Pericyclic reactions of some highly fluorinated cyclohexa-1,3-dienes and derived compounds

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PERICYCLIC REACTIONS OF SOME HIGHLY FLUORINATED CYCLOHEXA-1,3-DIENES AND DERIVED COMPOUNDS

by

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to the University of Durham

1971

To Mary

SUMMARY

Pericyclic reactions of some polyfluorocyclohexa-1,3-dienes and derived compounds

This work describes a study of the preparation and reactions of polyfluorocyclohexa-1,3-dienes and some derived bicyclic compounds.

Perfluorocyclohexa-1,3-diene reacts as an electron-poor diene, giving good yields of Diels-Alder adducts with ethylene and allene. 2H,3H-hexafluorocyclohexa-1,3-diene gives 1:1 adducts when heated at 200° together with ethylene, allene and various substituted alkynes. However, with less reactive alkynes, adducts consisting of two molecules of diene to one of alkyne were also formed, since the 1:1 adducts contain a dienophilic -CH=CH- bond. The unsymmetrical diene 1H,2H-hexafluorocyclohexa-1,3-diene was found to give a Diels-Alder dimer slowly at room temperature but gave adducts with perfluorobut-2-yne and with 3,3,3-trifluoropropyne at 200° together with dimer. With the latter unsymmetrical acetylene only one of the two possible Diels-Alder adducts was formed and its structure was confirmed by pyrolysis to give tetrafluoroethylene and a single aromatic, whose structure was proved by alternative synthesis. 2,3-Dimethylhexafluorocyclohexa-1,3-diene gave a Diels-Alder adduct with ethylene at 200° but at this temperature 2,3-dimethoxyhexafluorocyclohexa-1,3-diene decomposed and none of the expected adduct was formed.

Photolysis of some 2,3-disubstituted-hexafluorocyclohexa-1,3-dienes (substituents X,Y: F, F; H, H; F, OMe; OMe, OMe) caused them to be cleanly isomerised to 2,3-disubstituted-hexafluorobicyclo[2,2,0]hex-2-enes. The reverse thermal reaction occurred between 300-400°.

Nucleophilic substitution reactions of Diels-Alder adducts of perfluorocyclohexa-1,3-diene with ethylene and alkynes and of perfluorobicyclo[2,2,0]-hex-2-ene were studied and vacuum pyrolysis of the products provided new routes to polyfluorocyclohexa-1,3-dienes and aromatics, some of which themselves were new.

Finally, the dienophilicity of 2,3-disubstituted-hexafluorobicyclo[2,2,0]-hex-2-enes towards electron-rich dienes was investigated.

ACKNOWLEDGEMENTS

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Assistance from members of the technical and laboratory staff is greatly appreciated and thanks are due to Mr. J. Yeadon and Mr. W.E. Preston for their help in checking the typescript.

The author gratefully acknowledges the award of a maintainance grant by the Science Research Council.

MEMORANDUM

The work in this thesis was carried out in the Chemistry Laboratories of The University of Durham between September 1968 and July 1971. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of the following publications.

1. Photochemical Isomerisation of Octafluorocyclohexa-1,3-diene by W.J. Feast, W.K.R. Musgrave and R.G. Weston, Chem. Comm., 1970, 1337.

2. Diels-Alder Reactions of Polyfluorocyclohexa-1,3-dienes. Part III, Addition of Alkynes, Ethylene and Allene to 2H,3H-Hexafluorocyclohexa-1,3-diene and Reaction of some Diels-Alder Adducts of Octafluorocyclohexa-1,3-diene with Lithium Aluminium Hydride, by W.J. Feast, W.K.R. Musgrave and R.G. Weston, J. Chem. Soc.(C), 1971, 937.

3. Diels-Alder Reactions of Polyfluorocyclohexa-1,3-dienes. Part IV, Addition of Alkynes to 1H,2H-hexafluorocyclohexa-1,3-diene, by W.J. Feast, W.K.R. Musgrave and R.G. Weston, J. Chem. Soc.(C), 1971, 1547.

4. Polyfluorobicyclo[2,2,0]hex-2-enes as Dienophiles; the Effect of Substituents on the Double Bond, by W.J. Feast, W.K.R. Musgrave and R.G. Weston, Chem. Comm., 1971, 709.

NOTE TO READER

Throughout this thesis compounds actually employed or made in the course of the work are designated by large Roman numerals, (I) to (L), whilst other compounds or hypothetical structures are designated by small arabic numerals, (1) to (343). In the back endpaper there is a Summary Reaction Scheme by means of which all the compounds, (I) to (L) may be correlated. The synthesis (and hence reactions) of any of these compounds may be located using APPENDIX D, which also includes an index to the n.m.r. and mass spectra.

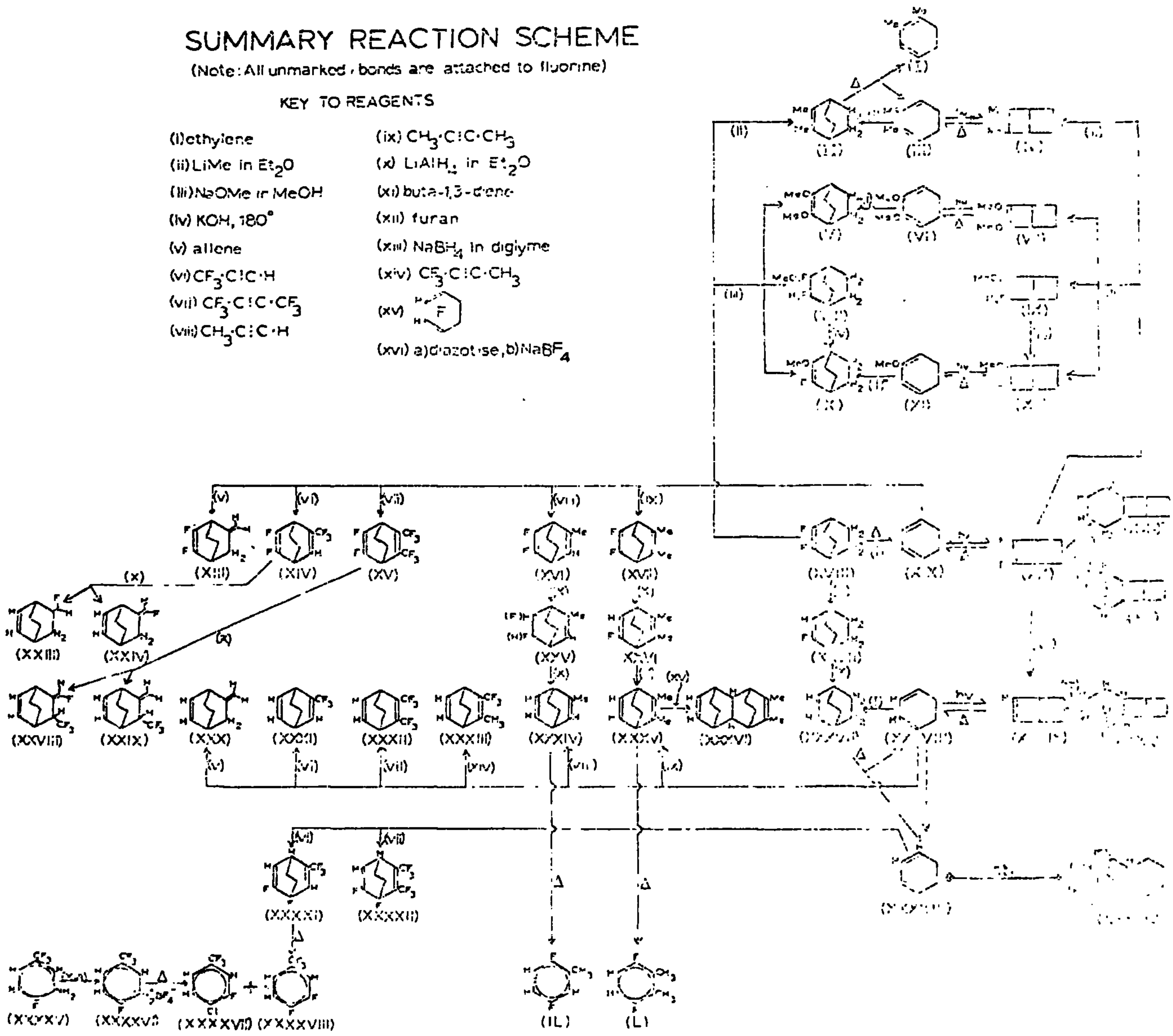
A letter F placed in the centre of a ring is used to denote that all unmarked bonds of the carbon atoms of that ring are attached to fluorine.

SUMMARY REACTION SCHEME

(Note: All unmarked bonds are attached to fluorine)

KEY TO REAGENTS

(i) ethylene
(ii) LiMe in Et_2O
(iii) NaOMe in MeOH
(iv) KOH, 180°
(v) allene
(vi) $CF_3{\cdot}C{:}C{\cdot}H$
(vii) $CF_3{\cdot}C{:}C{\cdot}CF_3$
(viii) $CH_3{\cdot}C{:}C{\cdot}H$
(ix) $CH_3{\cdot}C{:}C{\cdot}CH_3$
(x) $LiAlH_4$ in Et_2O
(xi) buta-1,3-diene
(xii) furan
(xiii) $NaBH_4$ in diglyme
(xiv) $CF_3{\cdot}C{:}C{\cdot}CH_3$
(xv)
(xvi) a) diazotise, b) $NaBF_4$



CONTENTS

CHAPTER 1

ROUTES TO POLYFLUOROCYCLOHEXA-1,3-DIENES

INTRODUCTION

1.1 Review of Synthetic Methods

The reported routes to polyfluorocyclohexa-1,3-dienes have all started from benzene as the basic raw material. Vapour phase fluorination of benzene over cobalt trifluoride gives a complex mixture of polyfluorocyclohexanes.[1] From this mixture have been obtained, by distillation and gas chromatography, perfluorocyclohexane m.p. 52° (sublimes); undecafluorocyclohexane[1,2] (b.p. 63°); six decafluorocyclohexanes,[1,3] (1)-(6) (Table 1.1); four nonafluorocyclohexanes,[4,5] (7)-(10) (Table 1.1); several octafluorocyclohexanes;[6] and traces of unsaturated products.[5]

1.1a. Dehydrofluorination of polyfluorocyclohexanes

Table 1.1 shows the products of dehydrofluorination of the decafluoro- and nonafluoro-cyclohexanes, using aqueous potassium hydroxide.[1,3,4,5] The general factors which appear to determine the products, rates and stereochemistry of the dehydrofluorination reactions of the polyfluorocyclohexanes seem to be[1]:

(i) The acidity of the hydrogens. This property appears to be greater for a -CHF- group flanked by two $-CF_2-$ groups than by one $-CF_2-$ group and, for example, one -CFH- group, and ease of dehydrofluorination appears to parallel acidity.

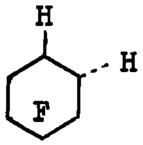
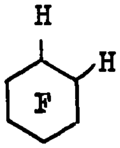
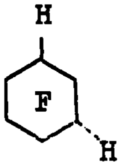
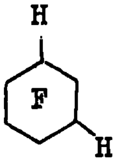
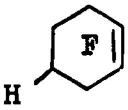
(ii) Dehydrofluorination via a trans-coplanar E_2 process occurs where this is possible; thus cyclohexanes which can easily assume a conformation having H and F trans-diaxial will be readily dehydrofluorinated compared with electronically equivalent cases where this is not possible.

(iii) In the elimination process, loss of a fluoride ion from $-CF_2-$ appears to be more difficult than from -CFH-, reflecting the increased stability of fluorine in $-CF_2-$ over that in -CFH-.

(iv) Cis-eliminations do proceed and may be faster than possible trans-eliminations in electronically favourable cases, that is where the proton of

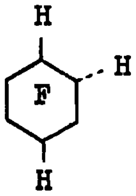
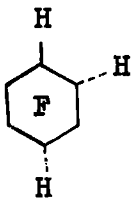
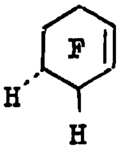
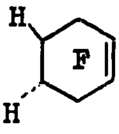
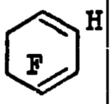
TABLE 1.1

Decafluoro- and Nonafluorocyclohexanes obtained from the Cobalt Trifluoride fluorination of Benzene and their Dehydrofluorination Products

Compound	Dehydrofluorination Products		Ref.
	Monoenes, 1,4-Dienes etc.	1,3-Dienes	
Decafluoro-Cyclohexanes  (1) b.p.70°	 (11)	+  (12)	1
 (2) b.p. 91°	(11)	-	1
 (3) b.p. 78°  (4) b.p. 89°	 +  +  (13) (14) (15)	+ (12)	3

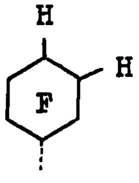
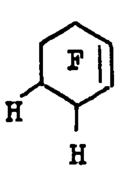
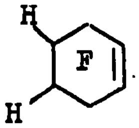
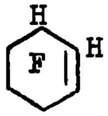
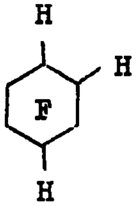
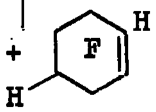
contd./

Table 1.1 contd.

Compound	Dehydrofluorination Products		Ref.
	Monoenes, 1,4-Dienes etc.	1,3-Dienes	
 (5) b.p. 78°  (6) b.p. 86°	(14) + (15)	+ (12)	3
Nonafluoro-Cyclohexanes  (7) b.p. 92°  (8) b.p. 101°	 +  +  +  (16) (17) (18) (19)	+  +  (20) (21)	4

contd./

Table 1.1 contd.

Compound	Dehydrofluorination Products		Ref.
	Monoenes, 1,4-Dienes etc.	1,3-Dienes	
 (9) b.p. 107°	 +  +  (22) (23) (24)	+ (19) + (20) + (21)	5
 (10) b.p. 124°	(22) + (23) + (24) + (19) +	 (25) + (20) + (21)	5

the eliminated HF is sufficiently acidic.

Using these considerations it is possible to rationalise the products of dehydrofluorination of the decafluorocyclohexanes (1)-(4). The 1H, 2H/- isomer, (2) is readily dehydrofluorinated[1] to give exclusively the monoene (11) by a trans-coplanar elimination with loss of fluorine from the electronically favoured -CFH- group. Monoene (11) is inert to further reaction. The 1H/2H-isomer (1) is dehydrofluorinated only slowly to give monoene (11) and perfluorocyclohexa-1,3-diene (12). In this case trans-coplanar elimination of HF with loss of fluorine from CFH is not possible and monoene (11) must arise via the less easy cis-coplanar elimination of HF from the boat form of (1). Diene (12) presumably arises by dehydrofluorination of the intermediate 3H-nonafluorocyclohexene which forms by trans-coplanar elimination of HF, with the loss of fluorine from the electronically disfavoured $\text{-}CF_2\text{-}$ group.

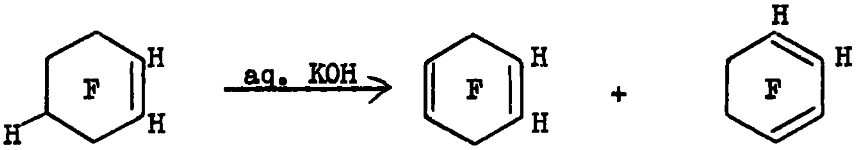
The 1H,3H-decafluorocyclohexanes (3) and (4) are readily dehydrofluorinated, each hydrogen being flanked by two $-CF_2-$ groups. Both the 1H/3H-isomer (3) and the 1H,3H/- isomer (4) give the two possible monoenes (13) and (14) together with perfluorocyclohexa-1,4-diene (15) and perfluorocyclohexa-1,3-diene (12). The 1H/4H- and 1H,4H/- isomers (5) and (6) each give the expected monoene (14) and both perfluorocyclohexadienes (15) and (12).

In practice the perfluorocyclohexadienes (12) and (15) are prepared in quantity by dehydrofluorination of the major fraction of the polyfluorocyclohexane mixture which distils at 78° and which has been shown to consist of a mixture of the 1H/4H- and 1H/3H-decafluorocyclohexanes (3) and (5). Prolonged reaction times can virtually remove all the monoenes and effect complete conversion to the dienes (12) and (15), however the 1,3-diene (12) is itself degraded by refluxing with concentrated potassium hydroxide and so highest yields of (12) are obtained before complete conversion of the monoenes.

1H- and 2H-heptafluorocyclohexa-1,3-dienes (20) and (21) have been obtained[4] by the dehydrofluorination of each of the possible 1H,2H,4H-nonafluorocyclohexanes (7)-(10) (Table 1.1). The 1H,4H/2H-isomer (7) and the 1H/2H,4H-isomer (8) each gave the same six products, (16)-(21), upon exhaustive dehydrofluorination, the main products being the monoenes (16) and (17). The dienes (20) and (21) were obtained as 21% by weight of the product mixture in the ratio 2.7:1 and hexafluorobenzene (18) and 1H-heptafluorocyclohexa-1,4-diene (19) were only minor products. Dehydrofluorination of 1H,2H/4H-nonafluorocyclohexane (9) gave six products[5] (19)-(24), and the 1H,2H,4H/-isomer (10) gave these same six products in addition to 1H,4H-octafluorocyclohexene (25).

1.1b. Dehydrofluorination of polyfluorocyclohexenes

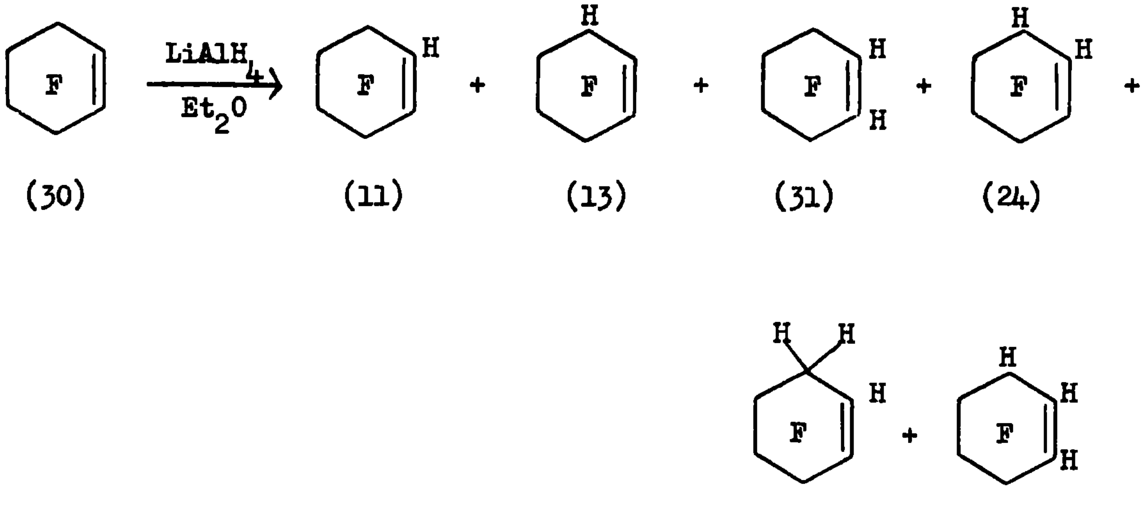
A very minor component of the product from the cobalt trifluoride fluorination ~~product~~ of benzene is 1H,2H,4H-heptafluorocyclohexene[5] (26). This olefin is also available, as a major product, by the fluorination of benzene with manganese trifluoride[5] or with a potassium cobaltifluoride complex.[5a] Dehydrofluorination of olefin (26) with aqueous potassium hydroxide gave the



(26) (27) (28)

1,4 diene (27), 1H,2H-hexafluorocyclohexa-1,3-diene (28) and recovered starting material, in respective yields of 36%, 20%, 18%.

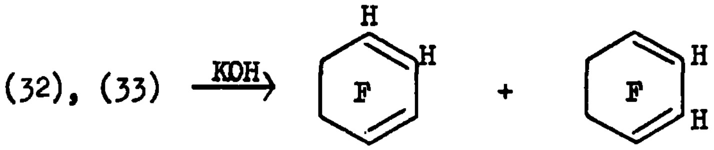
Perfluorocyclohexene (30) (made by dehydrofluorination of undecafluorocyclohexane), reacts with lithium aluminium hydride in ether to produce a complex mixture of hydrofluorocyclohexenes,[7] including (11), (13), (31), (24), (32), (33); further reduction products were not investigated. Although dehydrofluorination of monoene (24) with aqueous potassium hydroxide gives



(30) (11) (13) (31) (24)

(32) (33)

only a low yield of 2H-heptafluorocyclohexa-1,3-diene (21),[7] the action of molten potassium hydroxide upon the vapour of (24) gives (21) in ca. 60% yield.[8] In this reaction diene (21) is the sole product since either a 1,2 or 1,4 elimination of hydrogen fluoride leads to the same product. It has been shown[7] that olefins (32) and (33) upon dehydrofluorination separately each give the same two product dienes (28) and (34).



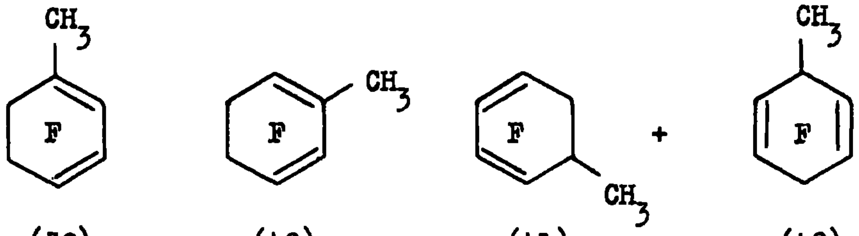
(28) (34)

Reaction of olefin (24) with lithium aluminium hydride in ether gives[9] a mixture of (33), (35) and (36); dehydrofluorination of (36) has given the 1H,2H,3H-pentafluorocyclohexa-1,3-diene (37) in low overall yield, together with 1,2,3,4-tetrafluorobenzene (38).[9]

(35) (36) (37) (38)

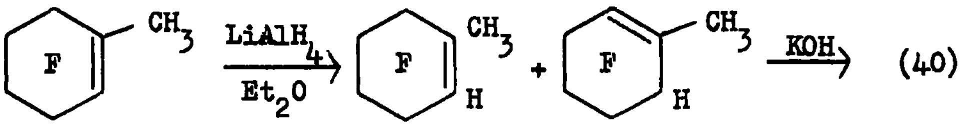
1.1c. Direct nucleophilic substitution of perfluorocyclohexa-1,3-diene[10]

With an equimolar quantity of methyllithium in ether, substitution of perfluorocyclohexa-1,3-diene occurs predominantly in the 2-position, giving products (39), (40), (41), (42) in the ratio 2:90:1:3.



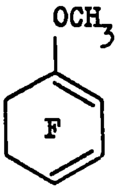
(39) (40) (41) (42)

Small amounts of polysubstitution products were also obtained but not investigated. All the products may be explained by an addition-elimination mechanism. Dienes (39) and (41) were only obtained from this reaction as a mixture identified by ^{19}F and ^{1}H n.m.r. spectroscopy. A pure specimen of (39) was obtained in very low yield by pyrolytic isomerisation of 1-methyl-heptafluorocyclohexa-1,4-diene. The structure of diene (40) was proved by alternative synthesis; (43) with lithium aluminium hydride in ether gave (44) and (45) in the ratio 3:1. Dehydrofluorination of the relatively unreactive olefin (45) with molten KOH gave (40) exclusively.

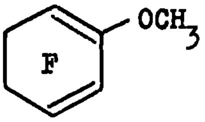


(43) (44) (45)

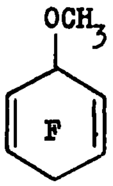
With an equimolar quantity of potassium hydroxide in methanol substitution again occurred predominantly in the 2-position to give (46), (47) and (48) in the ratio 1:12:2.



(46)



(47)

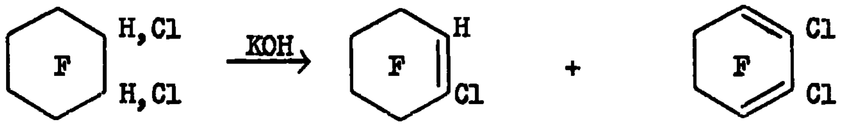


(48)

The 2-methoxy-diene (47) was also synthesised by the analogous route to that used for (40) above, starting from 1-methoxy-nonafluorocyclohexene.

1.1d. Other methods

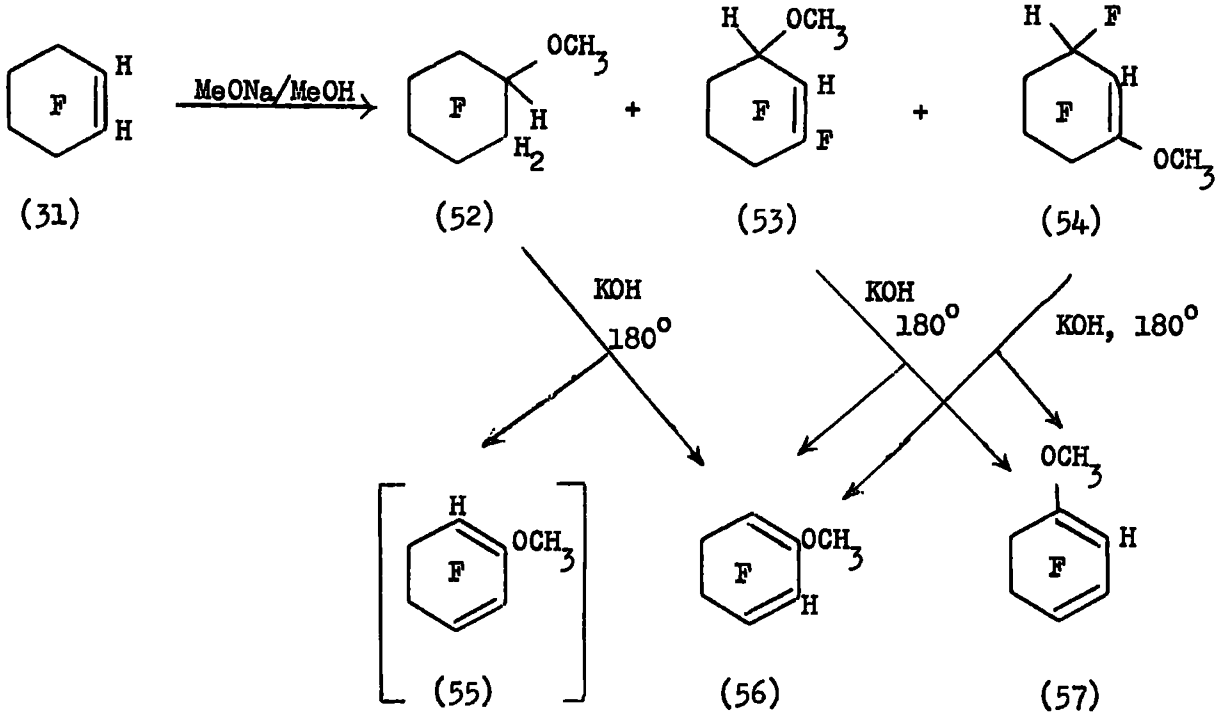
2,3-Dichloro-hexafluorocyclohexa-1,3-diene (51) has been obtained[7] in 4%



(49) (50) (51)

overall yield by dehydrochlorination of (49), as the minor coproduct of (50); (49) is a product of chlorination of 1H,2H-octafluorocyclohexene (31).

Recently three unstable monohydro-monomethoxy-hexafluorocyclohexa-1,3-dienes (55), (56), (57) have been reported,[10a] from the dehydrofluorination of products (52), (53), (54) obtained by the action of sodium methoxide in methanol on 1H,2H-octafluorocyclohexene (31). Diene (55) was only tentatively assigned; it was unstable and polymerised rapidly; (57) turned to a yellow paste at room temperature, whilst (56) was the most stable of the dienes.


MeONa/MeOH
KOH 180°
KOH 180°
KOH, 180°
F
H
OCH3
H2
(31)
(52)
(53)
(54)
(55)
(56)
(57)

CHAPTER 1

DISCUSSION

1.2 Two new routes to some mono- and di-substituted polyfluorocyclohexa-1,3-dienes

Both the routes (Fig.1.1) start from perfluorocyclohexa-1,3-diene and involve the same three basic steps:

(i) Formation of a bicyclic intermediate by introduction of a bridge between the 1,4-positions of the diene,

(ii) Nucleophilic substitution of either one or two of the vinylic fluorines of the bicyclic intermediate,

(iii) Pyrolysis of the products, which reverses the initial pericyclic reaction, (i), to give substituted cyclohexa-1,3-dienes.

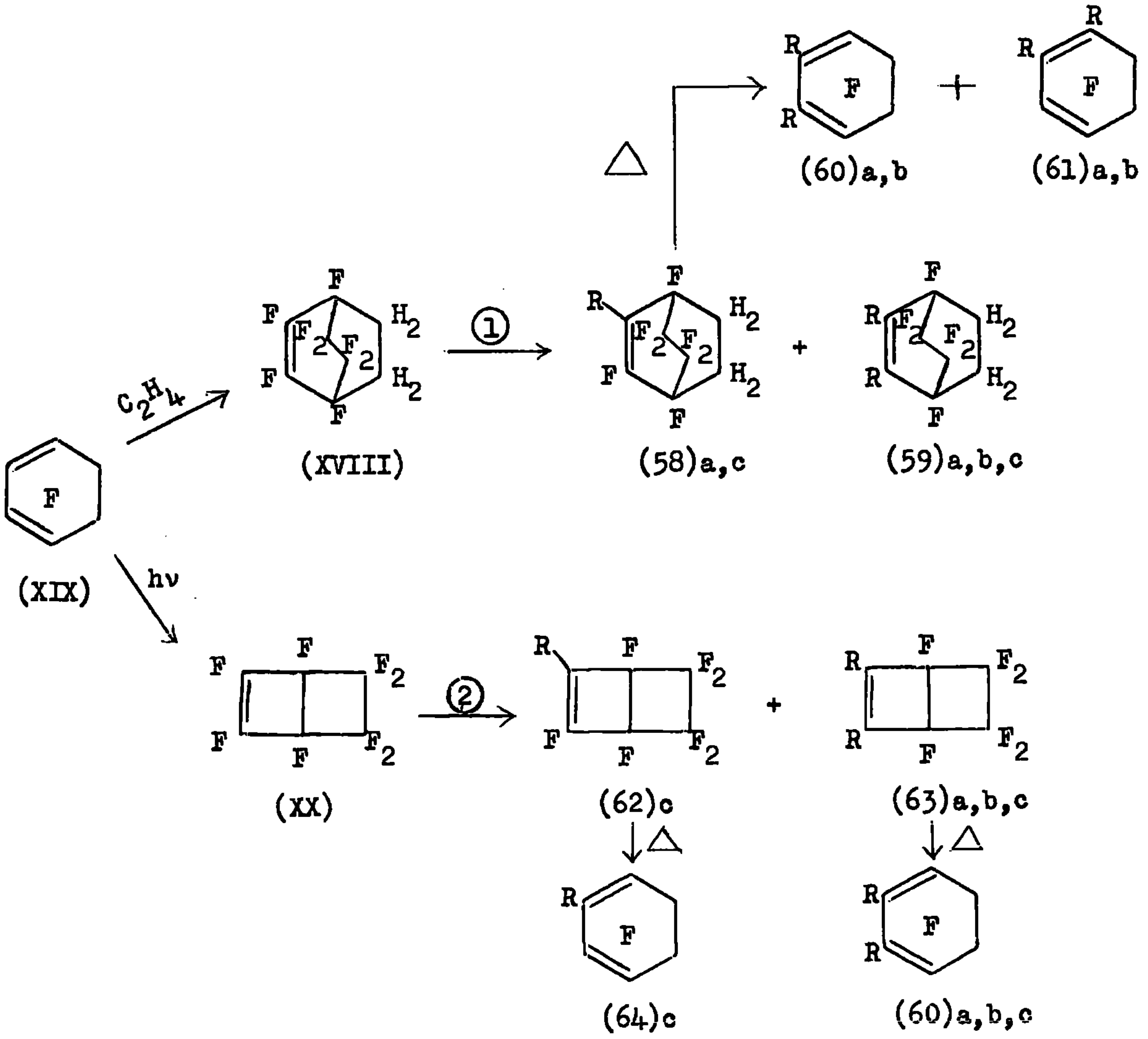


Fig.1.1

Fig.1.1 Key: a, (R = H); b, (R = Me); c, (R = OMe)

① Reaction with nucleophiles (a) $LiAlH_4$, (b) LiMe, (c) NaOMe

② Reaction with nucleophiles (a) $NaBH_4$, (b) LiMe, (c) NaOMe.

