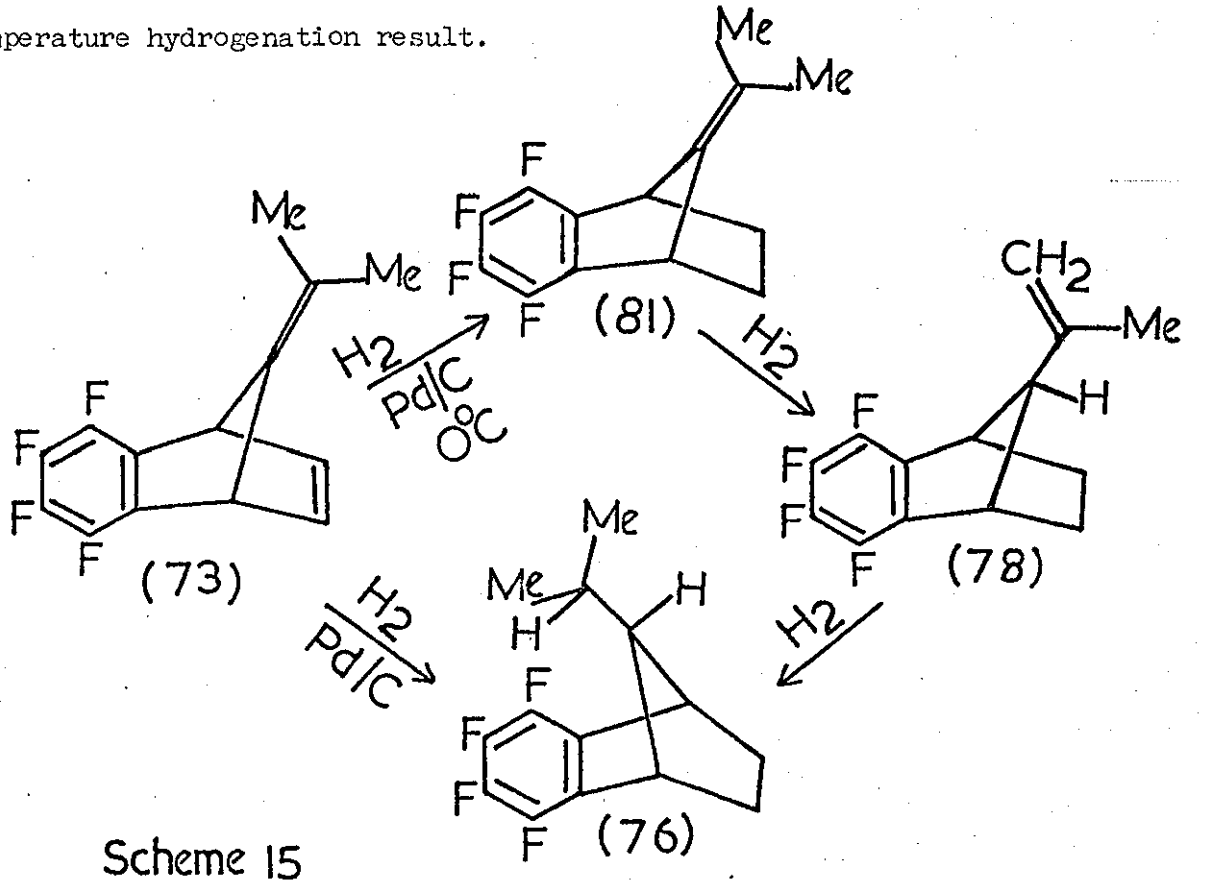


(75)

The catalytic hydrogenation of compound (73) has been carefully investigated.[35,57] It has been shown conclusively that, in spite of the presence of di- and tetra-substituted double bonds in the molecule, the hydrogenation in the presence of palladium-carbon at room temperature proceeds with the rapid uptake of 2 molar equivalents of hydrogen resulting in the formation of compound (76). G.l.c. however, showed the formation of two intermediate hydrogenation products. When the hydrogenation was carried out at $0^{\circ}C$ in

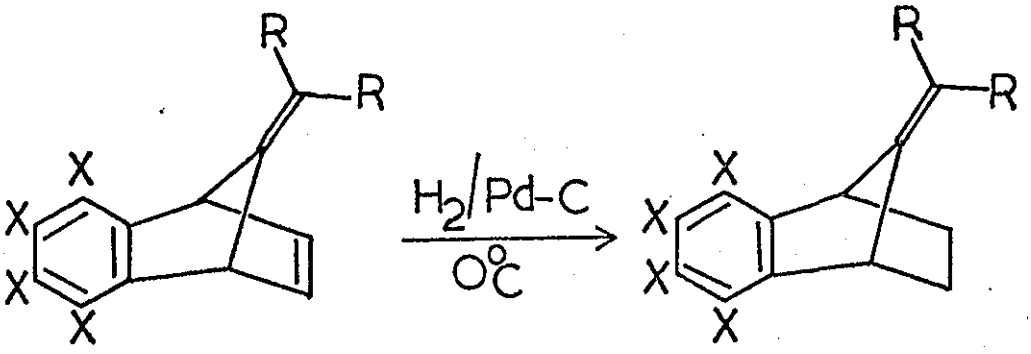
the presence of a small quantity of the catalyst, a break in the uptake of hydrogen occurred after exactly one molar equivalent of hydrogen had been taken up, and the dihydro-derivative (81) was obtained in a high yield. Moreover, the hydrogenation of compound (81) has been shown to proceed <u>via</u> a compound (78) which on further hydrogenation gave rise to the compound (76). (Scheme 15). The driving force for the isomerisation of the double-bond was attributed to the release of strain associated with the bridging sp^2-hybridised carbon atom in compound (81). This presumably also explains the room temperature hydrogenation result.



Scheme 15

The adducts [(71)-(74)] were therefore selectively hydrogenated in the presence of palladium-carbon at 0°C and in each case the reaction was terminated after the uptake of one molar equivalent of hydrogen. The standard work-up produced 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methano-naphthalene (79), 1,2,3,4-tetrahydro-9-(diphenylmethylene)-1,4-methano-naphthalene (80), 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-

1,4-methanonaphthalene (81) and 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro--9-isopropylidene-1,4-methanonaphthalene (82) in high yield (Scheme 16). The structures [(79)-(82)] were confirmed from their spectral data. Elemental analysis of the compound (80) was also in accord with the assigned molecular formula. The compound (76) was prepared by the complete hydrogenation of compound (73) (Scheme 15).



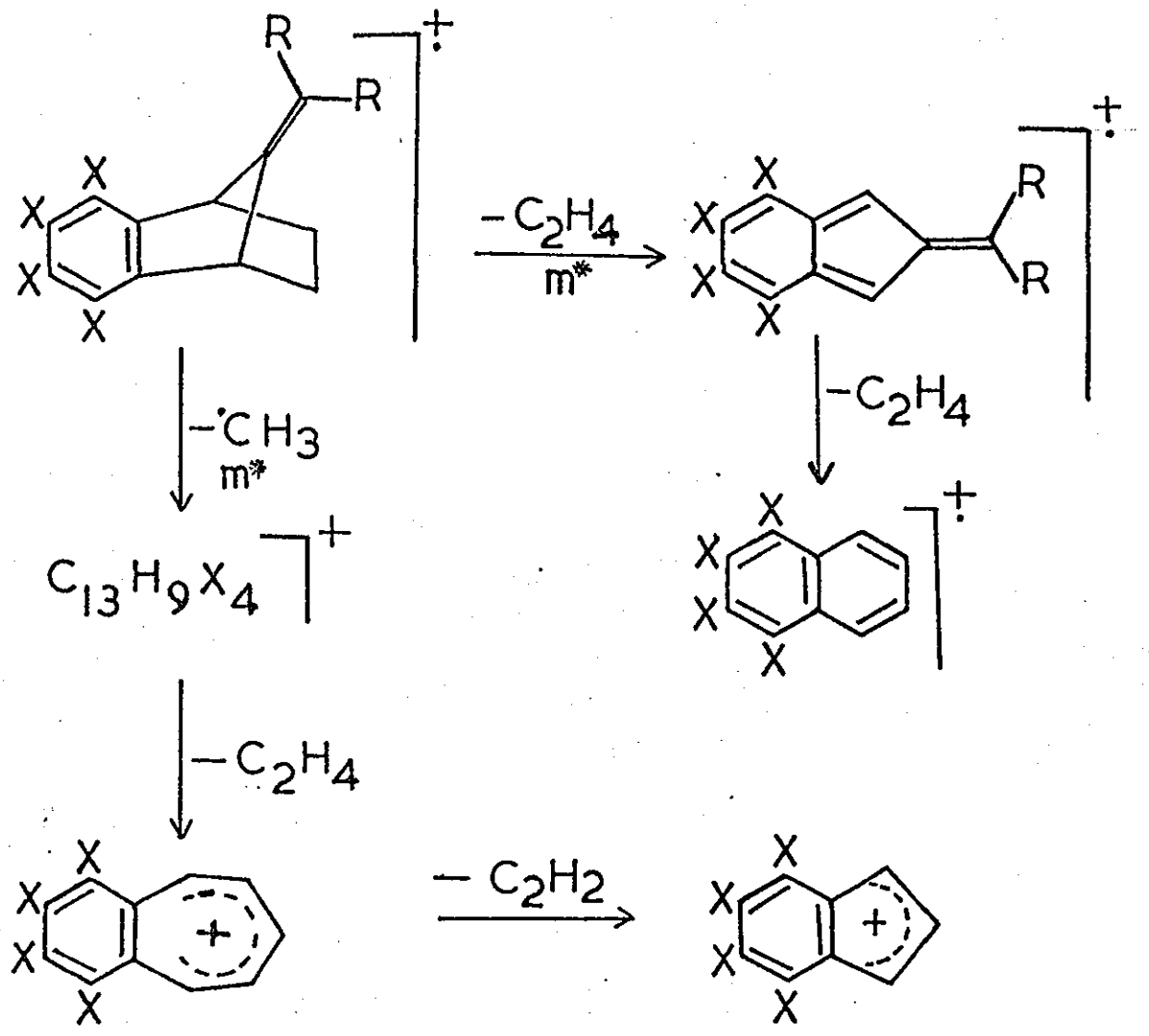
R = Me, X = H (71)
R = Ph, X = H (72)
R = Me, X = F (73)
R = Me, X = Cl (74)

R = Me, X = H (79)
R = Ph, X = H (80)
R = Me, X = F (81)
R = Me, X = Cl (82)

Scheme 16

Interestingly, the mass spectra of the compounds [(79)-(82)] each showed that the loss of m/e 28 was the major mode of fragmentation of the molecular ions. High resolution mass spectrometry for each compound together with the observation of the appropriate metastable peaks in the mass spectra, established that the loss was of a molecule of ethylene (Tables 2 and 3). This suggests that the molecular ions of each of these compounds are undergoing retro-Diels-Alder reactions in the mass spectrometer resulting in the formation of $M^{+\cdot}$ - 28 ions which may formally be regarded as possessing an isobenzofulvene structure (Scheme 17). We have already reported the loss of an ethylene molecule in the mass spectral fragmentation of the compounds (58) and (59).[46] These observations,and

the interest in apparent similarities between mass spectral and thermal processes,[61] led us to investigate the high temperature pyrolysis reactions of compounds [(79)-(82)] which it was hoped could provide a potential route for generating the so far undescribed isobenzofulvene-derivatives. It is, however, worth mentioning that when this work was in progress two different groups[62,63] simultaneously reported the transient existence of 8,8--dimethylisobenzofulvene (83) which dimerises instantaneously but forms cycloadducts with a variety of dienophiles.



Scheme 17

Results available so far have indicated that isobenzofulvenes are unstable and chemically very reactive compounds.[62,63] The stability of these compounds presumably should increase with electron donating

substituents at the endocyclic carbon atom due to the increased cyclic conjugation with the ring-system.

Table 2

Mass spectral data

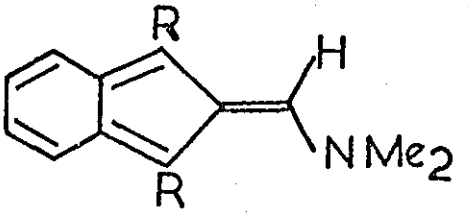
Compound	m/e	Relative abundance %	Ion	m^*	Transition
73	254	100	M^+		
	239	70	$M-CH_3$	224.9	254— 239
	213	33	$239-C_2H_2$		
	200	63	$M-C_4H_6$		
	187	33	$213-C_2H_2$		
81	256	20	M^+		
	241	27	$M-CH_3$	226.9	256— 241
	228	100	$M-C_2H_4$	203.0	256— 228
	213	56	$241-C_2H_4$		
	200	41	$228-C_2H_4$		
	187	24	$213-C_2H_2$		
82	322	22	M^+		
	307	33	$M-CH_3$		
	294	100	$M-C_2H_4$	268.3	322— 294
	279	20	$307-C_2H_4$		
	266	27	$294-C_2H_4$	240.7	294— 266
	257	11	292-Cl		
79	184	25	M^+		
	169	63	$M-CH_3$		
	156	100	$M-C_2H_4$	125.5	184— 156
	141	70			
	128	43	$156-C_2H_4$		
	115	30	$141-C_2H_2$		

Table 3

Precision mass measurements

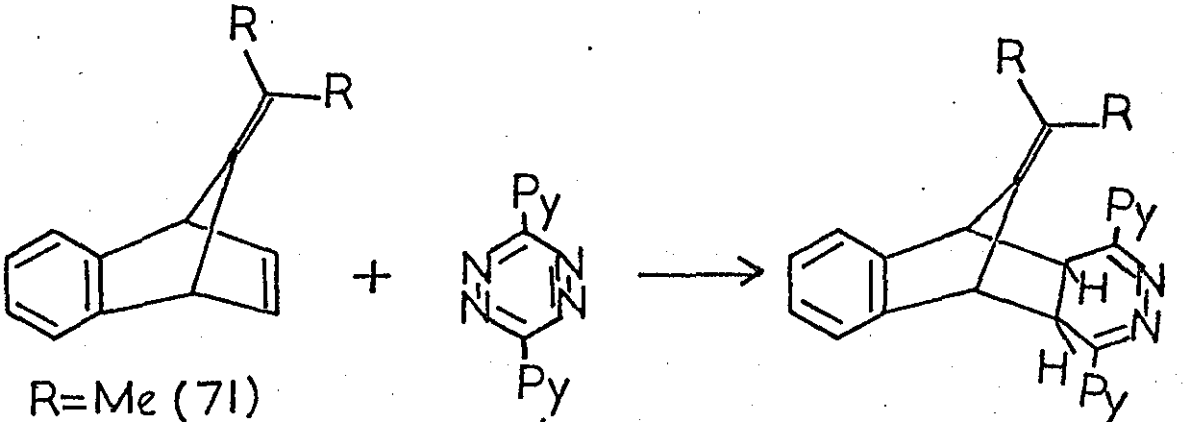
Compound	Measured mass	Formula	Calculated mass
73	254-0721	$C_{14}H_{10}F_4$	254.0718
	200.0248	$C_{10}H_4F_4$	200.0248
	187.0165	$C_9H_3F_4$	187.0171
81	256.0878	$C_{14}H_{12}F_4$	256.0876
	228.0561	$C_{12}H_8F_4$	228.0562
	213.0325	$C_{11}H_5F_4$	213.0327
	200.0243	$C_{10}H_4F_4$	200.0248
82	319.9713	$C_{14}H_{12}{}^{35}Cl_4$	319.9695
	291.9367	$C_{12}H_8{}^{35}Cl_4$	291.9380
79	184.1246	$C_{14}H_{16}$	184.1252
	156.0931	$C_{12}H_{12}$	156.0938
80	308.1556	$C_{24}H_{20}$	308.1565
	280.1255	$C_{22}H_{16}$	280.1252

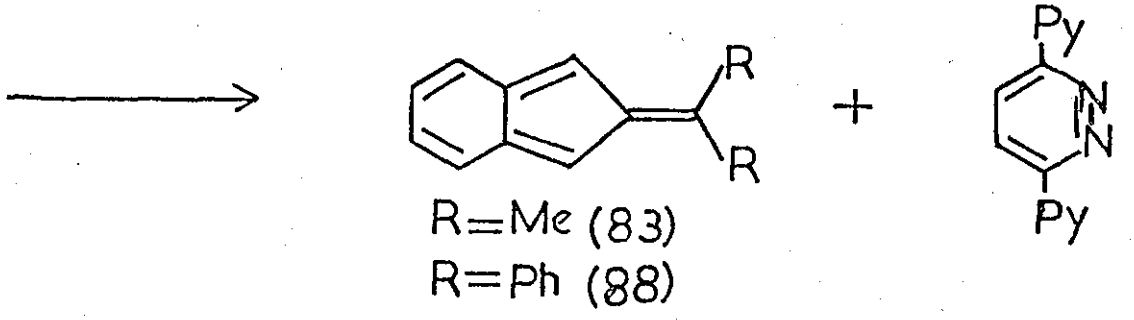
Hafner and Bauer[64] were the first to isolate a stable crystalline isobenzofulvene [8-(dimethylamino)-1,3-diphenylisobenzofulvene (84)]. They also detected the intermediacy of 8-(dimethylamino)isobenzofulvene (85).

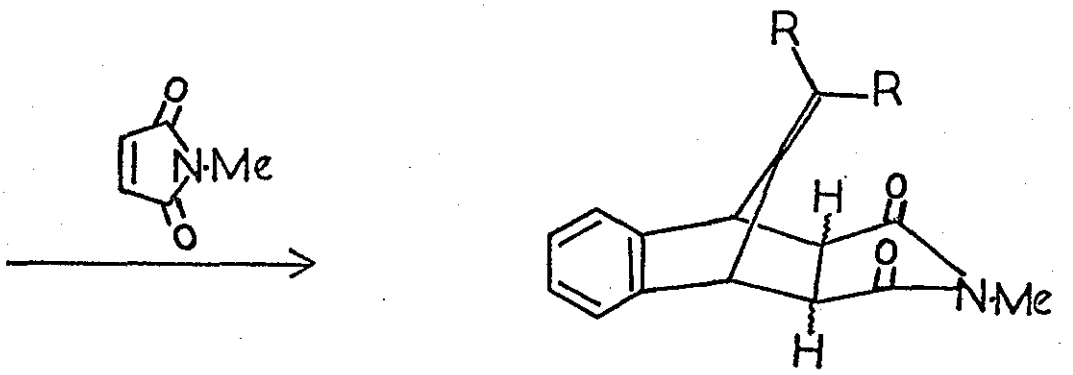


R = Ph (84)
R = H (85)

An excellent approach for the generation of isobenzofulvenes involves the mild pyrolysis of adducts (86) which are obtained from the reactions of compounds (71) and (72) with 3,6-di(2'-pyridyl)-s-tetrazine (87) (Scheme 18). Warrener and his co-workers[62] have employed this route for the generation of the 8,8-dimethyl-compound (83) and 8,8-diphenylisobenzofulvene (88) while Tanida's group[63] has used the same route for 8,8-dimethylisobenzofulvene (83).



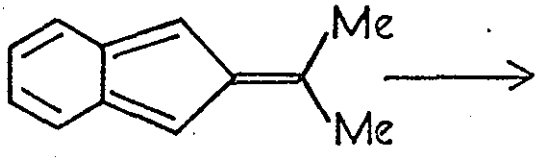




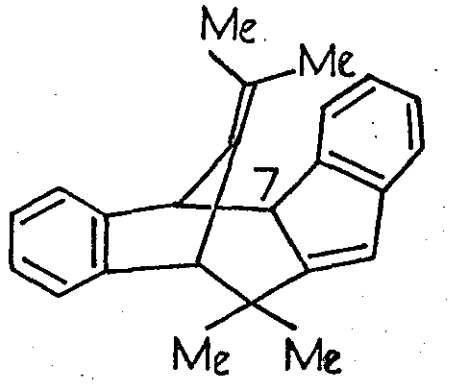
exo/endo mixture

Scheme 18

The dimerisation of isobenzofulvene (83) was first suggested as a single dimer by Tanida.[63] However, later observations by Warrener and his workers[62] have shown the product to be a mixture of two isomeric compounds (89) which differ in stereochemistry of the hydrogen atom at position 7.

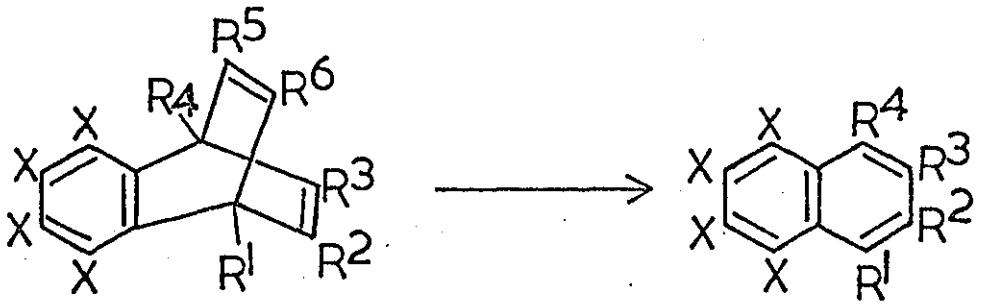


(83)



(89)

The thermal decomposition of benzobarrelene-derivatives (90) in vacuo around 300°C has been shown to form naphthalene-derivatives (91) in high yield.[23a, 65] So initially, the pyrolysis was carried out in an evacuated sealed tube.



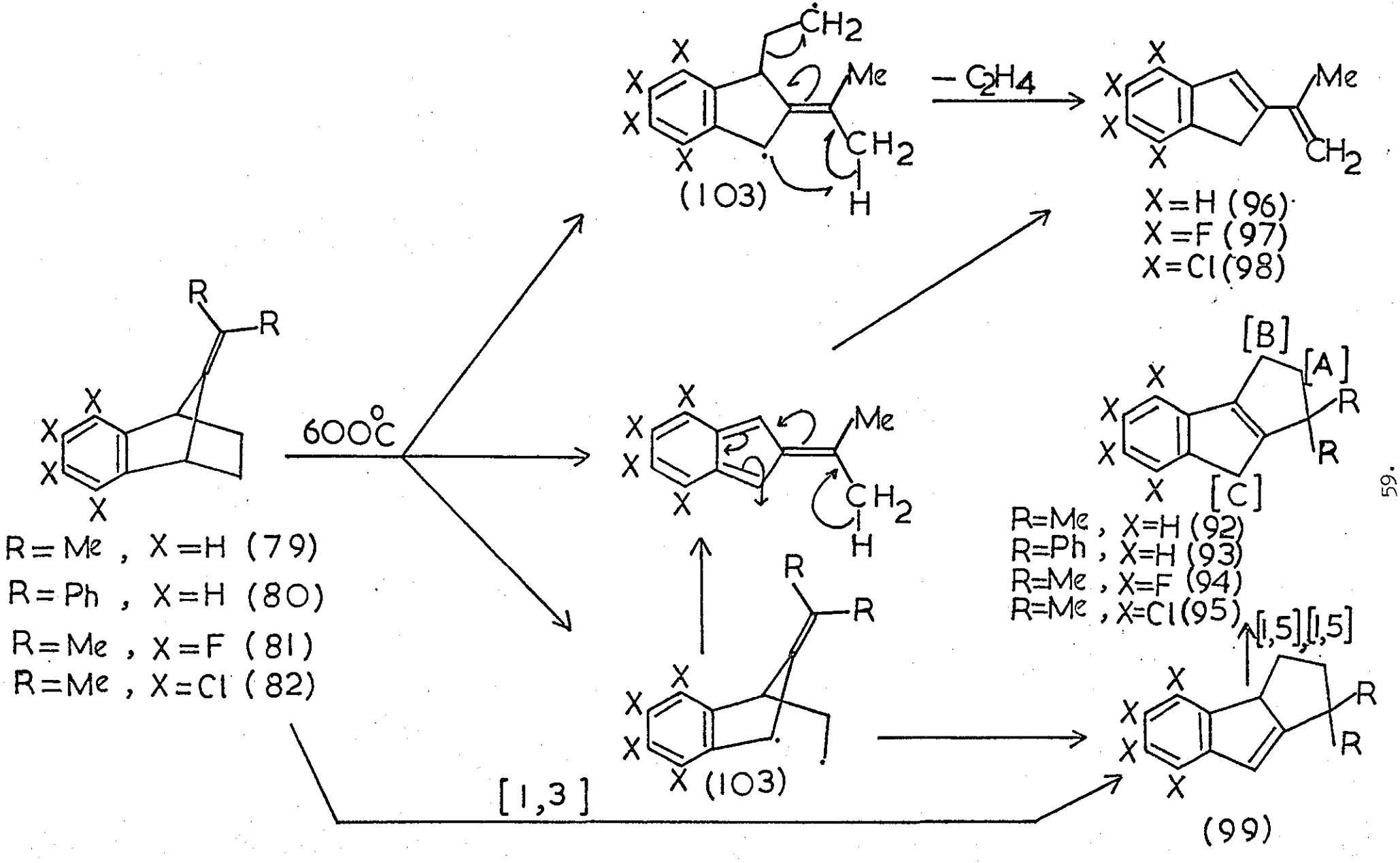
(90) (91)

When the compounds (74) and (81) were heated in benzene at 300°C and 200°C respectively for 14-16 hours, the former pyrolysis resulted only in the formation of an intractable polymeric material,while in the latter case unchanged starting material was recovered. This suggested that much higher temperatures and a flow system was needed in order to effect the thermal fragmentation of the compounds [(79)-(82)].

A series of small scale trial experiments using a silica flow system and temperatures in the range 300-600° established that clean reactions occurred at ca. 600° and ca. 3mm Hg. At lower temperatures significant amounts of unchanged starting materials were isolated in the pyrolysate, while the new products were identical with those obtained at 600°. No cycloadducts were obtained in any examples where the pyrolysate was condensed onto a cold trap at -195° which was coated with N-phenylmaleimide. When preparative scale pyrolyses at 600° and 3 mm Hg were conducted using the compounds (79), (81) and (82), each gave a mixture of products which was collected in a cold trap at -195°. Gas liquid chromatography established that two major components were present in each case. After subsequent isolation and identification it was established that the combined yields of the two products ranged from 55 to 75%. In the pyrolysis of the compound (80) only one product was obtained using a temperature of 600° (Scheme 9).

Thus, from the pyrolysis of the compound (79), 1,2,3,8-tetrahydro--1,1-dimethyl-cyclopent[a]indene (92) in 54% yield and 2-isopropenylindene (96) in 23% yield were obtained (Scheme 19). The structures of these compounds were assigned on the basis of elemental analytical and spectroscopic evidence. In the compound (92), for instance, IR spectrum ($\nu_{max.}$ at 1630 and 1610 cm.$^{-1}$) and the UV spectrum [$\lambda_{max.}$ (cyclohexane) 270 (log ϵ 4.00), 265 (4.06) and 260 (4.10) nm] were indicative of the presence of a double bond conjugated with the aromatic ring. In the 220 M Hz ^{1}H n.m.r. spectrum it showed methyl signals at τ 8.8 and the methylene signals at τ 7.83 (t., |J|= 7 Hz., [A], 7.45 (m., [B]) and 6.90 (t., |J|= 2.5 Hz., [C]). Spin-spin decoupling experiments revealed that the methylene group [B] was coupled to the other two methylene groups. The magnitude of the homoallylic coupling constant is in the predicted range. The indene (96) decomposed slowly at room temperature and did not produce correct elemental analysis. However, its composition was determined by an accurate mass measurement of the molecular ion in the mass spectrum. The infrared ($\nu_{max.}$ 1650 and 1610 cm.$^{-1}$) and the ultraviolet [$\lambda_{max.}$ (cyclohexane) 314 (log ϵ 3.97), 294 (4.26) and 288 (4.23) nm.] spectra were compatible with the structure (96). The ^{1}H n.m.r. spectrum displayed multiplets at τ 2.5-3.0 (aromatic protons), 3.22 (olefinic proton), 4.75 and 5.00 (=CH_2 protons) and broad singlets at τ 6.42 (methylene) and 7.93 (methyl).

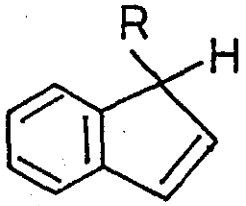
Similarly, the compounds [(80)-(82)] at 600°C after the standard work-up procedure gave 1,2,3,8-tetrahydro-1,1-diphenylcyclopent[a]indene (93) in 54% yield; 4,5,6,7-tetrafluoro-1,2,3,8-tetrahydro-1,1-dimethyl-cyclopent[a]indene (94) and 4,5,6,7-tetrafluoro-2-isopropenylindene (97) in 52.5% and 13% yield; and 4,5,6,7-tetra-chloro-1,2,3,8-tetrahydro-1,1--dimethylcyclopent[a]indene (95) in 45% and 4,5,6,7-tetrachloro-2-isopropenylindene (98) in 11.5% yield (Scheme 19). The structure of these


R
R
X
X
X
600°C
R=Me , X=H (79)
R=Ph , X=H (80)
R=Me , X=F (81)
R=Me , X=Cl (82)
CH2
Me
CH2
H
(103)
−C2H4
X=H (96)
X=F (97)
X=Cl (98)
[B]
[A]
[C]
R=Me , X=H (92)
R=Ph , X=H (93)
R=Me , X=F (94)
R=Me , X=Cl (95)
[1,5],[1,5]
[1,3]
(99)

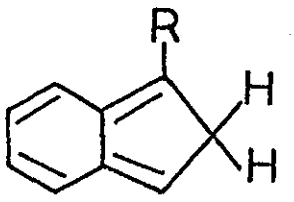
Scheme 19

compounds were established by elemental analysis and by spectroscopic methods (see experimental). The compound (97) also decomposed slowly at room temperature. We did not investigate the reactivity of the isopropenylindenes[(96)-(98)] but these compounds might be expected to undergo cycloaddition reactions with reactive dienophiles.

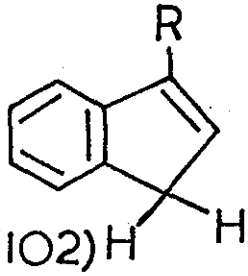
The reaction sequence for the isomerisation of compounds [(79)-(82)] to the compounds [(92)-(95)] can be rationalised in Scheme 19 which illustrates two possible pathways by the intermediacy of compounds of type (99). The formation of the thermodynamically more stable cyclopent[a]indene derivatives [(92)-(95)] is not surprising in view of the well documented isomerisation of indenes [e.g. (100)-(102)] by a series of [1,5]sigmatropic shifts.[66] The fact that the isomerisation



(100)



(101)



(102)

of the compounds [(79)-(82)] can occur via intermediates of type (99) involving a thermally allowed [1,3]sigmatropic shift[67] seems to support the implied view[42b, 44b] that stepwise retro-Diels-Alder reactions occur in carbon-carbon bridged systems which do not have alternative symmetry-allowed pathways. We cannot comment further on this point since we do not have a stereochemical reference point in the compounds (79-82).

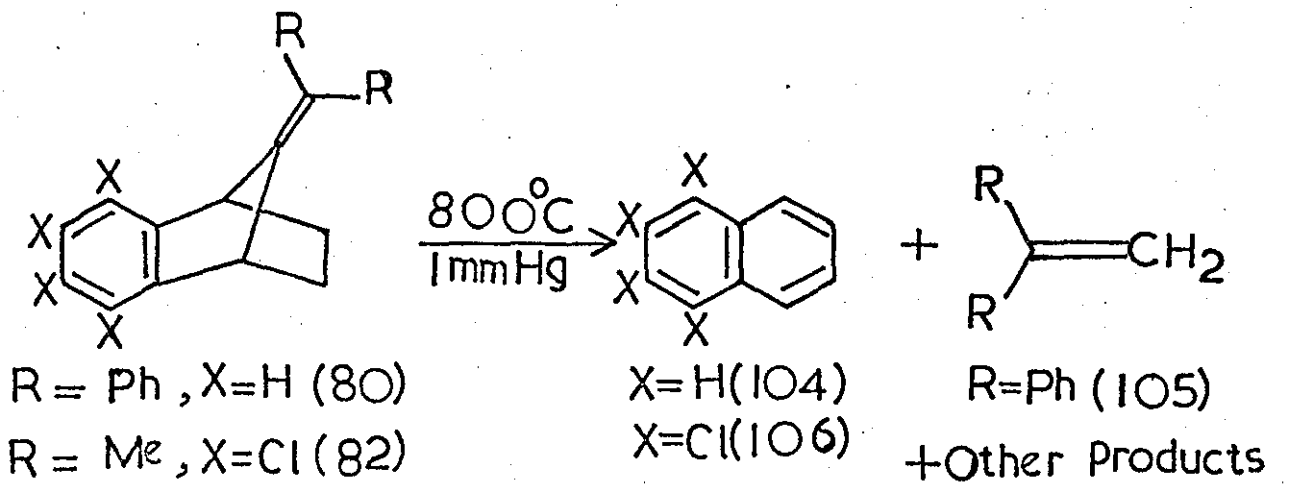
The isolation of small amounts of the isopropenylindenes [(96)-(98)] suggests that they are formed either by retro-Diels-Alder reactions which logically give rise to the respective 8,8-dimethyl-isobenzofulvene-derivatives or are derived from the diradical (103) as indicated (Scheme 19).

If the 8,8-dimethylisobenzofulvene derivatives are involved in the formation of the products (96-98) the subsequent [1,4]hydrogen shift is either an orbital symmetry disallowed reaction[68] or is a base-catalysed prototropic shift.[62]

It is perhaps significant that the flash vacuum pyrolysis of compounds (73) and (76) at 600°C at 3 mm Hg each resulted in the recovery of unchanged starting material. No new product was obtained in each experiment.

The fact that the isomerisation was the major pyrolysis product in the previous experiments led us to perform flash vacuum pyrolysis at much higher temperature (800°C) but this resulted in the formation of complex mixture of products. However, some of the products isolated in these experiments although obtained in poor yield were quite interesting.

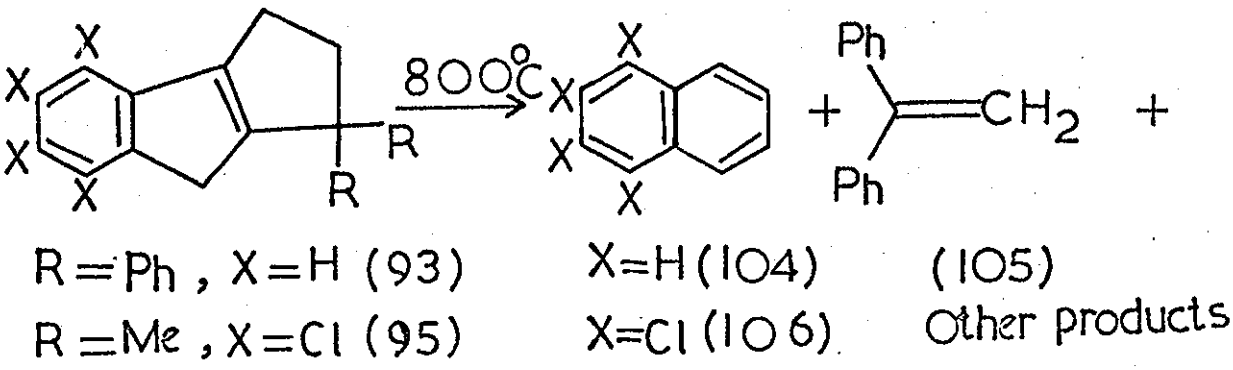
When the compound (80) was sublimed through the tube at 800°C at 1 mm Hg, a brown liquid was obtained. Preparative layer chromatography afforded naphthalene (104) which was confirmed by its mixed m.p. and comparison of ultraviolet spectra; and a second compound shown to be 1,1-diphenylethylene (105) (Scheme 20). The compound (105) was prepared by standard literature procedure[69] and shown to be the same by g.l.c. and ^{1}H n.m.r. spectroscopy. In the case of pyrolysis of the compound (82)



Scheme 20.

at 800°C, the only product isolated was tetrachloronaphthalene (106) confirmed by its mixed m.p. measurement with authentic material (Scheme 20). No attempt to trap isobutene was made. The pyrolysis of compound (81) under these conditions resulted in the formation of a complex mixture of products which was not investigated further. However, no evidence for the formation of tetrafluoronaphthalene could be obtained.

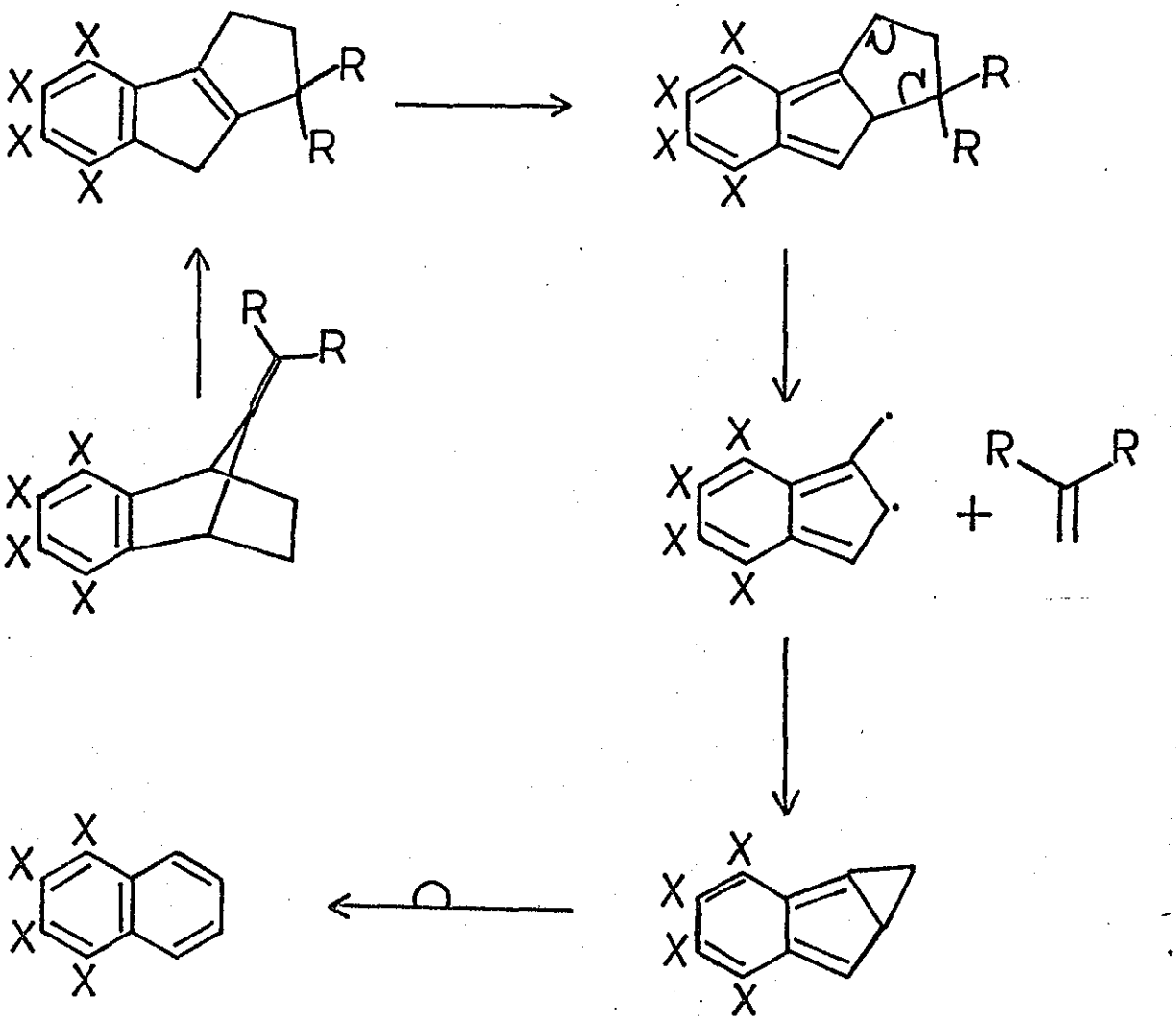
The pyrolysis of the compounds (93) and (95) at 800°C gave, after the standard work-up procedure, naphthalene (104) and 1,1-diphenylethylene (105) and tetrachloronaphthalene (106) respectively (Scheme 21). The



Scheme 21

compound (94) at 800°C gave only a complex mixture of products and no tetrafluoronaphthalene was obtained.