(58a) = (XXVII), (58c) = (X), (59a) = (XXXVII), (59b) = (II), (59c) = (V), (60a) = (XXXVIII), (60b) = (III), (60c) = (VI), (61a) = (XXXXIII), (61b) = (I), (62c) = (XII), (63a) = (XXXIX), (63b) = (IV), (63c) = (VII), (64c) = (XI).

In this chapter the synthetic routes will be described in broad outline; the details of the various stages and the description of the characterisation of the new compounds will be given in later chapters as indicated by references 12 to 17.

The first method involves, (i) addition of ethylene to perfluorocyclohexa-1,3-diene (XIX) at 200° to give the Diels-Alder adduct (XVIII) in good yield;[12] (ii) Nucleophilic substitution of (XVIII) gives good yields of mono- and di-substituted products (58a,c) and (59a,b,c);[13] (iii) Pyrolysis[14] of the bicyclo[2,2,2]oct-2-enes (XVIII), (59a) and (59b) in a flow system at 700°, 0.1 mm.Hg causes exclusive elimination of ethylene rather than tetrafluoroethylene. With the substituted derivatives (59a and 59b) the major products of the pyrolysis are the 2,3-disubstituted diene (60a), (60b) and the 1,2-disubstituted diene (61a), (61b). The high temperature is necessary to effect the pyrolysis stage in good yield although under these conditions there is some partial thermal degradation with formation of silicon tetrafluoride from the silica pyrolysis tube.

The second method involves, (i) formation of perfluorobicyclo[2,2,0]hex-2-ene (XX) by photolysis of perfluorocyclohexa-1,3-diene (XIX) in the vapour phase.[15] This process is quantitative using a sufficiently long irradiation period; (ii) Reaction of (XX) with mildly nucleophilic reagents gives the mono- and di-substituted derivatives (62) and (63),[16] which are stable and readily isolable; (iii) Pyrolysis of (62) and (63) at between 300-400°, 10^{-3} mm.Hg. gives the corresponding dienes (64) and (60) quantitatively.[15]

1.3 Limitations of the methods

In the first method overall yields of the bicyclic diene precursors (58), (59) can be very high, however the difficult nature of the pyrolysis step, with low conversion or breakdown of the product dienes (60), (61) is a severe limitation. Dienes (60), (61) generally have very similar properties and are difficult to separate by preparative g.l.c. Thermally unstable dienes (such as VI) could not be prepared using this method.

The second method scores over the first in that the final pyrolysis stage is effected under comparatively mild conditions and proceeds quantitatively to give one product diene which does not require purification. However the method is limited by the range of nucleophiles which can be used to substitute into (XX). Only mildly nucleophilic reagents (e.g. sodium borohydride, methyllithium, sodium methoxide) can be used; with the more reactive nucleophilic reagents (e.g. lithium aluminium hydride and phenyllithium) complex mixtures or polymers were formed.[16]

1.4 Improved preparation of 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes from perfluorocyclohexene

These dienes were prepared in quantity by a modified version of the published route[7] (see section 1.1b). In the original work the combined yield of the $C_6H_3F_7$ diene precursors, (32) and (33) obtained after separation was 18%. By increasing the molar ratio of perfluorocyclohexene to lithium aluminium from 1:0.65 to 1:1.38, the $C_6F_7H_3$ fraction was obtained as the major product and, after separation, was obtained in a yield of 62%.

In the original work[7] the dehydrofluorination stage was accomplished using refluxing aqueous potassium hydroxide and the recovery of materials and yields of the dienes were low. In the present work, application of the method of dehydrofluorination using the action of molten potassium hydroxide upon the vapour of the fluorocarbon to be dehydrofluorinated,[11] gave the dienes (28) = (XXXXIII) and (34) = (XXXVIII) in a combined yield of 84%. The preparative scale separation of dienes (XXXXIII) and (XXXVIII) by g.l.c. is slow and tedious owing to their very similar gas chromatographic retention times.

1.5 Spectroscopic Data for Polyfluorocyclohexa-1,3-dienes

Table 1.2 gives the known spectral parameters for seventeen polyfluorocyclohexa-1,3-dienes. Three of the dienes, (I), (III), and (VI) are new. The ^{19}F and ^{1}H spectra of the known dienes (28) = (XXXXIII) and (34) = (XXXVIII) have not been given previously.

(i) ^{19}F N.M.R. Spectra

In the ^{19}F spectra of polyfluorocyclohexa-1,3-dienes the difluoromethylene resonances are distinguishable from the vinylic fluorine resonances by their integrated intensities. With the exception of 1H,4H-cyclohexa-1,3-diene, the $-CF_2-$ resonances lie to lower field than the vinylic fluorine resonances in any given compound. The spin-spin splittings are generally complex and only for perfluorocyclohexa-1,3-diene has a complete analysis of the ^{19}F n.m.r. spectrum been carried out.[21]

(ii) Ultraviolet Spectra

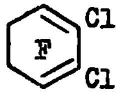
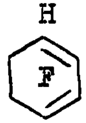
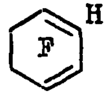
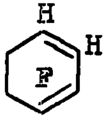
The conjugated diene system in these polyfluorinated molecules gives a broad absorbtion with the maximum lying in the region 252.0-284.0 nm, ϵ(1500-13,000). These values are comparable to those observed in cyclohexa-1,3-diene itself - λ_{max} 256.0 ($\epsilon \sim 8,000$).[22]

(iii) Infrared Spectra

The conjugated diene system in these molecules gives rise to two bands

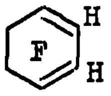
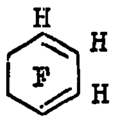
TABLE 1.2

Spectroscopic Data for Polyfluorocyclohexa-1,3-dienes

Diene	b.p.	References*	^{19}F N.M.R.			^{1}H N.M.R.		Ultraviolet		I.R.
			$-CF_2-$	Vinylic F	*	Shift τ	Assignment	λ_{max}(nm)	$\varepsilon^{\neq}$	ν_{max}(cm^{-1})
(12)  (XIX)	63°	10,19,22a	126.4	154.6 164.0	d	-	-	256.0	3200^{e}	1712 1746
(51) 	-	9,20	-	-	-	-	-	274.0	1700	1685
(20) 	72°	4	-	-	-	-	-	254.0	3720^{f}	1682 1743
(21) 	76°	4	-	-	-	-	-	262.5	3070^{f}	1679 1732
(28)  (XXXXIII)	-	5,P	112.1 120.6	131.7 160.2	o P	3.3	vinylic H	252.0	6300^{e}	1635 1734

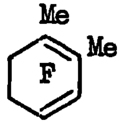
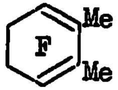
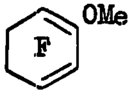
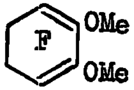
contd./

Table 1.2 contd.

Diene	b.p.	References*	^{19}F N.M.R.			^{1}H N.M.R.		Ultraviolet		I.R.
			$-CF_2-$	Vinylic F	*	Shift τ	Assignment	λ_{max}(nm)	ε ≠	ν_{max}(cm^{-1})
(34)  (XXXVIII)	98°	7,P	122.5	129.1	c P	4.25	vinylic H	266.0	3300^f	1655 1702
	-	18	121.8	115.9	a	4.23	vinylic H	-	-	-
(37) 	112°	9	-	-		-	-	262.5	4000^f	1620 1690
(39) 	-	10	121.0 126.4	132.4 152.1 162.8	d	8.45	$-CH_3$	-	-	-
(40) 	106°	10	126.4 127.2	140.1 157.0 169.0	d	8.37	$-CH_3$	264.0	3400^f	1684 1743

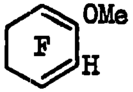
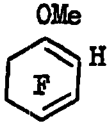
contd./

Table 1.2 contd.

Diene		b.p.	References[*]	^{19}F N.M.R.			^{1}H N.M.R.		Ultraviolet		I.R.
				$-CF_2-$	Vinylic F	*	Shift τ	Assignment	λ_{max}(nm)	ε ≠	ν_{max}(cm^{-1})
(I)		-	P	123.6 128.4	141.7 160.1	a P	8.11	$-CH_3$	266.5	5800^g	1645 1731
(III)		-	P	127.2	140.5	a P	8.15	$-CH_3$	269.0	2300^g	1660 1715
(46)		112°	10	123.0 138.0	160.1 146.9 164.7	d	6.55	$-OCH_3$	255.0	3070^f	1710 1745
(47) (XI)		123°	10,P	123.7 125.9	149.2 167.4 171.6	d	6.20	$-OCH_3$	270.0	4650^f	1690 1742
(VI)		175°	P	124.2	171.3	b	6.34	$-OCH_3$	274.5	1550^g	1678 1718

contd./

Table 1.2 contd.

Diene	b.p.	References※	^{19}F N.M.R.			^{1}H N.M.R.		Ultraviolet		I.R.
			$-CF_2-$	Vinylic F	*	Shift τ	Assignment	λ_{max}(nm)	ε ≠	ν_{max}(cm^{-1})
(56) 	-	10a	121.0 126.4	132.4 152.1 162.8	b	4.91 6.34	vinylic H $-OCH_3$	284.0	5150^f	1649
(57) 	-	10a	-	-	-	3.9 6.5	vinylic H $-OCH_3$	245.0	13,100^f	1675 1710

* ^{19}F N.M.R. shifts in p.p.m. upfield from $CFCl_3$

a - $CFCl_3$ internal reference

b - $CFCl_3$ external reference

c - C_6F_6 external reference

d - CF_3COOH external reference

※ P - indicates the present work

Shifts have all been related to $CFCl_3$ using the relationships:

$$\delta_{CFCl_3} = \delta_{C_6F_6} + 162.3 = \delta_{CF_3COOH} + 88.6 \text{ ppm.}$$

≠ ultraviolet spectra measured in the solvents indicated

e - diethyl ether
f - ethanol
g - cyclohexane

in the C=C stretching region (1600-1800 cm^{-1}), the positions of the bands depending on the substituents. One of the bands may be very weak and in certain cases is not observed.

(iv) Mass Spectra

The mass spectra of dienes (XIX), (I), (III), and (VI) are tabulated in Appendix B. The mass spectrum of perfluorocyclohexa-1,3-diene, (XIX) has been given before[22b] and shows the base peak at m/e 155, corresponding to loss of CF_3. For dienes (I), (III) and (VI) the parent peaks were also the base peaks.

CHAPTER 1

EXPERIMENTAL

1.6 Preparation of 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes

Perfluorocyclohexene (50.0 g., 192 mmole) was added dropwise over 3 hours to a stirred suspension of lithium aluminium hydride (10 g., 264 mmole) in refluxing ether (50 ml.) and refluxing was continued for 3 hours. The excess lithium aluminium hydride was destroyed by cautious addition of water in an atmosphere of nitrogen, followed by 50% (v/v) sulphuric acid (120 ml.) then water (100 ml.). The ether layer was separated, dried ($MgSO_4$) and fractionally evaporated (14" x $\frac{3}{4}$" diam. column, filled with glass helices). The still residue was distilled in vacuo from phosphoric oxide to give a liquid mixture (45.6 g.), which was separated in two portions by preparative g.l.c. (column A, 94°) to give (i) ether (7.9 g.); (ii) a mixture of nonafluoro- and octafluorocyclohexenes (2.3 g.); (iii) 1H,6H,6H- and 1H,2H,3H-heptafluorocyclohexenes (24.7 g., 119 mmole, 62%); and (iv) small amounts of longer retained materials (ca. 1 g.).

Dehydrofluorination of the heptafluorocyclohexene mixture

In a typical experiment, the heptafluorocyclohexene mixture (18.3 g.) was bubbled through molten potassium hydroxide at 180° in a slow stream of nitrogen and the product vapours were trapped in a collector cooled in liquid air. The analytical g.l.c. of the product (13.88 g., 84%) showed a trace of starting material and a mixture of 1H,2H- and 2H,3H-hexafluorocyclohexa-1,3-dienes, the latter diene being present in larger amount than the former. The mixture was separated by preparative g.l.c. (column B, 70°, pressure 1.6 atm. using the machine in the automatic mode with an injection size of ca. 50μl). From a typical dehydrofluorination product (18.4 g.) was obtained (i) 1H,2H-hexafluorocyclohexa-1,3-diene (XXXXIII) (3.60 g.); (ii) 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII) (6.96 g.); (iii) an interfraction (0.426 g.) of (XXXXIII), (XXXVIII) and unreatced nonafluorocyclohexenes.

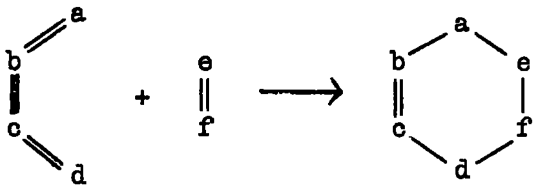
CHAPTER 2

DIELS-ALDER REACTIONS OF POLYFLUOROCYCLOHEXA-1,3-DIENES

INTRODUCTION

The Diels-Alder Reaction.[24]

In 1928 Diels and Alder first recognised the 1,4 addition of an unsaturated reactant to a conjugated diene,[23] and in subsequent years the wide scope of the reaction has been demonstrated by them and others. The basic reaction may be formulated as shown in the following equation:



The almost unlimited possibilities of variation of both the diene (abcd) and the dienophile (ef) make the Diels-Alder reaction a synthetic method of outstanding utility for the preparation of six-membered rings.[24]

2.1 The diene[24]

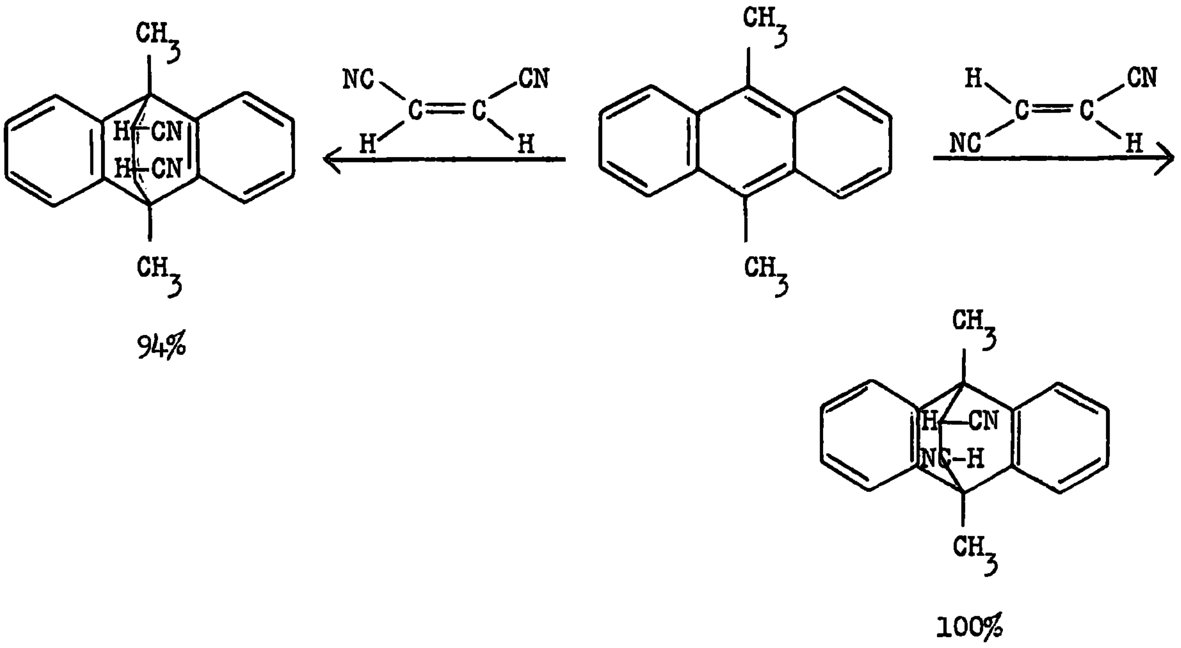
The conjugated diene, abcd, may be in an open chain or in a ring and it is necessary for the reaction that the diene be in, or be capable of assuming, a cisoid form. The diene may be part of a linear or cyclic polyene; even aromatic compounds can act as dienes with sufficiently reactive dienophiles, reactivity increasing in the order benzene < naphthalene < anthracene. For the heterocyclic dienes furan, pyrrole, thiophene, the reactivity in the Diels-Alder reaction falls dramatically from furan, which is an active diene, to thiophene, which is of very low reactivity.

2.2 The Dienophile[24]

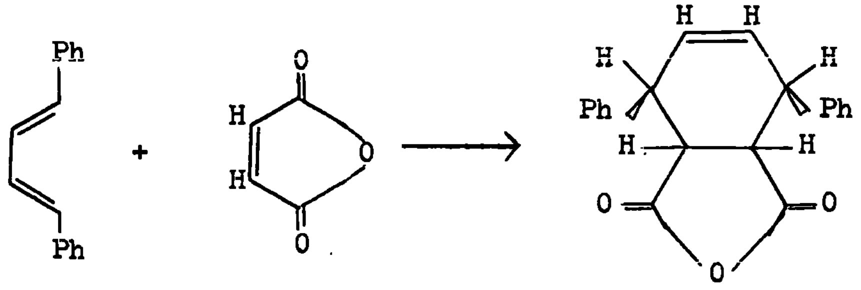
The unsaturated dienophilic species, (ef), may be a simple alkene or alkyne derivative, an allene, a cycloalkene or aryne. Heteroatomic groups which can show dienophilic properties are $\mathrm{C{=}O}$, $\mathrm{C{=}S}$, $\mathrm{C{\equiv}N{-}}$, $\mathrm{{-}C{\equiv}N}$, $\mathrm{{-}N{=}N{-}}$, $\mathrm{{-}N{=}O}$, $\mathrm{{-}N{=}SO}$, and a number of heterocyclic unsaturated compounds.

2.3 The stereochemistry of the Diels-Alder Reaction

In 1937 Alder and Stein[25] formulated the "cis principle" to rationalise a large body of experimental evidence which had by then been accumulated. This states that the configurational relationship of the diene and the dienophile is retained in the adduct. Thus, for example, the cis-trans isomeric 1,2-dicyanoethylenes react with 9,10-dimethyl anthracene to give high yields of pure diastereoisomeric 1:1 adducts,[24] as shown below.



The configuration of the diene component is also retained, as illustrated by the reaction of maleic anhydride with trans-trans-1,4-diphenylbuta-1,3-diene to give exclusively the adduct in which the phenyl groups are cis.[26]



The cis-principle is now recognised to be a consequence of the concerted nature of the Diels-Alder Reaction. Thus Woodward and Hoffmann state[27] that although a diradical mechanism has been advanced on numerous occasions, the overwhelming body of experimental facts is consistent only with a concerted mechanism,[28] (Rare examples of established diradical mechanisms are given in Reference 28a). Discussion and understanding of cycloaddition reactions has been greatly facilitated by the widespread acceptance of the concepts and nomenclature of Woodward and Hoffmann[27] used in the application of the "Principle of Conservation of Orbital Symmetry". The Diels-Alder reaction is classified as a $[\pi 2_s + \pi 4_s]$ cycloaddition, this being a special case of the general two-component cycloaddition $[_{\pi}m + _{\pi}n]$, where m,n represent the number of π electrons in the respective reacting systems. The subscript s̲ indicates that the cycloaddition occurs suprafacially on the termini of the π system. An a̲ would indicate that the process occurred antarafacially.

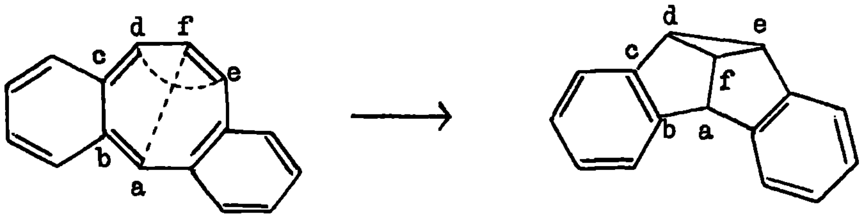
The general selection rules for concerted cycloadditions[27] are given in the table below.

Selection Rules for m + n additions

m + n	Allowed ground state reaction
4q	$m_s + n_a$
	$m_a + n_s$
4q + 2	$m_s + n_s$
	$m_a + n_a$

q = 0,1,2 .... (the smallest possible integer)

The Diels-Alder Reaction is the specific case where m = 2, n = 4, i.e. 4q + 2 = 6, q = 1, and is seen to be symmetry allowed in the ground state only for the $[_{\pi}2_s + _{\pi}4_s]$ or $[_{\pi}2_a + _{\pi}4_a]$ processes. It appears that the a-a process though symmetry allowed is energetically very unfavourable and the s-s process is the one normally observed experimentally as the Diels-Alder Reaction. However in certain cases, where the reacting π-electron systems are suitably twisted the $[\pi 2_a + \pi 4_a]$ process may operate, e.g. at room temperature molecule (65) is converted to (66).[29] The portion of molecule (65) acting as the diene is marked (abcd) and the dienophilic portion is marked (ef).



(65) (66)

Thus the Woodward-Hoffmann Rules give a very satisfactory explanation of the "cis-principle". The stereochemistry of the Diels-Alder reaction has been reviewed.[29a]

2.4 Reactivities in the Diels-Alder Reaction

The kinetic studies of Sauer et al[30-33] have done much to elucidate the nature of the Diels-Alder reaction. After an early suggestion by Bachman and Deno[36] Sauer clearly recognised two extreme reaction types: the Normal Diels-Alder reaction and the Diels-Alder reaction with Inverse Electron demand.

In the normal reaction the diene is an electron-rich species whilst the dienophile is electron poor; the empirical Alder Rule,[34] inferred from preparative experiments, recognised that reaction rate is increased by electron-donating substituents (e.g. $-NMe_2$, $-OMe$, $-CH_3$) in the diene and by electron attracting substituents (e.g. $-CN$, $-CO_2Me$, $-CHO$, $-NO_2$) in the dienophile.

The Diels-Alder reaction with inverse electron demand refers to the opposite state of affairs, in which the diene is an electron-poor species, whilst the dienophile is an electron-rich species. In this case the reverse of the Alder Rule applies; reaction rate is enhanced by electron attracting substituents in the diene and by electron donating substituents in the dienophile.

If both components in the Diels-Alder reaction are either electron-rich or electron-poor the reaction is generally sluggish or does not occur. The greater the difference in character the faster the reaction proceeds.

2.4a Electron-rich dienes with electron-poor dienophiles

(i) Effect of substituents in the diene

Sauer et al[32] measured the second order rate constants ($k_2 \times 10^8$ litre mole^{-1}sec^{-1} given in parentheses) for the reaction of the electron-poor dienophile maleic anhydride with a range of cyclic and acyclic dienes in dioxan at 30°.

The effect of substitution on the reactivity of butadiene is shown in the following order: 1-methoxy-butadiene (8.41×10^4), 2-phenyl- (6.00×10^4), 2,3-dimethyl- (3.36×10^4), trans-1-methyl- (2.27×10^4), butadiene (6.83×10^3) trans-1-phenyl- (4.28×10^3), 2-chloro- (6.90×10^2), trans-trans-1,4-diphenyl- (2.96×10^2). Thus the electron-donating substituents methyl, methoxy- enhance the rate, whilst the electron-withdrawing substituent chlorine reduce the rate relative to unsubstituted butadiene. A phenyl group is activating in the 2-position and deactivating in the 1,4-positions. The deactivating effect is attributed to its electron-attracting nature, and the rate enhancing effect in the 2-position to its large bulk, which favours the quasi-cis conformation of the diene. The high reactivity of dienes fixed in the cis-conformation is seen in the following order: cyclopentadiene (9.21×10^6), 9,10-dimethylanthracene (1.60×10^6), bis-1,2-methylene-cyclohexane (7.55×10^5), cyclohexa-1,3-diene (1.32×10^4), hexachlorocyclopentadiene (1.14). It is seen that the five-membered ring hydrocarbon diene is very much more reactive than the six-membered ring diene, whilst cycloocta-1,3-diene is even less reactive.[30] This effect may be attributed to the favourable (shorter) internuclear distance of the termini of the diene system in five-membered rings, compared to six-membered rings. The very low reactivity of hexachlorocyclopentadiene is attributable to the electron-withdrawing effect of the chlorine atoms. It is in fact a typical electron-poor diene.

(ii) Effect of substituents in the dienophile

In the addition of ethylenic dienophiles to the electron-rich diene 9,10-dimethylanthracene, progressive substitution of hydrogen atoms by powerfully electron-attracting cyano groups causes a marked increase in rate ($k_2 \times 10^5$ l. mole^{-1}sec^{-1} measured in dioxan at 20° given in parentheses):[31]

CH_2=CH-CN (0.89), cis-CH(CN)=CH(CN) (131), trans-CH(CN)=CH(CN) (139), $C(CN)_2$=CH_2 (1.27×10^5), $C(CN)_2$=CH(CN) (5.90×10^6), $C(CN)_2$=$C(CN)_2$ (1.30×10^{10}).

With the same diene and solvent, but at 30°, the rates of reaction of equivalently substituted alkenes and alkynes were measured[31] to be: trans($CH(CO_2Me)$=$CH(CO_2Me)$) (2.15×10^3), MeO_2C-C≡C-CO_2Me (1.40×10^3), CH_2=CH-CO_2Me (7.18×10^2), H-C≡C-CO_2Me (1.13×10^2). The rate-enhancing effect of the electron-withdrawing ester groupings is observed in both the alkenes and alkynes, but in each case the alkyne is less reactive than the equivalently substituted alkene.

2.4b Electron-poor dienes with electron-rich dienophiles

The effect of Inverse Electron Demand in the reaction of an electron-poor diene with an electron-rich dienophile[31] is clearly demonstrated in Table 2-1. Hexachlorocyclopentadiene reacts only slowly with maleic anhydride, reacting more quickly with the simple electron-rich olefin cyclopentene whilst this behaviour is reversed for 9,10-dimethylanthracene. Norbornene reacts more quickly with both dienes than cyclopentene; this shows the general effect of increase of dienophilicity of a double bond with increasing ring strain. This effect is rate enhancing in either the "Normal" or "Inverse" Diels-Alder reactions.

TABLE 2.1

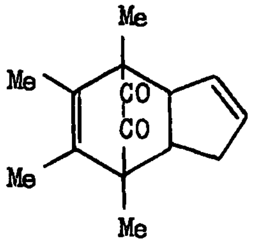
Kinetics of the reactions of hexachlorocyclopentadiene and 9,10-dimethylanthracene with dienophiles in dioxan at 130°

Dienophile	$k_2 \times 10^6$ l.mole^{-1}sec^{-1}	
	hexachlorocyclopentadiene	9,10-dimethylanthracene
p-methoxystyrene	1580	50
styrene	793	70
p-nitrostyrene	538	602
norbornene	72	36
cyclopentene	59	7.8
maleic anhydride	29	1,410,000

Considering the reactions of styrene it is seen that the electron withdrawing nitro-group decreases reactivity towards hexachlorocyclopentadiene whilst increasing the reactivity towards 9,10-dimethylanthracene. The opposite behaviour is observed for substitution of styrene with the electron-releasing methoxy-group.

2.5 Electron-poor dienes in the Diels-Alder Reaction

Quite a number of dienes containing electron-withdrawing groups have been observed to react qualitatively as electron-poor dienes, and readily give adducts with electron-rich olefins.[30] The electron-withdrawing effects of the carbonyl groups in ortho-benzoquinones confer electron-poor character upon their carbocyclic diene system; thus tetramethyl-o-benzoquinone reacts as a diene with cyclopentadiene to give adduct (67). Tetrachloro-o-benzoquinone (68) shows the ability to add dienophiles either to its cyclohexadiene system or to its heterodiene system (the 1,2-diketo grouping). With cyclopentadiene as dienophile both systems react to comparable extents.[30] α-Pyrones e.g. (69)[41,35]



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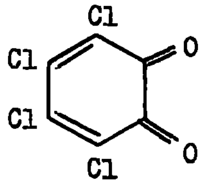

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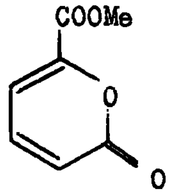

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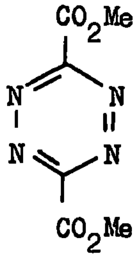

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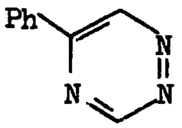
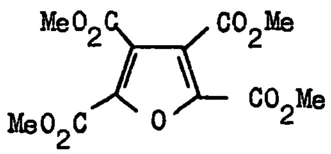


(71)

react with electron-rich olefins such as 1,1-diethoxyethylene in refluxing benzene to give Diels-Alder adducts in high yield. 1,2,4,5-tetrazines (e.g. (70))[31] and 1,2,4-triazines (e.g. (71))[42] react as dienes with electron-rich olefins; with (71) addition occurs across the 3,6-carbon atoms.

Other examples of electron-poor dienes are (72), (73) and (74). Though



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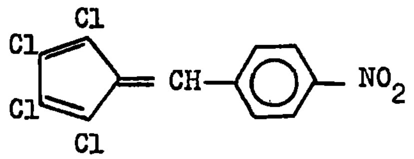

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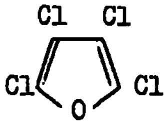

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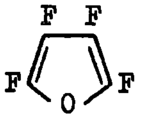
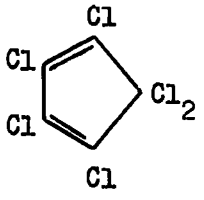


(75)

furan and fulvene are very reactive electron-rich dienes, (72) and (73) do not add the electron-poor dienophile maleic anhydride even under forcing conditions.[31] Tetrachlorofuran (74) gives exo- and endo-Diels-Alder adducts with the electron-rich olefin 2,5-dihydrofuran.[39] Tetrafluorofuran[40] polymerises rapidly and no attempts at Diels-Alder reaction have been possible. The polymer is not thought to arise by a Diels-Alder reaction.

The most extensively investigated electron-poor diene is hexachlorocyclopentadiene (76).[43,44] Dozens of adducts have been prepared using electron-rich



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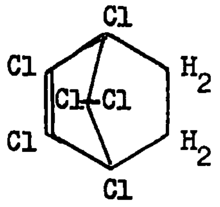

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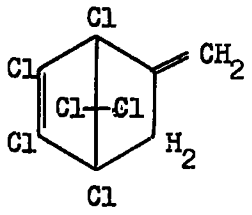
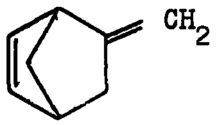


(78)

alkenes and alkynes and the kinetic studies of Sauer[31] have already been discussed. The interest in hexachlorocyclopentadiene centred around preparation of insecticides and heat resistant polymers.[43] The insecticide "Aldrin" is the adduct of (76) with norbornadiene. Hexachlorocyclopentadiene is very stable as a monomer and shows no tendency to dimerise. With ethylene (55 atm., 180°, 5.5h) adduct (77) was formed in 74% yield.[45] By bubbling ethylene through molten (76) at 200° (77) was obtained in 94% yield.[46] Allene reacts as a dienophile with (76) at 150-200° to give adduct (78) in 76% yield after purification.[47] That the addition of allene to (76) occurs in a synchromous [4 + 2] process, rather than via a diradical intermediate has been substantiated by a study using 1,1-dideuteroallene.[48] Although Sauer states[30] that 'allene exhibits sufficient activity only with respect to electron-deficient dienes - e.g. hexachlorocyclopentadiene', (quoting reference 47), in that same paper[47] it is observed that equimolar proportions of electron-rich cyclopentadiene (C_5H_6) and allene react at 200° to give the 1:1 adduct (79) (47%), together with the 2:1 adduct (80) (12%) and the 3:1 adduct (81) (9%), together with some polymer which was assumed to have arisen from allene.



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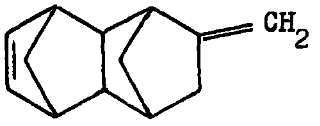

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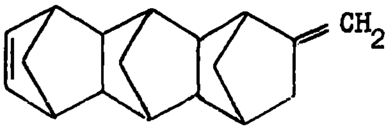
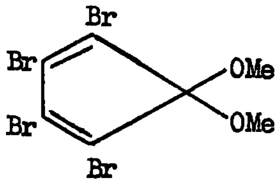


(81)

In view of the formation of (80) and (81) in only relatively small amounts it would seem that allene must be at least as dienophilic as the strained reactive endocyclic double bond in (79), since it is evidently able to compete successfully with (79), (80) and (81) for cyclopentadiene. This high reactivity of the electron-rich molecule allene even with electron-rich cyclopentadiene, might be ascribed to its high strain energy.

Hexabromocyclopentadiene[49] is stable and acts as a diene towards cyclopentadiene as dienophile. Its dimethoxy-derivative (82)[49] is said to react as an electron-rich diene, since on the basis of yields it reacts more readily with maleic anhydride, maleimide and benzoquinone than with allyl alcohol or cyclopentadiene. Possibly in (82) the electron-donating methoxyls have a greater effect than the electron-withdrawing bromines.



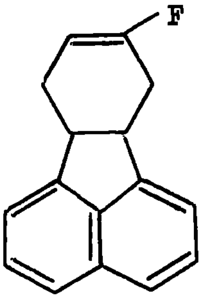
(82)

2.6 Fluorinated dienes in the Diels-Alder Reaction

The work up to 1966 in this field has been reviewed by Perry.[50]

(a) Acyclic fluorinated dienes

2-Fluorobuta-1,3-diene (fluoroprene) reacts with the electron-rich double bond of acenaphthene to give a low yield of adduct (83) and Dewar[51] cited this as



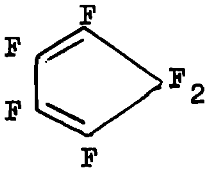
(83)

evidence for the electron-deficient nature of fluoroprene. However since fluoroprene gives quite good yields of Diels-Alder adducts with electron-poor olefins (e.g. acrylonitrile)[52] the electron-deficient nature of fluoroprene should not be overestimated.

1,1,4,4-tetrafluorobuta-1,3-diene[50] gives an adduct which apparently arises by Diels-Alder reaction with trifluoronitrosomethane, however with acrylonitrile 1,2 addition occurs; at 175° the diene dimerises by 1,2 addition.[53] Additions with trifluoronitrosomethane may well not be true [2 + 4] cyclo additions, since the molecule contains an odd electron. Perfluorobuta-1,3-diene displays very little tendency to give Diels-Alder adducts[50] with dienophiles, and only appears to have given[54] an adduct with trifluoronitrosomethane. It fails to react with maleic anhydride and appears[50] to react by 1,2 addition rather than by 1,4 addition.

(b) Polyfluorocyclopentadienes

Perfluorocyclopentadiene (84) dimerises quickly at room temperature and slowly even at -22° to give the Diels-Alder dimer (85),[57] which has been



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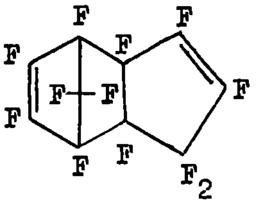


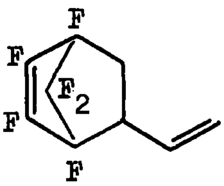
(85)

assigned the endo- configuration on the basis of a detailed analysis of its ^{19}F n.m.r. spectrum.[60] The thermal stability of the perfluoro-dimer (85) is very much greater than that of dicyclopentadiene; (85) is unaffected by storage at 475° for 45 min.[57] whereas dicylopentadiene breaks down quantitatively when heated to 160°. (The endo-stereochemistry of (85) was confirmed by the fact that endo-tetrahydrodicyclopentadiene and (85) both gave the same saturated fluorocarbon ($C_{10}F_{16}$) upon vapour-phase fluorination over cobalt trifluoride).[61]

Like hexachlorocyclopentadiene (76), perfluorocyclopentadiene appears to be a reactive electron-poor diene, however formation of dimer often seriously reduces the yields of adducts sought in Diels-Alder reactions.[57] Perfluorocyclopentadiene, (84) gave[56] adducts with the following compounds (reaction temperature, reaction time, yield of 1:1 adduct[57a] and yield of perfluorocyclopentadiene dimer are given in that order in parentheses): norbornadiene (100°, 6d., 99%, 0%), trifluoronitrosomethane (20°, overnight, 98%, 0%), cyclopentadiene (125°, 4d., 98%. o%), diethyl maleate (110°, 3d., 66%. 34%),[59] butadiene (100°, 4.5d., 64% -%), ethylene (106°, 8d., 51%. 41%), diethyl fumarate (110°, 3d., 50%, 50%),[59] acetylene (115° 65h., 42%, 22%), maleic anhydride (110°, 2d., 41%, 53%), N-allyltrifluoroacetamide (50°, 64h., 30%, -%),[62] anthracene (120°, 5d., 27%, -%), dimethyl acetylene dicarboxylic ester (133°, 3d., 22%. 50%).

Thus diene (84) gives adducts with electron-rich dienophiles ethylene and acetylene; the angle-strained molecule norbornadiene gives a quantitative yield of adduct. The electron-poor dienophiles maleic anhydride, dimethyl acetylene dicarboxylic ester, diethyl maleate and diethyl fumarate also react to give moderate yields of adducts. The last two dienophiles retain their configuration into the adduct[59] in accord with the cis-principle. Diene (84) gives a quantitative yield of adduct with trifluoronitrosomethane although hexachlorocyclopentadiene did not react even at 100°. With butadiene perfluorocyclopentadiene reacts purely as a diene to give, in addition to the 1:1 adduct

(86), a small amount (less than 1%) of the 2:1 adduct (87); with cyclopentadiene it reacts as a diene and as a dienophile to give (88) and (89) respectively in



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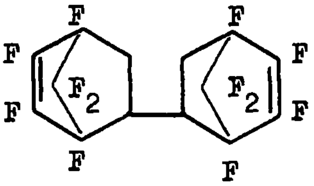

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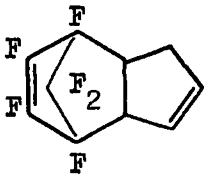

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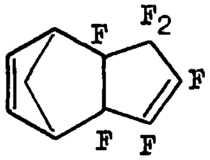
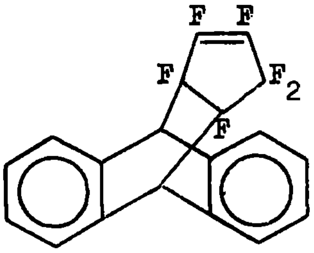


(89)

the constant ratio 16:84, independently of the reaction conditions such as temperature and solvent. This observation had led to the suggestion[58] that the reaction giving (88) and (89) proceeds via a common transition state. With anthracene perfluorocyclopentadiene reacts as a dienophile to give (90), in contrast to perchlorocyclopentadiene which reacts as a diene to give mianly (91).[43]



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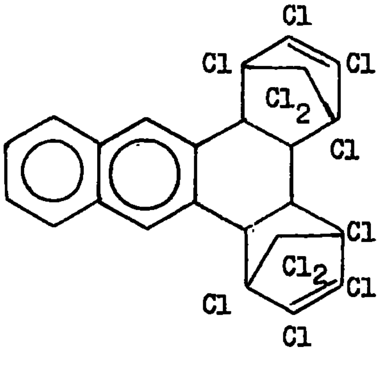
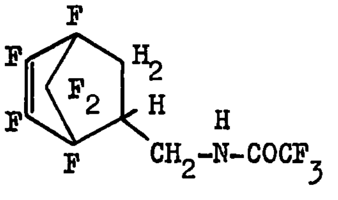


(91)

Like perchlorocyclopentadiene, perfluorocyclopentadiene shows no reactivity towards tetracyanoethylene or tetrafluoroethylene. It did not react with perchlorocyclopentadiene, perfluorobutadiene or perchlorobutadiene.

Chemical methods have shown[62] that N-allyltrifluoroacetamide reacts with (84) to give the adduct (92) which is predominantly or even exclusively the endo-isomer. Thus hydrolysis of (92) gives the free amine (93), which cyclises



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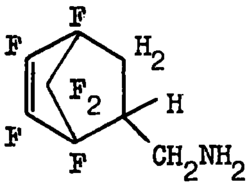

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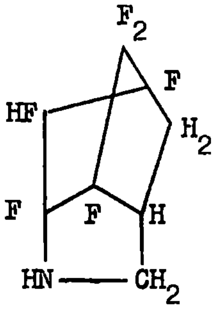
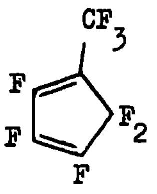


(94)

to the tricyclic amine (94) in 68% yield. Only for the endo-amine is it stereochemically feasible to effect the intramolecular cyclisation. The exo-amine would be expected to react intermolecularly.

The adduct of diethyl maleate with perfluorocyclopentadiene is believed[59] to be endo- on the basis of its n.m.r. spectrum. This same adduct is obtained by hydrolysis and esterification of the corresponding adduct of maleic anhydride, thus confirming the endo-stereochemistry of the maleic anhydride adduct. Perfluorocyclopentadiene dimer also has the endo-configuration, so it seems reasonable to expect the other Diels-Alder adducts of perfluorocyclopentadiene to be endo.

Several other polyfluorocyclopentadienes are known. Perfluoro(1-methylcyclopentadiene)[63] (95) is reasonably stable being only 40% converted to dimer (96) after 50 hours at 80°. Perfluoro(2-methylcyclopentadiene) (97), besides giving an unspecified dimer, is also partly rearranged thermally to diene (95), a process previously unknown under these conditions.[63] 2H-penta fluorocyclopentadiene (98), dimerises extremely rapidly[64] to give the endo isomer of (99).[60] 1H-pentafluorocyclopentadiene (100) is more stable towards dimerisation than (98) and appears[64] to give two dimers in the ratio 5:2. Diene (100) gave[64] no adduct with ethyl vinyl ether or, less surprisingly, with tetracyanoethylene.



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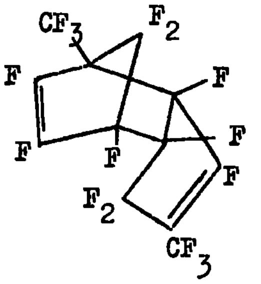

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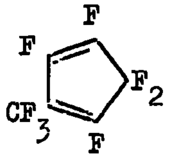

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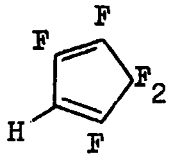

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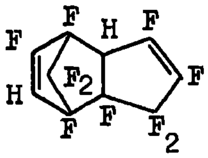

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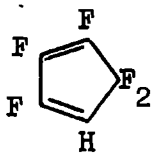

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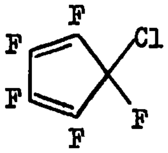

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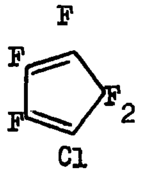

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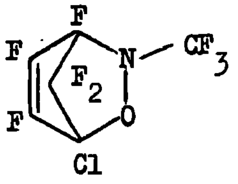

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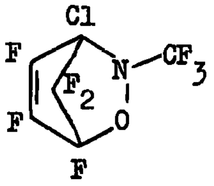
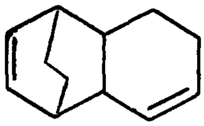


(104)

5-Chloropentafluorocyclopentadiene (101)[65] appears to be reasonably stable with respect to dimerisation, it gives mixtures of syn and anti isomers of the Diels-Alder adducts with trifluoronitrosomethane at room temperature and with dimethyl acetylene dicarboxylate at 135°. The higher stability of diene (101) with respect to dimerisation than of perfluorocyclopentadiene is not unexpected since the tendency towards dimerisation of 1,2,3,4-tetrachlorocyclopentadienes depends upon the 5-substituents[66] and falls in the order $F_2 > H_2 > H,Cl \gg Cl_2$. 1-Chloropentafluorocyclopentadiene (102) dimerises completely at room temperature over 3 days. With trifluoronitrosomethane at room temperature adduct (103) was obtained in 96% yield; the alternative adduct (104) may have been present in trace amount.

(c) Polyfluorocyclohexa-1,3-dienes

Cyclohexa-1,3-diene (C_6H_8) is moderately stable with respect to dimerisation and thus contrasts with cyclopentadiene (C_5H_6). Cyclohexa-1,3-diene held for 24 hours at 180° is reported[67] to give unchanged monomer (14%), endo- and exo-Diels-Alder dimers (105) (57%) and polymeric material (28%). Other workers report that at 200° the endo-, exo-dimers were obtained in the ratio of 4:1 in a combined yield of 32%.[67a]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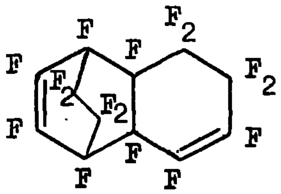

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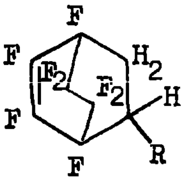
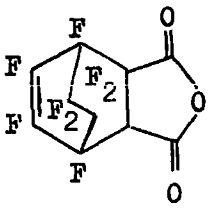
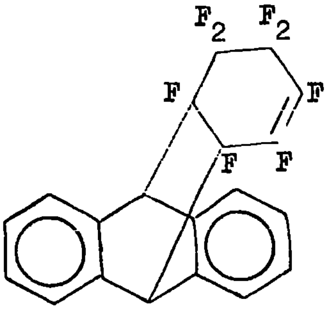
Perfluorocyclohexa-1,3-diene (XIX) is stable with respect to dimerisation up to 250° for preparative purposes, but when heated at 390° for 144 hours it produced[68] in 40% yield a mixture of endo- and exo-Diels-Alder dimers (106) in the ratio 9:1. Thus Diels-Alder additions of perfluorocyclohexa-1,3-diene with moderately reactive dienophiles are not affected by concomitant formation of the diene-dimer as are those with perfluorocyclopentadiene. Perfluorocyclohexa-1,3-diene was the first polyfluorinated diene to be shown to undergo Diels-Alder addition.[69] With alkenes, CH_2=CH-R good yields of the Diels-Alder adducts (107) were obtained;[69,70] after purification, yields obtained under the reaction



(107)



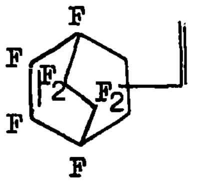
(108)



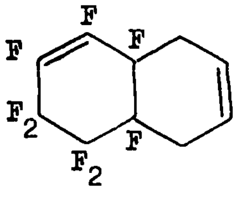
(109)

conditions shown were, for R = $-COCH_3$ (73%, 114°, 2.5h), -OEt (78%, 114°, 2.5h), -Ph (94%, 98°, 7h), $-CO_2Me$ (34%, 100°, 6h), -CN (65%, 170°, 5h). Here perfluorocyclohexa-1,3-diene is observed to display qualitatively the properties of a typical electron-poor diene giving high yields of adduct with the electron-rich olefins methyl vinyl ketone, ethyl vinyl ether, and styrene, whilst the yield with the relatively electron-poor methyl acrylate is lower and acrylonitrile requires a higher temperature for reaction.

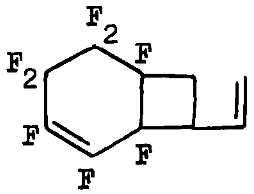
The adduct of perfluorocyclohexa-1,3-diene with N-allyltrifluoroacetamide (107) (R = $-CH_2-NHCOCF_3$) has been shown[71] to be predominantly or even exclusively the endo-isomer, by a method similar to that used for the analogous perfluorocyclopentadiene adduct (Section 2.6b). In this case the free amine (107) (R=$-CH_2NH_2$) was slower to cyclise than was amine (93), in keeping with the lower reactivity of the less strained (and hence less reactive) -CF=CF- double bond in the bicyclo [2,2,2] system, and the larger distance between the $-NH_2$ group and the proximate -CF= group.[71] Perfluorocyclohexa-1,3-diene reacted[69,70] with maleic anhydride at 190° to give (108) in 68% yield; with anthracene at 99° to give (109) in 7% yield; and with butadiene to give (110) (41%), (111) (34%) (112) (18%) and two other unidentified products (3% and 4%), At 350° both (110) and (112) were isomerised to (111). Thus perfluorocyclohexa-1,3-diene



(110)



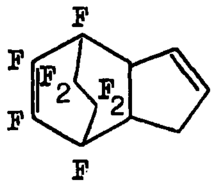
(111)



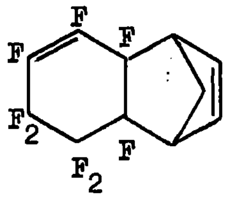
(112)

resembles perfluorocyclopentadiene in acting as a dienophile with anthracene but contrasts with it in acting both as diene and as dienophile with butadiene, with which perfluorocyclopentadiene only acts as diene. The 1,2 addition product (112) is quite remarkable; only in one other case, with tetrafluoroethylene at 400° has 1,2 addition been observed with perfluorocyclohexa-1,3-diene.[68]

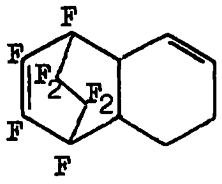
With the conjugated cyclic olefins cyclopentadiene and cyclohexa-1,3-diene, perfluorocyclohexa-1,3-diene reacts as both diene and dienophile;[71] thus (113) and (114) were obtained in the ratio 19:81 after 24 hours at 75° and (115) and (116) were obtained in the ratio 10:1 together with polymer after 24 hours at 60°. Thus the dienic behaviour of cyclopentadiene prevailed over that of perfluorocyclohexa-1,3-diene to give (114) as the major isomer. Similar behaviour was observed with perfluorocyclopentadiene and cyclopentadiene.[56] With cyclohexa-1,3-diene and perfluorocyclohexa-1,3-diene the situation is reversed and the dienic character of perfluorocyclohexa-1,3-diene predominates to give (115) as the major isomer.



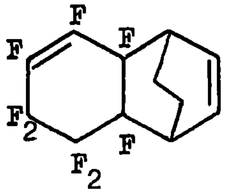
(113)



(114)

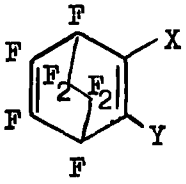


(115)



(116)

When an equimolar mixture of perfluorocyclohexa-1,3-diene and perfluorocyclopentadiene were heated at 110° for 2 days no cross reaction was observed[71] and perfluorocyclopentadiene dimer and unchanged ~~the~~ hexadiene were obtained quantitatively.



(117)

Perfluorocyclohexa-1,3-diene reacts with alkynes (X-C≡C-Y) at temperatures between 175-225° to give[68,72] Diels-Alder adducts (117) in the yields shown in Table 2.2. (Yields are of pure adduct actually obtained).

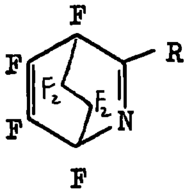
TABLE 2.2

Adducts of perfluorocyclohexa-1,3-diene with alkynes X-C≡C-Y

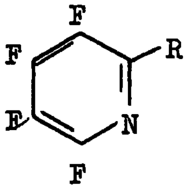
	Alkyne		Yield of adduct	Reaction temperature	Reaction time (hours)
	X	Y			
(i)	H	CH_3	94%	180°	40
(ii)	H	CF_3	92%	200°	100
(iii)	H	CH_2Cl	88%	180°	17
(iv)	CH_3	CH_3	71%	200°	19
(v)	CH_2Cl	CH_2Cl	62%	200°	40
(vi)	H	Ph	54%	175°	20
(vii)	CH_3	CF_3	49%	220°	63
(viii)	CO_2Et	CO_2Et	47%	215	18
(ix)	CF_3	CF_3	36%	225°	18
			(90%)[73]	(264°)	(22)

Thus under roughly comparable conditions the yields of adducts given by the symmetrical acetylenes are seen to fall in the order, according to X = Y, $CH_3 > CH_2Cl > CO_2Et > CF_3$ and hence the expected effect of inverse electron demand appears to be operating. The mono-substituted alkynes (i), (ii) and (iii) may be more reactive simply on steric grounds. It is likely that all the adducts (117) could be obtained in essentially quantitative yield; thus at the higher temperature of 264° perfluorobut-2-yne gave adduct (117) (X = Y = CF_3) in approximately 90% yield in 22 hours.[73]

Under forcing conditions perfluorocyclohexa-1,3-diene has been shown[74,75] to react with nitriles (R-C≡N, R an electronegative substituent, CF_3, Br, C_6F_5, $-(CF_2)_3CN$) see Table 2.3). In only two cases were the intermediate adducts (118) isolated. At the high temperatures necessary, the adducts (118) lose tetrafluoroethylene to give 2-substituted tetrafluoropyridines (119).



(118)



(119)

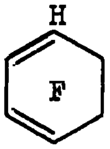
TABLE 2.3

Reaction of perfluorocyclohexa-1,3-diene with nitriles R-C≡N

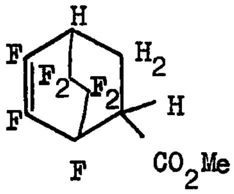
	Nitrile R-C≡N	Molar ratio (diene:nitrile)	Reaction Temperature	Reaction Time (hours)	Yield (118)	Yield (119)
(i)	R = CF_3	1:1	400°	16	-	40%
(ii)	R = Br	1:3	400°	15	-	40%
		2:3	380°	12	9%	18%
(iii)	R = C_6F_5	1:1	390°	64	-	4%
(iv)	R = $-(CF_2)_3CN$	1:2	350°	16	4%	1%
		1:2	350°	64	-	10%

The high reaction temperatures necessitated by the low reactivity of the C≡N group as a dienophile limit the reaction to nitriles of high thermal stability. For example acetonitrile heated with perfluorocyclohexa-1,3-diene in a Pyrex ampoule at 400° for 24 hours gave only silicon tetrafluoride and intractable black solids.[68]

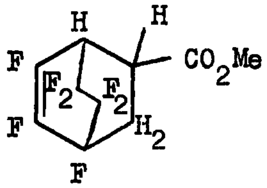
1H-heptafluorocyclohexa-1,3-diene (20) reacts with methyl acrylate at 130° for 15 hours to give the two possible positional isomers (120) and (121) in a combined yield of ca. 68%, which were presumed to possess endostereochemistry.[76] No dimerisation of diene (20) appears to have been observed.



(20)



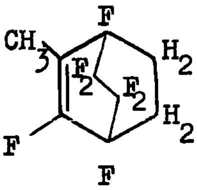
(120)



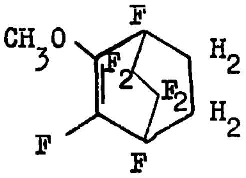
(121)

No attempt was made to differentiate the isomers (120) and (121); one was a solid, m.p.67-69° and the other a liquid b.p.88°, 10 mm.Hg. From the data given[76] it appears that the two isomers were produced in roughly equal amounts.

2-methyl- and 2-methoxy-heptafluorocyclohexa-1,3-dienes (40) and (47) each reacted with ethylene at 250° over 42 hours to give (122) (76% yield) and (123) (92% yield) respectively.[10] Thus these dienes, like perfluorocyclohexa-1,3-diene still behave as typical electron-poor dienes towards the electron-rich dienophile ethylene in spite of substitution with electron-donating substituents in the two-position. Again no dimerisation of these dienes was reported.



(122)



(123)

CHAPTER 2

DISCUSSION

2.7 Spectral Parameters of Diels-Alder adducts of polyfluorocyclohexa-1,3-dienes

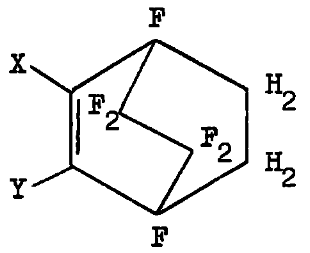
Since much of the subsequent discussion depends upon spectroscopic analysis, it is convenient to discuss together the spectroscopic parameters of the new polyfluorobicyclo[2,2,2]oct-2-enes (Table 2.4), polyfluorobicyclo[2,2,2] octa-2,5-dienes (Table 2.5) and polyfluoro-5-methylenebicyclo[2,2,2] oct-2-enes (Table 2.6) obtained in the course of the present work. All the compounds in Tables 2.4, 2.5, 2.6 are formally Diels-Alder adducts of polyfluorocyclohexa-1,3-dienes, though some were derived indirectly by nucleophilic substitution reactions (See Chapter 3).

(a) N.m.r. spectra

In these compounds both the ^1H and ^{19}F resonancaes are generally complex and broad owing to long-range H-F and F-F coupling between many nuclei, however the chemical shifts of the bridgehead, $-CF_2-CF_2-$ and vinylic fluorine resonances lie in characteristic regions. Thus in these compounds and other adducts of perfluorocyclohexa-1,3-diene with alkenes[70,65] and alkynes[72] the fluorine resonances lie in the regions: bridgehead fluorine (184-219 p.p.m. w.r.t. $CFCl_3$)(35 examples); $-CF_2-CF_2-$group (115-137 p.p.m.) (35); vinylic fluorine: -CF=CF- (150-163 p.p.m.) (17), -CF=CH- (119-124 p.p.m.) (4), -CF=CMe- (133.6) (1), -CF=C(OMe)- (160.7 p.p.m.) (1); >C=CFH (126-131.3 p.p.m.)(3); CF_3 (53.5-69.5 p.p.m.) (10). Although the $-CF_2-CF_2-$ region overlaps the vinylic fluorine regions, the integrated intensities of the observed signals generally enable the resonances to be assigned with confidence. The $-CF_2-CF_2-$ group in these molecules normally gives a very complex pattern as expected for such a AA'BB' system further coupled to other nuclei. However in certain asymmetrically substituted derivatives the environment of the two $-CF_2-$ groups appears to be sufficiently different for one of the difluoromethylene group resonances to approximate to an AB quartet, and in all such cases the geminal coupling constant, J_{AB}, is in the range 220-234 Hz (8 examples).

TABLE 2.4

Spectral Parameters for 2,3-disubstituted-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-enes



			^{19}F n.m.r.			^{1}H n.m.r. τ			i.r.
Compound	X	Y	$-CF_2-CF_2-$	$=CF-$	>-F	$-CH_2-CH_2-$	CH_3/OCH_3	$=CH-$	ν(C=C) cm^{-1}
(II)	CH_3	CH_3	132.2(4)	-	195.0(2)	7.89 (4)	8.14(6) (CH_3)	-	-
(V)	CH_3O	CH_3O	129.1(4)	-	196.8(2)	8.08 (4)	6.25(6) (OCH_3)	-	1695
(X)	CH_3O	F	128.2(2) 129.0(2)	160.7(1)	196.3(1) 199.5(1)	7.90 (4)	6.00(3) (OCH_3)	-	1718
(XVIII)^{abc}	F	F	129.2(4)	152.4(2)	200.7(2)	7.80 (4)	-	-	1751

contd./

TABLE 2.4 contd.

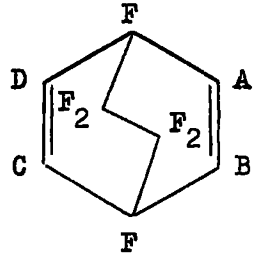
			^{19}F n.m.r.			^{1}H n.m.r. τ			i.r.
Compound	X	Y	$-CF_2-CF_2-$	$=CF-$	$\succ$F	$-CH_2-CH_2-$	CH_3/OCH_3	$=CH-$	ν(C=C) cm^{-1}
(XXVII)^a	H	F	126.7(1)^d 130.4(1)^d 126.4(2)	119.5(1)	184.9(1) 200.9(1)	8.00 (4)	-	4.50(1)	1686
(XXXVII)^a	H	H	127.1(4)^e	-	187.6(2)	8.00 (4)	-	3.75(2)	1623
(122)^{10}	CH_3	F	128.0(2)^f 129.7(2)^f	133.6(1)	191.8(1) 201.3(1)	7.82 (4)	8.02(3) (CH_3)	-	1715

NOTES: ^{1}H and ^{19}F chemical shifts are in p.p.m. from external Me_4Si and external $CFCl_3$ unless otherwise stated.

a, solution in CCl_4; b, internal Me_4Si as reference; c, internal $CFCl_3$ as reference; d, AB quartet $\delta_A = 126.7$, $\delta_B = 130.4$, $J_{AB} = 220$ Hz; e, centre of apparent AB quartet pattern, $J_{AB} = 230$ Hz; f, AB quartets.[10]

TABLE 2.5

Spectral Parameters for 2,3,5,6-tetrasubstituted-hexafluorobicyclo[2,2,2]octa-2,5-dienes



	Substituents				^{19}F n.m.r.				^{1}H n.m.r. (τ scale)			I.R.
Compound	A	B	C	D	$-CF_2-CF_2-$	$=CF-$	F	CF_3	$-CH=CH-$	$-CH=CX-$	CH_3	ν(C=C) cm^{-1}
(XXV)^c	CH_3 H	H CH_3	H H	F F	d	d	198.4(1) 214.2(1) 201.7(1) 210.3(1)			4.2(2) (X = F,CH_3)	8.15 (3)	1625 (CH=CMe) 1690 (CH=CF)
(XXVI)^c	CH_3	CH_3	H	F	121.1(2) 125.8(2)	124.3(1)	199.1(1) 211.0(1)	-	-	4.52(1) (X = F)	8.29(6)	1669 (CMe=CMe) 1700 (CH=CF)

contd./

TABLE 2.5 contd.