These results however, indicate that the compounds (80) and (82) at 800°C first undergo isomerisation to the appropriate cyclopent[a]-indene derivative which then fragment to the respective naphthalenes and other products. A tentative sequence is set out in Scheme 22.



Scheme 22.

Experimental

All general methods were those as described in Chapter 1.

1. Preparation of 6,6-dimethylfulvene.

Freshly prepared cyclopentadiene (26.8 g., 0.4 mole) and dry acetone (23.0 g., 0.4 mole) were added dropwise to a stirred solution of sodium methoxide [from sodium(9.2 g.) and methanol (180 ml.)] at room temperature. When the addition was complete, cold water (500 ml.) was added and the mixture was extracted with ether (2 x 100 ml.), washed with water and dried (Na_2SO_4). The solvent was evaporated carefully leaving behind a yellow oil, which on distillation under reduced pressure afforded 6,6-dimethylfulvene (69), (32.0g., 74%), a yellow liquid, b.p. 26°C at 1 mm Hg. (lit.[58] b.p. 77°C at 500 mm Hg.). 6,6-Dimethylfulvene was either used immediately for further reactions or stored in a refrigerator.

2. Preparation of 1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene.

A solution of o-fluorobromobenzene (19.7 g., 0.11 mole) and 6,6--dimethylfulvene (11.8 g., 0.11 mole) in dry tetrahydrofuran (150 ml.) was added slowly over magnesium turnings (2.75 g., 0.11 mole). When the addition was complete, the mixture was warmed gently with stirring on a waterbath for about 30 minutes. The solvent was removed and water (100 ml.) was added. The mixture was extracted with ether (3 x 50 ml.), washed with water, dried (Na_2SO_4) and the solvent was removed. The crude reaction product was placed on a column of silica-gel and elution with light petroleum gave 1,4-dihydro-9-isopropylidene-1,4-methano-naphthalene (71), (8.6 g., 42%), m.p. 90-92°C (from methanol) (lit.[56] m.p. 91°C).

3. Preparation of 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene--1,4-methanonaphthalene.

Bromopentafluorobenzene (24.7 g., 0.1 mole) in ether (100 ml.) was

stirred at -70°C and a solution of n-butyl-lithium in pentane (47.2 ml., 0.11 mole) was added dropwise. The mixture was stirred for a further period of one hour at the same temperature and 6,6-dimethylfulvene (11.0 g., 0.1 mole) in ether (50 ml.) was added. The external cooling was then removed and the mixture was allowed to warm to room temperature. After 12 hours it was washed with aqueous hydrochloric acid (100 ml., 2N) and water. The organic layer was then dried and evaporated to leave a pale brown oil, which on distillation under reduced pressure afforded 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (73), (9.0 g., 35%) based on bromopentafluorobenzene, b.p. 110°C at 0.2 mm. Hg., m.p. 83-85°C (from light petroleum) (lit.[57] m.p. 80-82°C). ^{1}H n.m.r. ($CDCl_3$) τ 3.15-3.65 (m., 2 protons), 5.18-5.40 (m., 2 protons), and 8.66 (s., 6 protons).

ν_{max} 3050, 3035, 2990, 2950, 2930, 2880, 2870, 1505, 1480, 1302, 1283, 1176, 1121, 1060, 1048, 955, 825 and 758 cm.$^{-1}$

4. Preparation of tetrachloroanthranilic acid.

Ammonia solution (80 ml., 0.880) was added to tetrachlorophthalic anhydride (114 g., 0.4 mole) and stirred vigorously with a glass rod for exactly 30 seconds. The suspension was poured into an ice cold sulphuric acid solution (80 ml., conc H_2SO_4 in one litre of crushed ice) and the bulky tetrachlorophthalamic acid formed was filtered, washed with water until free from acid and while still wet added to an alkaline solution of sodium hypobromite [from bromine (32 ml.) and sodium hydroxide (120 g.) in one litre iced water]. The mixture was heated on a water bath at ca. 80°C for one hour and filtered to remove any suspended solid. After cooling the red solution was acidified with conc. hydrochloric acid and the precipitated acid extracted into ether. The ethereal layer was dried and the solvent removed to give tetrachloroanthranilic acid (70-85 g., 64-77%), m.p. 184°C from aqueous methanol) (lit.[60] m.p. 184°C).

ν_{max} 3510, 3400 (NH_2), 1690 (C=O).

5. Preparation of 5,6,7,8-tetrachloro-1,4-dihydro-9-isopropylidene-1,4--methanonaphthalene.

Tetrachloroanthranilic acid (22.0 g., 0.08 mole) in 1,2-dichloroethane (100 ml.) and ether (30 ml.) and isoamyl nitrite (18 ml.) in 1,2-dichloroethane (100 ml.) were added concurrently to a stirred solution of 6,6-dimethylfulvene (17.0 g., 0.16 mole) in 1,2-dichloroethane (100 ml.) at 50°C. After the addition was complete the mixture was stirred at the same temperature for a further period of 2 hours. The solvents were removed to give a dark brown viscous liquid which was placed on a column of neutral alumina and elution with ether-light petroleum (1:1) gave 5,6,7,8-tetrachloro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (74), (5.5 g., 21%), m.p. 129-131°C (from methanol) (lit.[57] m.p. 129-131°C).

ν_{max} 3030, 2990, 2945, 2915, 2870, 1403, 1378, 1368, 1294, 1207, 1168, 1136, 796, 758, 711, 704 and 699 $cm.^{-1}$

6. Preparation of 6,6-diphenylfulvene.

Freshly prepared cyclopentadiene (11.0 g., 0.17 mole) was added slowly to a stirred solution of sodium ethoxide [from sodium (4.0 g.) and ethanol (120 ml.)] and benzophenone (28.8 g., 0.16 mole) at room temperature. After the addition was over the resulting red solution was heated (ca. 50°C) gently on a water bath for about 10 minutes and cooled. All operations were carried out under nitrogen. Orange crystals started separating out and the mixture was allowed to stand overnight in a refrigerator. The orange crystals were filtered and after recrystallisation from ethanol yielded 6,6-diphenylfulvene (70), (21.0 g., 54%), m.p. 82-83°C (lit.[59] m.p. 82°C).

7. Preparation of 1,4-dihydro-9-(diphenylmethylene)-1,4-methanonaphthalene.

Anthranilic acid (13.0 g., 0.09 mole) in acetonitrile (60 ml.) and isoamyl nitrite (13 ml.) in acetonitrile (60 ml.) were added concurrently to a stirred solution of 6,6-diphenylfulvene (10.8 g., 0.047 mole) in

acetonitrile (70 ml.) during one hour at 60-70°C. The reaction mixture was further stirred at this temperature for one more hour and the work-up in the usual way afforded a dark brown viscous liquid which was then chromatographed over neutral alumina and elution with ether-light petroleum (1:1) gave 1,4-dihydro-9-(diphenylmethylene)-1,4-methano-naphthalene (72), (12.8 g., 88%), m.p. 135-136°C (from methanol) (lit.[70] m.p. 131-132.5°C).

^{1}H n.m.r. ($CDCl_3$) τ 2.65-3.16 (m., 16 protons),
5.62 (m., 2 protons).

ν_{max} 3060, 3030, 1675, 1600, 1495, 1445, 1300, 1155, 1072, 1030, 1010, 920, 840, 788, 765, 745, 700 cm.$^{-1}$

Found: C, 94.1; H, 6.0%; M (mass spectrometry), 306.

Calculated for C, 94.1; H, 5.9%; M, 306.

8. Preparation of 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methano-naphthalene.

The compound (71), (2.0 g., 0.011 mole) in ethanol (300 ml.) was hydrogenated at atmospheric pressure over prereduced palladium-carbon (80 mg., 5%) at 0°C. The reaction was monitored by g.l.c. and terminated after the uptake of one mole equivalent of hydrogen. The work-up followed by recrystallisation from methanol yielded 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (79), (1.4 g., 70%), m.p. 90°C (lit. [56] m.p. 90.5-91.5°C).

^{1}H n.m.r. ($CDCl_3$) τ 2.74-3.0 (m., 4 protons),
6.15-6.3 (m., 2 protons), 8.0-8.85 (m., 4 protons) and
8.38 (s., 6 protons).

$\nu_{max.}$ 3080, 3030, 2970, 2940, 2875, 1470, 1450, 1370, 1280, 1250, 1110, 1010, 925, 840, 750, 730 and 690 cm.$^{-1}$

High resolution mass spectrometry:

	Measured mass	Calculated mass	Formula
M^{+}	184.1246	184.1252	$C_{14}H_{16}$
M^{+}-28	156.0931	156.0938	$C_{12}H_{12}$

9. Preparation of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene.

The compound (73), (8.2 g., 0.032 mole) in ethanol (500 ml.) on hydrogenation over prereduced palladium-carbon (350 mg., 10%) under identical reaction conditions and the work-up precedure as described in experiment 7. afforded 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (81), (8.3 g., 100%), m.p. 102°C (from light petroleum) (lit.[57] m.p. 101-102°C).

^{1}H n.m.r. ($CDCl_3$) τ 5.79-5.95 (m., 2 protons), 7.85-8.80 (m., 4 protons), and 8.36 (s., 6 protons).

High resolution mass spectrometry:

	Measured mass	Calculated mass	Formula
M^{+}	256.0878	256.0876	$C_{14}H_{12}F_4$
M^{+}-28	228.0561	228.0562	$C_{12}H_8F_4$

10. Preparation of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene.

Compound (74), (3.0 g., 0.01 mole) in ethanol (300 ml.) on hydrogenation over prereduced palladium-carbon (120 mg., 5%) under identical conditions described previously in experiment No. 8 gave 5,6,7,8-tetrachloro-1,2,3,4--tetrahydro-9-isopropylidene-1,4-methanonaphthalene (82), (2.7 g., 90%), m.p. 154-155°C (from methanol) (lit.[57] m.p. 154-155°C).

^{1}H n.m.r. ($CDCl_3$) τ 5.92 (m., 2 protons), 7.82-8.2 (m., 2 protons), 8.36 (s., 6 protons) and 8.56-8.90 (m., 2 protons).

$\nu_{max.}$ 3020, 2980, 2955, 2920, 2885, 1450, 1365, 1300, 1285, 1240, 1240, 1205, 1170, 1150, 1115, 1040, 970, 800, 755, 740 and 680 $cm.^{-1}$

High resolution mass spectrometry:

	Measured mass	Calculated mass	Formula
M^+	319.9713	319.9695	$C_{14}H_{12}{}^{35}Cl_4$
M^+-28	291.9367	291.9380	$C_{12}H_8{}^{35}Cl_4$

11. Preparation of 1,2,3,4-tetrahydro-9-(diphenylmethylene)-1,4--methanonaphthalene.

Compound (72), (4.15 g., 0.013 mole) in ethyl acetate (500 ml.) was hydrogenated over prereduced palladium-carbon (160 mg., 5%) at 0°C in the usual way and the standard work-up afforded 1,2,3,4-tetrahydro-9--(diphenylmethylene)-1,4-methanonaphthalene (80), (3.98 g., 96%), m.p. 137-137.5°C (from methanol) (lit.[70] m.p. 135.5-136.5°C).

^{1}H n.m.r. ($CDCl_3$) τ 2.65-3.1 (m., 14 protons), 6.15 (m., 2 protons), 7.8-8.05 (m., 2 protons), and 8.5-8.75 (m., 2 protons).

$\nu_{max.}$ 3080, 3060, 3030, 3010, 2975, 2945, 2875, 1670, 1600, 1490, 1470, 1440, 1170, 1150, 1110, 1072, 1030, 920, 770, 760, 710 and 700 cm.$^{-1}$

Found: C, 93.3; H, 6.7%; M (mass spectrometry), 308.

Calculated for $C_{24}H_{20}$ C, 93.5; H, 6.5%; M, 308.

High resolution mass spectrometry:

	Measured mass	Calculated mass	Formula
M^+	308.1556	308.1565	$C_{24}H_{20}$
M^+-28	280.1255	280.1252	$C_{22}H_{16}$

12. Preparation of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl--1,4-methanonaphthalene.

Compound (73), (1.0 g., 0.004 mole) in ethanol (150 ml.) was hydrogenated at atmospheric pressure over palladium-carbon (50 mg., 5%) at room temperature and the reaction was terminated after the uptake of 2 mole equivalent of hydrogen. The usual work-up then gave 5,6,7,8-tetrafluoro--1,2,3,4-tetrahydro-9-isopropyl-1,4-methanonaphthalene (76), (0.9 g., 90%),

m.p. 59°C (from light petroleum) (lit.[57] m.p. 58-59°C).

^{1}H n.m.r. ($CDCl_3$) τ 6.35-6.58 (m., 2 protons), 7.78-9.93 (m., 6 protons) and 9.16 (s., 6 protons).

13. Pyrolysis of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene--1,4-methanonaphthalene (81).

The compound (81), (0.1 g.) in benzene (2 ml.) was placed in a pyrolysis tube and the tube was evacuated (0.5 mm. Hg.). It was flushed with oxygen-free nitrogen, re-evacuated, sealed and heated at 200°C for 16 hours. The cold tube was opened and the product extracted with ether. Thin layer chromatography showed a single spot identical with the starting material. Column chromatography over silica-gel and elution with light petroleum gave only recovered starting material (81), (90 mg.), m.p., mixed m.p. and n.m.r. identical.

14. Pyrolysis of 5,6,7,8-tetrachloro-1,4-dihydro-9-isopropylidene-1,4-methanonaphthalene (74).

Compound (74), (0.2 g.) in benzene (1 ml.) was heated at 300°C for 14 hours in a manner described already in the previous experiment. The work-up resulted only in an intractable polymeric material.

Flash vacuum pyrolysis.

General procedure:

The pyrolysis was carried out in an apparatus[39] (ca. 90 cm. tube). The tube was flushed with nitrogen and heated at the pyrolysis temperature. The compound was then submitted slowly into the tube under a constant flow of nitrogen at 3 mm. Hg. pressure. The products formed were collected on a cold finger cooled under liquid nitrogen. The heating was then switched off and the cold finger was allowed to warm to room temperature. The products were washed with ether or chloroform and were purified by column chromatography and recrystallisation.

15. Pyrolysis of 1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (79).

The compound (79), (0.5 g., 0.003 mole) at ca. 600°C gave an oil (0.37 g.) which was placed on a column of neutral alumina (250 g., activity 1) and elution with light petroleum afforded two fractions :

(i) 1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]indene (92), (0.28 g., 54%), b.p. 110°C at 0.5 mm. Hg. ^{1}H n.m.r. ($CDCl_3$, 220 MHz.) τ 2.60-2.97 (m., 4 protons), 6.90 (t., 2 protons, /J/ = 2.5 Hz.), 7.45 (m., 2 protons), 7.83 (t., 2 protons, /J/ = 7 Hz.) and 8.8 (s., 6 protons)

$\nu_{max.}$ 3060, 2960, 2870, 1630, 1610, 1470, 1400, 1360, 1200, 1105, 1020, 750 and 720 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 270 (log ϵ 4.00), 265 (4.06), 260 (4.10), 225 (400), 217 (4.15) and 210 (4.22) nm.

Found: C, 90.5; H, 8.8%. M (High resolution mass spectrometry), 184.1257.

$C_{14}H_{16}$ requires C, 91.3; H, 8.7%; M, 184.1252.

And (ii) 2-isopropenylindene (96), (0.1 g., 23%), m.p. 88-90°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 2.5-3.0 (m., 4 protons), 3.22 (m., one proton), 4.75 (m., one proton), 5.10 (m., one proton), 6.42 (br.s., 2 protons), and 7.93 (br. 3 protons).

ν_{max} 3080, 3040, 2940, 2860, 1650, 1610, 1500, 1490, 1460, 1380, 1305, 1260, 1090, 1005, 940, 830, 770, 745 and 725 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 314 (log ϵ 3.97), 294 (4.26), 288 (4.23), 241 (4.06), 293 (4.15), 226 (4.12) and 212 (4.14) nm.

Found: C, 89.65; H, 6.4%; M (High resolution mass spectrometry), 156.0925. $C_{12}H_{12}$ requires C, 92.3; H, 7.7%; M, 156.0939.

This compound decomposed slowly at room temperature

16. Pyrolysis of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (81).

Compound (81), (0.4 g., 0.0016 mole) at ca. 600°C afforded a dark

brown oil (0.29 g.) which on column chromatography over neutral alumina (200 g.) and elution with light petroleum gave two fractions :

(i) 4,5,6,7-tetrafluoro-1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]-indene (94), (0.21 g., 52.5%), m.p. 102-103°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 6.80 (m., 2 protons), 7.26 (t.xt., 2 protons, /J/ = 7 and 2 Hz.), 7.78 (t., 2 protons, /J/ = 7 Hz.)and 8.77 (s., 6 protons).

$\nu_{max.}$ 2970, 2870, 1650, 1630, 1505, 1490, 1460, 1400, 1365, 1312, 1110, 1050, 960 and 790 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 296 (log ϵ 3.23), 280 (3.46), 266 (4.00), 257 (4.06), 217 (4.18) abd 209 (4.20) nm.

Found: C, 65.72; H, 4.72%; M (mass spectrometry), 256. $C_{14}H_{12}F_4$ requires C, 65.60; H, 4.70%; M, 256.

m/e 256, 241, 213, 200 and 187.