Compound	Substituents				^{19}F n.m.r.				^{1}H n.m.r. (τ scale)			I.R.
	A	B	C	D	$-CF_2-CF_2-$	=CF-	F	CF_3	-CH=CH-	-CH=CX-	CH_3	ν(C=C) cm^{-1}
(XXXI)^{b}	CF_3	H	H	H	115.8(2) 120.4(2)	-	194.5(1) 201.5(1)	60.9(3)	3.21(2)	2.81(1)	-	1612 (CH=CH) 1677 ($C(CF_3)=CH$)
(XXXII)^{b}	CF_3	CF_3	H	H	118.7(4)	-	196.7(2)	54.3(6)	3.20(2)	-	-	1631 (CH=CH) 1684 ($C(CF_3)=C(CF_3)$)
(XXXIII)^{b}	CH_3	CF_3	H	H	117.3(4)	-	195.9(1) 199.7(1)	55.3(3)	3.25(2)	-	7.62(3)	1629 (CH=CH) 1692 ($C(CF_3)=CMe$)
(XXXIV)^{b}	CH_3	H	H	H	117.1(4)	-	193.5(1) 197.9(1)	-	3.37(2)	3.74(1) ($X=CH_3$)	7.87(3)	1610 (CH=CH) 1667 (CH=CMe)
(XXXV)^{a,b}	CH_3	CH_3	H	H	118.1(4)	-	196.7(2)	-	3.20(2)	-	-	-

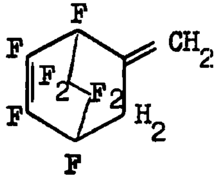
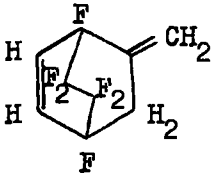
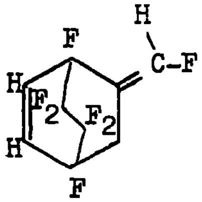
TABLE 2.5 contd.

NOTE: Chemical shifts are given in p.p.m. relative to $CFCl_3$ and Me_4Si as external references unless otherwise stated. Integrated intensities in parentheses.

a, measured relative to internal Me_4Si; b, measured relative to internal C_6F_6 and converted into δ_{CFCl_3} shifts by using the relation, $\delta(CFCl_3) = \delta(C_6F_6) + 162.3$ p.p.m.; c, measured relative to internal $CFCl_3$; d, in the range 121·4–126·2, total intensity (5).

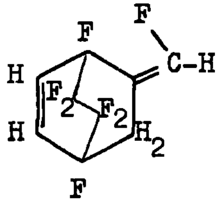
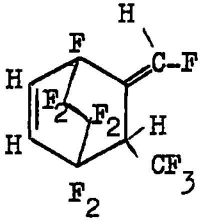
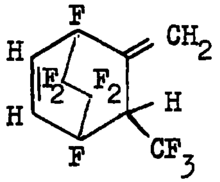
TABLE 2.6

Spectral Parameters for polyfluoro-5-methylenebicyclo[2.2.2]oct-2-enes

		^{19}F n.m.r.				^{1}H n.m.r. (τ scale)					I.R.
Number	Compound	$-CF_2-CF_2-$	$\succ$F	C=CHF	$-CF_3$	-CH=CH-	CH_2	$C=CH_2$	C=CHF	$-CH(CF_3)$	ν(C=C) cm^{-1}
(XIII)^{a,b}		127.8(4)	204.4(1) 209.0(1)	-	-	-	7.08(2)	4.30(1) 4.57(1)	-	-	1767 (CF=CF) 1669 ($C=CH_2$)
(XXX)^{f}		125.0(1) 129.7(1) 127.0(2)	190.9(1) 198.2(1)	-	-	4.02(2)	7.47(2)	4.75(1) 5.02(1)	-	-	1669 $C=CH_2$
(XXIII)^{a}		125.6(1) 129.2(1) 127.8(2)	191.7(1) 200.7(1)	131.3(1)^{c}	-	4.52(2)	7.96(2)	-	3.94(1)^{c}	-	1712 C=CFH

contd./

TABLE 2.6 contd.

		^{19}F n.m.r.				^{1}H n.m.r. (τ scale)					I.R.
Number	Compound	$-CF_2-CF_2-$	≻F	C=CHF	$-CF_3$	-CH=CH-	CH_2	$C=CH_2$	C=CHF	$-CH(CF_3)$	ν(C=C) cm^{-1}
(XXIV)		124.6(1) 128.8(1) 126.9(2)	190.8(1) 198.8(1)	127.9(1)^{d}	-	3.99(2)	7.65(2)	-	3.64(1)^{d}		1631 (CH=CH) 1712 C=CFH
(XXVIII)^{b}		120.0(2) 126.8(2)	191.1(1) 199.1(1)	ca.126(1)^{e}	59.9(3)	3.35(2)	-	-	3.05(1)^{e}	6.32(1)	1692 C=CHF
(XXIX)		120.7(1) 123.1(1) 128.0(2)	192.5(1) 197.6(1)	-	61.3(3)	3.88(2)	-	4.34(2)	-	6.60(1)	- -

NOTE Chemical shifts are in p.p.m. relative to external $CFCl_3$ and external Me_4Si unless otherwise stated. Integrated intensities are given in parentheses. a, measured relative to internal Me_4Si; b, measured relative to internal $CFCl_3$; c, J(GEM.HF) = 80 Hz; d, J(GEM.HF) = 79 Hz; e, J(GEM.HF) = 83 Hz.; f, vinylic resonance positions at 152·0 p.p.m. and 154·0 p.p.m. (each 1F).

(b) Infrared C=C stretching frequencies

The stretching frequencies of -CX=CY- double bonds in these polyfluorobicyclo[2,2,2] systems are characteristic of X and Y and lie in the following regions: -CH=CH- (1610-1631 cm^{-1}, weak or not observed) (six examples); -CH=CF- (1686-1700 cm^{-1}, medium strong) (6); -CF=CF- (1751-1772 cm^{-1}, strong) (17); -CF=C(OMe)- (1718 cm^{-1}, medium strong) (1); -C(OMe)=C(OMe)- (1695 cm^{-1}, medium) (1); >C=CH_2 (1669 cm^{-1}, weak) (1); >C=CHF (1692-1712 cm^{-1}, strong) (3).

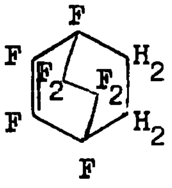
(c) Mass Spectra

The mass spectra of the new compounds in Tables 2.4, 2.5, and 2.6 are summarised in Appendix B, sections c, d and e respectively and discussed further in the text where relevant. In general the compounds shown an abundant parent peak and breakdown pattern consistent with the proposed structure.

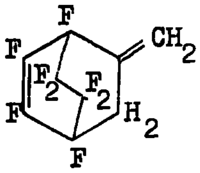
The polyfluorobicyclo[2,2,2]oct-2-enes of Table 2.4, each show a large peak for loss of C_2F_4 in their mass spectra, whilst the peak corresponding to loss of C_2H_4 is generally much smaller. The polyfluorobicyclo[2,2,2]octa-2,5-dienes of Table 2.5 all have the base peak of the mass spectrum corresponding to loss of C_2F_4 from the molecular ion, as also observed for related adducts of perfluorocyclohexa-1,3-diene.[68,72] The mass spectra of the compounds in Table 2.6 are discussed at the appropriate point in the text.

2.8 Diels-Alder Reactions of perfluorocyclohexa-1,3-diene with ethylene and allene

Perfluorocyclohexa-1,3-diene (XIX) reacts with ethylene at 200° and with allene at 190° to give the Diels-Alder Adducts (XVIII) and (XIII) respectively in yields estimated by analytical g.l.c. of over 90%.



(XVIII)



(XIII)

After separation adduct (XVIII) was obtained pure in 80% yield and adduct (XIII) in 57% yield, the latter yield reflecting losses during gas chromatographic separation.

The symmetrical nature of the ethylene adduct (XVIII) is reflected in its ^{19}F n.m.r. spectrum (Table 2.4) which shows only single resonances in the bridgehead and vinylic regions. Thus the alternative unsymmetircal adduct structure arising by 1,2-addition of ethylene to the diene is ruled out. The nucleophilic replacement reactions of adduct (XVIII) are discussed in Chapter 3 and its pyrolytic breakdown in Chapter 4.

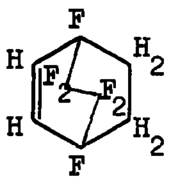
The structure of the allene adduct (XIII) is fully established by its ^{1}H and ^{19}F n.m.r. spectra by comparison with other polyfluoro-5-methylenebicyclo [2,2,2]oct-2-enes (Table 2.6), in particular adduct (XXX), whose structure unequivocally arises by 1,4 addition of allene to 2H,3H-hexafluorocyclohexa-1,3-diene (see section 2.9a). The mass spectrum of adduct (XIII) (Appendix B) shows an abundant parent peak (30%) and the base peak corresponds to loss of C_2F_4 from the molecular ion. The loss of H from the base peak gives a strong peak (61%) at m/e 163 ($C_7F_5H_2$), presumably a stable benzyl-tropylium ion. Thus in its reactions with ethylene and allene, perfluorocyclohexa-1,3-diene closely resembles the electron-poor diene hexachlorocyclopentadiene.

2.9 Diels-Alder reactions of 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII)

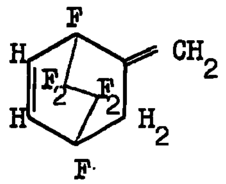
2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII) is a volatile liquid and appears to be stable indefinitely when stored in the dark at room temperature.

(a) Reaction with ethylene and allene

2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII) appears to be of similar reactivity to perfluorocyclohexa-1,3-diene (XIX) and reacts as an electron-poor diene to give with ethylene at 200° and allene at 196° good yields of the Diels-Alder adducts (XXXVII) and (XXX). Adduct (XXXVII) was obtained in 91% (pure) yield and adduct (XXX) in 49.5% yield after separation, however



(XXXVII)



(XXX)

consumption of allene and absence of involatile products suggested that the reaction with allene proceeded to the extent of about 90%. The structures of the adducts are fully substantiated by their ^{1}H and ^{19}F n.m.r. spectra (Tables 2.4 and 2.6). (Structures arising from 1,2 addition to 2H,3H-hexafluorocyclohexa-1,3-diene are readily discounted since such structures would contain the -CH=CF- group which would display a strong infrared absorbtion in the region 1680-1700 cm^{-1}, which is not observed). The mass spectra of adduct (XXX) (Appendix B) shows an abundant parent peak (27%), the base peak occurs at m/e 128 corresponding to loss of C_2F_4 from the molecular ion, and loss of hydrogen (H) from the base peak gives a strong peak at m/e 127 (80%).

(b) Reaction with alkynes

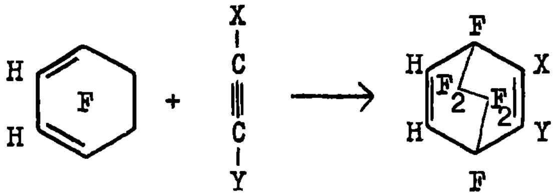
Five alkynes (X-C≡C-Y) reacted with 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII) in sealed pyrex ampoules at ca.200° to give adducts (XXXI)-(XXXV) respectively, as shown in Table 2.7 (yields quoted are after purification).

The adducts were characterised by analysis, spectroscopy and in the case of (XXXIV) and (XXXV) by pyrolysis and alternative synthesis (see Chapters 3 and 4). Elemental analysis and mass spectrometry confirmed the molecular formulae of the adducts (Appendix B), and i.r., ^{19}F and ^{1}H n.m.r. spectroscopy confirmed the assigned bicyclo[2,2,2]octa-2,5-diene structures (Table 2.5).

The yields of 1:1 adducts from these reactions were low in certain cases, when compared to those obtained from the analogous reactions of perfluorocyclohexa-1,3-diene (see Table 2.2), since the primary adducts are themselves sufficiently dienophilic to compete with the alkyne for the remaining diene.

TABLE 2.7

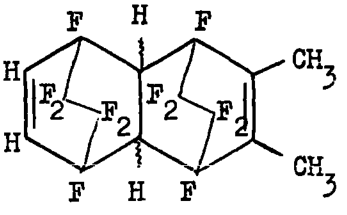
1:1 Adducts of 2H,3H-hexafluorocyclohexa-1,3-diene with alkynes



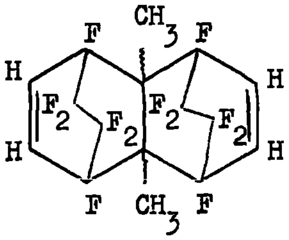
Alkyne (X-C≡C-Y)	X	Y	1:1 Adduct	Yield
(i)	CF_3	H	(XXXI)	75%
(ii)	CF_3	CF_3	(XXXII)	31%
(iii)	CF_3	CH_3	(XXXIII)	37%
(iv)	CH_3	H	(XXXIV)	58%
(v)	CH_3	CH_3	(XXXV)	30%

Consequently the products contained, in addition to the expected 1:1 adduct, less volatile polyaddition products. Only in one reaction (with but-2-yne) were the polyaddition products investigated.

In the reaction between but-2-yne and 2H,3H-hexafluorocyclohexa-1,3-diene a 1:1 molar ratio of reactants was used and an appreciable proportion of the 2:1 adduct (XXXVI) was formed. At 200° this adduct was formed in 41.3% yield. Elemental analysis and mass spectroscopy established that different samples of



(XXXVI)



(124)

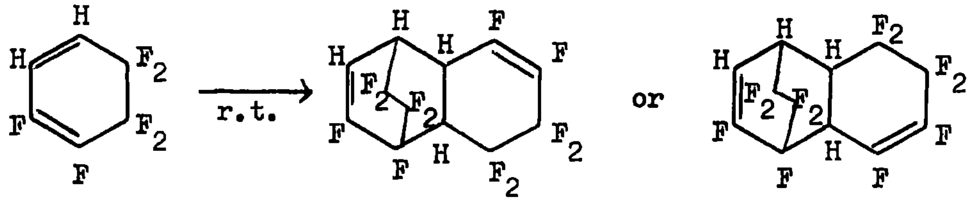
the products obtained by sublimation and recrystallisation, although differing in their melting points and the relative intensities of bands in their i.r. spectra, were all adducts of two molecules of diene (XXXVIII) with one molecule of but-2-yne. The ^{1}H n.m.r. spectrum ($CDCl_3$) showed five resonances which could not be rationalised when they were separately integrated; however the total integrated area of the resonances in the vinylic region (4.07τ and 4.37τ) and those for hydrogen attached to saturated carbon atoms (6.87 , 7.43 , 8.47τ) were in the ratio 1:4, consistent with a mixture of stereoisomers of (XXXVI) and excluding the alternative structures (124) which require a ratio of 2:3.

In the reaction of diene (XXXVIII) with the other alkynes an excess of alkyne over diene was used in an attempt to decrease the amounts of the 2:1 adducts. Of the alkynes studied 3,3,3-trifluoropropyne appeared to be the most reactive, since the yield of 1:1 adduct was high and very little less volatile material was produced.

The dienophilicity of the -CH=CH- electron-poor double bond in adduct (XXXV) towards the electron-poor diene, 2H,3H-hexafluorocyclohexa-1,3-diene at 200° is surprisingly high; it appears to be attributable to the effect of ring strain since 1H,2H-octafluorocyclohexene and 1H,2H-hexafluorocyclopentene require[8] a temperature of 330° for reaction to give Diels-Alder adducts with perfluorocyclohexa-1,3-diene in yields of ca.20% and ca.60%. (The effect of ring-strain upon dienophilicity of C=C bonds is discussed further in Chapter 7.

2.10 Diels-Alder Reactions with 1H,2H-hexafluorocyclohexa-1,3-diene

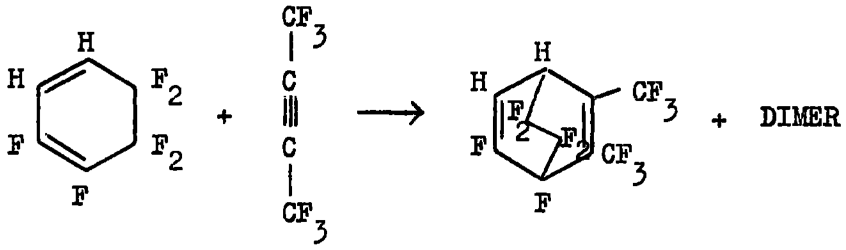
In contrast to perfluorocyclohexa-1,3-diene and 2H,3H-hexafluorocyclohexa-1,3-diene, 1H,2H-hexafluorocyclohexa-1,3-diene (XXXXIII) undergoes slow dimerisation at room temperature giving 1H,2H,7H,10H-dodecafluorotricyclo $[6,2,2,0^{2,7}]$dodeca-3,9-diene (XXXXIVa) or its -5,9-diene isomer (XXXXIVb). A sample stored at room temperature for three months was found to have dimerised to the extent of ca.66%. The product dimer appeared to be a single component and was separated by gas chromatography giving a white solid. Elemental analysis



(XXXXIII) (XXXXIVa) (XXXXIVb)

and mass spectroscopy established the molecular formula $C_{12}H_4F_{12}$ and suggested a Diels-Alder dimer since the base peak (m/e 188, $C_6H_2F_6^+$) presumably arises from a retero-diene reaction of the parent ion. Many structures can be postulated for dimers of (XXXXIII), however the observation of two strong absorbtions in the i.r. spectrum at 1742 and 1686 cm^{-1} characteristic of -CF=CF- and -CH=CF- substituted double bonds established that the adduct arises from a 1,4-cycloaddition with the C-1,C-2 double bond of (XXXXIII) acting as dienophile, since none of the alternative modes of dimerisation give this combination of substituted double bonds in the product. Thus the structure of the dimer must be either (XXXXIVa or b). The ^{1}H n.m.r. spectrum supports this assignment since the vinylic proton (a multiplet at 4.5τ) and aliphatic protons (a complex band centred at 6.62τ) occur in the integrated intensity ratio 1:3. The ^{19}F n.m.r. spectrum was too complex for complete interpretation but supported the structural assignment showing one bridgehead fluorine at 203.4 p.p.m., one distinct vinylic fluorine at 146.1 p.p.m., and a complex set of resonances in the range 89.0 —— 131.7 p.p.m. integrating for ten fluorines from which one AB quartet (δ_A 113.0, δ_B 118.4 p.p.m., J_{AB} 230 Hz, integrating for two fluorines) could be picked out which had a J_{AB} value typical of a difluoromethylene in a perfluorodimethylene bridge of a bicyclo[2,2,2] system, (see section 2.1a). The dimer obtained appeared to be a pure single compound, from the symmetry of the peak on analytical gas chromatography and the single symmetrical bridgehead fluorine resonance in the ^{19}F n.m.r. spectrum. However it was not possible to distinguish between structures XXXXIVa or b or to ascertain whethet the dimer had endo- or exo-stereochemistry, from the available data. However endo- addition is to be expected since in the dimerisation of perfluorocyclohexa-1,3-diene at 400° the endo-dimer predominates over the exo- by a ratio of 9:1;[68] 1H-heptafluorocyclohexa-1,3-diene is reported to give endo adducts with methyl acrylate;[76] and the adduct of perfluorocyclohexa-1,3-diene with N-allyltrifluoroacetamide is predominantly or even exclusively endo.[71]

(a) With hexafluorobut-2-yne and 1H,2H-hexafluorocyclohexa-1,3-diene at 200° the major product was diene dimer (XXXXIV), however the Diels-Alder adduct (XXXXII) was obtained in 26% yield after purification.



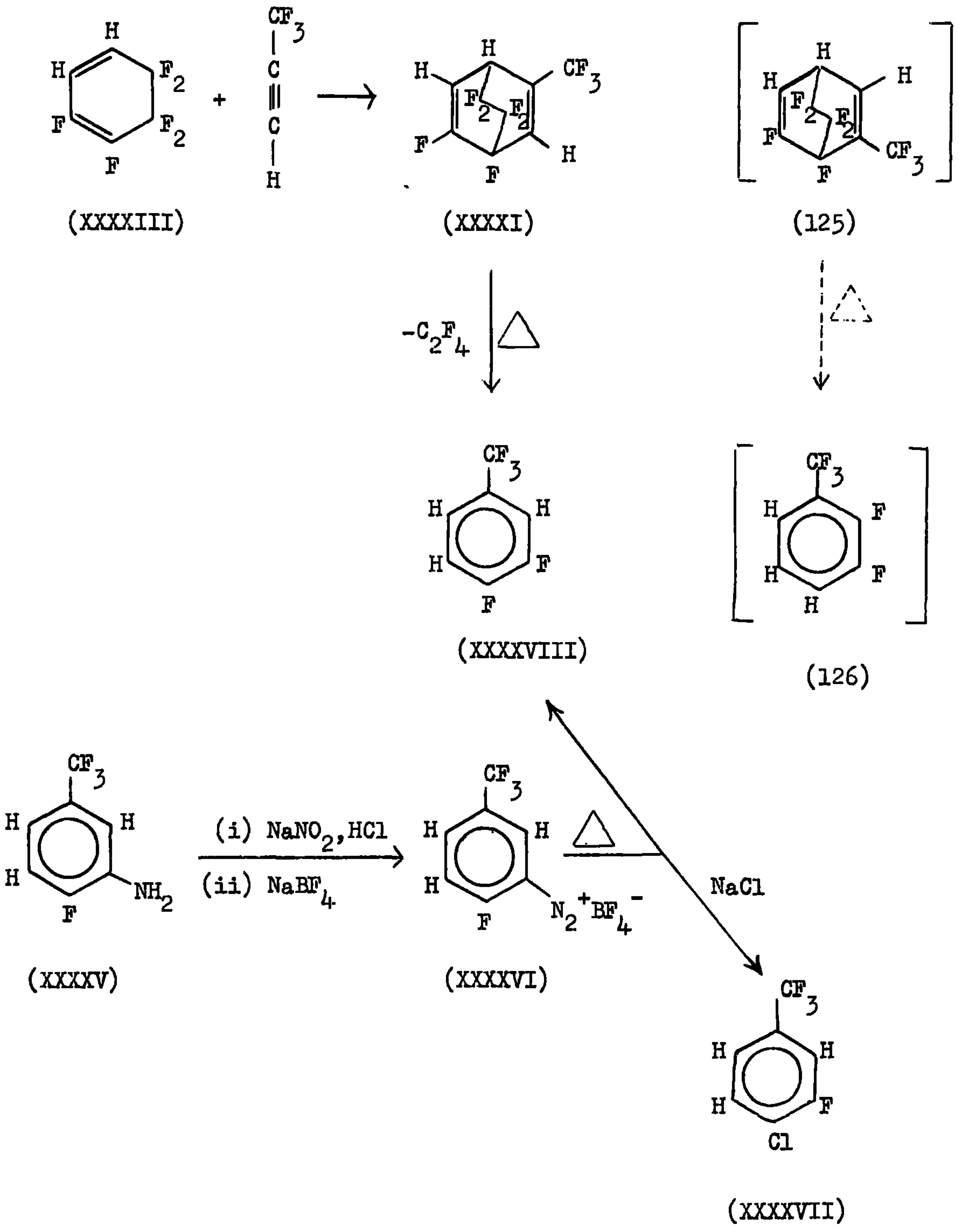
(XXXXIII) (XXXXII)

Analysis and mass spectrometry established the molecular formula, and the mass spectrum showed the typical elimination of the perfluorodimethylene bridge from the parent ion to generate the base peak. The i.r. spectrum indicated the expected double bonds, -CH=CF- (1703 cm^{-1}) and -C(CF$_3$)=C(CF$_3$)- (1676 cm^{-1}); and n.m.r. spectroscopy confirmed the assignment of structure showing one bridgehead fluorine (214.2 p.p.m., 1F), one vinylic fluorine (123.6 p.p.m., 1F), and AB quartet (δ_A 108.2, δ_B 111.3 p.p.m., J_{AB} 234 Hz, 2F) and two multiplets (124.8 and 125.4 p.p.m., each 1F) for the bridging difluoromethylenes, an unsymmetrical signal at 62.1 p.p.m. for the non-equivalent trifluoromethyls (6F), and two proton resonances (5.87τ and 4.43τ) of equal intensity ($>$CH and -CH= respectively). These parameters are in good agreement with those in the related systems recorded in Tables 2.4 and 2.5.

(b) With 3,3,3-trifluoropropyne and 1H,2H-hexafluorocyclohexa-1,3-diene at 200° a mixture of dimer and a single 1:1 adduct was obtained. In this case the lack of symmetry in both diene and dienophile allows two possible 1:1 adduct structures to be drawn. It was not possible to distinguish the two possible adducts on the basis of the i.r. spectrum which showed the expected double bond absorbtions at 1686 cm^{-1} (-CH=CF-) and 1665 ($-CH=C(CF_3)-$), or the n.m.r. spectra which showed a single bridgehead fluorine at 210.3 p.p.m., a resonance at 69.5 p.p.m. for the trifluoromethyl group, and a complex series of resonances between 108.1 and 123.5 p.p.m. integrating for the five remaining fluorine atoms; the ^1H spectrum indicated one tertiary and two vinylic hydrogens with resonances at 6.22, 4.43 and 3.23τ of equal intensity. Although the single symmetrical resonances for the bridgehead fluorine and the trifluoromethyl group indicated that only one of the two possible adducts had been formed, it was not possible on the basis of the spectroscopic data to assign the structure unambiguously.

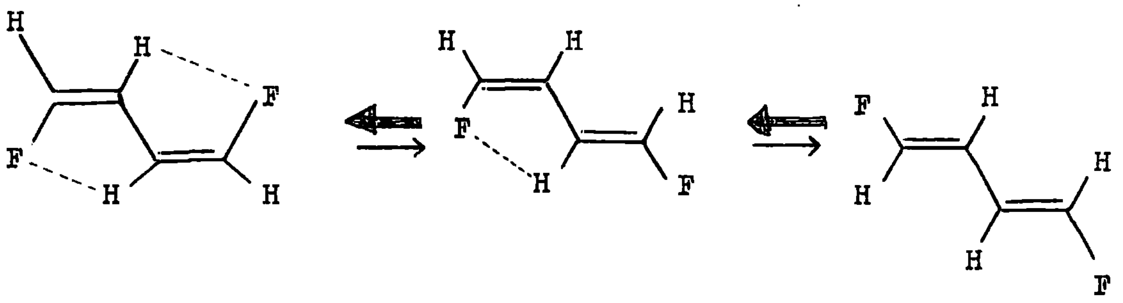
The adduct was shown to be (XXXXI) rather than (125) by pyrolysis of the adduct to give the aromatic (XXXXVIII) whose structure was proved by alternative synthesis as shown in the figure. Pyrolysis[14] of the adduct gave exclusively and in good yield 3,4-difluorobenzotrifluoride (XXXXVIII) with an identical i.r. to the aromatic prepared unambiguously by the Schiemann synthesis from amine (XXXXV).

A minor co-product obtained in the Schiemann synthesis was shown by elemental analysis and spectroscopy to be a monochloromonofluorobenzotrifluoride, which was assigned as 4-chloro-3-fluorobenzotrifluoride (XXXXVII) since it has been established by Finger[77] that, where the Schiemann reaction is applied to compounds having fluorine ortho to the amine function, it is the presence of coprecipitated sodium chloride in the derived diazonium fluoroborate which gives rise to the formation of chloro compounds during the pyrolysis stage by replacement of the fluorine ortho to the diazo group;



and replacement of the diazo group itself by chloride is a very minor reaction.

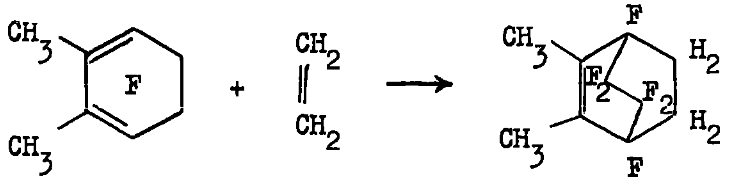
No satisfactory basis exists for explanation of the generally found predominance of one of the isomeric adducts formed in the 1,4-cycloaddition reactions of unsymmetrically substituted dienes and dienophiles.[31] In this case a rationalisation of the observed result can be made on the basis of a preferred orientation of diene and dienophile prior to reaction. Such an effect can be accounted for in terms of best steric approach and/or a favourable interaction of the fluorine atoms of the trifluoromethyl group with the hydrogens at C-1 and C-2 in the diene and of the alkyne hydrogen with the fluorine atoms at C-3 and C-4 in the diene. An interaction of this type has been postulated by Viehe to account for the predominance of cis over trans isomers in equilibrated mixtures of 1-fluoro- and 1,4-difluorobuta-1,3-dienes.[78] Thus equilibration of 1,4 difluorobutadienes with 1% iodine at 100° shows that cis-isomers are invariably more stable than trans isomers and this unusual behaviour is ascribed to maximisation of H...F interactions:



2.11 Diels-Alder addition of ethylene to other highly fluorinated cyclohexa-1,3-dienes

(a) Reaction of 2,3-dimethylhexafluorocyclohexa-1,3-diene(III) with ethylene

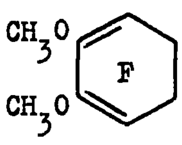
At 216° the expected adduct (II) was formed in 59% yield after purification, which was identified by its i.r. spectrum, (see Chapter 3 for the characterisation of adduct (II)).



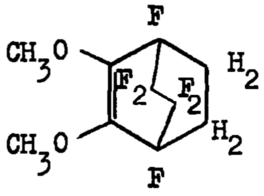
(III) (II)

(b) Attempted reaction of 2,3-dimethoxyhexafluorocyclohexa-1,3-diene (VI) with ethylene

The thermal instability of this diene precludes its use in the Diels-Alder reaction. When diene (VI) was heated with a fivefold excess of ethylene in a sealed pyrex ampoule at 200° for 63 hr. much silicon tetrafluoride was produced and the tube was badly etched. Ethylene was recovered unchanged and only a small amount of volatile liquid material was obtained, which consisted of at least eleven components, not including the expected product (V). The adduct (V) synthesised by a nucleophilic substitution reaction (see Chapter 3)



(VI)



(V)

appears to be stable. Thus the failure of diene (VI) to react with ethylene must be a consequence of its thermal instability. Indeed decomposition of the liquid diene (VI) occurs even at room temperature over a few days, especially on exposure to moisture. (See Chapter 5 for further discussion of the instability of this diene).

CHAPTER 2

EXPERIMENTAL

2.12 Reagents

Perfluorocyclohexa-1,3-diene, 3,3,3-trifluoropropyne, 1,1,1-trifluorobut-2-yne were prepared as detailed in reference 72. 2H,3H- and 1H,2H-hexafluorocyclohexa-1,3-dienes were prepared by the published route (see Chapter 1) and purified by gas chromatography. Reagents were dried (P_2O_5) and degassed before being inserted *in vacuo* in a Pyrex ampoule (Carius Tube) or an autoclave; 3-amino-4-fluorobenzotrifluoride was purchased from Peninsular Chemresearch Inc.

2.13 Reactions of Perfluorocyclohexa-1,3-diene (XIX)

(a) With ethylene. A mixture of perfluorocyclohexa-1,3-diene (56.9 g., 254 mmoles) and ethylene (6.7 g., 226 mmoles) was sealed under vacuum in a 100 ml. stainless steel autoclave fitted with a pressure gauge. The autoclave was rocked and heated to 200° (1.5 hrs.) and maintained at that temperature for a further 3 hrs. After the autoclave had cooled to room temperature the volatile materials (mainly perfluorocyclohexa-1,3-diene) were removed by vacuum transfer and the major product, a waxy solid, was dissolved in dry ether. Evaporation of the solvent and bulb to bulb vacuum transfer from P_2O_5 gave 1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]oct-2-ene (XVIII) (45.3 g., 180 mmoles, 80%) [Found: C,38.3; H,1.8; F,60.7%; M (mass spectrometry), 252. $C_8H_4F_8$ requires C,38.1; H,1.6; F,60.3%; M, 252], m.p. 98-99° (sealed tube), ν_{max} 1751 cm^{-1} (-CF=CF-). Small scale reactions using sealed Pyrex ampoules gave (XVIII) in yields >90%.