And (ii) 4,5,6,7-tetrafluoro-2-isopropenylindene (97), (0.05 g., 13%), m.p. 76-78°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.30 (m., one proton), 4.74 (m., one proton), 4.90 (m., one proton), 6.36 (br.s., 2 protons), and 7.95 (br., 3 protons).

$\nu_{max.}$ 2930, 2860, 1655, 1625, 1495, 1400, 1300, 1220, 1130, 1105, 980, 950, 900, 855 and 780 cm.$^{-1}$

Found: M (High resolution mass spectrometry), 228.0558.

$C_{12}H_8F_4$ requires M, 228.0562.

This compound decomposed slowly at room temperature.

17. Pyrolysis of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene-1,4-methanonaphthalene (82).

Compound (82), (1.5 g., 0.005 mole) at ca. 600°C gave a dark brown viscous oil (0.90 g.) which on column chromatography as usual yielded

two fractions :

(i) 4,5,6,7-tetrachloro-1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]-indene (95), (0.67 g., 45%), m.p. 153°C (from ethanol).

^{1}H n.m.r. ($CDCl_3$) τ 6.85 (m., 2 protons), 7.20 (m., 2 protons), 7.82 (m., 2 protons) and 8.78 (s., 6 protons).

$\nu_{max.}$ 2965, 2870, 1618, 1590, 1460, 1390, 1340, 1310, 1185, 1085, 785 and 700 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 287 (log ϵ 4.20), 277 (4.22), 243 (4.28), 235 (4.35), 228 (4.33), 221 (4.28) and 209 (4.22) nm.

Found: C, 52.5; H, 3.8%; M (mass spectrometry), 322. $C_{14}H_{12}Cl_4$ requires C, 52.5; H, 3.7%; M, 322.

m/e 322, 307, 266 and 200.

And (ii) 4,5,6,7-tetrachloro-2-isopropenylindene (98), (0.16 g., 11.5%), m.p. 145-146°C (from ethanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.29 (m., one proton), 4.70 (m., one proton), 4.90 (m., one proton), 6.38 (br., 2 protons), 7.95 (br., 3 protons).

$\nu_{max.}$ 2940, 1624, 1 565, 1390, 1300, 1225, 1170, 895, 850 and 770 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 319 (log ϵ 4.18), 307 (4.37), 299 (4.34), 255 (4.13), 246 (4.25), 238 (4.21) and 230 (4.19) nm.

Found: C, 48.6; H, 2.7%; M (mass spectrometry), 294. $C_{12}H_8Cl_4$ requires C, 48.98; H, 2.7%; M, 294.

m/e 294, 279, 259, 207.

18. Pyrolysis of 5,6,7,8-tetrafluoro-1,4-dihydro-9-isopropylidene--1,4-methanonaphthalene (73).

Compound (73), (0.4 g.) was pyrolysed at 600°C as usual and gave a white crystalline solid (0.262 g.) which was shown to be an unchanged starting material (73) by its g.l.c., comparison thin layer chromatography, ^{1}H n.m.r. spectrum and m.p.

19. Pyrolysis of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropyl--1,4-methanonaphthalene (76).

Compound (76), (0.343 g.) at ca. 600°C yielded only a recovered starting material (76), (0.257 g.). Thin layer chromatography, ^{1}H n.m.r. spectrum and m.p. identical to that of an authentic sample.

20. Pyrolysis of 1,2,3,4-tetrahydro-9-(diphenylmethylene)-1,4-methanonaphthalene (80).

Compound (80), (2.2 g., 0.007 mole) at 600°C as usual gave a dark brown oil (2.0 g.) which solidified at room temperature and on recrystallisation from light petroleum gave 1,2,3,8-tetrahydro-1,1-diphenylcyclopent[a]indene (93), (1.2 g., 54%), m.p. 120-122°C.

^{1}H n.m.r. ($CDCl_3$) τ 2.55-3.0 (m., 14 protons), 6.5-6.72 (m., 2 protons), 6.88-7.05 (m., 2 protons), and 7.13-7.35 (m., 2 protons).

$\nu_{max.}$ 3070, 3045, 2965, 2930, 2895, 2862, 1622, 1602, 1580, 1495, 1470, 1460, 1445, 1395, 1315, 1302, 1268, 1246, 1222, 1210, 1190, 1180, 1155, 1082, 1024, 1019, 940, 910, 888, 854, 763, 758, 738, 720 and 700 cm.$^{-1}$

Found: C, 93.5; H, 6.4%; M (mass spectrometry), 308. $C_{24}H_{20}$ requires C, 93.5; H, 6.5%; M, 308.

Flash Vacuum Pyrolysis at 800°C.

This was carried out in a much shorter tube (44 x 2 cm.) and exactly in a manner as described in the case of 600°C. The flow of nitrogen during the pyrolysis was also stopped and therefore, the pyrolysis was done at 0.5-1.0 mm. Hg. pressure. Work-up procedure was the same as already mentioned.

21. Pyrolysis of 5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-9-isopropylidene--1,4-methanonaphthalene (81).

Compound (81), (2.55 g., 0.01 mole) on pyrolysis at 800°C afforded

a dark brown oil (2.2 g.) which was placed on a column of silica-gel (300 g.) and elution with light petroleum yielded a complex mixture as indicated by g.l.c. and ^{1}H n.m.r. spectroscopy. This was not investigated further.

22. Pyrolysis of 4,5,6,7-tetrafluoro-1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]indene (94).

Compound (94), (0.8 g., 0.003 mole) at 800°C resulted only in a complex mixture (0.65 g.) as shown by g.l.c. and ^{1}H n.m.r. spectroscopy. This mixture was not investigated further.

23. Pyrolysis of 5,6,7,8-tetrachloro-1,2,3,4-tetrahydro-9-isopropylidene--1,4-methanonaphthalene (82).

Compound (82), (0.2 g., 0.0006 mole) at 800°C gave a dark solid (0.1 g.). Preparative layer chromatography (1 x 1 m. x 20 cm., 0.75 mm. thickness; eluant benzene) yielded tetrachloronaphthalene (106), (ca. 20 mg.), m.p., mixed m.p., i.r., ^{1}H n.m.r. and u.v. spectra identical to an authentic[27c] sample.

24. Pyrolysis of 4,5,6,7-tetrachloro-1,2,3,8-tetrahydro-1,1-dimethylcyclopent[a]indene (95).

Compound (95), (0.1 g., 0.0003 mole) at 800°C gave a solid (ca. 38 mg.) which on preparative layer chromatography as usual afforded tetrachloronaphthalene (106), (17 mg.), m.p., ^{1}H n.m.r. and u.v. spectra identical to an authentic sample.

25. Pyrolysis of 1,2,3,4-tetrahydro-9-(diphenylmethylene)-1,4-methanonaphthalene (80).

Compound (80), (0.32 g., 0.001 mole) at 800°C gave a brown liquid (0.2 g.). Preparative layer chromatography [2 x 1 m. x 20 cm., 0.75 thickness; eluant ether-light petroleum (1:5)] afforded :

(i) naphthalene (104), (ca. 30 mg.), m.p. and mixed m.p. 80° and u.v. spectrum identical to that of an authentic sample.

And (ii) 1,1-diphenylethylene (105), (40 mg.), i.r. and ^{1}H n.m.r. spectra, and g.l.c. identical to those of an authentic[69] sample.

26. Pyrolysis of 1,2,3,8-tetrahydro-1,1-diphenylcyclopent[a]indene (93).

Compound (93), (0.1 g.) on pyrolysis at 800°C as usual gave an oil (ca. 76 mg.) which on preparative layer chromatography yielded :

(i) naphthalene (104), (ca. 18 mg.), m.p. and mixed m.p. 80° and u.v. spectrum identical with an authentic sample.

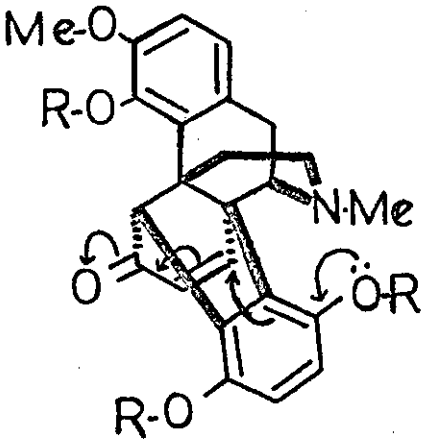
And (ii) 1,1-diphenylethylene (105), (ca. 21 mg.), i.r. spectrum and g.l.c. identical to an authentic material.

CHAPTER 3

THE SYNTHESIS AND REARRANGEMENT OF SOME BENZOBARRELENE DERIVATIVES

INTRODUCTION

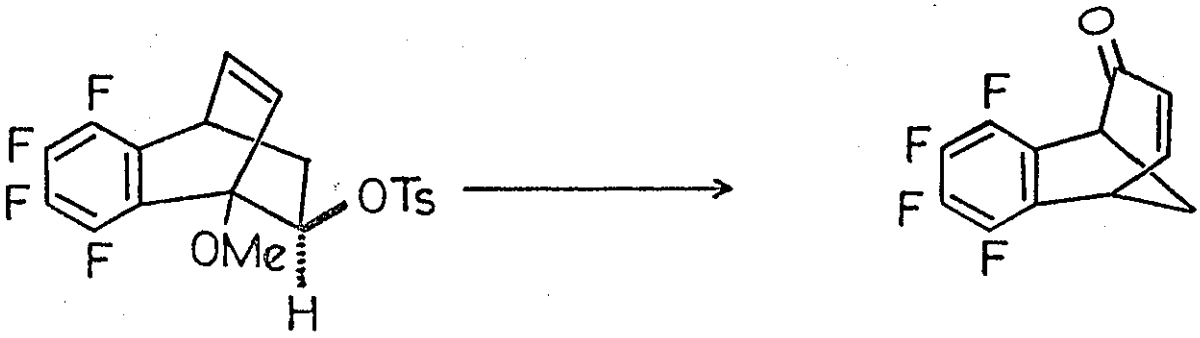
The ultraviolet spectrum of flavothebaone (107)[71] shows an unexpected maximum at 346 nm (log ε 3.56) and which is also observed in the case of its trimethyl ether (108) at 337 nm (log ε 3.49). However, it has been suggested that the enone chromophore interacts with the non-conjugated hydroquinone system as indicated in structure (107) and that this interaction is responsible for the abnormal spectrum.[71a]



R = H (107)
R = Me (108)

In order to rationalise this anomaly an appropriate model compound for flavothebaone molecule is necessary although earlier attempts to obtain such a system have been unsuccessful.[72]

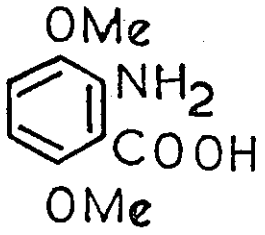
In view of these observations it was decided to synthesise a suitable model compound particularly for the u.v. spectral studies. It has already been established that 5,6,7,8-tetrafluoro-1-methoxy-2-exo-p-tolylsulphonyloxy--1,4-ethenotetralin (109) rearranges exclusively to compound (110)[27a] and it was anticipated that with the appropriate substituents in the aryl residue this approach could provide a route to the required model system.



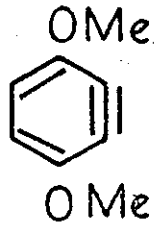
(109) (110)

DISCUSSION

It is well documented[1,14] that the mode of addition of dienes to arynes in the Diels-Alder reactions is controlled largely by the inductive effects of the substituents, particularly in the 3- and 6-positions in arynes. In the present study, the synthesis of a previously unreported 2-amino-3,6--dimethoxybenzoic acid (16)[28] was undertaken, in view of the fact that, like other anthranilic acids, it would also be a suitable precursor for reactions of 3,6-dimethoxybenzyne (17) with arenes.

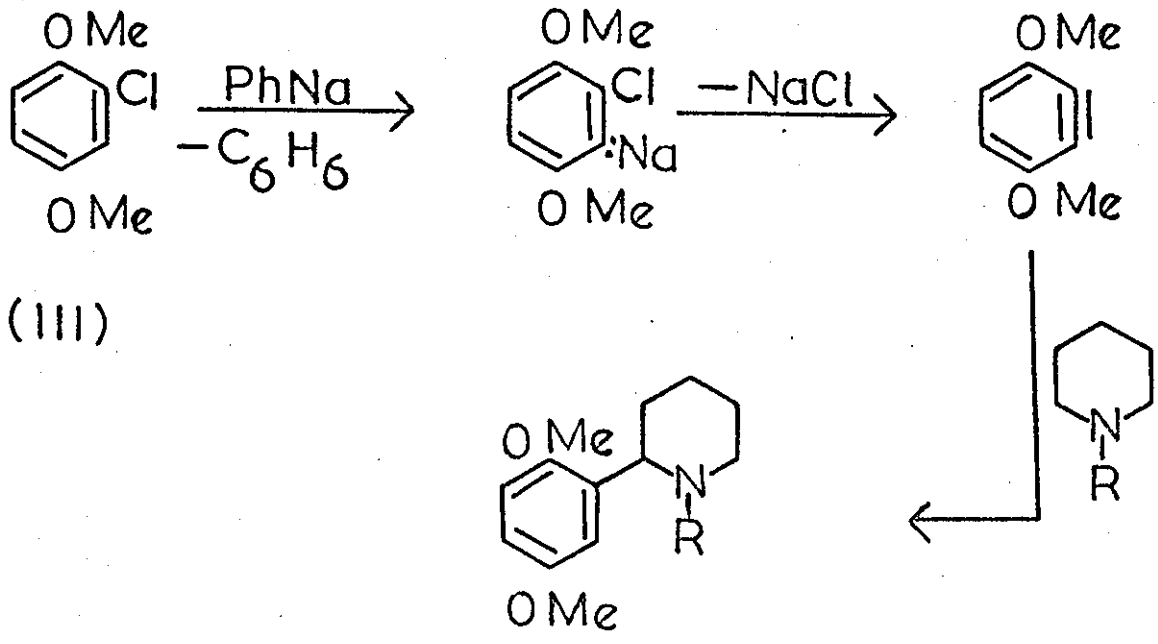


(16)



(17)

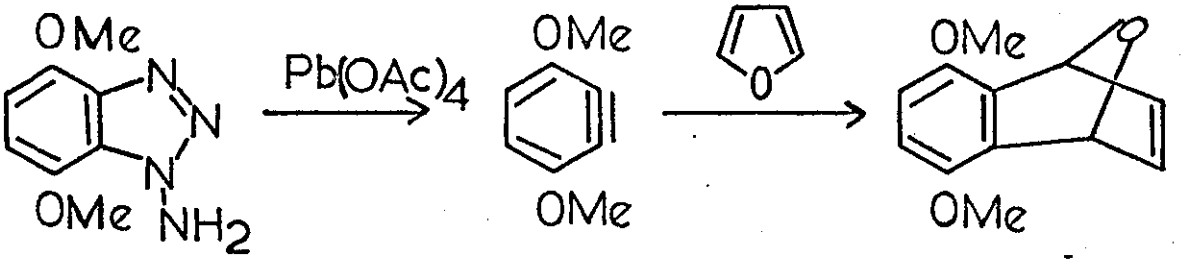
The aryne (17), however, is not unfamiliar. Gustav Ehrhart[73] generated it from compound (111) as illustrated in Scheme 23. In a more recent report, Rees and West[74] have shown the formation of



(111)

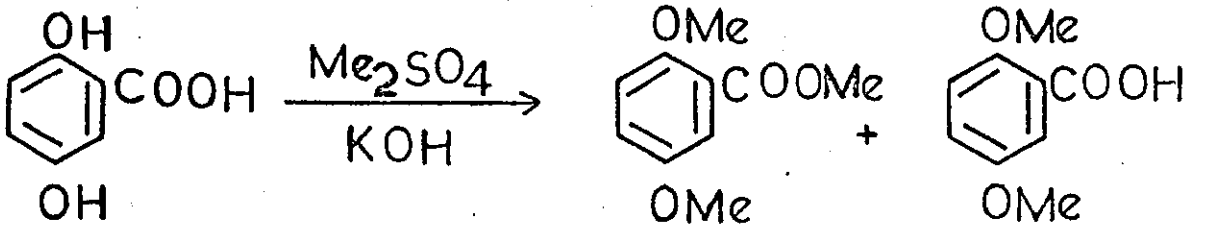
Scheme 23

3,6-dimethoxybenzyne by the oxidation of 1-amino-4,7-dimethoxybenzotriazole (112) in the presence of furan and obtained the adduct (113) in 63% yield.



(112) (113)

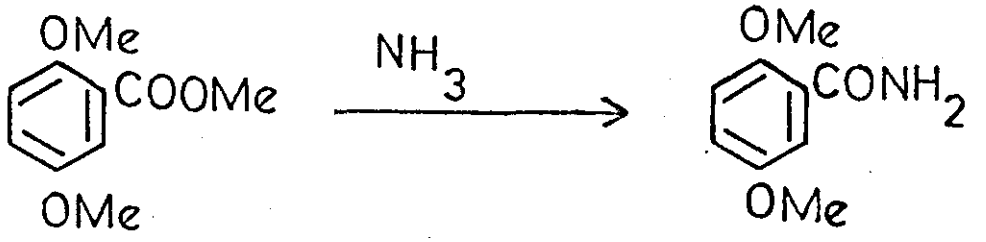
First of all, the methylation of 2,5-dihydroxybenzoic acid with dimethyl sulphate in concentrated aqueous potassium hydroxide following the standard literature procedure gave methyl 2,5-dimethoxybenzoate (114) in a high yield (88.5%) (Scheme 24). A small amount of 2,5-dimethoxybenzoic acid (115) was also produced.



(114) (115)

Scheme 24

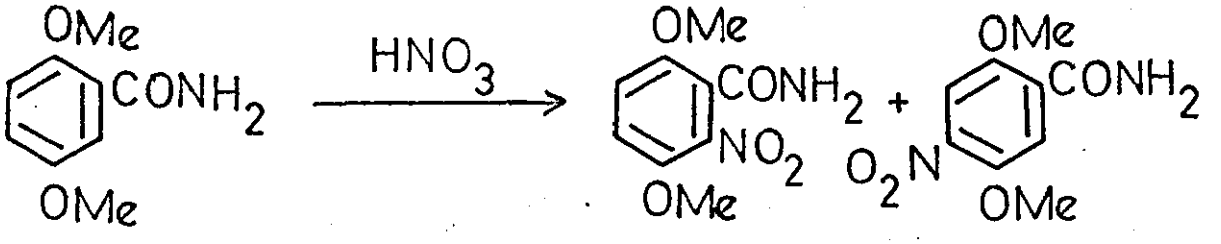
The ester (114) was stirred with an excess of concentrated ammonia solution at room temperature for 72 hours and gave white needles of 2,5-dimethoxybenzamide (116) in a quantitative yield (Scheme 25).



(114) (116)

Scheme 25

Rees and West[74] have reported that the amide (116) on treatment with concentrated nitric acid at low temperature forms an isomeric mixture of 3,6-dimethoxy-2-nitrobenzamide (117), obtained as the major component, and 2,5-dimethoxy-4-nitrobenzamide (118). The latter compound however, dissolves readily in hot benzene thereby enabling an easy separation of both the isomers from the reaction mixture. In this manner, the compound (117) was prepared in 69% yield (Scheme 26).

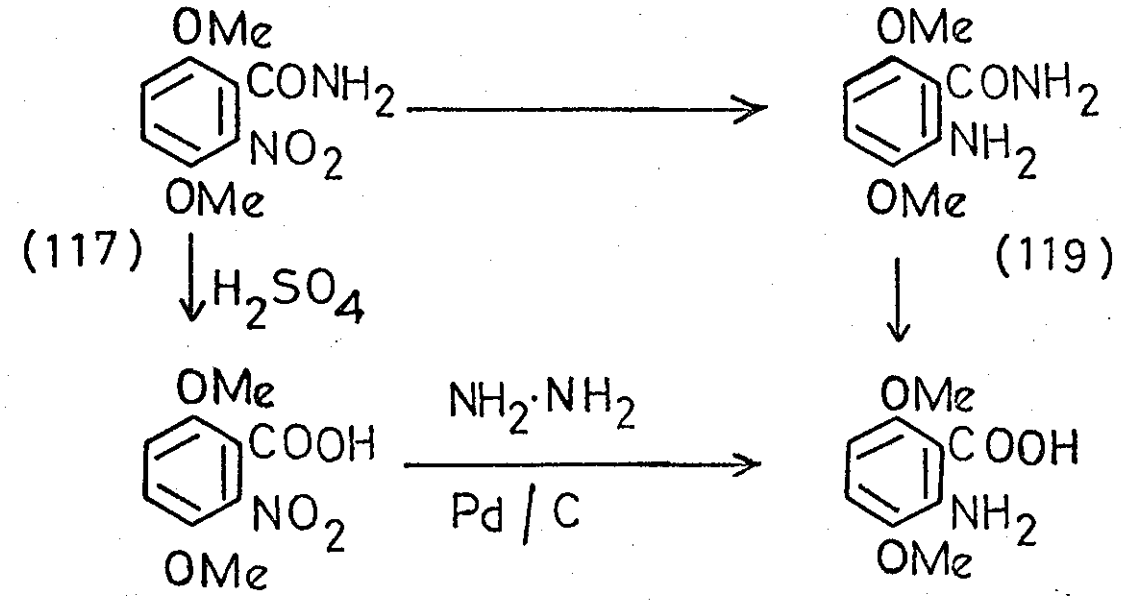


(116) (117) (118)

Scheme 26

After having obtained the nitroamide (117) two synthetic pathways to 2-amino-3,6-dimethoxybenzoic acid (16) as outlined in Scheme 27 seemed possible. One approach involved the reduction of nitro-group to form the compound (119) which on hydrolysis of the amide function could lead to the required acid (16). Nevertheless, this route proved inadequate.[75] The alternative procedure was to hydrolyse the hindered amide (117) first to the previously unreported 3,6-dimethoxy-2-nitrobenzoic

acid (120). However, after several initial unsuccessful attempts the nitroamide (117) was converted to nitroacid (120) in 88% yield by the treatment of the amide solution in concentrated sulphuric acid at low temperature with an excess of sodium nitrite.[76] The structure (120) was established by its elemental analysis and from spectral data. The



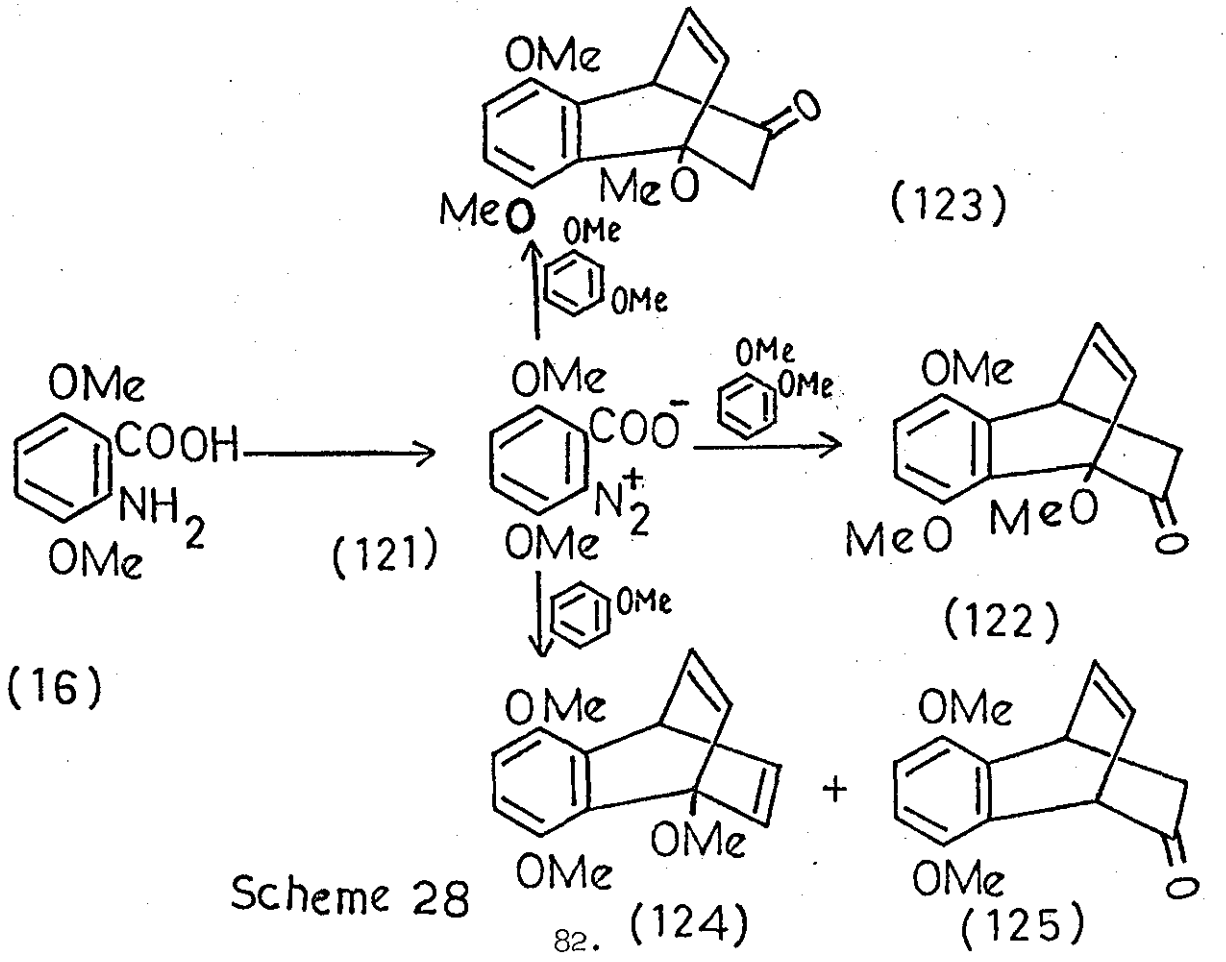
Scheme 27

nitro-group in compound (120) was reduced quantitatively by the method of Dewar and Mole[77] using hydrazine hydrate in the presence of palladium-carbon in ethanol. The structure (16) was compatible with its elemental analysis and spectral data.

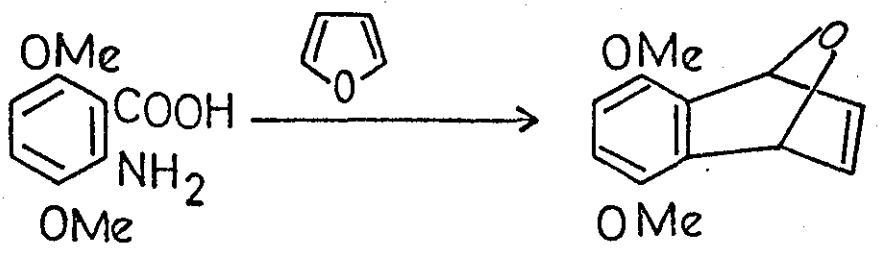
As anticipated 2-amino-3,6-dimethoxybenzoic acid (16) was found to be an efficient precursor for 3,6-dimethoxybenzyne (17). The aprotic diazotisation in the presence of furan produced the 1,4-cycloadduct (113) in 80% yield.[28]

The reactions of tetrahalogenobenzynes with methoxyarenes have revealed

that in the formation of the Diels-Alder adducts there is a marked preference for the methoxy-group to be retained at the bridgehead position.[65] The diazotisation of the anthranilic acid (16) afforded a dark-red crystalline 3,6-dimethoxybenzene-diazonium-2-carboxylate (121). When this compound was decomposed in an excess of o-dimethoxy- and m-dimethoxybenzene, each reaction mixture, after hydrolysis and the standard work-up procedure, gave the expected 1,4-cycloadducts, 1,5,8--trimethoxy-1,4-etheno-2-tetralone (122) in 47% yield and 1,5,8-trimethoxy--1,4-etheno-3-tetralone (123) in 39% yield. Likewise, in the reaction of anisole with the diazonium carboxylate (121) two products, 1,4-dihydro--1,5,8-trimethoxy-1,4-ethenonaphthalene (124) in 17% yield and 5,8--dimethoxy-1,4-etheno-2-tetralone (125) in 5% yield were isolated (Scheme 28). The structures of these compounds were established by elemental analyses and by spectroscopic methods. The i.r. spectra of the compounds (122), (123) and (125) showed carbonyl stretching frequencies at



Scheme 28

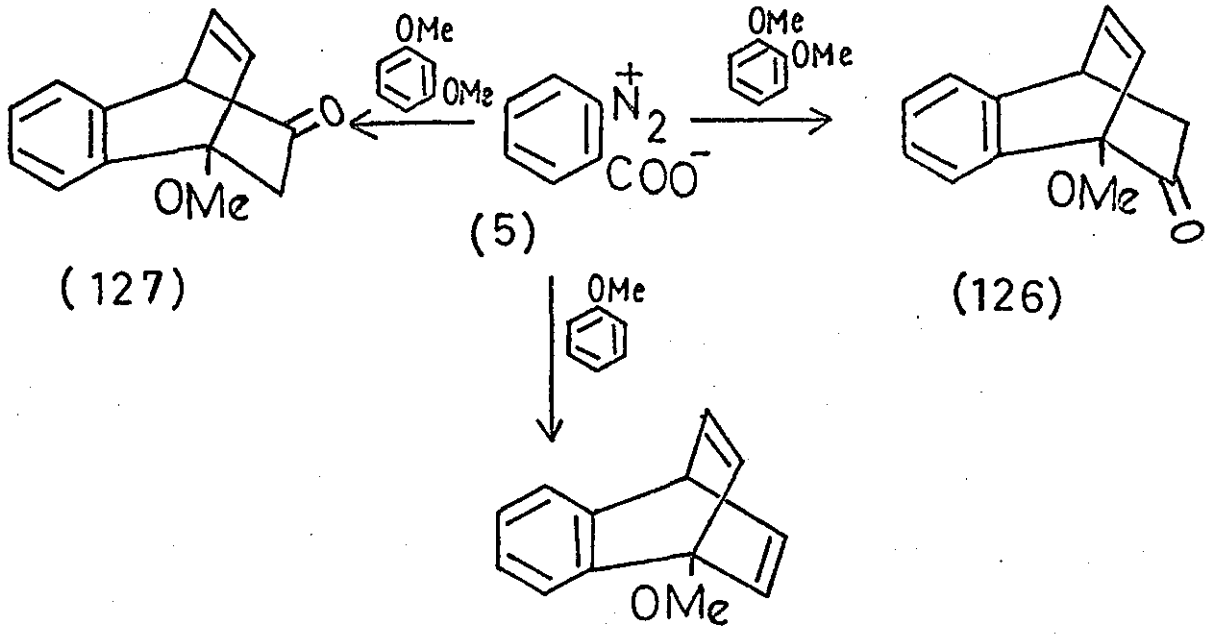


(16) (113)

Scheme 28

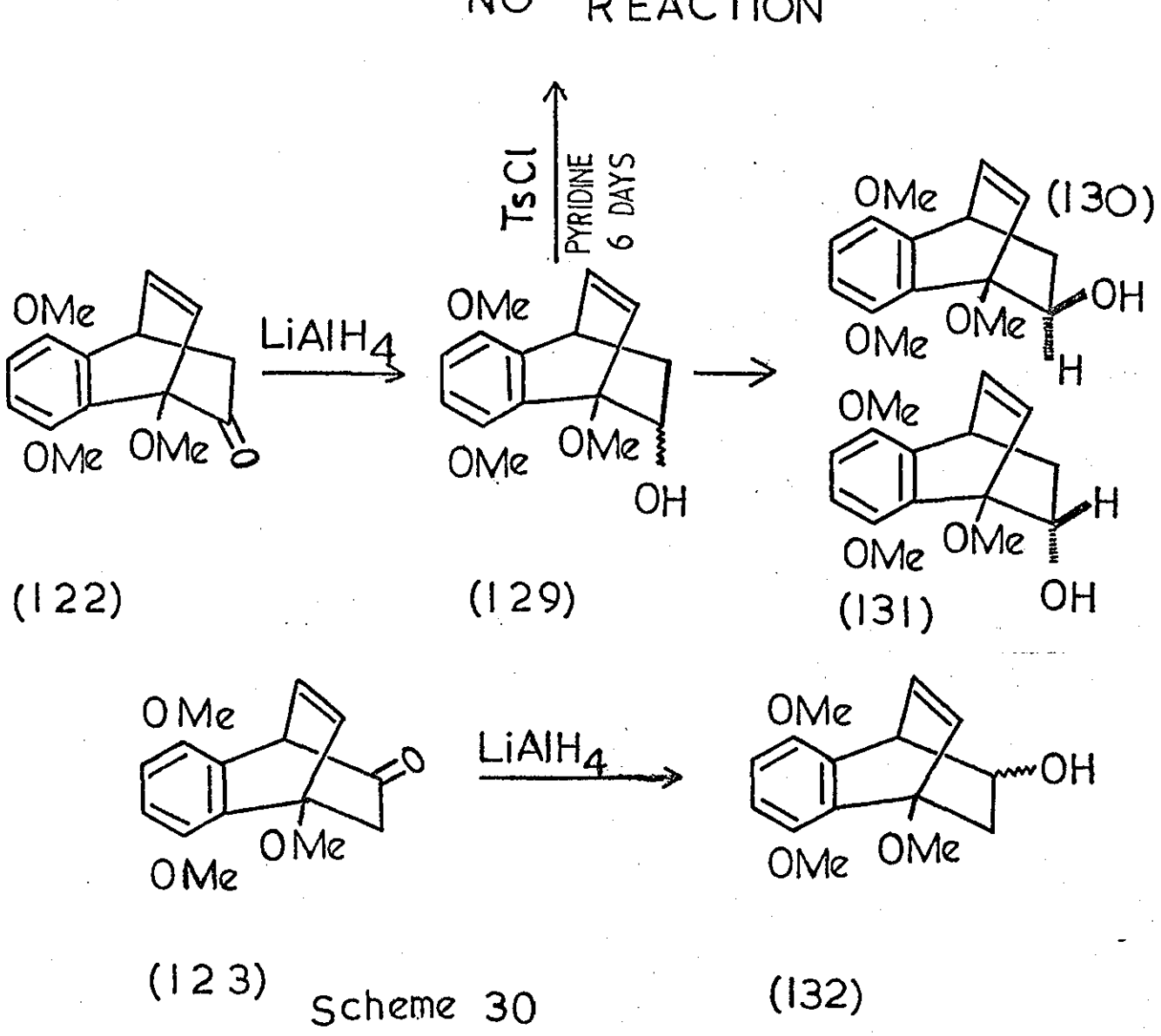
1745, 1730 and 1740 cm^{-1} respectively. The ^1H n.m.r. spectrum of the adduct (122) for instance, exhibited multiplets at τ 3.25 (aromatic and olefinic protons) and 5.35 (bridgehead methine proton), singlets at τ 6.2, 6.22 and 6.25 (methoxy-groups) and the methylene protons appeared as an AB quartet at τ 7.92, $|J_{AB}|$ = 18 Hz. However, in compound (123) the bridgehead methine proton and the methylene-group were observed as doublet of doublets at τ 5.12, $|J|$ = 6 and 2 Hz and a singlet at τ 7.61 respectively. In the case of the adduct (124) the bridgehead methine proton gave rise to a triplet of triplets centred at τ 4.72, $|J|$ = 5.8 and 1.8 Hz.

Interestingly, the reactions of benzyne generated from benzenediazonium--2-carboxylate (5) with o-dimethoxy- and m-dimethoxybenzene produced the expected 1,4-cycloadducts, (126) and (127) but in poor yield (Scheme 29). This is not surprising in view of the fact that benzyne reacts with anisole to form the adduct (128) in only 1.5% yield.[27a] The formation of the compounds (126) and (127) was evident from their infra-red and ^1H n.m.r. data. No further attempts were made to isolate these compounds in pure form. Nevertheless, the significance of these results lies in the fact that 3,6-dimethoxybenzyne is, as expected, far more reactive and electrophilic in character than the parent benzyne.



Scheme 29

The ketone (122) on treatment with lithium aluminium hydride in ether resulted in the formation of an epimeric mixture of alcohols (129). The separation of the mixture was however, achieved with considerable difficulty by multiple-elution preparative layer chromatography over silica-gel and 1,2,3,4-tetrahydro-1,5,8-trimethoxy-1,4-ethenonaphthalen--2-exo-ol (130) and 1,2,3,4-tetrahydro-1,5,8-trimethoxy-1,4-ethenonaphthalen--2-endo-ol (131) were obtained (Scheme 30). The structures of the individual alcohols were confirmed by elemental analysis and by spectroscopic techniques. The stereochemistry of each compound was assigned on the basis of ^{1}H n.m.r. spectra. For instance, the methine proton at position 2 in the case of exo-alcohol (130) was observed at higher field than that of the endo-isomer (131). Likewise, the compound (123) was reduced to a mixture of alcohols (132) in high yield.