(b) With allene. A mixture of perfluorocyclohexa-1,3-diene (10.58 g., 47.1 mmoles) and allene (1.27 g., 50.5 mmoles) was sealed *in vacuo* in a 150 ml. Pyrex ampoule which was heated at 190° for 14 hrs. to give: (i) a gaseous fraction (12.4 mmoles), whose i.r. spectrum was consistent with a mixture of perfluorocyclohexa-1,3-diene and allene; (ii) a liquid mixture (10.9 g.), separated by gas chromatography (Column B/120°) to give 2-methylene-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]oct-5-ene (XIII) (7.08 g., 26.8 mmoles, 57%)

[Found: C,41.0; H,1.6; F,57.9%; M (mass spectrometry), 264. $C_9H_4F_8$ requires C,40.9; H,1.5; F, 57.6%; M,264], b.p. 147°, ν_{max} 1767 cm^{-1} (-CF=CF-) and 1669 cm^{-1} (C=CH_2); (iii) a viscous yellow liquid (0.533 g.).

2.14 Reactions of 2H,3H-hexafluorocyclohexa-1,3-dienes

(a) With ethylene. 2H,3H-Hexafluorocyclohexa-1,3-diene (2.17 g., 11.5 mmoles) and ethylene (0.435 g., 12.1 mmoles) were heated at 200° for 14.5 hrs. in a 135 ml. Pyrex ampoule, which had been sealed *in vacuo*. The products were separated by conventional vacuum line techniques to give: (i) trace amounts of unreacted starting materials; (ii) 1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (XXXVII) (2.26 g., 10.5 mmoles, 91%) [Found: C,44.2; H,2.8; F,53.1%; M (mass spectrometry) 216. $C_8H_6F_6$ requires C,44.45; H,2.8; F,52.75%; M,216], m.p. 145-6° (sealed tube), ν_{max} 1623 cm^{-1} (-CH=CH-).

(b) With allene. Using the same procedure as in (a), 2H,3H-hexafluorocyclohexa-1,3-diene (1.57 g., 8.86 mmoles) and allene (0.183 g., 9.75 mmoles) were heated in a 30 ml. Pyrex ampoule at 196° for 47.5 hrs. to give: (i) a gaseous fraction (1.73 mmoles) of allene and 2H,3H-hexafluorocyclohexa-1,3-diene; (ii) a liquid mixture (0.44 g.), shown by analytical gas chromatography to consist of 2H,3H-hexafluorocyclohexa-1,3-diene and 2-methylene-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXX); (iii) 2-methylene-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXX) (1.0 g., 4.4 mmoles, 49.5%) [Found: C,47.6; H,2.5; F,50.5%; M (mass spectrometry), 228. $C_9H_6F_6$ requires C,47.4; H,2.6; F,50.0%; M, 228], b.p. 164°, ν_{max} 1669 cm^{-1} (>C=CH_2).

(c) With but-2-yne. Using the same procedure as in (a), 2H,3H-hexafluorocyclohexa-1,3-diene (2.0 g., 10.6 mmoles) and but-2-yne (0.574 g., 10.7 mmoles) were heated in a 30 ml. Pyrex ampoule at 200° for 22.5 hrs. to give: (i) but-2-yne; (ii) 2,3-dimethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXV) (0.72 g., 2.96 mmoles, 28%) [Found: C,49.3; H,3.4; F,47.5%; M (mass spectrometry), 242. $C_{10}H_8F_6$ requires C,49.6; H,3.3; F,47.1%; M, 242], b.p.

171-172°; (iii) a pale yellow solid (1.21 g.) which was sublimed (128°/10^{-3} mm.) to give white solid mixed stereoisomers of 4,5-dimethyl-1,3,6,8,11,11,12,12,13,13,14,14-dodecafluorotetracyclo[$6,2,2,2^{3,6},0^{2,7}$]tetradeca-4,9-diene (XXXVI) (0.94 g., 2.19 mmoles, 41.3% based on diene consumed) [Found: C,44.4; H,2.3%; M (mass spectrometry), 430. $C_{16}H_{10}F_{12}$ requires C,44.7; H,2.3; H,53.0%; M,430] m.r. 132-137°. Recrystallisation of (XXXVI) from petrol (80/100) gave a solid m.p. 158-159. [Found: C,44.6; H,2.3; F,52.8%]. Repetition of the experiment at 175° gave a 13.1% yield of the 2:1 adduct (XXXVI); a 30% yield of the 1:1 adduct (XXXV); and 30% of recovered diene. Samples of the 2:1 adduct (XXXVI) prepared in different experiments and recovered from recrystallisation had different melting ranges and variations in the relative intensities of some bands in their infrared spectra; they all had the same elemental analysis and mass spectrum.

(d) With propyne. Using the same procedure as in (a), 2H,3H-hexafluorocyclohexa-1,3-diene (2.42 g., 12.8 mmoles) and propyne (1.05 g., 26.2 mmoles) were heated in a 30 ml. Pyrex ampoule at 212° for 19 hrs. to give: (i) propyne (0.296 g., 9.6 mmoles); (ii) 2-methyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXIV) (1.69 g., 7.4 mmoles, 58%) [Found: C,47.2; H,2.9; F,50.5%; M (mass spectrometry), 228. $C_9H_6F_6$ requires C,47.4; H,2.7; F,50.0; M,228], b.p. 156°, ν_{max} 1667 (-(CH$_3$)C=CH-) and 1610 cm^{-1} (-CH=CH-); (iii) a brown viscous liquid (1.04 g.) which was not investigated.

(e) With hexafluorobut-2-yne. Using the same procedure as in (a), 2H,3H-hexafluorocyclohexa-1,3-diene (2.0 g., 10.6 mmoles) and hexafluorobut-2-yne (3.58 g., 22.1 mmoles) were heated in a 30 ml. Pyrex ampoule at 175° for 41 hrs. to give: (i) hexafluorobut-2-yne (2.56 g., 15.8 mmoles); (ii) a liquid mixture (2.45 g.), separated by preparative gas chromatography (Column C, 100°) to give 2H,3H-hexafluorocyclohexa-1,3-diene (0.68 g., 3.6 mmoles) and 2,3-bis-(trifluoromethyl)-1,4,7,7,8,8-hexafluorobicyclo 2,2,2 octa-2,5-diene (XXXII) (1.19 g., 3.4 mmoles, 31%) [Found: C,34.2; H,0.7; F,65.3%; M (mass spectrometry),

350. $C_{10}H_2F_{12}$ requires C,34.3; H,0.6; F,65.1%; M, 350], b.p. 150°, ν_{max} 1684 cm^{-1} [-C(CF$_3$)=C(CF$_3$)-] and 1631 cm^{-1} (-CH=CH-); (iii) solid residue (0.1 g.), not investigated.

(f) With 3,3,3-trifluoropropyne. Using the same procedure as in (a), 2H,3H-hexafluorocyclohexa-1,3-diene (2.1 g., 11.1 mmoles) and 3,3,3-trifluoropropyne (1.95 g., 20.8 mmoles) were heated in a 30 ml. Pyrex ampoule at 208° for 18 hrs. to give: (i) 3,3,3-trifluoropropyne (0.86 g., 9.1 mmoles); (ii) a liquid mixture (0.465 g.), shown by analytical gas chromatography to consist of starting materials and (XXXI); (iii) 2-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXI) (2.33 g., 8.26 mmoles, 74.5%) [Found: C,38.0; H,1.1; F,61.0%; M (mass spectrometry), 282. $C_9H_3F_9$ requires C,38.3; H,1.1; F,60.6%; M, 282], b.p. 144°, ν_{max} 1677 cm^{-1} [-C(CF$_3$)=CH-] and 1612 cm^{-1} (-CH=CH-); (iv) solid residue (0.1 g.), not investigated.

(g) With 1,1,1-trifluorobut-2-yne. Using the same procedure as in (a), 2H,3H-hexafluorocyclohexa-1,3-diene (2.0 g., 10,6 mmoles) and 1,1,1-trifluorobut-2-yne (1.55 g., 16.2 mmoles) were heated in a 30 ml. Pyrex ampoule at 210° for 14 hrs. to give: (i) 1,1,1-trifluorobut-2-yne (0.63 g., 4.1 mmoles); (ii) a liquid mixture (2.07 g.), separated by preparative gas chromatography (Column C, 100°) to give 2H,3H-hexafluorocyclohexa-1,3-diene and 2-methyl-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXIII) (1.17 g., 3.94 mmoles, 37%) [Found: C,40.8; H,1.8; F,58.0%; M (mass spectrometry), 296. $C_{10}H_5F_9$ requires C,40.5; H,1.7; F,57.7%; M, 296], b.p. 163°, ν_{max} 1692 cm^{-1} [-C(CF$_3$)=C(CH$_3$)-] and 1629 cm^{-1} (-CH=CH-), (iii) a viscous brown liquid (0.712 g.), which gave a white solid on sublimation.

2.15 Reactions of 1H,2H-hexafluorocyclohexa-1,3-diene (XXXXIII)

(a) Dimerisation. When stored at room temperature diene (XXXXIII) undergoes dimerisation, the reaction proceeding to the extent of 66% after 3 months. The product appeared as a single symmetrical peak on analytical gas chromatography and was separated (Column B, 120°) to give 1H,2H,7H,10H-dodecafluorotricyclo$[6,2,2,0^{2,7}]$dodeca-3,9 (or 5,9)-diene (XXXXIVa or b) [Found: C,38.5; H,1.1; F,61.0%; M (mass spectroscopy), 376. $C_{12}H_4F_{12}$ requires C,38.3; H,1.1; F,60.6%; M, 376] ν_{max} 1742 (-CF=CF-) and 1686 cm^{-1} (-CF=CH-).

(b) With hexafluorobut-2-yne. A mixture of diene (XXXXIII) (2.14 g., 11.4 mmoles) and hexafluorobut-2-yne (3.30 g., 20.4 mmoles) was sealed under vacuum in a Pyrex ampoule (160 ml.) which was heated at 200° for 23 hrs. to give: (i) hexafluorobut-2-yne (17.1 mmoles); (ii) a liquid mixture which was separated (Column B, 100°) to give dimer (XXXXIVa or b) (1.03 g., 2.75 mmoles, 48% and 2,3-bis(trifluoromethyl)-4,5,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXXII) (1.05 g., 3.00 mmoles, 26.3%) [Found: C,34.0; H,0.7; F,65.7; M (mass spectrometry), 350. $C_{10}H_2F_{12}$ requires C,34.3; H,0.6; F,65.1%; M, 350], ν_{max} 1703 (-CF=CH-) and 1676 (-(CF$_3$)=C(CF$_3$)-).

(c) With 3,3,3-trifluoropropyne. A mixture of diene (XXXXIII) (0.63 g., 3.15 mmoles) and 3,3,3-trifluoropropyne (1.88 g., 20 mmoles) were sealed under vacuum in a Pyrex ampoule (30 ml.) which was heated at 200° for 22 hrs. to give: (i) 3,3,3-trifluoropropyne (1.53 g., 16.2 mmoles); (ii) a liquid mixture which was separated (Column B, 100°) to give dimer (XXXXIVa or b) (ca. 0.1 g., 0.25 mmole, 16%) and 2-trifluoromethyl-4,5,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXXI) (0.40 g., 1.43 mmoles, 45%) [Found: C,38.5; H,1.1; F,60.8%; M (mass spectroscopy), 282.0086. $C_9H_3F_9$ requires C,38.3; H,1.1; F,60.6%; M, 282.0091], ν_{max} 1686 (-CF=CH-) and 1665 cm^{-1} (-CH=C(CF$_3$)-).

Pyrolysis of 2-trifluoromethyl-4,5,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXXI). Diene (XXXXI) (1.806 g., 6.40 mmole) was pyrolysed at 600°/0.001 mm to give: (i) tetrafluoroethylene (5.08 mmoles, 79%) with the correct i.r.; (ii) 3,4-difluorobenzotrifluoride (XXXXVIII) (1.11 g., 6.05 mmole), 94.5%) [Found: C,46.3; H,1.7; F,52.5%; M (mass spectrometry), 182. $C_7H_3F_5$ requires C,46.2; H,1.7; F,52.2%; M, 182], b.p. 105°, ν_{max} 1631, 1529, 1449, 1340, 917, 885, 826, 781 cm^{-1} ν_{max} (0.22 g./l. in cyclohexane) 267.0 nm (ϵ - 6.94 x 10^2), 261.5 nm (ϵ - 7.32 x 10^2), 257.5 nm (ϵ - 6.07 x 10^2), 253.5 nm

(ϵ - 4.66 x 10^2), ^{19}F n.m.r. (external $CFCl_3$) 64.5 (multiplet, $-CF_3$), 134.1 and 137.4 p.p.m. (multiplets, aromatic fluorines), ^1H n.m.r. (external T.M.S.) 3.12 (complex multiplet, aromatic protons).

Schiemann synthesis of 3,4-difluorobenzotrifluoride (XXXXVIII). A mixture of 3-amino-4-fluorobenzotrifluoride (5.0 g., 28 mmoles) in a 16.8 ml. of concentrated HCl was diazotised at 0° with a solution of sodium nitrite (2.14 g., 31 mmoles) dissolved in water (2.8 ml.). A solution of sodium fluoroborate (6.15 g., 56 mmoles) in water (7.4 ml.) was added and the precipitated diazonium fluoroborate was filtered off, washed successively with 5% $NaBF_4$ solution (10 ml.), ice-cold methanol (3 ml.) and ether (six 10 ml. portions) and dried overnight in a vacuum dessicator over P_2O_5, to give a white solid (5.57 g.) (XXXXVI). 5.09 g. of the white solid was pyrolysed to give a volatule liquid which was collected in a trap cooled in an ice-salt bath. Sodium bicarbonate (ca. 0.1 g.) and P_2O_5 (ca. 0.1 g.) were added and the product was distilled *in vacuo* to give 2.245 g. of a two-component liquid mixture which was separated by g.l.c. (column B, 120°) to give: (i) 3,4-difluorobenzotrifluoride (XXXXVIII) (1.258 g., 6.92 mmole, 27% on amine) with the correct i.r. spectrum; (ii) 4-chloro-3-fluorobenzotrifluoride (XXXXVII) (0.372 g., 1.87 mmoles, 7.4% on amine) [Found: C,42.6; H,1.7; Cl,18.1; F,37.9%; M (mass spectrometry), parent ion m/e 198, parent+2 ion indicating 1 chlorine atom. $C_7H_3ClF_4$ requires C,42.3; H,1.5; Cl,17.9; F,38.3%; M,198.55], ν_{max} 1433, 1335, 909, 885, 746 cm^{-1} ν_{max} (0.087 g./l in cyclohexane) 274.0 nm (ϵ - 302), 269.0 (s) nm (ϵ - 258), 266.5 nm (ϵ - 284), 262.0 (s) nm (ϵ - 195), ^{19}F n.m.r. 63.8 p.p.m. (multiplet, $-CF_3$, 3F), 112.5 p.p.m. (multiplet, aromatic fluorine, 1F), ^1H n.m.r. 2.63τ (multiplet, aromatic protons).

2.16 Reaction of 2,3-Dimethylhexafluorocyclohexa-1,3-diene with ethylene

2,3-Dimethylhexafluorocyclohexa-1,3-diene (III) (0.12 g., 0.58 mmoles) and ethylene (1.49 mmoles) were heated at 216° for 23 hrs. in a 76 ml. Pyrex ampoule to give 2,3-dimethyl-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (II) (0.08 g., 0.33 mmoles, 59%) with the correct i.r. spectrum, (see Chapter 4).

2.17 Attempted Reaction of 2,3-dimethoxyhexafluorocyclohexa-1,3-diene (VI) with ethylene

2,3-Dimethoxyhexafluorocyclohexa-1,3-diene (VI) (0.496 g., 2.0 mmoles) and ethylene (2.5 mmoles) were heated in a 170 ml. Pyrex ampoule at 200° for 63 hrs. On cooling the tube was observed to be blackened and etched. The contents of the tube were separated into (a) a gaseous fraction (5.36 mmoles) consisting of a mixture of SiF_4 and ethylene (by i.r.); (b) a liquid mixture (ca. 0.05 g.) which showed the presence of at least eleven components by analytical g.l.c. (Column A, 150°), including (VI). Mixed injection with an authentic sample of 2,3-dimethoxy-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (V) showed that this expected product was not present.

CHAPTER 3

REACTIONS OF DIELS-ALDER ADDUCTS OF PERFLUOROCYCLOHEXA-1,3-DIENE WITH NUCLEOPHILIC REAGENTS

INTRODUCTION

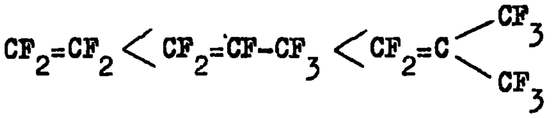
3.1 Reactions of fluoroolefins with nucleophiles[79,80]

Replacement of the hydrogen atoms in ethylene with the highly electronegative element fluorine to give tetrafluoroethylene results in contraction of the π-electron 'cloud' of the double bond and renders the system much less susceptible to attack by electrophiles. In general the ionic reactions of fluoroolefins are those involving nucleophilic attack and the number of genuine electrophilic additions to fluoroolefins appears to be quite limited.

Active nucleophiles are alkoxides, thioalkoxides, amines, alkyllithiums, Grignard reagents, fluoride ion and complex metal hydrides (e.g. lithium aluminium hydride and sodium borohydride).

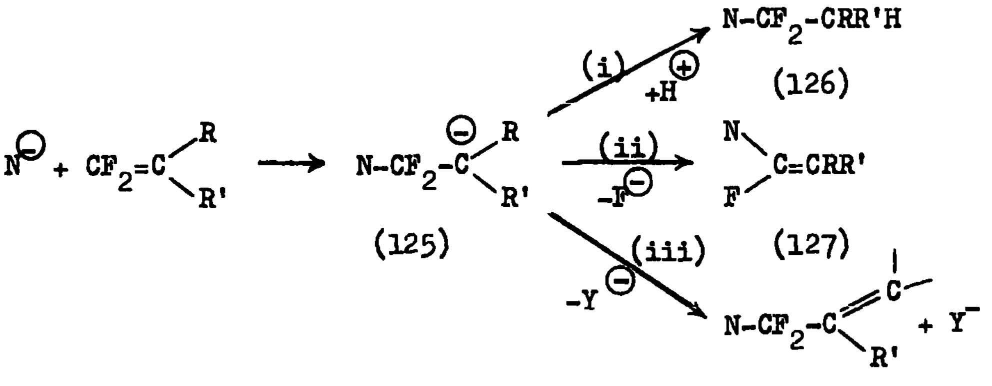
(a) Reactions of acyclic fluoroolefins

There is some difficulty in comparing reactivities of olefins unless reactions have been carried out under identical conditions. However it appears that fluoroolefins containing a terminal difluoromethylene group are particularly reactive. Reactivity towards nucleophiles increases in the series



$$CF_2{=}CF_2 < CF_2{=}CF{-}CF_3 < CF_2{=}C(CF_3)_2$$

In general if a fluoroethylene contains a difluoromethylene group nucleophilic attack occurs exclusively at the difluoromethylene carbon. The general scheme for nucleophilic attack on such fluoroolefins (where N^- is the nucleophile) is as follows:



(125) (126) (127) (128)

(Y = F,Cl,Br,I)

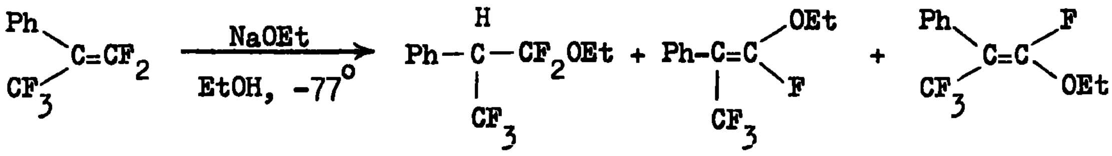
The nucleophile attacks the fluoroolefin producing the most stable carbanionic intermediate (125), which then has three reaction paths (i), (ii) and (iii) open to it. If the reaction is carried out in a protic solvent, (i) the carbanion (125) can abstract a proton to produce the adduct (126), or (ii) (in any solvent) it may lose a fluoride ion from the NCF_2- group to give the substituted olefin (127) or (iii) it may lose a halide ion ($Y^- = F^-, Cl^-, Br^-, I^-$) from another carbon atom α to the carbanion to give the rearranged olefin (128).

An illustrative example is the reaction of methanolic potassium hydroxide with perfluoropropene in an autoclave:[81]

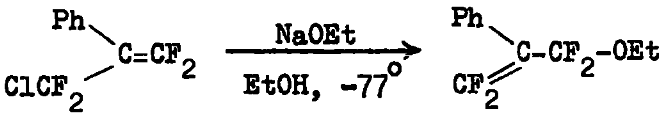
$$CF_2{=}CF{-}CF_3 \xrightarrow[60^\circ]{CH_3OH/KOH} CH_3O{-}CF_2{-}CHF{-}CF_3 \ (83\%) + CH_3O{-}CF{=}CF{-}CF_3$$

The proportions of saturated to unsaturated products depend upon the nature of the substituents, reaction conditions and solvent, but in general acyclic olefins with alcohols in the presence of base give mainly addition products.

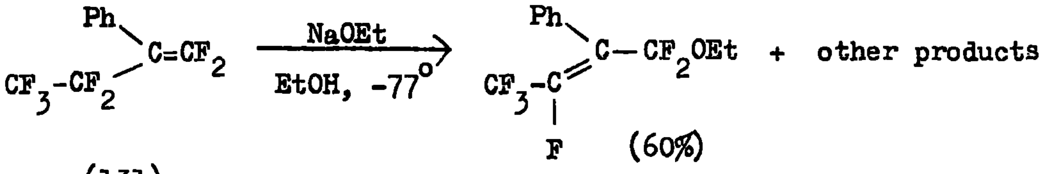
A recent kinetic study[84] has leant support for the intermediacy of a carbanion in the nucleophilic displacement of fluoroolefins. The very similar reaction rates of olefins (129), (130) and (131) with sodium ethoxide in ethanol suggested that the rate determining step in all three cases is the initial attack of ethoxide ion on the difluoromethylene group to form an intermediate carbanion, subsequent steps to products being rapid by comparison.



(129) (15%) (76%) (9%)



(130) (sole product)



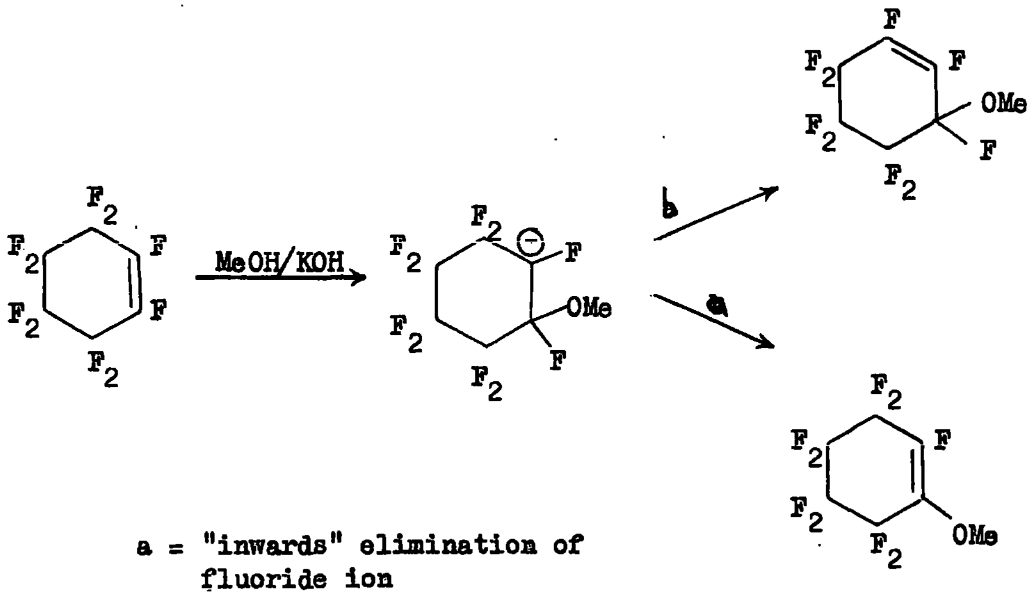
(131)

From the products produced in these reactions it is clear that loss of a β chloride is the fastest process, however loss of fluoride ion is competitive with the rate of protonating the carbanion intermediate.

(b) Reactions of cyclic fluoroolefins

It appears that virtually all the reactions of nucleophiles with polyfluorocycloalkenes under ionic conditions can be rationalised as addition of the nucleophilic species to the electron-deficient double-bond, followed by protonation of, or β-elimination of fluoride ion from, the carbanionic species produced.

The reactions of polyfluorocycloalkenes with alcohols in the presence of base have been studied extensively.[10a,83] In contrast to reactions with acyclic olefins under these conditions the major product of the reaction arises by displacement of fluoride ion rather than addition of the alcohol across the double bond, as in the following example:[83]

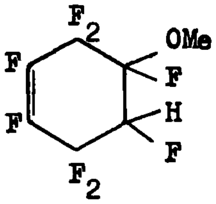


a = "inwards" elimination of fluoride ion

b = "outwards" elimination of fluoride ion

The "outwards" elimination product predominates over the "inwards" elimination product by a ratio of ca. 3:1.

Perfluorocyclohexa-1,4-diene(15) with methanolic potassium hydroxide was observed[10] to give a methanol adduct (132), of unspecified stereochemistry, as a minor product, together with (132a) as the major product.



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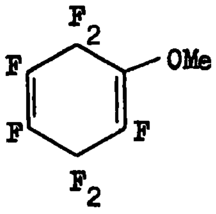
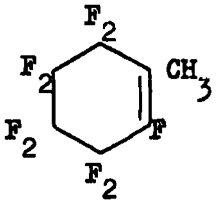


(132a)

Dehydrofluorination of (132) was sluggish but proceeded in fair yield to give (132a) on refluxing for 3 hours with aqueous potassium hydroxide.

In reactions of cyclic fluoroolefins with methyllithium and lithium aluminium hydride products of inwards rather than outwards elimination predominate. Thus perfluorocyclohexene reacts with methyllithium in ether to give[83a] the 1-methyl- and 1,2-dimethyl-cyclohexenes, (133) and (134), as the major products. In these reactions CH_3^- is the apparent nucleophile, although in solution methyl lithium is tetrameric.



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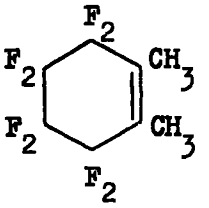
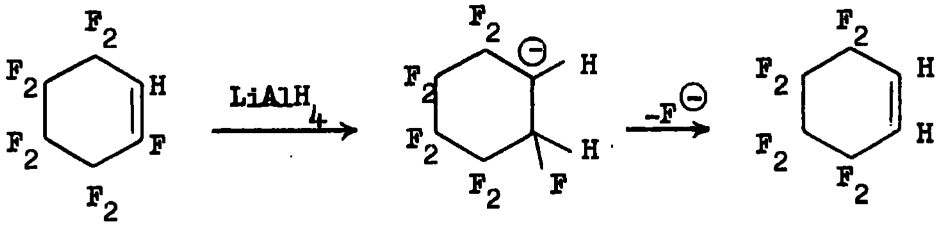


(134)

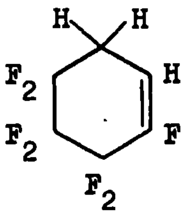
The reactions of cyclic fluoroolefins with lithium aluminium hydride have received considerable attention and have been reviewed.[80] Fluorine atoms on saturated, non-allylic carbon are in general inert to attack by lithium aluminium hydride, but fluorine atoms attached to unsaturated carbon are readily replaced by an apparent addition-elimination process with H^- as the nucleophile. When the reaction is carried out by adding the fluoroolefin to a slurry of lithium aluminium hydride in ether, the hydride is always in large excess and complex mixtures are usually formed by replacement of several fluorine atoms in several stages. As examples the reaction of perfluorocyclohexene (Section 1.1b) may be cited. Perfluorocyclopentene gives a complex mixture which has been shown[85] to contain 1H- and 3H-heptafluorocyclopentene; 1H,2H-, 1H,3H- and 2H,3H-hexafluorocyclopentene; 1H,2H,3H- and 2H,3H,3H-pentafluorocyclopentenes; and 1H,2H,3H,3H- and 2H,3H,3H,4H-tetrafluorocyclopentenes. The ratio of the products in such cases depends upon reaction time and conditions; some products only occur in trace amounts. The initial position of attack on substituted derivatives appears to be governed by the stability of the intermediate anion so formed, and the ability of substituents to stabilise the negative charge on the ionic carbon, this order being:[85] $I \sim Br > Cl > H > F$. The destabilising effect of the fluorine can be attributed to the large repulsive $I\pi$ effect[86] of the lone pair electrons on fluorine.

Thus (11) is attacked as shown to put the anion on the carbon bearing H rather than F, and elimination occurs predominantly "inwards" by loss of fluorine from the electronically favoured CHF group rather than "outwards" from the $>CF_2$ group.



(11) (31)

The reactivity of C=C double bonds to nucleophilic attack depends upon both vinylic, alpha and possibly more remote substituents. Thus olefin (32) is insufficiently activated to react with lithium aluminium hydride, although the balance of factors determining reactivity is clearly very delicate since its isomer (33) does react.



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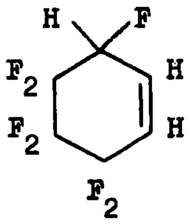
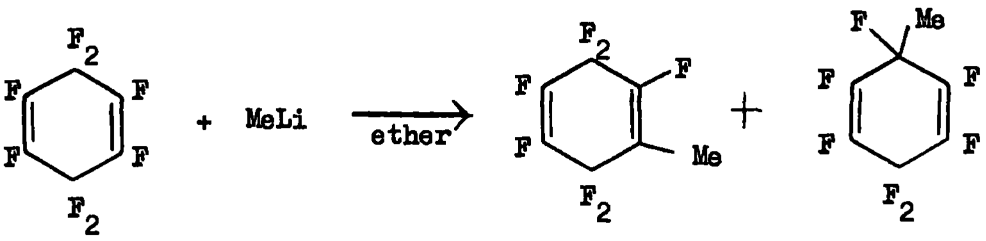


(33)

In only one case does unambiguous direct allylic substitution of fluorine appear to have been observed[10] in the reaction of perfluorocyclohexa-1,4-diene with methyllithium to produce 3-methyl-heptafluorocyclohexa-1,4-diene (136) as a minor product. The major isomer (135) was that expected from the conventional addition-elimination process.



(135) (136)

This observation may be explained by the abnormally high reactivity of the fluorine atoms in the CF_2 groups of perfluorocyclohexa-1,4-diene. With the weaker nucleophilic reagent methanolic potassium hydroxide no allylic displacement was observed.