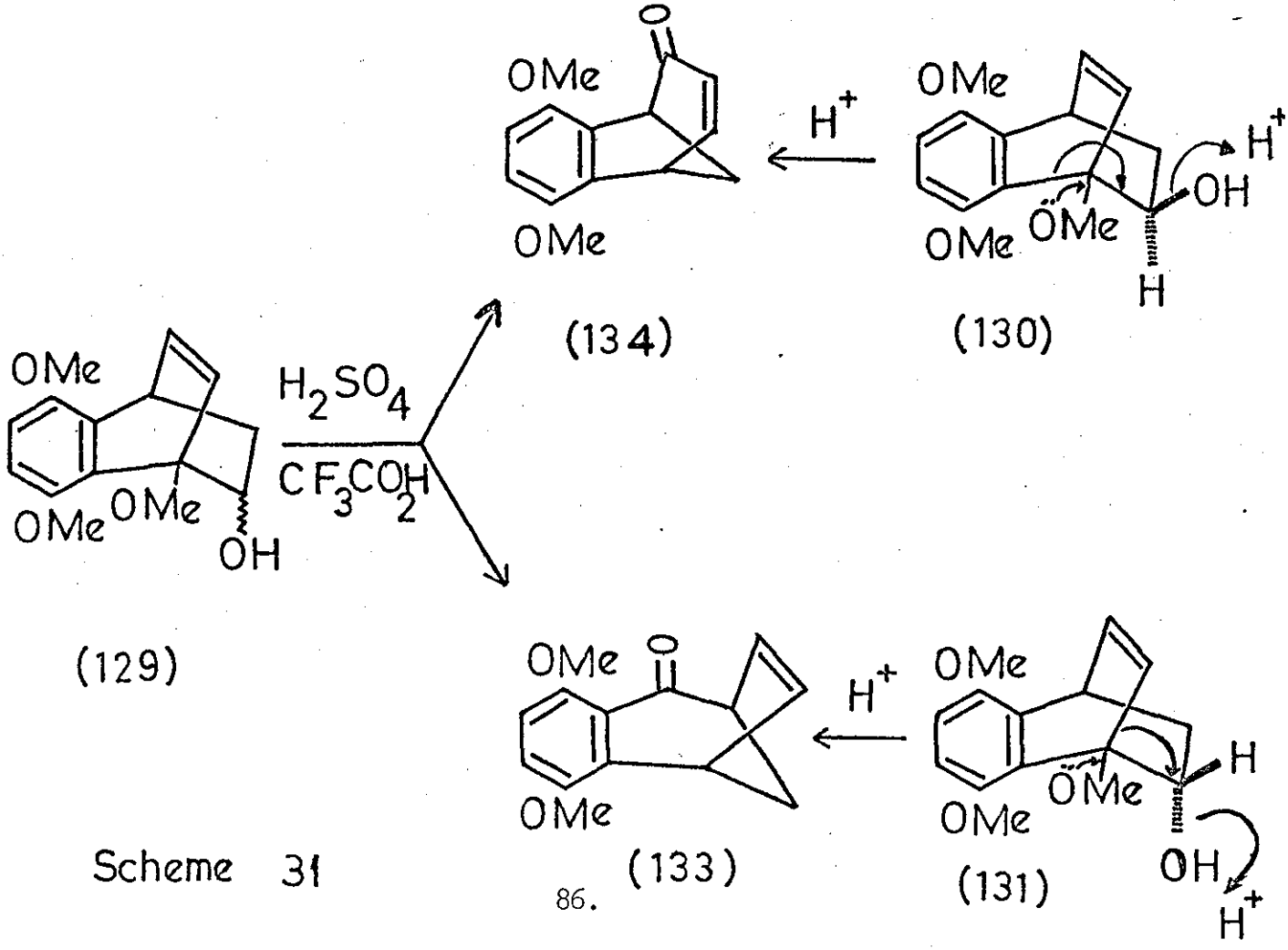
Scheme 30

In view of the difficulty of separating the mixture (129) it was decided to convert it into an epimeric mixture of p-tolylsulphonyl derivatives which could enable an easy separation of the endo- and exo-compounds. Surprisingly, the alcohols (129) did not undergo any reaction with tosyl chloride in pyridine and only the starting material was recovered in this reaction. It may be possible that the interactions of the methoxy-groups present in the aryl system hinder the formation of the tosylates.

Acid-catalysed rearrangement reactions of bicyclic molecules have been investigated extensively during the past few years.[78] Workers in these laboratories have established that compounds of the type

1-methoxybenzobarrelenes (12, X=H, F or Cl) in the presence of strong mineral acids rearrange readily to an isomeric mixture of ketones [(13)-(15)] and that the formation of the minor components (14) and (15) depends largely on the reaction conditions used.[27a]

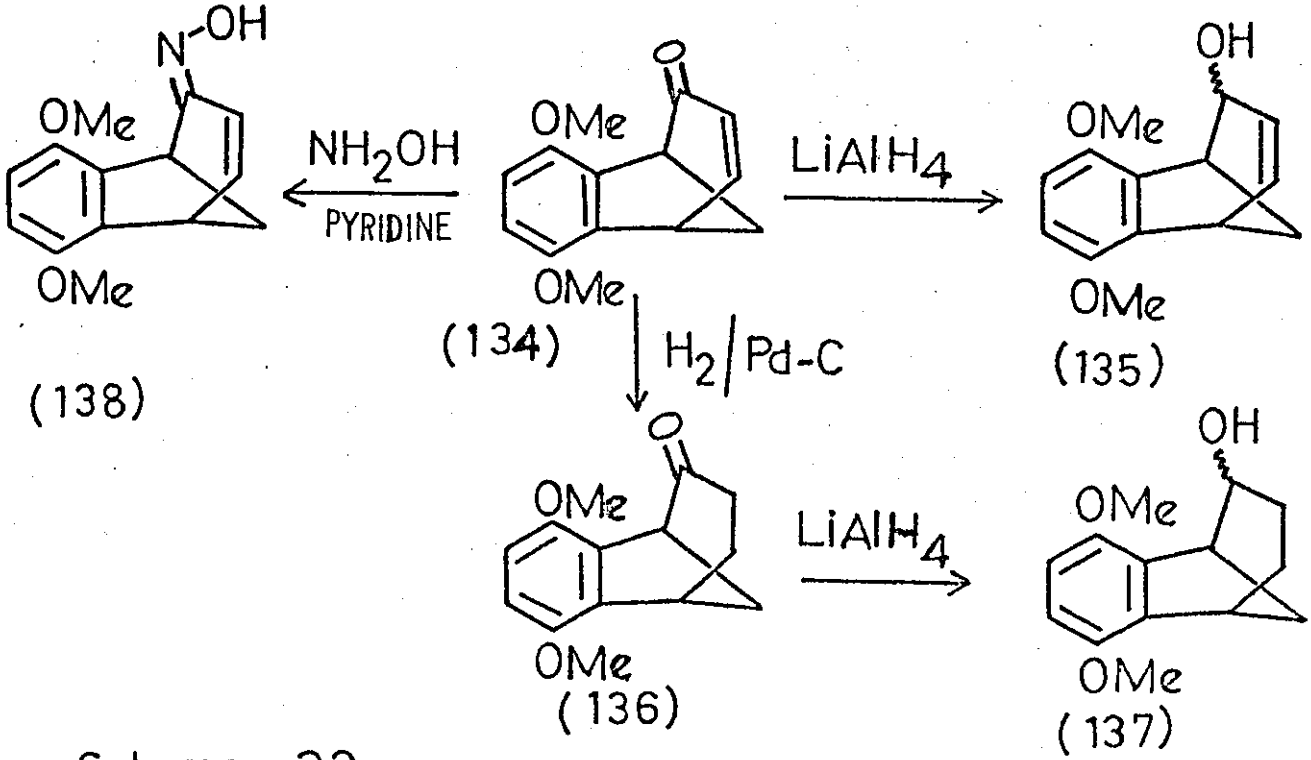
Treatment of the epimeric alcohols (129) with a mixture of trifluoroacetic and sulphuric acids at room temperature after the standard work-up procedure produced a mixture of two products (t.l.c.). Preparative layer chromatography as usual afforded 5,8-dimethoxy-2,4-etheno-1-tetralone (133) in 50% yield and the model compound, 5,9-dihydro-1,4-dimethoxy-5,9--methanobenzocyclohepten-6-one (134) in 28% yield (Scheme 31). Furthermore, the alcohols (130) and (131) underwent the expected stereospecific rearrangements to the compounds (134) and (133) respectively. This was shown by carrying out small-scale rearrangements of the individual alcohols using analytical t.l.c. and i.r. spectroscopy to identify the products formed.



Scheme 31

The structures of the compounds (133) and (134) were established largely by analysis and by spectroscopic methods.

As illustrated in Scheme 32, a number of derivatives of the model compound (134) were also prepared particularly for the ultraviolet spectroscopic studies. Thus, the reduction of (134) with lithium aluminium hydride following the standard procedure produced 6,9-dihydro-1,4--dimethoxy-5,9-methano-5H-benzocyclohepten-6-ol (135). The catalytic hydrogenation of ketone (134) in the presence of palladium-carbon at room temperature resulted in the formation of 5,7,8,9-tetrahydro-1,4--dimethoxy-5,9-methanobenzocyclohepten-6-one (136) which on further treatment with lithium aluminium hydride in the usual way formed 6,7,8,9-tetrahydro-1,4-dimethoxy-5,9-methano-5H-benzocyclohepten-6-ol (137). Finally, the reaction of the compound (134) with hydroxylamine in pyridine after the work-up gave 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-oxime (138). It is interesting that the yields of the products obtained in all these reactions were reasonably high (75-100%). The structures of the compounds [(135)-(138)] were established on the basis of their analytical and spectral data (experimental).



Scheme 32

The ultraviolet spectra of the compounds [(134)-(138)] are recorded in Table 4 and in Figures 1 and 2. The close similarity between the spectra of the compounds (134) and (138) (Figure 2) and flavothebaone trimethyl ether (108) and the corresponding oxime[71b] (Figure 3) reveals that the original aromatic ring of the alkaloid makes an insignificant contribution to the abnormal spectrum. The spectra of the saturated ketone (136), the unsaturated alcohol (135), and the saturated alcohol (137) (Figure 1) are very similar and are typical of simple 2,3--dialkylquinol dimethyl ethers.[72,79]

Table 4

U.v. spectra of compounds (134)-(138)

Compound	Solvent	λ max./nm (log ϵ)
134	Ethanol	380 (2.75), 360 (3.10), 350 (3.19), 340 (3.28), 330 (3.35), 320 (3.37), 310 (3.30), 300 (3.13), 290 (3.00), 280 (3.00), 270 (3.16), 260 (3.19), 250 (3.28), 240 (3.63), 230 (3.91), and 220 (4.11).
	cyclohexane	380 (2.29), 372 (2.51), 366 (2.47), 356 (2.69), 350 (2.63), 340 (2.98), 330 (3.29), 320 (3.43), 315 (3.45), 300 (3.26), 290 (2.98), 280 (2.69), 270 (2.84), 260 (2.96), 250 (3.01), 240 (3.37), and 230 (4.12).
135	cyclohexane	310 (2.39), 300 (3.45), 298 (3.50), 295 (3.51), 290 (3.52), 280 (3.29), 270 (2.90), 260 (2.48), 250 (2.48), 240 (3.33), 230 (3.88), and 220 (4.12).
136	cyclohexane	321 (2.50), 320 (2.50), 315 (2.62), 310 (3.04), 300 (3.53), 295 (3.54), 292 (3.56), 280 (3.29), 270 (2.86), 260 (2.42), 250 (2.62), 240 (3.40), 230 (3.91), and 220 (4.13).
137	Ethanol	305 (2.36), 300 (3.06), 295 (3.41), 293 (3.43), 290 (3.44), 286 (3.47), 280 (3.36), 270 (3.03), 260 (2.59), 250 (2.36), 240 (3.00), 230 (3.86), 224 (3.94), and 220 (3.97).
138	Ethanol	325 (3.18), 320 (3.37), 315 (3.48), 310 (3.56), 305 (3.58), 303 (3.60), 300 (3.58), 290 (3.50), 283 (3.43), 275 (3.52), 265 (3.68), 260 (3.79), 250 (3.92), 245 (3.95), 240 (3.94), 235 (3.95), 225 (4.07), and 215 (4.15).

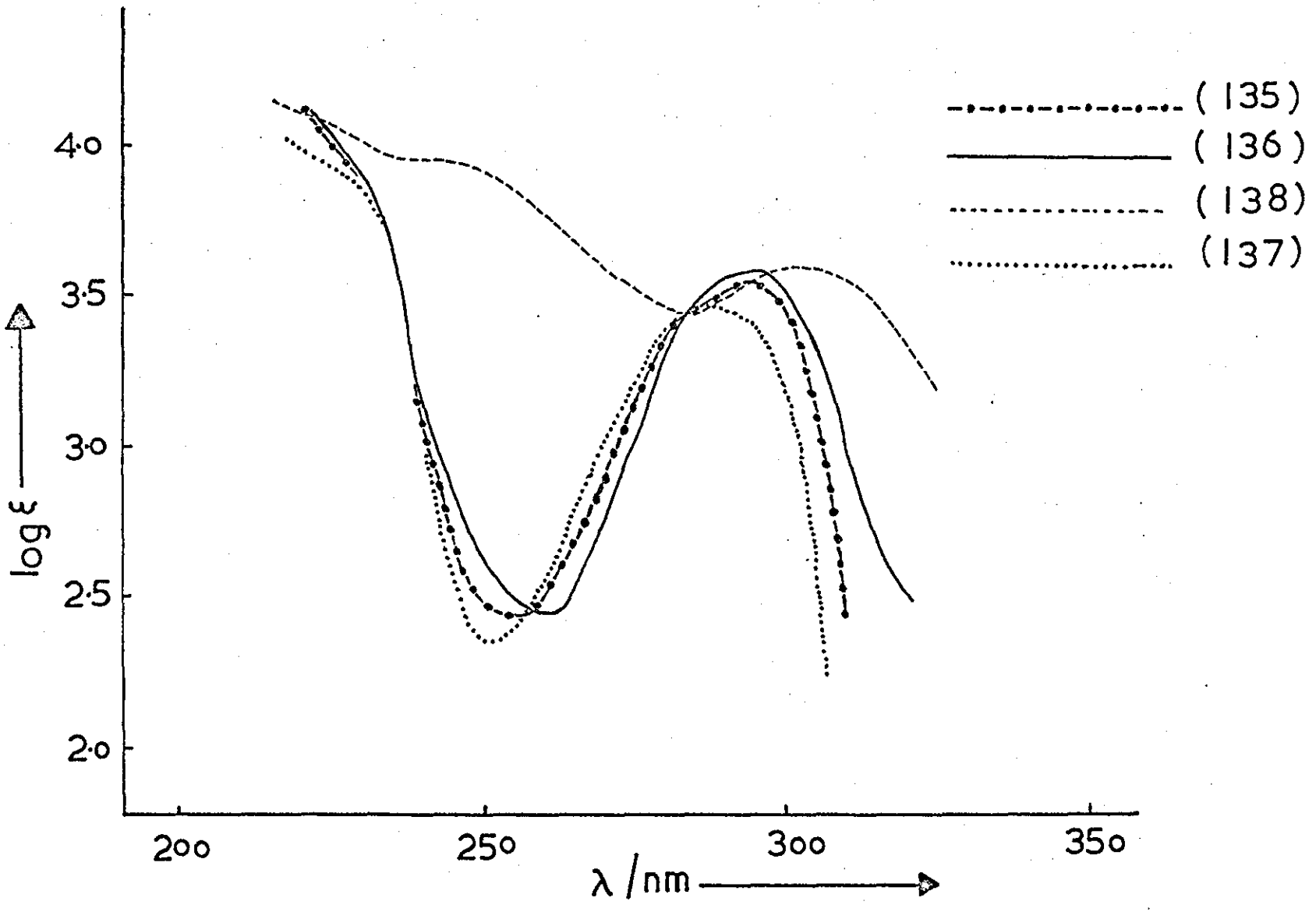


FIGURE I U.V. Spectra of compounds [(135)-(138)].

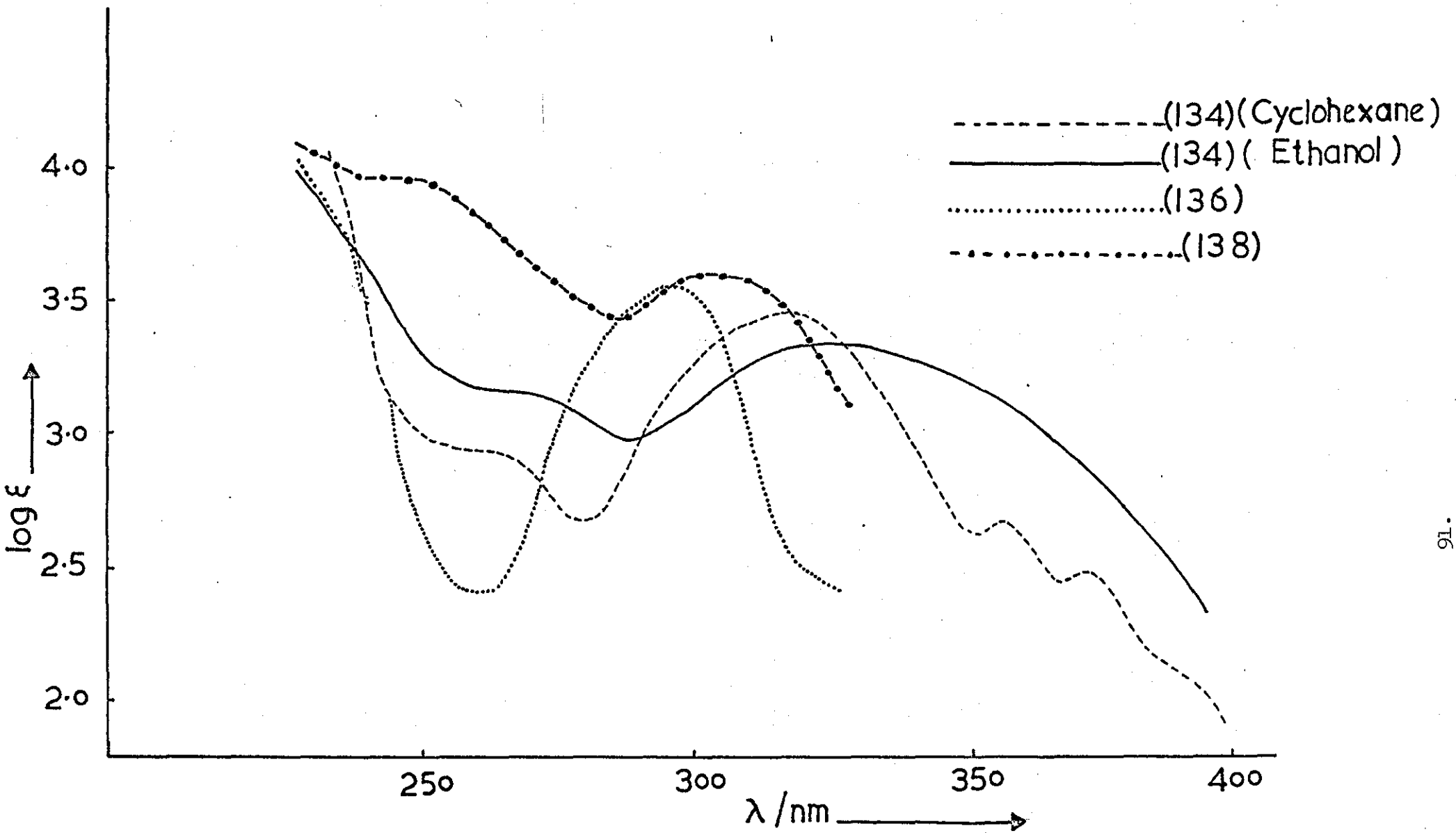


FIGURE 2 U.V. Spectra of compounds (134), (138) and (136) .