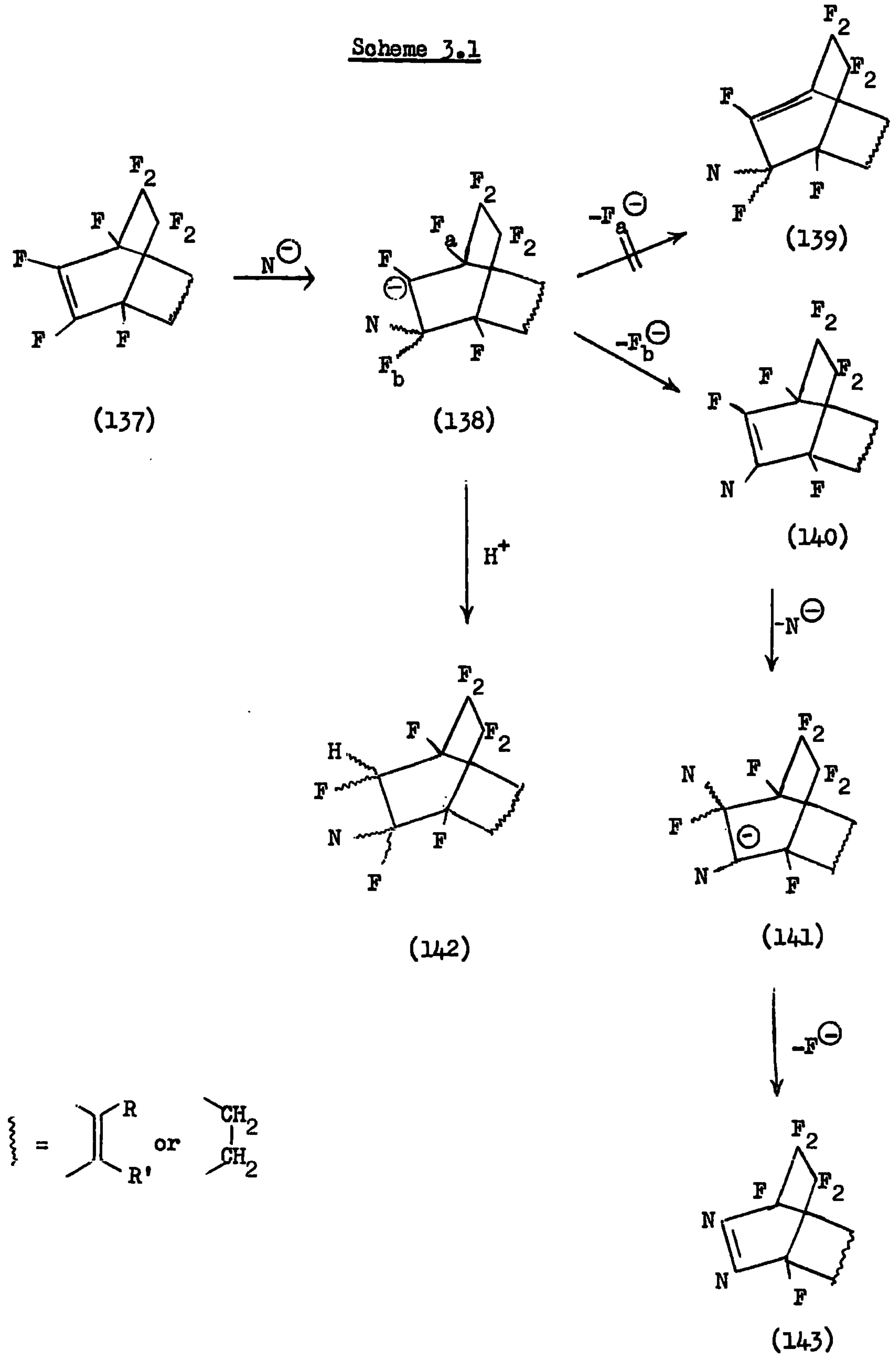
CHAPTER 3

DISCUSSION

3.2 Reaction of Diels-Alder Adducts of Perfluorocyclohexa-1,3-diene with Nucleophilic Reagents

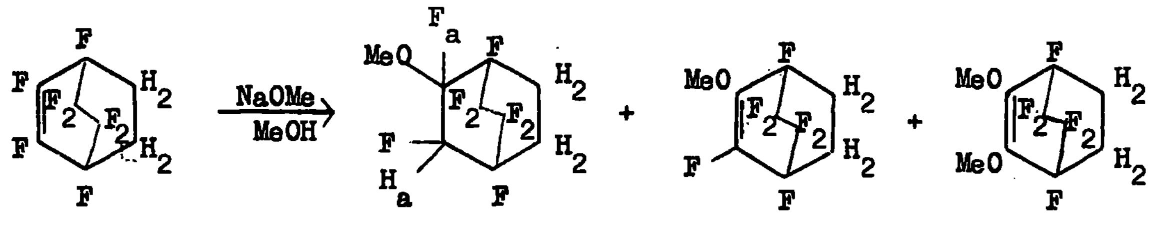
In this section reactions of compounds containing the system (137) (Scheme 3.1) with nucleophiles will be considered. In these reactions the usual

Scheme 3.1



complications met with monocyclic fluoroolefins are avoided since the bridgehead fluorines and the fluorines in the $-CF_2CF_2-$ bridge are found to be completely inert to nucleophilic displacement owing to the constraints imposed by the bicyclic system. Thus (Scheme 3.1) the nucleophile, (N^-) attacks at one of the vinylic positions to produce the intermediate carbanion (138); this carbanion can only eliminate one β fluorine atom (F_b) as a fluoride ion to give the monosubstituted product (140). Loss of the other β fluorine atom (F_b) as a fluoride ion to give the product (139) would require the formation of a double bond at a bridgehead in a bicyclo[2,2,2] system, a situation which would be extremely unfavourable energetically. In a protic solvent the intermediate anion (138) can also be protonated to give the adduct (142). Further attack on (140) gives the disubstituted product (143) via the intermediate anion (141).

(a) Reaction of 1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]oct-2-ene (XVIII) with sodium methoxide in methanol

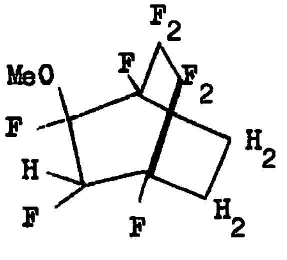


(XVIII) (VIII) (X) (V)

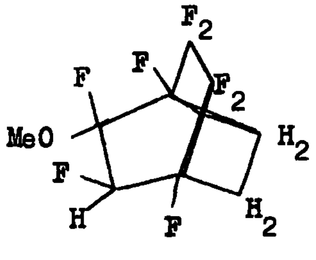
Reaction of adduct (XVIII) (1 mole) with sodium methoxide (3 mole) in methanol at reflux for 67 hours produced the methanol adduct (VIII) and the mono- and di-methoxy derivatives (X) and (V) in the ratio (estimated by g.l.c.) of ca. 3:2:2. The monomethoxy compound (X) has been made previously by addition of ethylene to 2-methoxy-heptafluorocyclohexa-1,3-diene and spectroscopic data (Table 2.4) are consistent with those published.[10] The dimethoxy derivative (V) was characterised by spectroscopy (Table 2.4) and elemental analysis. The methanol adduct (VIII) was characterised by elemental analysis, spectroscopy and chemical conversion with molten potassium hydroxide to adduct (X). The mass spectrum of (VIII) showed the parent peak and the i.r. spectrum was transparent between 1600-1750 cm^{-1} (C=C stretching region), indicating a saturated system. The ^{1}H n.m.r. spectrum showed the expected features: a broad band at 7.94τ (4H, $-CH_2-CH_2-$), a sharp singlet at 5.40τ (3H, $-OCH_3$) and a very broad doublet at 4.23τ (1H, CHF, J(GEM.HF) = ca. 50 Hz). The ^{19}F n.m.r. spectrum showed a complex broad band at +125.4 p.p.m. with respect to external $CFCl_3$ (4F, $-CF_2CF_2-$), a broad band at +140.8 p.p.m. (1F, CF(OMe)), two sharp bands at +188.5 and 197.7 p.p.m. (2F, bridgehead fluorines) and a very broad band at 202.6 p.p.m. (1F, CHF). It was not possible to assign the stereochemistry of the -CHF-CF(OMe)- grouping in adduct (VIII) from n.m.r. spectroscopy; however the symmetry of the resonances (other than of the overlapping $-CF_2-$ bands) suggested that the adduct was predominantly one isomer.

That the adduct (VIII) was the major product of the reaction of excess sodium methoxide with (XVIII) indicates the inertness of this compound to dehydrofluorination. When a sample of the product containing (VIII), (X) and (V) was refluxed with strong aqueous potassium hydroxide for 18 hours very little, if any, conversion of (VIII) occurred. However treatment with molten potassium hydroxide at 260° in a flow system effected complete conversion of (VIII) to (X). The presence of the monomethoxy-derivative (X) in the reaction products from the reaction of (XVIII) with excess sodium methoxide under forcing conditions reflects the deactivating effect of the methoxyl group already present in (X).

The great inertness of the methanol adduct (VIII) with respect to dehydrofluorination suggests that there is no easy pathway by which elimination of HF can proceed. The all-boat rings of the bicyclo[2,2,2]octane system would mean that if H_a and F_a of adduct (VIII) were cis-disposed they would be held rigidly eclipsed and in such a situation cis-coplanar elimination would be expected to occur quite readily. The inertness of (VIII) would seem to suggest that H_a and F_a are trans-disposed; the impossibility of an easy coplanar elimination of H_a and F_a in this situation might then explain the inertness of (VIII) towards dehydrofluorination. If H_a and F_a are trans, there still remain two stereochemical possibilities (144) and (145) for the structure of (VIII).



(144)

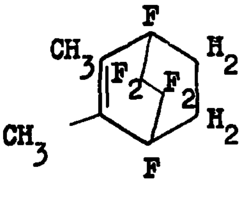


(145)

If methoxide is considered to approach from the least hindered side of adduct (XVIII), in the reaction in which (VIII) is formed, then perhaps (145) is the more likely structure. The formation of (145) would then arise by the unusual cis addition of methanol to the double bond of (XVIII).

(b) Reaction of 1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2] oct-2-ene (XVIII) with methyllithium in ether

With an excess of methyllithium in ether complete conversion of olefin (XVIII) to the dimethyl derivative (II) occurred.



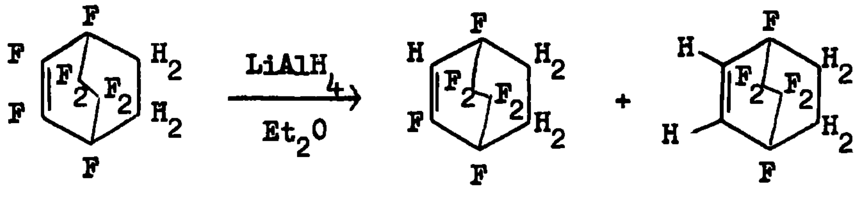
(II)

Olefin (II), obtained in 86% yield after purification, was the sole product and was characterised by elemental analysis and spectroscopy (Table 2.4).

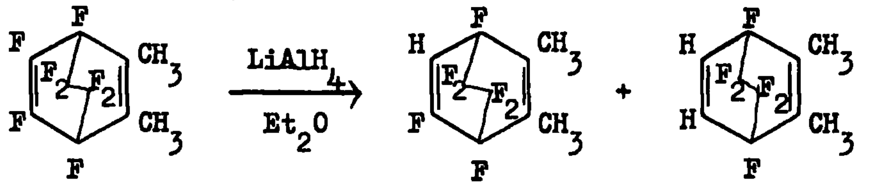
(c) Reactions with lithium aluminium hydride in ether

Compounds (XVIII), (XVI) and (XVII) reacted as expected to give the products of replacement of both one and two vinylic fluorines by hydrogen;

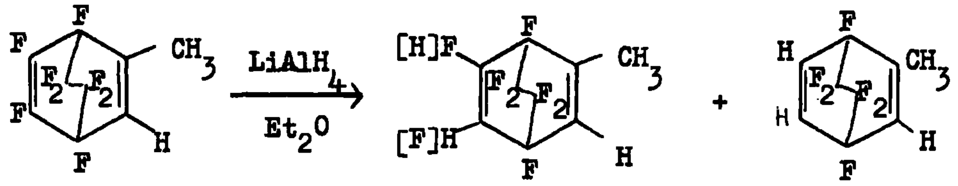
excess lithium aluminium hydride was used in each case. The adducts (XXXVII),



(XVIII) (XXVII) (XXXVII)



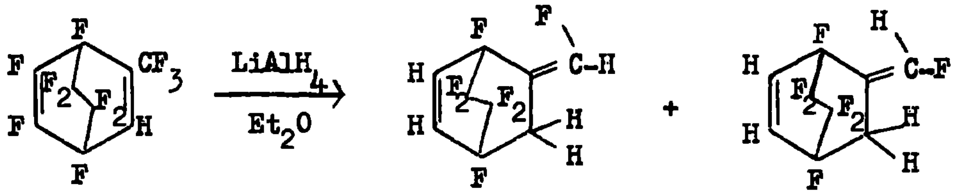
(XVII) (XXVI) (XXXV)



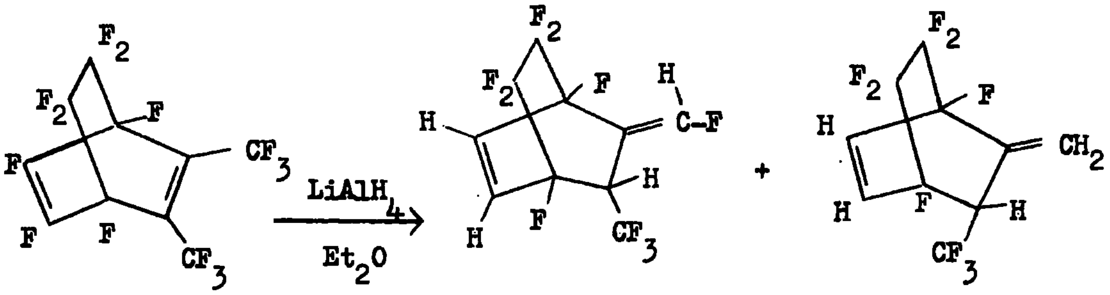
(XVI) (XXV(a) and (b)) (XXXIV)

(XXXV) and (XXXIV) produced in these reactions were identical with the materials produced from the Diels-Alder reactions of 2H,3H-hexafluorocyclohexa-1,3-diene (Chapter 2). The monosubstituted products were characterised by analysis and spectroscopy. Thus, (XXVII) showed a strong absorbtion in its i.r. spectrum at 1686 cm^{-1} (CH=CF) and its ^{19}F n.m.r. spectrum indicated one vinylic fluorine, four fluorines in the perfluorodimethylene bridge and two tertiary fluorines Table 2.4). The unsymmetrical substitution of the double bond in this case makes the environments of the two difluoromethylenes in the perfluorodimethylene bridge different and the fluorine resonances appear as a single line (δ, 126.4, 2F) imposed on an AB-quartet (δ_A, 126.7, δ_B, 130.4, J_{AB} 220 Hz, 2F). Compound (XXVI) showed a strong absorbtion at 1700 cm^{-1} in its i.r. spectrum (-CH=CF-); the n.m.r. spectra (Table 2.5) confirm the structure, the unsymmetrical substitution of the double bond again causes the resonances of the bridging difluoromethylene groups to appear at different chemical shifts although in this case both appear as broad resonances. The monosubstitution product of (XVI) consisted of a mixture of the two possible products (XXVa and b) which could not be separated on available gas chromatographic packings. The i.r. spectrum of the mixed isomers showed two sharp absorbtions in the double bond region at 1690 cm^{-1} (CF=CH) and 1625 cm^{-1} (CH=C(CH$_3$)). The ^{1}H n.m.r. spectrum (Table 2.5) indicated a ratio of vinylic to methyl hydrogens of 2:3, and the ^{19}F spectrum allowed the determination of the ratio of the isomers although it was not possible to establish which isomer was the major product. The resonances for bridging perfluorodimethylene and vinylic fluorine atoms appeared as a complex overlapping set between 121.4 and 126.2 p.p.m., however in the bridgehead region four distinct resonances could be distinguished and integrated with the aid of a computer of average transients. The pair of resonances at 198.4 and 214.2 p.p.m. were of equal intensity and their total integrated intensity was two and a half times that of the other pair of equal intensity resonances at 201.7 and 210.3 p.p.m; thus, in the product mixture obtained in this experiment, one of the isomers (XXVa or b) is found in two and a half times the abundance of the other. This observation implies either an interaction between the reacting C-5,C-6 double bond and the unsymmetrically substituted C-2,C-3 double bond in (XVI); and/or preferential further reduction of (XXVa or b) to (XXXIV).

The reactions of 2-trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (XIV) and perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5-diene (XV) with lithium aluminium hydride resulted in the replacement of vinylic fluorines by hydrogen as expected; however, in these adducts the C-2,C-3 double bond is also susceptible to attack by lithium aluminium hydride due to the activating effect of the trifluoromethyl substituent(s). Consequently reduction

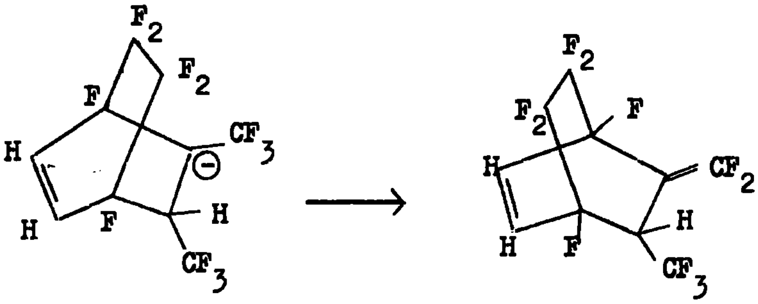


(XIV) (XXIII) (XXIV)



(XV) (XXVIII) (XXIX)

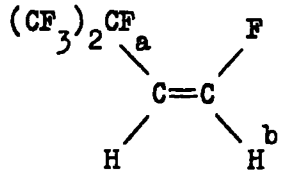
of adduct (XV) can lead to the intermediate anion (146) which is able to eliminate a β-fluorine atom, as fluoride ion, from the trifluoromethyl group giving 2-difluoromethylene-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo [2,2,2]oct-5-ene (147). Intermediate (147) can react further with lithium



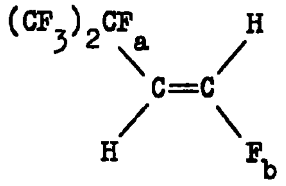
(146) (147)

aluminium hydride and it can be seen that a complex micture of products may be expected from these reactions. In order to minimize the complexity of the product mixtures obtained in these reactions a considerable excess of lithium aluminium hydride was used, together with prolonged reaction times, in the hope that comparatively reactive intermediates would react further giving a few final products amenable to separation and characterisation.

Two compounds (XXIII) and (XXIV) were isolated from the reduction of adduct (XIV) and were shown by analysis and spectroscopy to be the *Z* and *E* isomers of 2-fluoromethylene-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene. Elemental analysis and mass spectrometry established the molecular formulae, the mass spectra of both isomers were identical, the major fragmentation being the elimination of the perfluorodimethylene bridge from the molecular ion (m/e 246, 8%) to give an ion at m/e 146 ($C_7H_5F_3^+$, 81%) which then loses either a hydrogen or a fluorine atom to give, presumably, the trifluorotropylium (m/e 145, 100%) or difluorotropylium ion (m/e 127, 36%). The i.r. spectra of both isomers showed a strong absorbtion at 1712 cm^{-1} ($>C{=}CHF$) but were otherwise quite different. The n.m.r. spectra (Table 2.6) establish the structures and the stereochemistry at the 2-fluoromethylene. In the ^{19}F n.m.r. spectra of both (XXIII) and (XXIV) the two difluoromethylenes of the perfluorodimethylene bridge appeared as a broad line integrating for two fluorines imposed on an AB quartet (J_{AB}, 234 Hz); both spectra showed two distinct resonances in the region appropriate for bridgehead fluorines, the higher field resonance in the spectra of one isomer being split into a doublet (J = 44 Hz) through coupling with the vinylic fluorine; both spectra showed the expected geminal H-F coupling for the vinylic fluorines of the fluoromethylene groups (J_{HF} = 79-80 Hz, lit.[87] range 72 —— 85 Hz). The observed F-F coupling between bridgehead and vinylic fluorines (44 Hz) may be assigned to isomer (XXIII) by analogy with halogenated propenes where J_{CF_3-F} for $-CF_3$ and -F in a *cis* disposition (~23 Hz) is greater than for the *trans*-disposed case (~9.5 Hz), and with *cis*- and *trans*-1-fluoro-2-(perfluoroisopropyl)ethylenes (148) and (149) where $J_{F_aF_b}$ for *cis*-disposed F_a and F_b (148) is 31.0 Hz and for the *trans* case (149) is 5.0 Hz.[87] In the completely rigid systems (XXIII) and (XXIV) the F-F coupling constant for *cis*-disposed fluorines (i.e. in (XXIII) increases to 44 Hz while that for

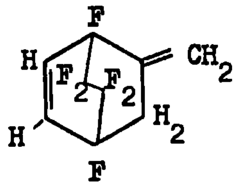


(148)



(149)

trans-disposed fluorines (XXIV) is too small to be detected. The boiling points (156° (XXIV) and 181° (XXIII)) and chromatographic gas retention times on dinonylphthalate stationary phase ((XXIII) longer than (XXIV)) are qualitatively in agreement with the structural assignment, since it has been found in fluorohydrocarbons where conformational restrictions exist that the isomers with most of the hydrogen atoms close to each other in space have higher boiling points and longer retention times than their isomers where hydrogen and fluorine atoms are more evenly distributed.[9,88] The expected final reaction product of (XIV), 2-methylene-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXX), was not produced in this reaction even after prolonged treatment with an excess of lithium aluminium hydride in refluxing ether. Gas chromatographic analysis of



(XXX)

the crude product mixture, using enrichment with an authentic sample of (XXX),[12] showed that (XXX) was not produced in detectable quantities. Presumably the double bonds in (XXIII) and (XXIV) are not sufficiently substituted with electronegative groups to render them susceptible to attack by lithium aluminium hydride. Previous reports have suggested that the reactivity of cyclic fluoro olefins towards this reagent depends on the number of vinylic and allylic fluorine atoms in the molecule.[9,89] If this is the correct explanation for the absence of (XXX) from the product mixture the reactivity must be very sensitive to substituents since adduct (XV) gives the completely reduced product (XXIX) in >31% yield. Two products were isolated from the reaction of adduct (XV) with lithium aluminium hydride, they were characterised by analysis and spectroscopy; again the n.m.r. spectra (Table 2.6) were the major factor in assigning structures. The minor product (XXVIII) showed two bridgehead fluorine resonances neither of which showed the large coupling (44 Hz) found in (XXIII). Consequently the stereochemistry shown (XXVIII) was assigned. The bridge perfluorodimethylene and the vinylic resonances formed a complex overlapping set which were not resolved. The expected large geminal H-F coupling for the fluoromethylene group was detected in the ^{1}H spectrum (J_{HF} = 83 Hz). The i.r. spectrum showed a strong absorbtion at 1692 cm^{-1} ($>C=CHF$). The mass spectrum had an abundant molecular ion (m/e 314, 30%) and two fragmentation routes, either loss of the perfluorodimethylene bridge (m/e 214, 12%) and subsequently trifluoromethyl, or loss of trifluoromethyl (m/e 245, 47%) and subsequently the perfluorodimethylene bridge, to give the base peak (m/e 145, $C_7H_4F_3^+$), presumably the trifluorotropylium ion. Diene (XXIX) was characterised in a similar manner; the ^{19}F n.m.r. spectrum showed two bridgehead fluorines, a broad single band for one of the difluoromethylene groups and an AB quartet (J_{AB} 240 Hz) for the other, and a symmetrical nine line system for the trifluoromethyl resonance. The mass spectrum of (XXIX) was dominated by loss of the perfluorodimethylene bridge and the trifluoromethyl group from the molecular ion to give difluorotropylium as base peak. In (XXVIII) and (XXIX) it was not possible to specify the stereochemistry at C-3, however the observation of single symmetrical resonances for the trifluoromethyl fluorines in the ^{19}F n.m.r. spectra suggested that only one isomer was present and construction of Courtald space filling models suggest that the most likely configuration is endo as shown in the figure (page 80).

CHAPTER 3

EXPERIMENTAL

Reagents: The 2,3-disubstituted-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-dienes (XIV), (XV), (XVI) and (XVII) were prepared by the published route.[72]

3.3 Reaction of 1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]oct-2-ene (XVIII) with sodium methoxide in methanol

Olefin (XVIII) (20.0 g., 79.2 mmoles) and sodium methoxide (13.3 g., 250 mmoles) in dry methanol (50 ml.) were heated under reflux for 67 hr. The solution was then shaken with 2N HCl (200 ml.) and the lower organic layer separated. The liquid product (16.1 g.) when examined by analytical g.l.c. (Column A, 150°) showed three components (i) retention time 5 min; (ii) retention time 12 min.; (iii) retention time 15 min. in the approximate ratio of 2:2:3. Preparative scale g.l.c. (Column B, 120°, N_2 carrier 2 atm) enabled (i) to be separated easily but (ii) and (iii) overlapped and it was only possible to obtain a small amount of (iii) pure. Component (ii) was obtained pure by reaction of a portion of the liquid product consisting of (i), (ii) and (iii) with molten potassium hydroxide (see later) which gave a mixture of (i) and (ii) only, which was readily separated on Column B.

A portion of the liquid mixture (8.61 g.) was separated (Column B, 150°, nitrogen carrier 2 atm) and gave component (i) 2-methoxy 1,3,4,5,5,6,6-heptafluorobicyclo[2,2,2]oct-2-ene (X) (1.959 g.) [Found: C,41.03; H,2.61; F,50.9%; M (mass spectrometry), 264. Calculated for $C_9H_7F_7O$: C,40.92; H,2.67; F,50.35%; M, 264], with i.r. and n.m.r. spectra (Table 2.4) in agreement with the literature;[10] a mixture of components (ii) and (iii) and a pure fraction of (iii), 2-methoxy-1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]octane (VIII) (1.25 g.) [Found: C,38.30; H,2.47; F,53.8%; M (mass spectrometry), 284 , $C_9H_8F_8O$ requires C,38.04; H,2.84; F,53.4%; M, 284], b.p. 233°, ^{19}F and ^{1}H n.m.r. see discussion page 76.

Reaction of liquid product containing components (i), (ii) and (iii) with aqueous potassium hydroxide.

A portion of the liquid mixture (16.0 g.) (obtained from a reaction as above) was refluxed with a solution of potassium hydroxide (20 g.) in water (15 ml.) for 18 hrs. Water (100 ml.) was added and the lower layer separated and washed with water to give a liquid mixture (13.3 g.) whose g.l.c. analysis (Column A, 150°) differed from that before reaction only by a very slight relative decrease of the proportion of component (iii) (VIII) relative to (i) and (ii).

Reaction of the liquid product with molten KOH

A portion of the liquid product containing components (i), (ii) and (iii) (5.53 g.) was passed in a stream of nitrogen through molten potassium hydroxide contained in a flask heated to 260° in an oil-bath. The product vapours were collected in a trap cooled in liquid air. The contents of the trap were distilled from phosphoric oxide to give a liquid mixture (4.12 g.) whose analytical g.l.c. (Column A, 150°) now showed the presence of only components (i) and (ii), component (iii) being completely absent. This liquid product was readily separated by preparative g.l.c. (Column D, 200°) to give (i) 2-methoxy-1,3,4,5,5,6,6-heptafluorobicyclo[2,2,2]oct-2-ene (X) (1.98 g.) and (ii) 2,3-dimethoxy-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (V) (1.07 g.) [Found: C,43.77; H,3.43; F,41.68%; M (mass spectrometry), 276. $C_{10}H_{10}F_6O_2$ requires C,43.48; H,3.65; F,41.28%; M, 276], b.p. 220°, ν_{max} 1687 cm^{-1} (-C(OMe)=C(OMe)-).

3.4 Reaction of 1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]oct-2-ene (XVIII) with methyl lithium in ether.

1,2,3,4,5,5,6,6-Octafluorobicyclo[2,2,2]oct-2-ene (XVIII) (10.0 g., 39.6 mmoles) in ether (10 ml.) was added dropwise to a stirred solution of methyl lithium (100 mmoles) in ether (80 ml.) at -30°. The mixture was allowed to warm up to room temperature and was then refluxed for 31 hrs. Water (25 ml.) was added, the ether layer was separated washed with water (25 ml.), dried

($MgSO_4$) and the ether removed by distillation. The brown solid residue was sublimed under vacuum at room temperature to give 2,3-dimethyl-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (II) (7.70 g., 34.0 mmoles, 86%) [Found: C,49.0; H,4.3; F,46.4%; M (mass spectrometry), 244. $C_{10}H_{10}F_6$ requires C,49.2; H,4.1; F,46.7%; M, 244], m.p. 35-36°.

3.5 Reactions with lithium aluminium hydride

General procedure: A solution of the fluoro-olefin or diene in ether was added dropwise at room temperature to a stirred suspension of lithium aluminium hydride in ether. The mixture was refluxed and the excess lithium aluminium hydride was destroyed by cautious dropwise addition of water to the vigorously stirred mixture which was maintained at room temperature by a large water bath. To reduce fire hazard the whole operation was carried out under an atmosphere of dry nitrogen. Sufficient dilute sulphuric acid was added to dissolve all the inorganic salts and the ether layer was then separated, dried ($MgSO_4$), and fractionally evaporated (vacuum jacketed, Vigreux column, 12 cm. x 1 cm.) to remove the bulk of the ether; P_2O_5 was added to the residue and the volatile materials recovered by vacuum transfer and separated by gas chromatography (Column B, 100°).

(a) 1,2,3,4,5,5,6,6,-Octafluorobicyclo[2,2,2]oct-2-ene (XVIII) (3.52 g., 13.95 mmoles) in ether (5 ml.) with lithium aluminium hydride (1.16 g., 30 mmoles) in ether (20 ml.), after refluxing for 3 hrs., gave: (i) 1,2,4,5,5,6,6-heptafluorobicyclo[2,2,2]oct-2-ene (XXVII) (1.47 g., 6.3 mmoles, 45%) [Found: C,40.7; H,2.2; F,56.6%; M (mass spectrometry), 234. $C_8H_5F_7$ requires C,41.0; H,2.2; F,56.8%; M, 234], m.p. 120-121° (sealed tube), ν_{max} 1686 cm^{-1} (-CH=CF-); and (ii) 1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (XXXVII) (0.50 g., 2.3 mmoles, 16.5%), with correct i.r. spectrum.

(b) 2,3-Dimethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (XVII) (4.98 g., 17.9 mmoles) with lithium aluminium hydride (2.02 g., 54 mmoles) in ether, after refluxing for 45 mins., gave: (i) 2,3-dimethyl-

1,4,5,7,7,8,8-heptafluorobicyclo[2,2,2]octa-2,5-diene (XXVI) (0.55 g., 2.12 mmoles, 11.9%) M (mass spectrometry), 260.0440. $C_{10}H_7F_7$ requires M, 260.0436 ν_{max} 1700 cm^{-1} (-CH=CF-) and 1669 cm^{-1} (-C(CH$_3$)=C(CH$_3$)-); and (ii) 2,3-dimethyl-2,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXV) (1.90 g., 7.83 mmoles, 41.5%) with correct i.r. spectrum.

(c) 2-Methyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (XVI) (5.13 g., 19.4 mmoles) with lithium aluminium hydride (1.5 g., 40 mmoles), after refluxing for 30 mins., gave: (i) a mixture of 2-methyl-1,4,5,7,7,8,8- and -1,4,6,7,7,8,8-heptafluorobicyclo[2,2,2]octa-2,5-dienes (XXVa and b) (0.56 g., 2.28 mmoles, 11.8%) M (mass spectrometry), 246.0279. $C_9H_5F_7$ requires M, 246.0278 , ν_{max} 1690 cm^{-1} (-CF=CH-) and 1625 cm^{-1} (-C(CH$_3$)=CH-); and (ii) 2-methyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXIV) (1.95 g., 8.55 mmoles, 45%) with correct i.r. spectrum.

(d) Perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5-diene (XV) (5.29 g., 13.7 mmoles) with lithium aluminium hydride (2.0 g., 53 mmoles) in ether (35 ml.), after refluxing for 43 hours, gave a complex mixture of at least eight components. The major product was 2-methylene-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXIX) (1.25 g., 4.12 mmoles, 31%) [Found: C,40.3; H,1.9; F,58.2%; M (mass spectrometry), 296.0235. $C_{10}H_5F_9$ requires C,40.6; H,1.7; F,57.7%; M, 296.0247], b.p. 187°, ν_{max} 1667 cm^{-1} (C=CH$_2$) and 1623 cm^{-1} (-CH=CH-).