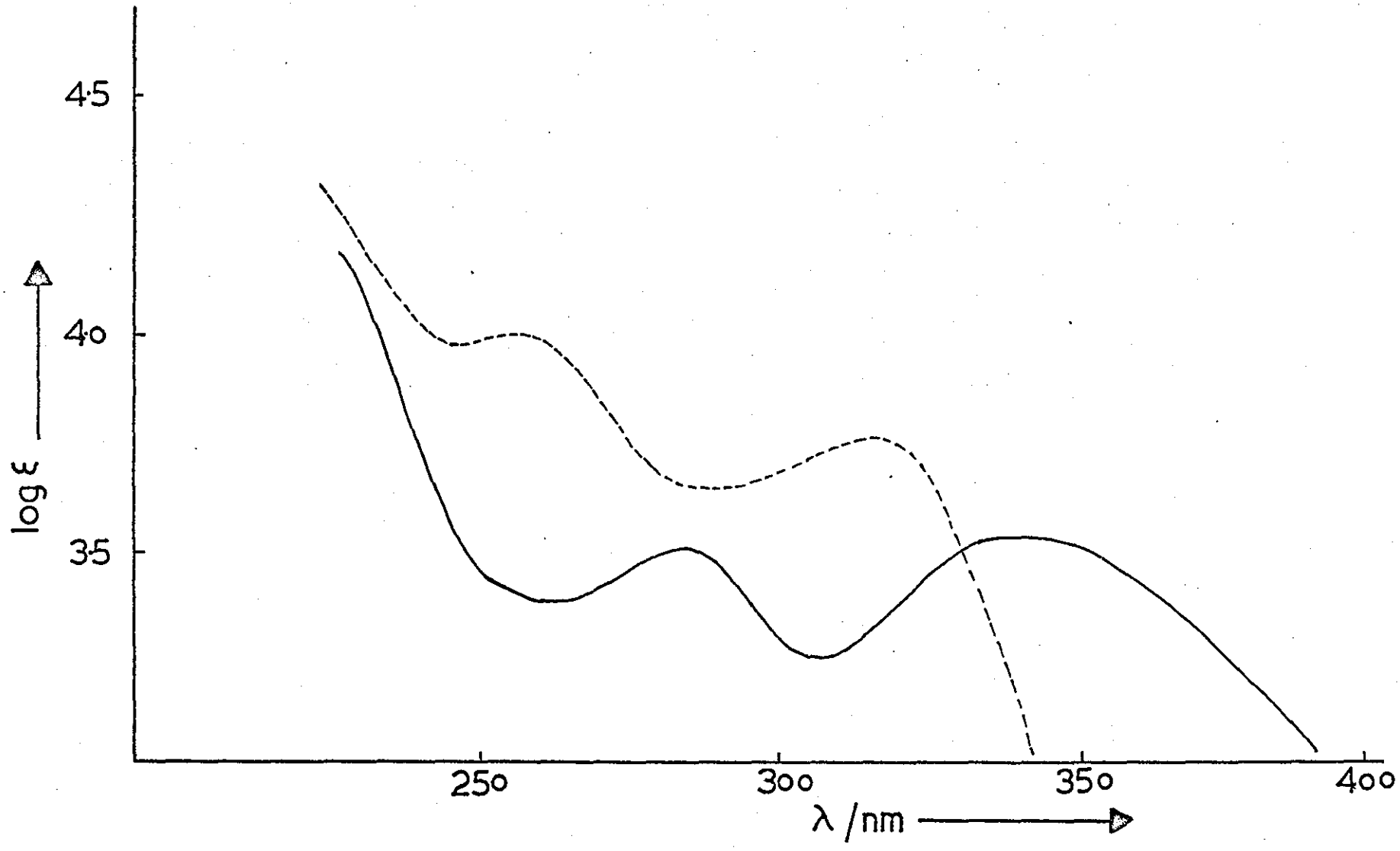


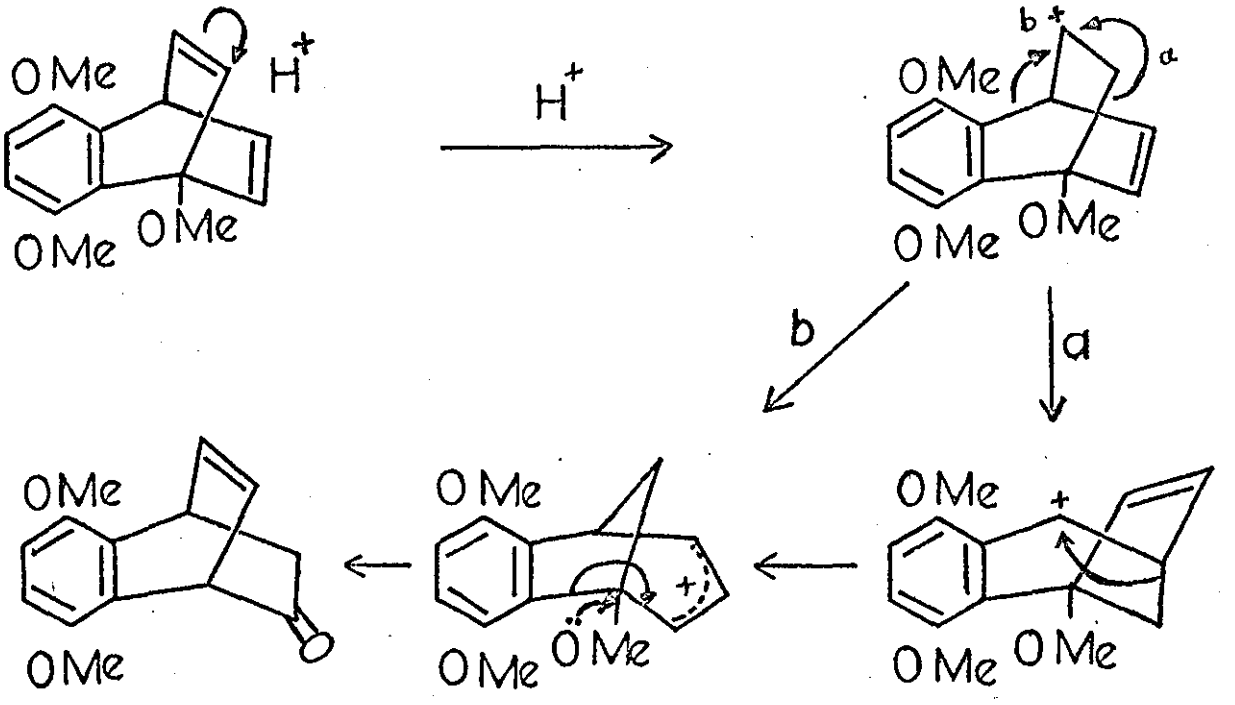
FIGURE 3 U.V. Spectra of Flavothebaone trimethyl ether (——) and Flavothebaone trimethyl ether oxime (--------).

The u.v. spectra of other analogues of the compound (134), for instance (15, X=F or H), show only very low intensity maxima in the region 225-250 nm (log ϵ ca. 2.3). The high extinction coefficient in the case of the compound (134), as compared with those observed for the compounds (15, X=F or H) is attributed to the presence of the methoxy-groups.

It therefore seems reasonable that the abnormal spectrum of flavothebaone trimethyl ether is, as originally predicted,[71a] due to the homoconjugation of the alkoxybenzene ring with the α,β-unsaturated ketone chromophore.

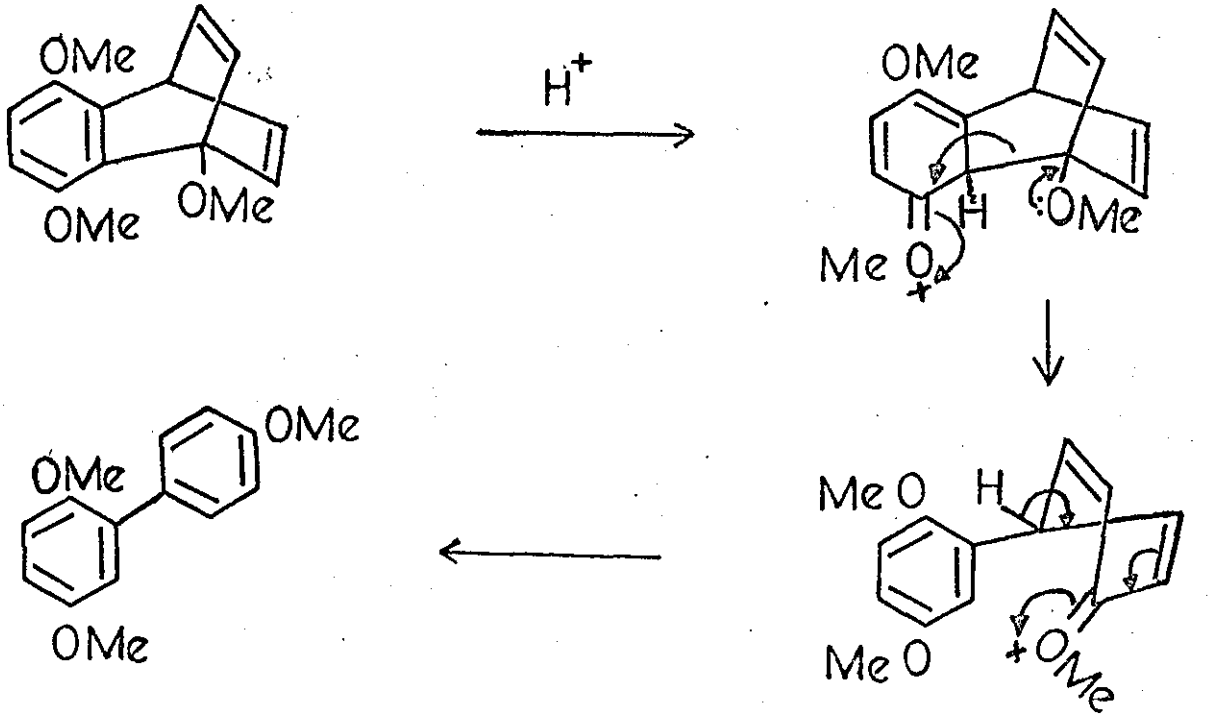
Interestingly, the compound (124) on treatment with perchloric acid (60%) for 1.5 hours at room temperature or when heated under reflux in trifluoroacetic acid for two hours afforded in each case a mixture of four products shown by analytical t.l.c. Preparative layer chromatography over silica-gel gave two of the four components, which by i.r., ^{1}H n.m.r., u.v. spectral data, mass spectrometry and by elemental analysis shown to be 2,4,5-trimethoxybiphenyl (139) in 21% yield and the ketone (125) in 42% yield. The remaining products in the mixture were not isolated in pure form. However, further work is in progress in these laboratories.

The formation of ketone (125) is illustrated in Scheme 33 as this type of mechanism has already been established in analogous systems.[27a] However, the rearrangement of the benzobarrelene (124) to the trimethoxybiphenyl (139) is quite unusual and has never been observed before. Presumably the high electron density in the aryl residue allows ready protonation. Addition of a proton at position-8a could afford a σ-complex (an arenonium ion) which could undergo a retro-Friedel-Crafts alkylation to give a new ion which, by loss of a proton, would result in the formation of 2,4',5-trimethoxybiphenyl (139), as shown in Scheme 34.



(125)

Scheme 33



(139)

Scheme 34

EXPERIMENTAL

All general procedures used were those as described in Chapter 1.

1. Preparation of methyl 2,5-dimethoxybenzoate

Dimethyl sulphate (375 ml.) and aqueous potassium hydroxide (375 ml., 50%) were added in small portions to a stirred solution of 2,5-dihydroxybenzoic acid (75 g.) in ethanol (150 ml.) and potassium hydroxide (75 ml., 50%). After the addition was complete the mixture was heated on a water-bath (ca. 80°C) for about 2 hours, cooled and a brown oil was separated from the aqueous layer. The aqueous phase was extracted with chloroform (2 x 100 ml.). The combined organic layer was washed successively with sodium hydroxide (2 x 50 ml., 2N) and water and dried (Na_2SO_4). The solvent was evaporated and distillation of the crude product under reduced pressure gave methyl 2,5-dimethoxybenzoate (114), (84.6 g., 88.5%), b.p. 90-95°C at 0.5 mm. Hg. (lit.[80] b.p. 95-98°C at 1 mm. Hg.).

$\nu_{max.}$ 3000, 2955, 2840, 1737, 1620, 1590, 1470, 1320, 1290, 1250, 1220, 1180, 812 and 735 $cm.^{-1}$

2. Preparation of 2,5-dimethoxybenzamide

Methyl 2,5-dimethoxybenzoate (84.6 g.) was stirred with ammonia solution (500 ml.) at room temperature for 72 hours. The white crystalline solid obtained was filtered, washed thoroughly with cold water. Recrystallisatic from hot water gave white needles of 2,5-dimethoxybenzamide (116), (78.5 g., 100%), m.p. 140-141°C (lit.[81] m.p. 140°C).

3. Preparation of 3,6-dimethoxy-2-nitrobenzamide

Concentrated nitric acid (800 ml.) was cooled in an ice-salt mixture and stirred whilst 2,5-dimethoxybenzamide (78.0 g.) was added to it in small portions. After the addition was complete the mixture was stirred for a further period of 1 hour at 0-5°C and then poured onto ice (1000 g.). The yellow crystalline solid was filtered, washed well with water and dried.

It was then treated with hot benzene (3 x 500 ml.) and filtered. The yellow crystalline solid thus obtained was recrystallised from acetone and afforded 3,6-dimethoxy-2-nitrobenzamide (117), (67.0 g., 68.7%), m.p. 231°C (lit.[74] m.p. 225-226°C).

$\nu_{max.}$ 3400, 3185, 2850, 1665, 1630, 1585, 1535, 1495, 1372, 1297, 1272, 1195, 1120, 1055, 935, 815, 800 and 720 $cm.^{-1}$

4. Preparation of 3,6-dimethoxy-2-nitrobenzoic acid

3,6-Dimethoxy-2-nitrobenzamide (25.0 g., 0.11 mole) was dissolved in sulphuric acid (750 g., 90%) and cooled in ice-salt mixture (ca. -5°C) and stirred. Sodium nitrite (8.0 g., 0.11 mole) in water (12 ml.) was slowly and carefully added below the surface of the acid and the mixture was stirred for a period of about 30 minutes. It was then allowed to come to room temperature and heated (ca. 60°C) on a water-bath until gas evolution ceased. The whole process was repeated twice (total sodium nitrite added 24.0 g.) and the cold mixture was then added to ice (ca. 2 kg.). The precipitate obtained was filtered, washed with water, dried and recrystallisation from aqueous ethanol gave 3,6-dimethoxy-2-nitrobenzoic acid (120), (22.0 g., 88%), m.p. 192-194°C.

$\nu_{max.}$ 3000 (br.), 2855, 1745, 1710, 1620, 1580, 1540, 1495, 1465, 1452, 1435, 1370, 1290, 1250 (br.), 1190, 1140, 1055, 935, 810, 800, 790, 760, 720 and 690 $cm.^{-1}$

Found: C, 47.7; H, 4.1; N, 6.4%.

$C_9H_9NO_6$ requires C, 47.6; H, 4.0; N, 6.2%.

5. Preparation of 2-amino-3,6-dimethoxybenzoic acid

3,6-Dimethoxy-2-nitrobenzoic acid (22.0 g., 0.1 mole) was dissolved in hot ethanol (300 ml.) and palladium-carbon (300 mg., 10%) was added. Hydrazine hydrate (31 ml.) was added to it during 30 minutes. After the addition was complete, more palladium-carbon (100 mg.) was added and the

mixture was heated under reflux for 3 hours, cooled and filtered. The filtrate was evaporated to a small volume and cooled and gave 2-amino--3,6-dimethoxybenzoic acid (16), (19.0 g., 100%), m.p. 96-97°C (from ethanol).

$\nu_{max.}$ 3480, 3365, 3100 (br.), 2940, 2850, 1700, 1625, 1600, 1550, 1480, 1365, 1270, 1222, 1160, 1115, 1055, 960, 800 and 720 $cm.^{-1}$

Found: C, 55.0; H, 5.7; N, 7.0%.

$C_9H_{11}NO_4$ requires C, 54.8; H, 5.6; N, 7.1%.

6. Preparation of 1,5,8-trimethoxy-1,4-etheno-2-tetralone

2-Amino-3,6-dimethoxybenzoic acid (5.4 g., 0.027 mole) was dissolved in tetrahydrofuran (30 ml.) and diethylether (30 ml.) and trichloroacetic acid (50 mg.) was added. Pentyl nitrite (7.5 ml.) was then added and the mixture was stirred at room temperature for 2 hours. The supernatant liquid was poured off and the dark red solid was washed with 1,2-dichloroethane (3 x 10 ml.), slurried in 1,2-dichloroethane (10 ml.) and was added to preheated veratrole (250 g.) at 60°C and kept at this temperature for three hours. Ether (300 ml.) was added to the cooled solution which was then washed with hydrochloric acid (150 ml., 2N), sodium hydroxide (4 x 100 ml., 2N) and water (2 x 100 ml.), dried, the solvent and the excess of veratrole were removed under reduced pressure to afford a dark oil. Preparative layer chromatography [14 x 1 m. x 20 cm., 0.75 mm. thickness; eluant ether-light petroleum (b.p. 40-60°C), 10:1] gave 1,5,8-trimethoxy-1,4-etheno-2-tetralone (122), (3.2 g., 47%), m.p. 64-66°C (from light petroleum).

^1H n.m.r. ($CDCl_3$) τ 3.25 (m., 4 protons), 5.35 (m., one proton), 6.2 (s., 3 protons), 6.22 (s., 3 protons), 6.25 (s., 3 protons), and 7.92 (ABq., $|J_{AB}|$ = 18 Hz., 2 protons).

$\nu_{max.}$ 3015, 2845, 1745, 1600, 1495, 1465, 1390, 1345, 1260, 1067, 1020, 975, 900, 840, 800, 755, 720 and 695 $cm.^{-1}$

λ_{max} (Ethanol) 305 (log ϵ 3.51), 297 (3.56), 296 (3.56) and 210 (4.28) nm.

Found: C, 69.7; H, 6.4%; M (mass spectrometry), 260. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.15%; M, 260.

High resolution mass spectrometry:

	Measured mass	Calculated mass	Formula
$M^{+\cdot}$	260.1045	260.1049	$C_{15}H_{16}O_4$
$M^{+\cdot}-42$	218.0938	218.0943	$C_{13}H_{14}O_3$

7. Reduction of 1,5,8-trimethoxy-1,4-etheno-2-tetralone (122)

The ketone (122) (0.5 g., 0.002 mole) in ether (10 ml.) was added to a suspension of lithium aluminium hydride (250 mg.) in ether (15 ml.) and the mixture was stirred at room temperature for 20 minutes. Sulphuric acid (25 ml., 2N) was then added slowly and the ether layer was separated and washed with water (2 x 10 ml.). The aqueous acid layer was extracted with chloroform (2 x 10 ml.) and the combined organic layers were dried and evaporated to afford an epimeric mixture of alcohols (129), (472 mg., 94%).

A portion of the mixture (100 mg.) was separated by preparative layer chromatography (1 x 1 m. x 20 cm. x 0.75 mm. thickness) by elution (x 6) with benzene:chloroform (1:4) and gave an upper band of 1,2,3,4--tetrahydro-1,5,8-trimethoxy-1,4-ethanonaphthalen-2-exo-ol (130), (31 mg.), m.p. 191-192°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.25-3.45 (m., 4 protons), 5.6-5.8 (m., one proton), 6.06 (d.x d., one proton, $|J|$ = ca. 12 and 3 Hz.), 6.18 (s., 3 protons), 6.24 (s., 3 protons), 6.25 (s., 3 protons), 7.3 (m., one proton, exchangeable), 8.1 (m., one proton) and 8.7 (d. x t., one proton, $|J|$ = ca. 12 and 3 Hz.).