When this reaction was carried out with a molar ratio of diene to lithium aluminium hydride of 1:2.9 and a reflux time of 30 mins., as compared to 1:3.9 and 43 hrs. above, a similar complex mixture was obtained from which only two of the components were isolated in a pure state: (i) 2-monofluoromethylene (E)-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXVIII) (0.16 g., 0.50 mmoles, 3.7%) [Found: M (mass spectrometry), 314.0156. $C_{10}H_4F_{10}$ requires M, 314.0153], ν_{max} 1692 cm^{-1} (C=CHF); and (ii) 2-methylene-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-2-ene (XXIX) (0.07 g., 0.23 mmoles, 1.7%) with correct i.r. spectrum.

(e) 2-Trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (XIV) (5.61 g., 17.7 mmoles) with lithium aluminium hydride (2.3 g., 58 mmoles) in ether (35 ml.), after refluxing for 50 hrs., gave a complex mixture of at least seven components. The two major products were obtained pure and identified as: (i) 2-fluoromethylene(E)-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXIV) (0.88 g., 3.6 mmoles, 20%) [Found: C,43.9; H,2.3; F,54.2%; M (mass spectrometry), 246. $C_9H_5F_7$ requires C,43.9; H,2.1; F,54.0%; M, 246] b.p. 156°, ν_{max} 1712 cm^{-1} (C=CHF); and (ii) 2-fluoromethylene(Z)-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXIII) (0.69 g., 2.8 mmoles, 15%) [Found: C,44.0; H,2.3; F,54.0%; M (mass spectrometry), 246. $C_9H_5F_7$ requires C,43.9; H,2.1; F,54.0%; M, 246], b.p. 181°, ν_{max} 1712 cm^{-1} (C=CHF) and 1631 cm^{-1} (-CH=CH-).

When this reaction was carried out using a five fold excess of lithium aluminium hydride and a reflux time of 96 hrs. analytical gas chromatography on the product indicated a mixture of the same components as before, the major product in this case being 2-fluoromethylene(Z)-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXIII). Analytical gas chromatography on the product mixture enriched with an authentic specimen of 2-methylene-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene (XXX) showed that this expected product was not present in detectable concentration.

CHAPTER 4

PYROLYSIS OF SOME 2,3-DISUBSTITUTED-POLYFLUOROBICYCLO[2.2.2]OCT-2-ENES

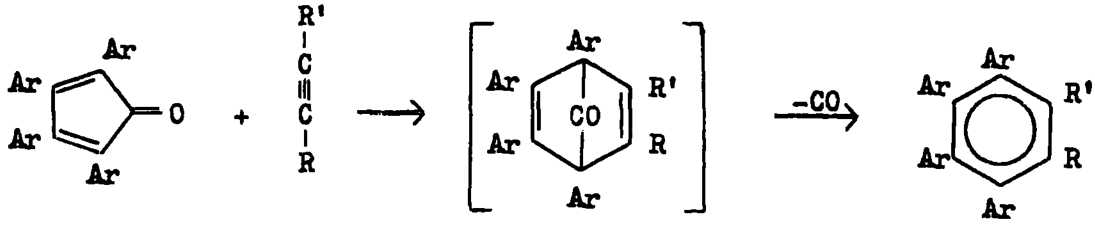
INTRODUCTION

4.1 The Reverse Diels-Alder Reaction[90]

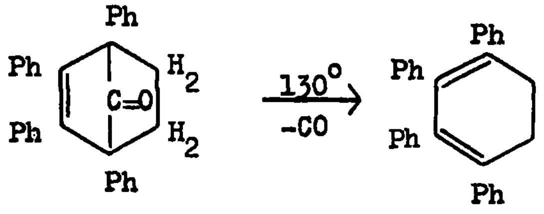
In general Diels-Alder adducts of cyclic hydrocarbon dienes are less stable than those of acyclic dienes with respect to dissociation into their addends. Adducts of cyclopentadienes decompose more readily than those of cyclohexa-1,3-dienes; thus the adduct of maleic anhydride with cyclopentadiene dissociates into its addends at 200°, whilst the adduct with cyclohexa-1,3-diene requires a temperature of 310°. It is also true that Diels-Alder adducts of cyclic dienes with alkynes are more stable than those with alkenes with respect to dissociation to the addends. Thus the adduct of furan with maleic anhydride is extremely labile and decomposes at its melting point (125°),[93] whereas the adduct of furan with diethyl acetylene dicarboxylic ester is much more stable.

These results obey the general empirical rule of Schmidt[94] - the so-called "double-bond rule", which states that in any olefin pyrolysis it is the bond β to the double bond that cleaves; a single C-C bond in this position appears to be weaker than a normal C-C bond, while the position α to the double bond is one of strength. This effect is not confined to C-C bonds as demonstrated by the lability of allyl halides.

Bicyclic adducts may also decompose thermally by a route other than that which gives back the addends, and in such cases where there is a choice of pathways, it is generally found that the mode of retrogression observed is that which leads to the most stable of the possible products. Decompositions which give aromatic products are expected to proceed readily. Thus the highly strained adducts of tetracyclones with acetylenes, (150) are normally not isolable and lose carbon monoxide readily to give aromatic (151). Adducts of tetracyclones with alkenes are more stable, the product cyclohexa-1,3-diene being less favoured energetically than aromatics, however carbon monoxide is expelled upon heating. Thus adduct (152) of tetraphenylcyclopentadienone and ethylene decomposes at 130°. The adduct of maleic anhydride with tetraphenylcyclopentadienone loses carbon monoxide only at 235° and is readily isolated.

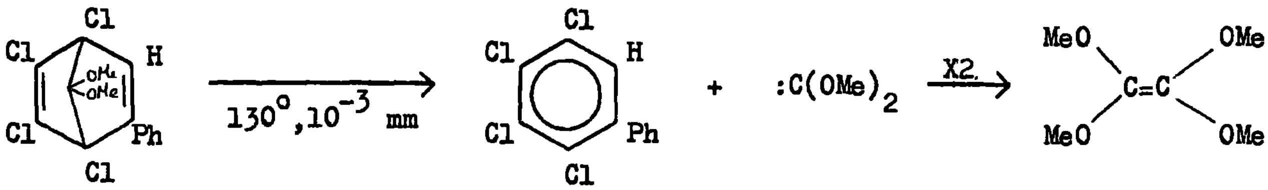


(150) (151)



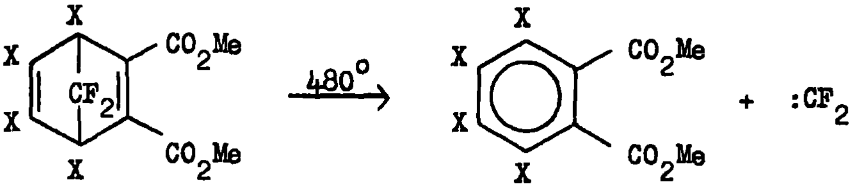
(152)

The retrodiene reaction of tetracyclone adducts involves breakage of two bonds from the same carbon atom to produce a carbene, in this case the very stable carbene carbon monoxide. Adducts of cyclopentadiene with alkynes and alkenes cannot decompose by the loss of the unstable carbene methylene, since thus would be very unfavourable energetically and decomposition to the original addends generally occurs. However it is possible to eliminate less unstable carbenes from other bicyclo[2,2,1]heptadiene systems. Thus pyrolysis of the adduct of 5,5-dimethoxy-tetrachlorocyclopentadiene and phenyl acetylene, (153), causes elimination of dimethoxycarbene, which dimerises to give tetramethoxyethylene.[91] There does not appear to be any report of the pyrolysis of adducts of hexachlorocyclopentadiene with alkynes with elimination of dichlorocarbene; however the corresponding aromatics can be prepared by the ready conversion of the $>CCl_2$ group of the adducts to $>C(OMe)_2$ using methoxide ion. The adducts are then readily pyrolysed as above.



(153)

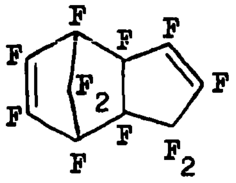
Difluorocarbene was eliminated when adducts (154)[92] and (155)[56] were pyrolysed at 480° to give the corresponding aromatics; in the second case, the



(154) (X = Cl)
(155) (X = F)

intermediacy of difluorocarbene was clearly demonstrated by trapping with cyclohexene to give 7,7-difluoronorcarane in a yield of over 57%.

The high thermal stability of the polyhalogenated adducts (154) and (155) with respect to dissociation into its addends (halocyclopentadiene and dimethyl acetylene dicarboxylate) is noteworthy. In particular fluorine substituents increase the stability of carbocyclic systems. Thus perfluorocyclopentadiene dimer (156) in striking contrast to dicyclopentadiene itself is exceedingly



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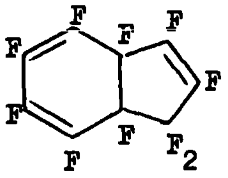

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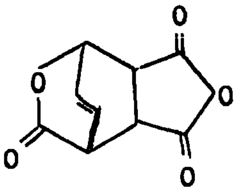
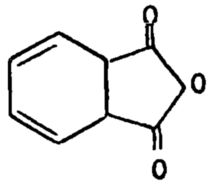


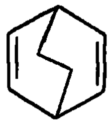
(158)



(159)

stable[57] and does not appreciably revert to monomer but eventually loses difluorocarbene at 680° to give (157).

Pyrolyses of Diels-Alder adducts in the bicyclo[2,2,2]octane series again proceed to give the most stable products, e.g. an aromatic and a stable small molecule. Thus the adducts of α-pyrones with alkenes and alkynes lose carbon dioxide easily, for example the adduct of α-pyrone with maleic anhydride (158) gives (159) at 130° by loss of carbon dioxide. Ethylene is eliminated from bicyclo[2,2,2]octa-2,5-diene (160)[95] at 200° to give benzene. Bicyclo[2,2,2]octa-2,5,7-triene (161)[96] requires a higher temperature (250°)[97] for decomposition to give benzene and acetylene. The substituted triene (162)[97] decomposes at 150° by both available retro-reactions giving both durene and (163).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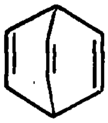
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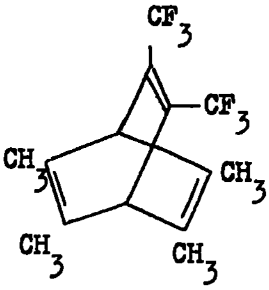

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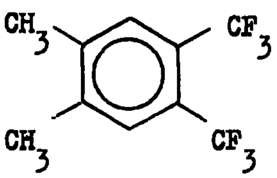
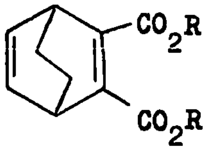
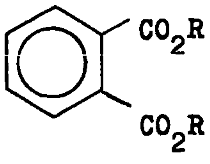


(163)

Adducts of acetylenes and cyclohexa-1,3-diene (such as (164) which form at 0°), lose ethylene under similar conditions to the parent compound (160) to give aromatics (165).[98] The thermal decomposition of bicyclo[2,2,2]oct-2-ene (166) occurs unimolecularly in the vapour phase at 376-445° to give ethylene and cyclohexa-1,3-diene,[98a] and the kinetic results favour a concerted rather than a



(164)



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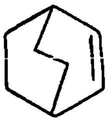
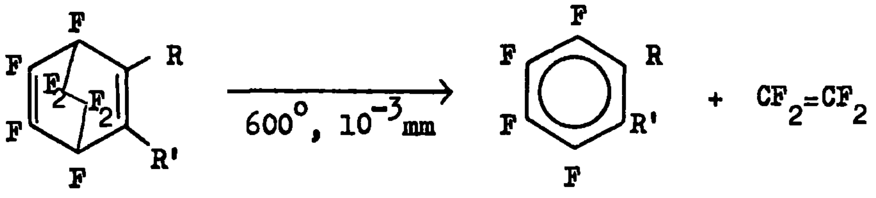

(166)

biradical pathway. The reaction is an equilibrium one, and the diene decomposes further to produce benzene, cyclohexene and hydrogen by radical pathways.

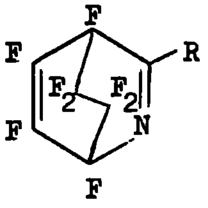
Adducts of perfluorocyclohexa-1,3-diene with simple alkynes (167) eliminate



(167) (168)

tetrafluroethylene on pyrolysis at 600°, 10^{-3}mm.Hg to give 1,2-disubstituted-tetrafluorobenzenes (168) in virtually quantitative yield.[72] The adducts (167) are completely stable up to at least 250° in contrast to the hydrocarbon analogues (e.g. (160) and (164) which lose ethylene at 200°, this stability again being conferred by the fluorine substituents).

The Diels-Alder adducts of perfluorocyclohexa-1,3-diene with nitriles, (169) decompose[75] by loss of nitrile in competition with loss of tetrafluoroethylene



(169)

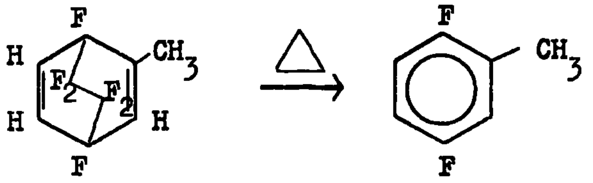
at 600°, giving both perfluorocyclohexa-1,3-diene and 2-substituted tetrafluoropyridines.

CHAPTER 4

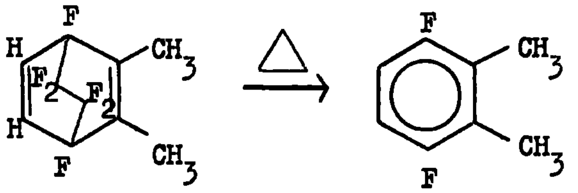
DISCUSSION

4.2 Pyrolysis of 2-methyl- and 2,3-dimethyl-1,4,7,7,8,8-hexafluorobicyclo [2.2.2]octa-2,5-diene (XXXIV) and (XXXV)

Adducts (XXXIV) and (XXXV) were prepared by Diels-Alder addition of 2H,3H-hexafluorocyclohexa-1,3-diene (with propyne and but-2-yne respectively, Chapter 2) and also by lithium aluminium hydride reduction of the corresponding adducts of perfluorocyclohexa-1,3-diene (Chapter 3); pyrolysis in a flow system at 600°, 10^{-3}mm.Hg causes quantitative expulsion of the perfluorodimethylene bridge giving the expected para-difluorobenzene derivatives, (IL) and (L).



(XXXIV) (IL)



(XXXV) (L)

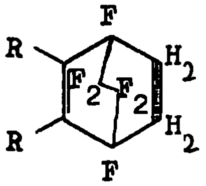
Both these aromatics had been prepared previously[99,100] by the Schiemann reaction and boiling points measured were in reasonable agreement with the literature values, but no spectroscopic data were given.

2,5-difluorotoluene (IL) shows a strong parent peak in the mass spectrum (see Appendix B) at m/e, 128 (62%) and the base peak of the spectrum (m/e 127) corresponds to loss of a hydrogen atom from the molecular ion to give the stable difluorobenzyl or tropylium ion $C_7F_2H_5^+$. 1,4-Difluoro-2,3-dimethylbenzene (L) gives a strong parent peak in the mass spectrum at m/e, 142 (66%). The base peak (at m/e, 127) arises by loss of a methyl group as indicated by observation of the appropriate metastable ion (Appendix B). Presumably the ion at m/e 127 is the same stabilised benzyl or tropylium ion $C_7F_2H_5^+$ as observed in the spectrum of (IL). Loss of a hydrogen atom from the parent ion to give another stabilised benzyl or tropylium ion at m/e 141 (39%), presumably $C_7F_2H_4(CH_3)^+$ was also an important breakdown route. The ^{19}F and ^1H n.m.r. and u.v. spectra were in agreement with the assigned structures of (IL) and (L) (see Experimental Section 4.4a and b).

The pyrolysis of 2-trifluoromethyl-4,5,7,7,8,8-hexafluorobicyclo[2,2,2]-octa-2,5-diene (XXXXI) proceeded normally by loss of tetrafluoroethylene to give the expected aromatic (see Section 2.10).

4.3 Pyrolysis of some 2,3-disubstituted-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]-oct-2-enes

Three polyfluorobicyclo[2,2,2]oct-2-enes prepared either by Diels-Alder reaction of the corresponding polyfluorocyclohexa-1,3-diene and ethylene (Chapter 2) and/or nucleophilic substitution reactions (Chapter 3) of 1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]oct-2-ene (XVIII) were examined. The system (170) might be expected to be more thermally stable than the



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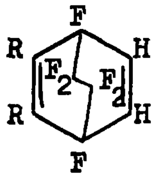
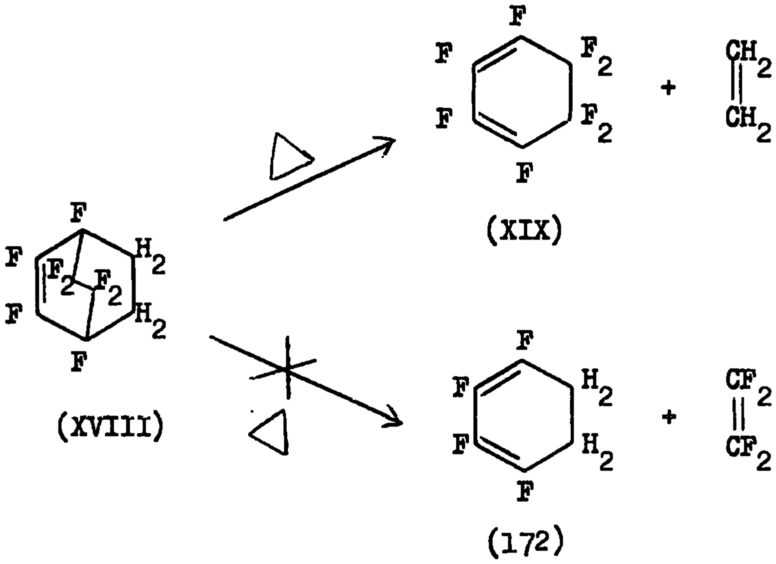


(171)

corresponding polyfluorobicyclo[2,2,2]octa-2,5-diene (171) since the possible conjugated products of thermolysis, cyclohexa-1,3-diene are less stabilised than the aromatic product of pyrolysis of (171). This expected behaviour is observed experimentally; thus pyrolysis of adduct (170) (R=F) at 600°, 10^{-3}mm. produces very little breakdown (170) being recovered substantially unchanged whereas under these conditions adducts (171) give aromatics quantitatively.

It was found that efficient pyrolytic breakdown of adducts (170) required a temperature of ca. 700°, and an increased residence time in the pyrolysis zone, obtained by increasing the pressure in the flow system to 10^{-1} mm.Hg.

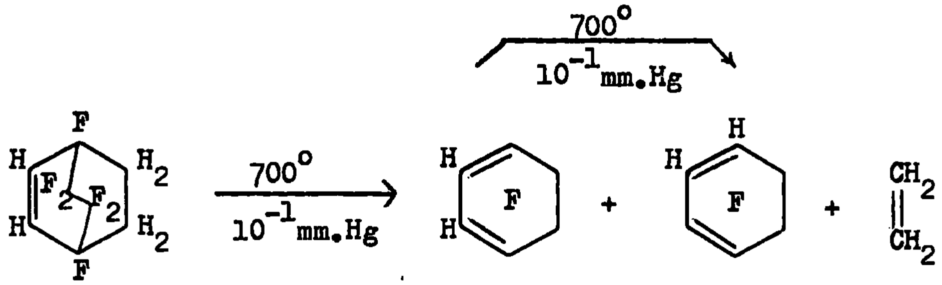
Under these conditions it was found that all three adducts (XVIII), (XXXVII) and (II) broke down by the exclusive elimination of ethylene rather than tetrafluoroethylene. Thus pyrolysis of adduct (XVIII) at 700°, 10^{-1}mm.Hg.



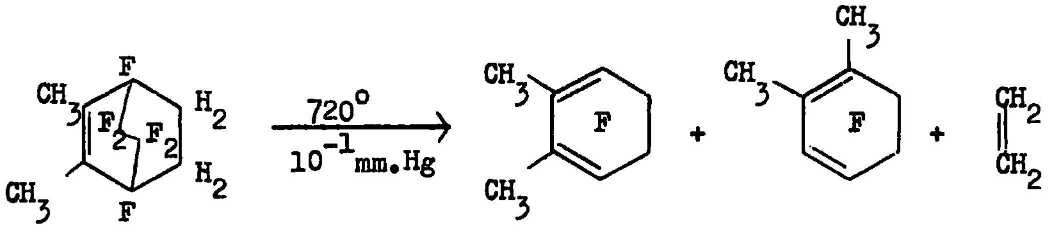
gave ethylene (86%), perfluorocyclohexa-1,3-diene (XIX) and unchanged (XVIII). Tetrafluoroethylene was not detected by i.r. in the product gases. (Since tetrafluoroethylene has very strong absorbtions in its i.r. spectrum relative to those of ethylene less than 1% of C_2F_4 in the product gases would have been readily detectable). Thus none of the alternative diene (172) was produced.

A possible qualitative rationalisation of the specific expulsion of ethylene rather than tetrafluoromethylene may be that it is the strength of the bonds broken in the reaction which determine the products. Thus in adduct (XVIII) the C_1-C_8 and C_4-C_7 bonds (F-C-CF_2-) are expected to be stronger than the C_1-C_6 and C_4-C_5 bonds (F-C-CH_2-). It is known that fluorine substitution in hydrocarbons at C_a and C_b generally increases the C_a-C_b bond strength. Thus $CF_3.CF_3$ only decomposes appreciably into CF_3 radicals at 1200° whereas $CH_3.CH_3$ decomposes at ca. 600°.[101]

The pyrolytic decomposition of adducts (XXXVII) and (II) proceeded by the same pathway to give mixtures of the expected 2,3-disubstituted-hexafluorocyclohexa-1,3-dienes (XXXVIII) and (III) together with their 1,2-disubstituted isomers (XXXXIII) and (I) as the major products, together with small amounts of other unidentified materials and unchanged adduct. Adducts (XXXVII) and (II)



(XXXVII) (XXXVIII) (XXXXIII)

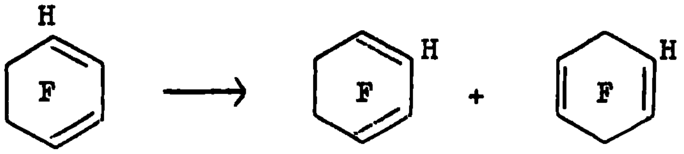


(II) (III) (I)

gave ca.52% and 62% respectively of ethylene from the pyrolysis. Since pyrolysis of diene (XXXVIII) alone under the same conditions results in its partial isomerisation to diene (XXXXIII) it seems likely that the initial product of these pyrolyses is the 2,3-disubstituted dienes (XXXVIII) and (III), which under the vigorous conditions of the pyrolysis rearrange to their 1,2 isomers (XXXXIII) and (I) respectively. This rearrangement which appears to involve a 1,3-fluorine shift, would of course not be observable with perfluorocyclohexa-1,3-diene itself.

The new dienes (I) and (III) were characterised by elemental analysis and spectroscopy (see Experimental Section 4.4f and Table 1.2).

Although isomerisations of polyfluorocyclohexa-1,3-dienes during pyrolysis have been reported previously, for example (20) gave (21) and (19) on pyrolysis at 260°,[102] these reactions have usually been carried out with 'aged' nickel



(20) (21) (19)

tubes in a nitrogen carrier and comparatively long reaction times and can be attributed to a surface reaction catalysed by fluoride ion, a process which cannot be invoked for pyrolyses in vacuo in silica tubes. Dienes (XXXVIII) and (III) are stable on pyrolysis at 300°, 10^{-3}mm in a silica tube packed with silica wool. (See Chapter 5).

CHAPTER 4

EXPERIMENTAL

Pyrolysis Apparatus

The apparatus consisted of a silica tube (59 cm x 1.4 cm internal diameter) lightly packed with silica wool. The middle 44 cm of the tube were heated in an electric furnace and the temperature at the outer surface of the silica tube was measured with a chrome-alumel thermocouple. Samples were admitted from a Pyrex reservoir at one end and the other end was connected to a trap cooled in liquid air, which in turn was connected to the vacuum system. The pressure in the vacuum system, as measured by a 'vacustat' gauge, was regulated by means of a dry-nitrogen bleed inlet.

Procedure

The material to be pyrolysed was admitted to the reservoir and cooled in liquid air before the system was evacuated to the desired pressure. On warming the material transferred through the pyrolysis zone into the trap. The contents of the trap were then transferred into the vacuum line for fractionation, gas measurements, etc.

4.4 Pyrolyses

(a) 2,3-Dimethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene (XXXV) (1.685 g., 6.96 mmoles) was pyrolysed at 600°/0.075 mm. to give: (i) tetrafluoroethylene (6.76 mmoles, 97%) with correct i.r. spectrum; (ii) 1,4-difluoro-2,3-dimethylbenzene (L) (0.989 g., 6.96 mmoles, 100%) [Found: C,67.7; H,5.6; F,26.7; M (mass spectroscopy), 142. Calculated for $C_8H_8F_2$, C,67.6; H,5.7; F,26.7; M, 142], b.p. 144° (Lit.^{100} 137-8°). ν_{max} 2907 cm^{-1} (C-H) and 806, 730 cm^{-1} (aromatic nucleus). λ_{max} 252.0(s) nm (ε - 6.4 x 10^2), 256.0(s) nm (ϵ - 9.8 x 10^2), 260.2 nm (ϵ - 1.5 x 10^3), 264.9 nm (ϵ - 1.7 x 10^3), 269.3 nm (ϵ 2.2 x 10^3), 274.1 nm (ϵ - 2.3 x 10^3) in cyclohexane (0.321 g./litre); ^{19}F n.m.r. a symmetrical multiplet at 123.3 p.p.m. (relative to external $CFCl_3$ and ^1H n.m.r. two symmetrical multiplets at 2.55τ and 7.53τ in the intensity ratio 1:3.

(b) <u>2-Methyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene</u> (XXXIV) (1.95 g., 8.55 mmoles) was pyrolysed at 600°/0.001 mm. to give: (i) tetrafluoroethylene (7.92 mmoles, 97%), with correct i.r. spectrum; (ii) 2,5-difluorotoluene (IL) (0.983 g., 7.68 mmoles, 90%) [Found: C,65.9; F,29.3%; M (mass spectrometry), 128.0442, calculated for $C_7H_6F_2$, C,65.6; F,29.7%; M, 128.0438], b.p. 120° (Lit.[99] 117°), ν_{max} 2933 cm^{-1} (C-H), 870, 813, 769, 763 724 cm^{-1}, λ_{max} 260.0(s) nm (ϵ - 17 x 10^3), 264.5 nm (ϵ - 2.3 x 10^3), 268.5 nm (ϵ - 2.7 x 10^3), 274.0 (ϵ - 2.6 x 10^3) in cyclohexane (0.342 g./litre); ^{19}F n.m.r. showed 2 multiplets of equal intensity at 120.1 and 126.2 p.p.m. measured relative to external C_6F_6 and converted to δ_{CFCl_3} using the expression $\delta_{CFCl_3} = \delta_{C_6F_6} + 162.3$ p.p.m. and ^1H n.m.r. multiplets of equal intensity at 3.33τ and 7.94τ.

(c) <u>1,2,3,4,5,5,6,6-Octafluorobicyclo[2,2,2]oct-2-ene</u> (XVIII) (1.064 g., 4.23 mmoles) was pyrolysed at 700°/0.1 mm. to give: (i) ethylene (3.66 mmoles, 86%), with correct i.r. spectrum; (ii) a liquid fraction (0.792 g.) the analytical gas chromatogram and i.r. spectra of which were completely consistent with a mixture of perfluorocyclohexa-1,3-diene and 1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]oct-2-ene (XVIII).

(d) <u>1,4,5,5,6,6-Hexafluorobicyclo[2,2,2]oct-2-ene</u> (XXXVII) (0.987 g., 4.57 mmoles) was pyrolysed at 700°/0.1 mm. to give: (i) ethylene (2.36 mmoles, 51.5%), with correct i.r. spectrum; (ii) a liquid mixture (0.893 g.), separated by preparative gas chromatography into 1H,2H-hexafluorocyclohexa-1,3-diene (XXXXIII) (ca. 25%), 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII) (ca. 25%) and 1,4,5,5,6,6-hexafluorobicylo[2,2,2]oct-2-ene (XXXVII) (ca. 50%), each with correct i.r. spectrum.

(e) <u>2H,3H-Hexafluorocyclohexa-1,3-diene</u> (XXXVIII) (0.273 g.) was pyrolysed at 700°/0.1 mm. to give a liquid (0.242 g.) the analytical gas chromatogram and i.r. spectrum of which were consistent with an approximately equimolar mixture of 1H,2H- (XXXXIII) and 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII).

(f) 2,3-Dimethyl-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene (II) (3.684 g., 15.1 mmoles) was pyrolysed at 720°/0.1 mm. to give: (i) a gaseous mixture (9.3 mmoles), shown by i.r. spectroscopy to be predominantly ethylene; (ii) a liquid mixture (2.309 g.) from which the two major components were separated by preparative gas chromatography and identified as 1,2-dimethylhexafluorocyclohexa-1,3-diene (I) (0.374 g., 1.73 mmoles, 11.5%) [Found: C,44.8; H,2.7%; M (mass spectrometry), 216. $C_8H_6F_6$ requires C,44.5; H,2.8%; M, 216], ν_{max} 1731s, 1645w cm^{-1} (conjugated diene), λ_{max} 266.5 nm (ϵ - 5.8 x 10^3), ^{19}F n.m.r. (30% soln. in CCl_4, int. $CFCl_3$ as reference) four bands 123.6(2) 128.4(2), 141.7(1) and 160.1(1), ^1H n.m.r. (int. t.m.s.) one band at 8.11τ (CH_3) and 2,3-dimethylhexafluorocyclohexa-1,3-diene (III) (0.314 g., 1.45 mmoles, 9.6%) [Found: C,44.7; H,2.8%; M (mass spectrometry), 216. $C_8H_6F_6$ requires C,44.5; H,2.8; M, 216], ν_{max} 1715m, 1660w cm^{-1} (conjugated diene), λ_{max} 269 nm (ε - 2.3 x 10^3), ^{19}F n.m.r. (30% soln. in CCl_4, int. $CFCl_3$) two bands at 127.2(4) and 140.5(2), ^1H n.m.r. one band at 8.15τ. The correctness of the above assignment was confirmed by addition of ethylene to (III) to give (II), see Chapter 2, section 2.

CHAPTER 5

PHOTOCHEMICAL ISOMERISATION OF POLYFLUOROCYCLOHEXA-1,3-DIENES

INTRODUCTION

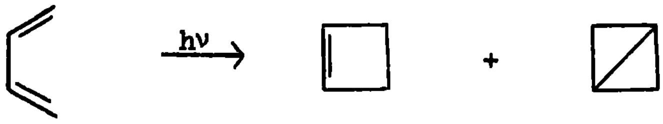
Photochemical Isomerisation of 1,3-dienes

The course of photochemical rearrangement of acyclic and cyclic dienes is only rarely simple and whilst there are general reaction types the individual structures of reactants, intermediates and products can have a marked influence. The rationalisation of the course of photochemical reactions of 1,3-dienes owes much to the concept of the Conservation of Orbital Symmetry.[27]

A comprehensive, though purely factual review of both unsensitised and sensitised photochemical reactions of 1,3-dienes is available.[102a] In the subsequent discussion only photochemical reactions carried out in the absence of triplet-sensitisers will be considered.