$\nu_{max.}$ 3520, 3060, 2990, 2970, 2940, 2905, 2840, 1625, 1592, 1495,

1465, 1360, 1262, 1200, 1100, 1080, 1015, 957, 860, 800, 720 and 710 cm.$^{-1}$

$\lambda_{max.}$ (EtOH) 300 (logϵ 3.44), 290 (3.54), 225 (3.89) and 207 (4.15)nm.

Found: C, 68.8; H, 7.0%; M (mass spectrometry), 262. $C_{15}H_{18}O_4$ requires C, 68.7; H, 6.9%; M, 262.

A lower band contained 1,2,3,4-tetrahydro-1,5,8-trimethoxy-1,4--ethenonaphthalen-2-endo-ol (131), (44 mg.), m.p. 186°C (from methanol). ^{1}H n.m.r. ($CDCl_3$) τ 3.28 (s., 2 protons), 3.44 (m., 2 protons), 5.68 (m., one proton), 5.95 (d.x d., one proton, $|J|$ = ca. 12 and 3 Hz.), 6.18 (s., 3 protons), 6.22 (s., 3 protons), 6.30 (s., 3 protons), 7.72 (m., one proton, exchangeable), 7.9 (octet, 1 proton) and 8.96 (d. x t., one proton $|J|$ = ca. 12 and 3 Hz.).

$\nu_{max.}$ 3520, 3060, 2942, 2890, 2840, 1625, 1592, 1495, 1460, 1440, 1350, 1315, 1260, 1190, 1080, 1060, 990, 805, 715, 700 cm.$^{-1}$

$\lambda_{max.}$ (EtOH) 300 (logϵ 3.36), 290 (3.52), 225 (3.94) and 209 (4.13) nm.

Found: C, 68.8; H, 6.9%; M (mass spectrometry), 262.

8. Rearrangement of an epimeric mixture of the alcohols (130) and (131)

A mixture of alcohols (129), (0.3 g., 0.0011 mole) was dissolved in a mixture of trifluoroacetic acid (2 ml.) and sulphuric acid (2 ml.) and stirred at room temperature for 30 minutes. The mixture was then added to ice (25 g.) and the products were extracted with ether (5 x 10 ml.). The ether extract was washed with sodium hydrogen carbonate and water and dried. The solvent evaporation afforded an oil (269 mg.), which was separated by preparative layer chromatography [eluant ether-light petroleum (b.p. 40-60°C), 4:1] and gave an upper band of 5,8-dimethoxy--2,4-etheno-1-tetralone (133), (130 mg., 50%), m.p. 83-84°C (from ether).

^{1}H n.m.r. ($CDCl_3$) τ 3.15 (q., 2 protons, $|J|$ = 9.5 Hz.), 3.64 (octet, 2 protons, $\Delta\delta$ = 48 Hz.), 5.78 (m., one proton, 6.18 (s., 3 protons), 6.21 (s., 3 protons), 6.62 (m., one proton) and 7.48 (m., 2 protons).

$\nu_{max.}$ 2970, 2945, 2845, 1695, 1585, 1485, 1440, 1265, 1235, 1198, 1143, 1105, 1087, 1045, 1010, 985, 965, 945, 900, 890, 817, 770, 730 and 722 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 350 (logϵ 3.56), 340 (3.62), 263 (3.35) and 216 (4.27) nm.

Found: C, 73.1; H, 6.4%; M (mass spectrometry), 230. $C_{14}H_{14}O_3$ requires C, 73.05; H, 6.1%; M, 230.

The lower band contained 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (134), (74 mg., 28%), m.p. 140-141°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 2.54 (q., one proton, $|J|$ = ca. 10 and 6 Hz.), 3.38 (s., 2 protons), 4.55 (q., one proton, $|J|$ = ca. 10 and 2 Hz.), 5.94 (m., one proton), 6.15 (m., one proton), 6.22 (s., 6 protons) and 7.32 (m., 2 protons).

$\nu_{max.}$ 3000, 2965, 2945, 2845, 1680, 1615, 1495, 1470, 1442, 1380, 1330, 1305, 1288, 1260, 1235, 1200, 1160, 1100, 1080, 1062, 970, 920, 830, 800, 750 and 708 cm.$^{-1}$

$\lambda_{max.}$ (EtOH) 380 (logϵ 2.75), 360 (3.10), 350 (3.19), 340 (3.28), 330 (3.35), 320 (3.37), 310 (3.30), 300 (3.13), 290 (3.00), 280 (3.00), 270 (3.16), 260 (3.19), 250 (3.28), 240 (3.63), 230 (3.91) and 220 (4.11) nm.

(cyclohexane) 380 (logϵ 2.29), 372 (2.51), 366 (2.47), 356 (2.69), 350 (2.63), 340 (2.98), 330 (3.29), 320 (3.43), 315 (3.45), 300 (3.26), 290 (2.98), 280 (2.69), 270 (2.84), 260 (2.96), 250 (3.01), 240 (3.37) and 230 (4.12) nm.

Found: C, 73.2; H, 6.2%; M (mass spectrometry), 230.

A sample (5 mg.) of the endo-alcohol (131) was shown to give only the tetralone (133) on rearrangement; similarly the exo-alcohol gave only the αβ-unsaturated ketone (134).

9. Reduction of 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten--6-one (134) with lithium aluminium hydride.

The ketone (134), (50 mg.) in ether (10 ml.) was added to a suspension of lithium aluminium hydride (30 mg.) in ether (10 ml.) and the mixture was stirred at room temperature for 20 minutes. Sulphuric acid (6 ml., 2N) was then slowly added and the ether layer was separated. The usual work-up gave 6,9-dihydro-1,4-dimethoxy-5,9-methano-5H-benzocyclohepten-6-ol (135), (42 mg., 84%), m.p. 103-104°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 3.36 (m., 2 protons), 3.70 (m., one proton), 4.78 (d. x t., one proton, $|J|$ = ca. 10 and 2 Hz.), 5.45 (m., one proton), 6.15 (m., one proton), 6.22 (s., 3 protons), 6.24 (s., 3 protons), 6.58 (m., one proton), 7.75 (m., 2 protons) and 8.20 (m., one proton exchangeable).

$\nu_{max.}$ 3460, 2945, 2840, 1608, 1498, 1470, 1440, 1255, 1205, 1165, 1090, 1067, 1005, 965, 927, 792, 738, and 710 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 310 (logϵ 2.39), 300 (3.45), 298 (3.50), 295 (3.51), 290 (3.52), 280 (3.29), 270 (2.90), 260 (2.48), 250 (2.48), 240 (3.33), 230 (3.88) and 220 (4.12) nm.

Found: C, 72.6; H, 7.1%; M (mass spectrometry), 232. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%; M, 232.

10. Catalytic hydrogenation of 5,9-dihydro-1,4-dimethoxy-5,9-methano-benzocyclohepten-6-one (134).

The compound (134), (94 mg.) in ethanol (50 ml.) was hydrogenated at atmospheric pressure over prereduced palladium-carbon (10 mg., 5%)

at room temperature. The normal work-up gave 5,7,8,9-tetrahydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (136), (95 mg., 100%), m.p. 103-103.5°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.32 (q., 2 protons, $|J|$ = ca. 9 Hz.), 6.16 (m., one proton), 6.20 (s., 3 protons), 6.26 (s., 3 protons), 6.45 (m., one proton), 7.40 (m., one proton), and 7.90 (m., 5 protons).

$\nu_{max.}$ 2945, 2870, 2840, 1720, 1500, 1465, 1440, 1300, 1260, 1218, 1180, 1085, 1060, 990, 962, 797 and 710 cm.$^{-1}$

$\lambda_{max.}$ (cyclohexane) 321 (logϵ 2.50), 320 (2.50), 315 (2.62), 310 (3.04), 300 (3.53), 295 (3.54), 292 (3.56), 280 (3.29), 270 (2.86), 260 (2.42), 250 (2.62), 240 (3.40), 230 (3.91), 220 (4.13) nm.

Found: C, 72.6; H, 7.1%; M (mass spectrometry), 232. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%; M, 232.

11. Reduction of 5,7,8,9-tetrahydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (136) with lithium aluminium hydride.

The compound (136), (75 mg.) in ether (15 ml.) was stirred with a suspension of lithium aluminium hydride (40 mg.) in ether (15 ml.) at room temperature for 30 minutes. Sulphuric acid (10 ml., 2N) was then added and the work-up in the usual manner afforded 6,7,8,9-tetrahydro-1,4-dimethoxy-5,9-methano-5H-benzocyclohepten-6-ol (137), (74 mg., 99%), m.p. 87-88°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 3.34 (m., 2 protons), 6.22 (s., 3 protons), 6.23 (s., 3 protons), 6.55 (m., one proton), 6.70 (m., one proton), 7.80 (m., one proton), 8.24 (m., one proton, exchangeable) and 8.45 (m., 6 protons).

$\nu_{max.}$ 3460, 3005, 2950, 2870, 2840, 1610, 1595, 1500, 1465, 1440, 1255, 1180, 1090, 1065, 1025, 970, 790 and 710 cm.$^{-1}$

$\lambda_{max.}$ (EtOH) 305 (logϵ 2.36), 300 (3.06), 295 (3.41), 293 (3.43),

290 (3.44), 286 (3.47), 280 (3.36), 270 (3.03), 260 (2.59), 250 (2.36), 240 (3.00), 230 (3.86), 224 (3.94) and 220 (3.97) nm.

Found: C, 72.4; H, 7.9%; M (high resolution mass spectrometry), 234.1256. $C_{14}H_{18}O_3$ requires C, 71.8; H, 7.7%; M, 234.1256.

12. Reaction of 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-one (134) with hydroxylamine.

The compound (134), (100 mg.) was taken in pyridine (10 ml.) and hydroxyammonium chloride (97 mg.) was added. The mixture was then heated (ca. 60-70°C) on a water bath for about an hour and kept overnight at room temperature. Water (50 ml.) was added and it was extracted with ether (2 x 25 ml.), washed well with water and dried. The solvent was removed under reduced pressure and gave 5,9-dihydro-1,4-dimethoxy-5,9-methanobenzocyclohepten-6-oxime (138), (80 mg., 75%), m.p. 188-190°C (from light petroleum).

^{1}H n.m.r. ($CDCl_3$) τ 3.36 (m., 2 protons), 3.45 (m., one proton), 4.28 (m., one proton), 5.00 (m., one proton), 5.90 (m., one proton), 6.20 (s., 3 protons), 6.22 (s., 3 protons), 6.30 (m., one proton), and 7.65 (m., 2 protons).

$\nu_{max.}$ 3220, 2940, 2840, 1595, 1485, 1495, 1440, 1255, 1080, 1060, 1030, 972, 950, 790, 745 and 700 cm.$^{-1}$

$\lambda_{max.}$ (EtOH) 325 (log ϵ 3.18), 320 (3.37), 315 (3.48), 310 (3.56), 305 (3.58), 303 (3.60), 300 (3.58), 290 (3.50), 283 (3.43), 275 (3.52), 265 (3.68), 260 (3.79), 250 (3.93), 245 (3.95), 240 (3.94), 235 (3.95), 225 (4.07) and 215 (4.15) nm.

Found: C, 68.8; H, 6.4; N, 5.7%; M (mass spectrometry), 245. $C_{14}H_{15}NO_3$ requires C, 68.6; H, 6.1; N, 5.7%; M, 245.

13. Preparation of 1,5,8-trimethoxy-1,4-etheno-3-tetralone.

The reaction was carried out exactly in a fashion described under the experiment number 6. The dark red solid [from 2-amino-3,6-dimethoxybenzoic acid (5.4 g., 0.027 mole)] was added to preheated m-dimethoxybenzene (200 g.) at 60°C and kept at this temperature for 3 hours. The standard work-up and column chromatography over silica-gel using ether: light petroleum (1:1) as eluant, gave 1,5,8-trimethoxy-1,4-etheno-3-tetralone (123), (2.65 g., 39%), m.p. 93°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.3 (m., 4 protons), 5.12 (d. x d., one proton, $|J|$ = 6 and 2 Hz.), 6.17 (s., 3 protons), 6.22 (s., 3 protons), 6.31 (s., 3 protons) and 7.61 (s., 2 protons).

$\nu_{max.}$ 2930, 2830, 1730, 1620, 1590, 1490, 1460, 1437, 1408, 1340, 1322, 1310, 1260 (br.), 1175, 1067, 1040, 1018, 955, 842, 790, 760, 715 and 685 cm.$^{-1}$

Found: C, 69.2; H, 6.1%; H (mass spectrometry), 260. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.2%; M, 260.

14. Reduction of 1,5,8-trimethoxy-1,4-etheno-3-tetralone (123).

The compound (123), (2.08 g., 0.008 mole) in ether (50 ml.) was added to a suspension of lithium aluminium hydride (1.0 g.) in ether (60 ml.) and the mixture was stirred at room temperature for 30 minutes. Sulphuric acid (80 ml., 2N) was slowly added and the work-up in the usual way afforded an epimeric mixture of alcohols (132), (1.76 g., 84%), m.p. 100-111°C (from methanol).

$\nu_{max.}$ 3410, 3065, 3000, 2940, 2880, 2840, 1625, 1597, 1495, 1465, 1447, 1350, 1325, 1290, 1260, 1160, 1100, 1080, 1055, 1020, 980, 960, 800, 790, 730, 718 and 700 cm.$^{-1}$

M.W. M (mass spectrometry), 262.

15. Reaction of 3,6-dimethoxybenzyne with anisole.

2-Amino-3,6-dimethoxybenzoic acid (8.1 g., 0.04 mole) was dissolved in tetrahydrofuran (40 ml.) and ether (40 ml.) and trichloroacetic acid (80 mg.) was added. Pentyl nitrite (10 ml.) was added and the mixture was stirred at room temperature for two hours. The dark red solid so obtained was filtered carefully, washed with ether (10 ml.) and was taken in 1,2-dichloroethane (50 ml.) and then added to preheated anisole (250 g.) at 60°C. It was maintained at this temperature for a further period of four hours. The solvents and the excess of anisole were removed under reduced pressure. The dark brown oil obtained was placed on a column of neutral alumina and elution with ether-light petroleum (1:2) afforded 1,4-dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene (124), (1.7 g., 17%), m.p. 78-79°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.1 (m., 4 protons), 3.49 (s., 2 protons), 4.72 (t.x t., one proton, $|J|$ = 5.8 and 1.8 Hz.), 6.18 (s., 3 protons), 6.2 (s., 3 protons) and 6.24 (s., 3 protons).

$\nu_{max.}$ 3085, 3000, 3965, 2940, 2915, 2840, 1640, 1590, 1500, 1460, 1445, 1345, 1315, 1260, 1240, 1195, 1180, 1150, 1108, 1080, 1065, 1042, 1025, 985, 955, 848, 808, 798, 722, 710 and 678 cm.$^{-1}$

Found: C, 74.0; H, 6.6%; M (mass spectrometry), 244. $C_{15}H_{16}O_3$ requires C, 73.8; H, 6.6%; M, 244.

Elution with ether-light petroleum (5:1) gave 5,8-dimethoxy-1,4-etheno-2-tetralone (125), (0.46 g., 5%), m.p. 104-106°C (from methanol).

^{1}H n.m.r. ($CDCl_3$) τ 3.2 (m., 4 protons), 5.13 (d. x d., one proton, $|J|$ = 6 and 2 Hz.), 5.35 (m., one proton), 6.18 (s., 3 protons), 6.22 (s., 3 protons) and 7.96 (ABq., 2 protons, $|J_{AB}|$ = 17 Hz.).

$\nu_{max.}$ 3080, 3010, 2950, 2840, 1740, 1600, 1500, 1470, 1445, 1337, 1292, 1260, 1150, 1130, 1090, 1010, 970, 770, 715 and 690 $cm.^{-1}$

M.W. M, 230 (mass spectrometry).

m/e, 230, 188, 173, 145

Caution: Dry 3,6-dimethoxybenzenediazonium-2-carboxylate could be explosive. Therefore, suitable precautions should be taken during its filtration and handling.

16. Reaction of 1,4-dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene (124) with acids.

(a) Perchloric acid.

The compound (124), (0.6 g.) was stirred with perchloric acid (50 ml., 60%) at room temperature for 1.5 hours. The mixture was then added to ice (200 g.), extracted with chloroform (3 x 50 ml.), washed with water and dried. The solvent removal gave an oil (0.62 g.), which was shown to be a mixture of four compounds by thin layer chromatography. Preparative layer chromatography [4 x 1 m. x 20 cm.; 0.75 mm. thickness; eluant ether-light petroleum (1:1)] afforded a fast running top band of 2,4',5-trimethoxybiphenyl (139), (127 mg., 21%), m.p. 49-50°C (from light petroleum).

^1H n.m.r. ($CDCl_3$) 2.50 (AA' of AA'BB', J_{AB} = 9 Hz, 2 protons) 2.95 - 3.20 (m., 5 protons), 6.18 (s., 3 protons), 6.23 (s., 3 protons) and 6.28 (s., 3 protons).

$\nu_{max.}$ 3000, 2945, 2915, 2840, 1618, 1595, 1580, 1520, 1500, 1465, 1445, 1405, 1300, 1265, 1250, 1220, 1180, 1055, 1027, 882, 835, 798, 745, 720, 692 and 682 $cm.^{-1}$

$\lambda_{max.}$ (cyclohexane) 325 ($\log\epsilon$ 3.11), 3.10 (3.77), 302 (3.83), 290 (3.72), 255 (4.11), 222 (4.22) and 211 (4.33) nm.

Found: C, 73.9; H, 6.7%; M (mass spectrometry), 244.

$C_{15}H_{16}O_3$ requires C, 73.8; H, 6.6%; M, 244.

A lower band contained 5,8-dimethoxy-1,4-etheno-2-tetralone (125), (225 mg., 42%), m.p., mixed m.p., i.r., and ^{1}H n.m.r. spectra identical to that of an authentic sample (isolated in experiment No. 15).

Two other compounds in the mixture were not investigated further.

(b) Perchloric acid using dioxane as solvent.

The compound (124), (45 mg.) was dissolved in dioxane (5 ml.) and perchloric acid (5 ml., 60%) was added. The reaction was carried out exactly in a manner as described under (a) and the usual work-up procedure gave only an unchanged starting material (40 mg.) shown by t.l.c., m.p., i.r. and ^{1}H n.m.r. spectra.

(c) Trifluoroacetic acid at room temperature.

The compound (124), (70 mg.) in trifluoroacetic acid (5 ml.) was stirred for 4.5 hours and the usual work-up afforded only an unchanged starting material, m.p., t.l.c. and i.r. spectra identical.

(d) Trifluoroacetic acid.

The compound (124), (160 mg.) in trifluoroacetic acid (5 ml.) was heated under reflux for 2 hours and the standard work-up procedure gave an oil (151 mg.) which by comparison t.l.c. and i.r. spectroscopy was shown to be identical with the mixture obtained in experiment (a).

17. Attempted tosylation of an epimeric mixture of the alcohols (130) and (131).

A mixture of the alcohols (130) and (131), (0.12 g.) in dry pyridine (4 ml.) was cooled to ca. -5°C and tosyl chloride (95 mg.) in pyridine (2 ml.) was added slowly maintaining the same temperature. The mixture was then stirred at room temperature for 6 days and the standard work-up gave an unchanged starting material (129), (95 mg.), m.p., comparison thin layer chromatography and i.r. spectra identical.

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