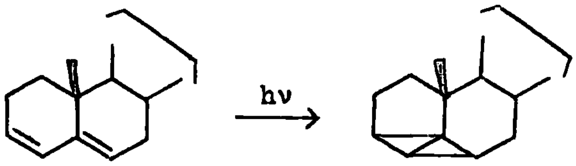
5.1 Photochemical Isomerisation of Acyclic Conjugated Dienes

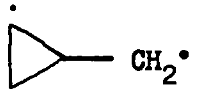
The simplest acyclic diene, buta-1,3-diene (173) on irradiation with ultraviolet light of wavelength 253.7 nm in cyclohexane as solvent, gives[103] cyclobutene (174) and bicyclo[1,1,0]butane (175) in the ratio 10:1.



(173) (174) (175)

Cyclobutene (174) arises from the excited state of butadiene in a symmetry-allowed concerted electrocyclic reaction by disrotatory ring closure.[27] Cyclobutenes are the usual products obtained from ultraviolet irradiation of substituted buta-1,3-dienes. Bicyclobutanes are formed in favourable cases on irradiation of dienes fixed in a transoid conformation[104] as in the following example,[105] (176) → (177), in which (176) is a steroidal diene.





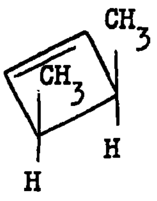
(176) (177) (178)

It has been suggested[106] that the formation of bicyclobutane (175) from butadiene (173) is not a concerted process and proceeds via the diradical intermediate (178), which then ring closes.

In the photochemical isomerisation of certain substituted buta-1,3-dienes the reaction can be complicated by cis-trans isomerisation of the diene, and/or by sigmatropic hydrogen shifts. For example irradiation[106] of a solution of the trans-trans diene (179) caused a rapid equilibration to a mixture containing

(179) (180) (181)

also the cis-trans diene (180) and the cis-cis diene (181). At the stationary state the ratio of (179):(180):(181) was calculated to be 35.7:30.5:33.7. In a slower process then this equilibration, cyclobutenes and other products were formed. The major product, which accounted for 33% of the hexadiene consumed



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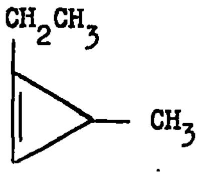

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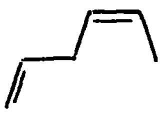

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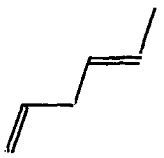
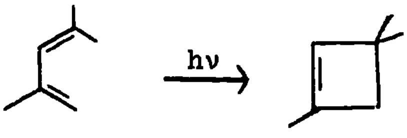


(185)

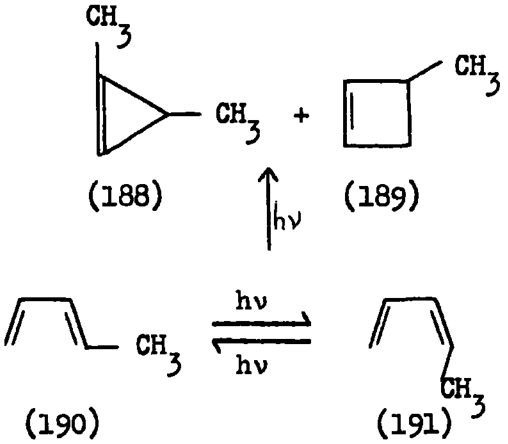
was the cis-dimethylcyclobutene (182), which was shown to arise exclusively from (179) rather than (180) or (181) by short irradiation of the pure diene. Cyclobutene (182) is the expected product of the symmetry allowed disrotatory ring closure[27] of diene (179). The cyclopropene (183), found as a minor product (ca. 3% of the hexadiene consumed), is believed[106] to arise via rearrangement of a diradical analogous to (178). Other minor products were the non-conjugated dienes (184) and (185), each formed in about 1-2% yield.

The course of photochemical reaction of buta-1,3-dienes may differ in the gas phase to that in solution. Thus the cyclobutene (187) is produced readily by irradiation of diene (186) in the vapour phase, but only negative results



(186) (187)

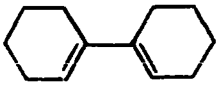
are obtained in solution.[107]



(188) (189) (190) (191)

Irradiation of trans-1-methylbuta-1,3-diene (190) at 253.7 nm. in cyclohexane solution gives[108] the cis isomer (191), 3-methylcyclobutene (189) and 1,3-dimethylcyclopropene (188), whereas direct irradiation of the vapour of (190) gives the non-conjugated molecule, penta-1,4-diene as the major product together with small amounts of (189) and other products.

The disrotatory ring-closure of 1,3-dienes to cyclobutenes is also observed in the transformation (192) → (193).[109,110]



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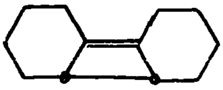
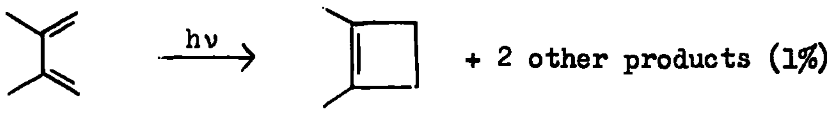


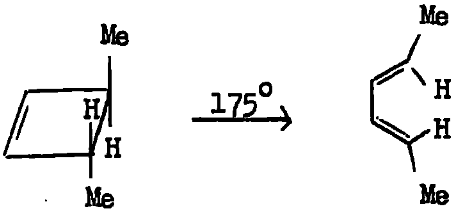
(193)

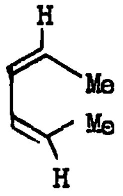
In certain cases the yields of cyclobutenes can be quite high; thus (195) was formed in 71% yield by irradiation of (194).[110]



(194) (195)

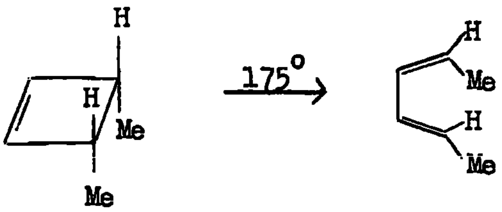
Cyclobutenes are generally stable at room temperature but upon heating they give buta-1,3-dienes by the symmetry allowed[27] ground state conrotatory ring-opening. Thus the trans-dimethyl cyclobutene (196) on pyrolysis gives exclusively (197).[111] The product of the alternative conrotatory process (198)





(196) (197) (198)

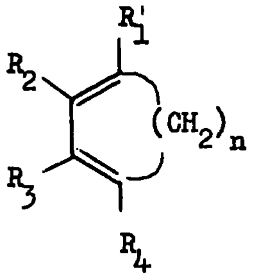
was not observed and this has been attributed[27] to the unfavourable steric interaction of the methyl groups in the transition state. Similarly the cis-isomer (199) gave the product of conrotatory ring opening (200) exclusively.[111-2]



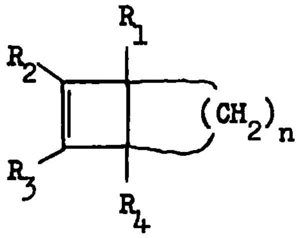
(199) (200)

5.2 Photochemical isomerisation of cyclic conjugated dienes

The course of photochemical reactions of cyclic 1,3 dienes (201) (n = 1,2,3 ...) is markedly dependent upon n. As for open-chain dienes it is possible to



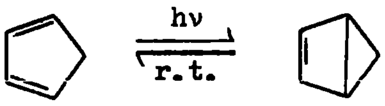
(201)



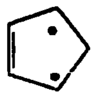
(202)

produce cyclobutene derivatives (202) by the symmetry-allowed disrotatory ring closure. For n = 1,3,4,5 this reaction appears to be the normal mode of photochemical rearrangement. However for the special case n = 2 (i.e. for cyclohexa-1,3-dienes) there is another symmetry-allowed electrolytic reaction pathway available whereby conrotatory ring opening occurs to give hexa-1,3,5-trienes, which can themselves undergo further photochemical transformations. In the majority of cases cyclohexa-1,3-dienes have been observed to give products derived from ring-opening to hexa-1,3,5-trienes rather than products of ring-closure to bicyclo[2,2,0]hex-2-enes. Since the behaviour of cyclohexa-1,3-dienes is complex, their photochemistry will be discussed last.

(a) Cyclopentadienes (201), n = 1

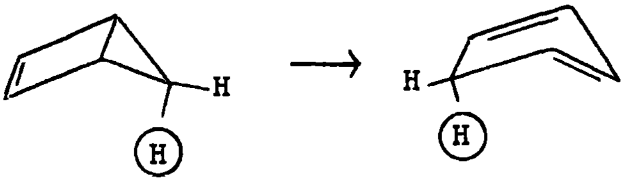


(203) (204)



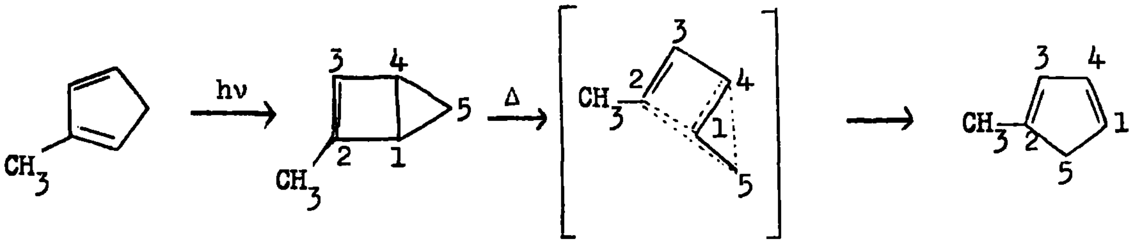
(205)

Only recently ~~less~~ formation of bicyclo[2,1,0]pentene (204) from cyclopentadiene has been observed,^{113} in spite of many reported unsuccessful attempts. Irradiation of cyclopentadiene (203) in ethanol at 0° gave (204) in ca. 10% yield. As might be expected for such a highly strained molecule, (204), is unstable and reverts mainly to cyclopentadiene with a half life of only 2 hours at room temperature. The thermal decomposition of (204) by the symmetry allowed conrotatory process is stereochemically impossible and it was thought that the decomposition must be non-concerted and proceed by breaking the 1,4 bond to give the diradical intermediate (205) and kinetic measurements[114] were consistent with such a mechanism. Deuteration studies[115] established that the methylene group of (204) survived intact, with no exchange, into the cyclopentadiene produced and hence ruled out mechanisms involving hydrogen shift from the methylene group to the double bond ((206) — (207)).



(206) (207)

However new light is shed on the process by the observation[116] that 2-methylbicyclo[2,1,0]pentene (209), obtained by irradiation of 2-methylcyclopentadiene (208), does not revert to (208) on heating but gives 1-methylcyclopentadiene (211). The process was ascribed[116] to valence isomerisation



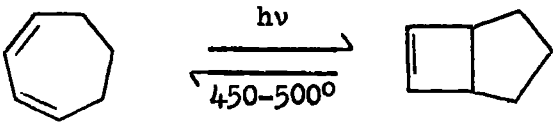
(208) (209) (210) (211)

involving the C(1)-C(2) and C(4)-C(5) bonds in a concerted symmetry allowed $[{}_{\sigma}2_s + {}_{\sigma}2_a]$ cycloreaction. Thus it seems likely that the decomposition of bicyclo[2,1,0]pentene (204) also occurs by this concerted mechanism rather than via diradical (205) in a stepwise reaction.

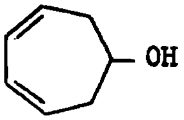
(b) Cyclohepta-1,3-dienes [(201), n = 3]

The simple cis-cis-cyclohepta-1,3-dienes have been shown to be very consistent in their photochemical behaviour and isomerisation to bicyclo[3,2,0] hept-6-enes has been observed in the vast majority of cases.

Cyclohepta-1,3-diene (212) gives[118] bicyclo[3,2,0]heptene (213) in 58% yield by disrotatory ring closure; pyrolysis of (213) at 450-500° gave (212) quantitatively, but very little reaction occurred in a flow system at temperatures lower than 300°. Other seven-membered ring dienes which give the expected derivatives of bicyclo[3,2,0]heptene on photolysis are (214),[118] (215),[117] (216)[119] and (217).[120]



(212) (213)



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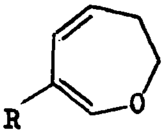
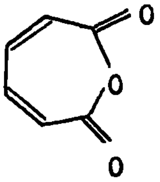


(215)
(R = H,Cl)



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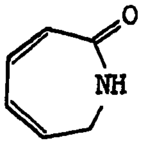

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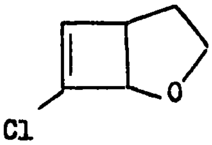
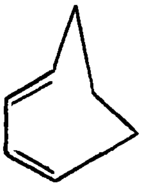


(218)

Yields in such reactions can be high, (e.g. (215) (R = Cl) gives[117] (218) in 81% yield) and the products are generally quite thermally stable.

The thermal stability of the photoisomers is a consequence of the great difficulty in opening the bicyclo[3,2,0]heptene ring system in the thermally allowed conrotatory fashion, which would produce a highly strained cis-trans-cyclohepta-1,3-diene (219). Cis-trans-cyclohepta-1,3-dienes have not been observed directly, (though they have been postulated as reaction intermediates which immediately ring-close to bicyclo[3,2,0]heptenes[121]) and in practice cis-cis-cyclohepta-1,3-dienes are the products of pyrolysis. The measured activation energy for the thermal isomerisation of (213) has been interpreted[122]



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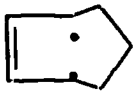
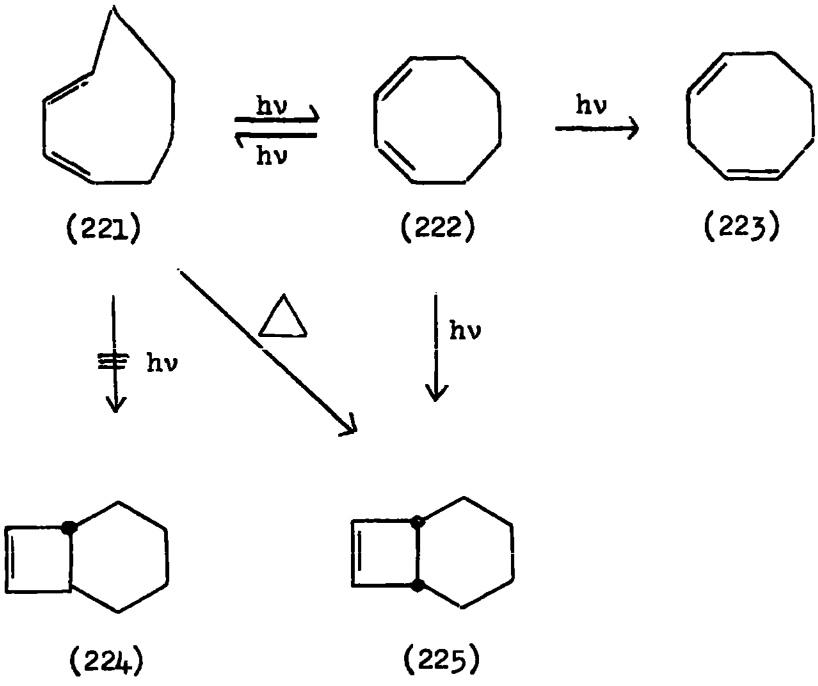


(220)

as indicating a symmetry-forbidden disrotatory mode of ring opening rather than indicating the intermediacy of a biradical (220).

(c) <u>Cycloocta-1,3-diene</u> [(201), n = 4]

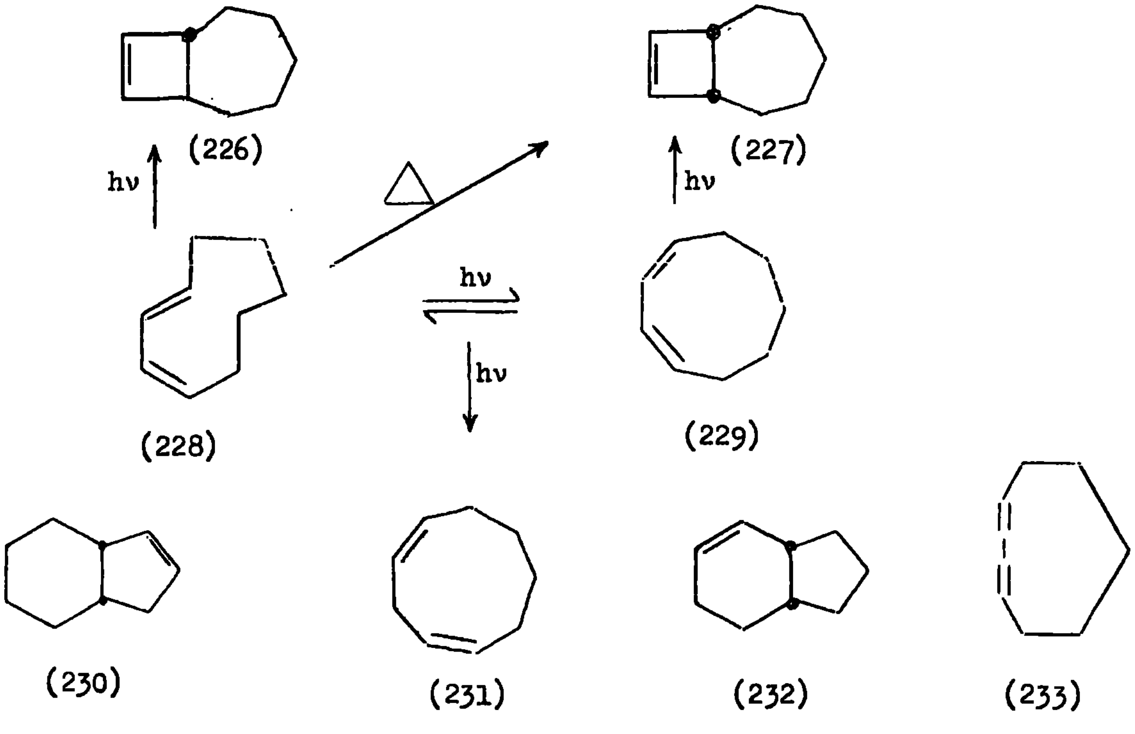
The lower strain of the eight-membered ring compared to the seven-membered and smaller rings means that cycloocta-1,3-dienes can exist in the cis-trans as well as cis, cis isomeric form, and this has a profound effect on their photochemical behaviour. Thus when cis-cis cycloocta-1,3-diene (222) is directly irradiated[123] at 248.0 nm. ± 4 nm. the major photochemical



transformation is the cis-trans isomerisation (222) $\rightleftharpoons$ (221). On short irradiation of diene (222) the major and minor products were (221) and (225) respectively. The cis-fused bicyclo[4,2,0]oct-7-ene (225) arises by symmetry-allowed disrotatory ring closure of (222) photochemically, and not under these conditions by the thermally-allowed conrotatory ring closure of (221). (The thermal process (221) ⟶ (225) occurs quantitatively at 80°).[124] Prolonged irradiation gives (225) as the major product together with the non-conjugated 1,4 diene (223), which is presumed[123] to arise by a suprafacial [1,3] sigmatropic shift - a process which is symmetry-allowed[27] photochemically. No photochemical transformation of the cis-trans octadiene (221) to the trans-fused bicyclo[4,2,0]oct-7-ene (224) although this process is symmetry allowed, probably because (224) is too strained to exist. (Eliel states[123a] that the seven-membered ring is the smallest cycle than can span a four-membered ring in trans fashion).

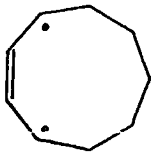
(d) Cyclonona-1,3-diene [(201), n = 5]

Increasing the ring size still further from eight to nine members gives still greater stereochemical freedom and further complexities are observed in the photochemistry of cyclononadiene, as shown below.



As in the cyclooctadiene case cis-trans isomerism of the diene itself is the fastest photochemical process operating and irradiation of either the cis-cis diene (229) or the cis-trans diene (228) at wavelengths below 300 nm. gives rise to an equilibrium mixture of (228) and (229) in which the cis-cis diene (229) predominates.[125] Slower processes which accompany the isomerisation lead to the formation of a complex micture of (226), (227), (230), (231), (232) and (233) in the ratio 14:25:23:4:6:1. The major product (227) arises by disrotatory ring closure of the cis-cis diene (229). In contrast to the cycloocta-1,3-diene system, photochemical disrotatory ring closure of the cis-trans diene (228) can and does occur to give the trans-fused bicyclo[5,2,0]non-8-ene (226) Isomerisation to the 1,4 diene (231) occurs as for cyclooctadiene. The products (231)-(233) were postulated[125] to result from photochemically induced hydrogen shifts and cyclisations of the sigmatropic type.

The Woodward Hoffman Rules for electrocyclic transformation receive elegant confirmation in the conversion of (228) into (227) at temperatures above 175° with the establishment of an equilibrium mixture of (228) and (227) by the thermally allowed conrotatory process. It is interesting that at temperatures above 250° irreversible isomerisation of (227) occurs[125] to give the cis-cis diene (213). Possibly at this temperature there is sufficient energy available to effect the symmetry disallowed disrotatory ring opening of (227) or to form the biradical (234).

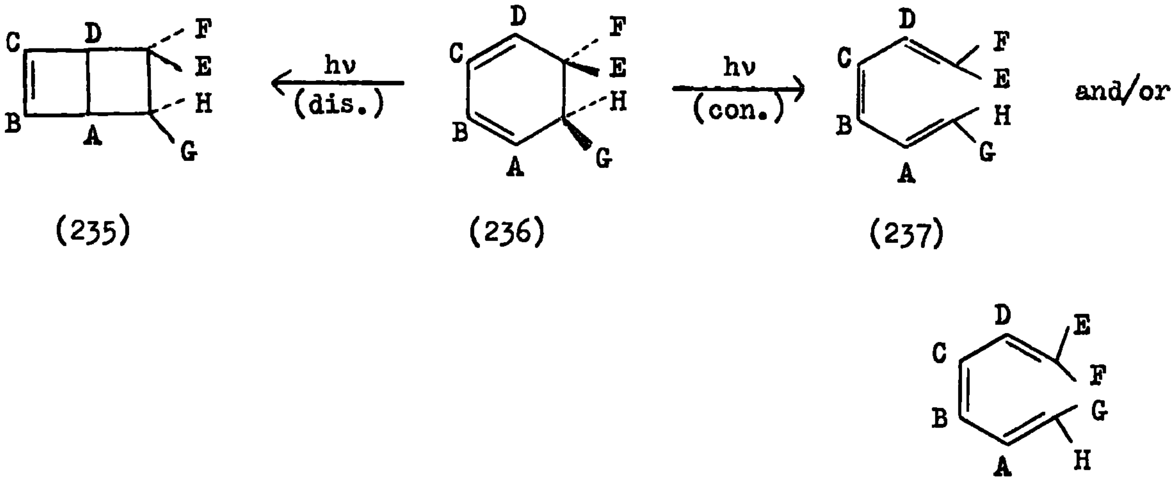


(234)

The photochemistry of larger ring 1,3 dienes apparently displays similar complexity,[125] but details have not yet been published.

(e) <u>Cyclohexa-1,3-dienes</u> [(201), n = 2]

The photochemistry of cyclohexa-1,3-dienes (236) is potentially more

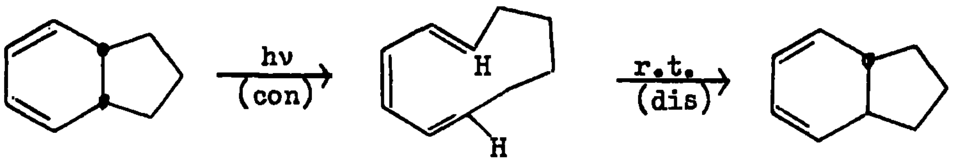


(235) (236) (237) (238)

complicated than that of cyclopentadienes or cyclohepta-1,3-dienes because, besides the possibility of ring closure to give the cyclobutene derivative (235) there exists another symmetry-allowed photochemical pathway, i.e. the conrotatory ring opening[27] reaction to give a cis-cis hexa-1,3,5-triene (237) and/or (238). In the great majority of cases cyclohexa-1,3-dienes have been found to ring-open to give hexa-1,3,5-trienes, which are themselves subject to further photochemical reactions and hence complex mixtures of products are often formed. In comparatively few cases six-membered cyclic 1,3 dienes have been observed to give derivatives of bicyclohex-2-ene (235) and in these cases special factors appear to be operating. Thus the "normal" photochemical reaction of cyclohexa-1,3-dienes is ring-opening. There has never been any substantiated case of bicyclo[2,1,1] hex-2-ene formation from photolysis of cyclohexa-1,3-dienes.[125a]

(i) Photolyses of cyclohexa-1,3-dienes which give hexa-1,3,5-trienes by ring opening

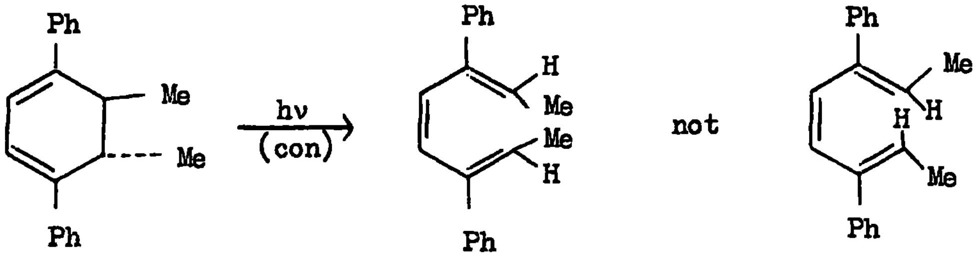
The stereospecific conrotatory nature of the photochemical ring-opening predicted in 1965 by Woodward and Hoffman[27] has been observed experimentally[126-129] with 5,6-disubstituted cyclohexa-1,3-dienes. Thus (239) on irradiation in methanol solution at -20° gave[126] the cis,cis,trans-1,3,5-nonatriene (240) by conrotatory ring opening; at room temperature (240)



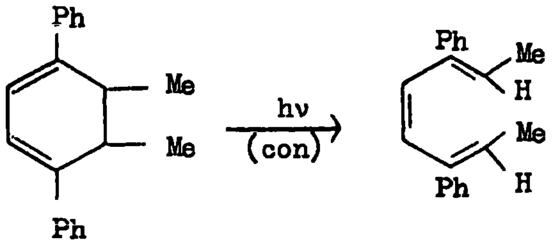
(239) (240) (241)

isomerised to the trans-fused isomer (225) by the thermally allowed disrotatory process.

The stereospecific disrotatory ring opening reaction is also demonstrated in the photoisomerisation of the cis-trans isomeric dienes (242) and (245) to give (243) and (246) respectively.

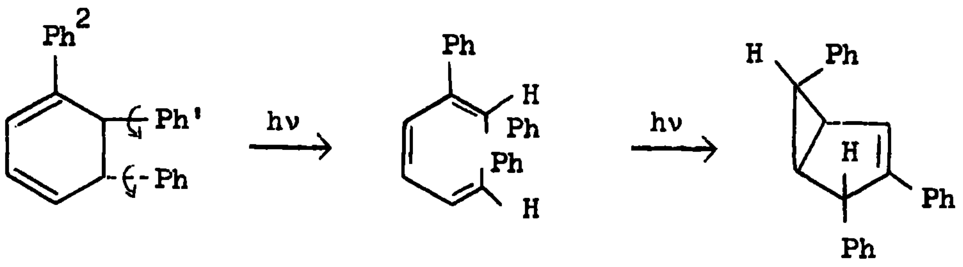


(242)(trans) (243) (244)

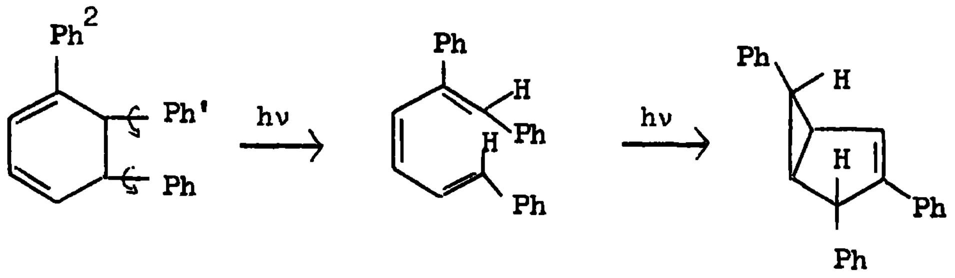


(245)(cis) (246)

In the photolysis of (242) conrotatory motion occurs only in one direction to give (243) rather than (244). A similar preference for only one of the two possible conrotatory modes is shown[129] in the photoisomerisation of (247) and (250) to give the trienes (248) and (251) exclusively by conrotation in the



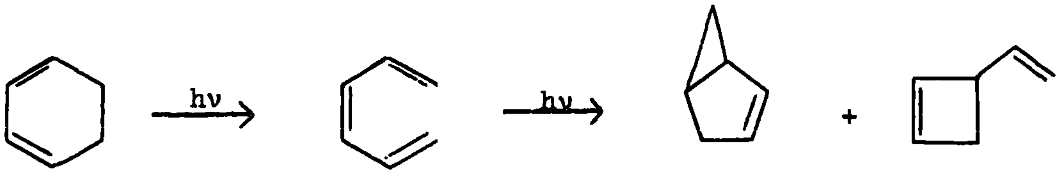
(247) (248) (249)



(250) (251) (252)

direction shown. This behaviour was attributed[129] to the unfavourable interaction of Ph' and Ph^2 in the transition state which would be engendered in the opposite conrotation to that shown. Further irradiation of (248) and (251) produced (249) and (252) stereospecifically in yields of 71% and 65% respectively. This photocyclisation of hexa-1,3,5-trienes (248) and (251) to bicyclo[3,1,0]hex-2-enes (249) and (252) occurs by a symmetry-allowed intermolecular $[_{\pi}4_{s} + {}_{\pi}2_{a}]$ cycloaddition and in this case the products are distinguishable from those which would have been formed in the alternative $[_{\pi}4_{a} + {}_{\pi}2_{s}]$ reaction, (cf. Reference 27,p.79).

Extended irradiation of unsubstituted cyclohexa-1,3-diene (253) as a 1% solution in ether yields[130,131] an approximately 1:1 mixture of bicyclo[3,1,0]-

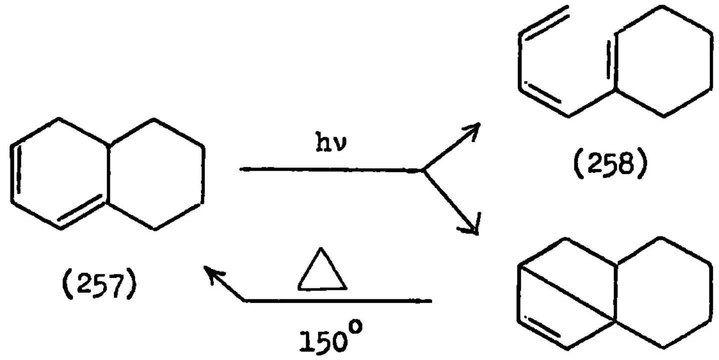


(253) (254) (255) (256)

hex-2-ene (255) and 3-vinylcyclobutene, via the acyclic triene (254). Product (256) is considered to arise by 1,4 cyclisation of the partial diene system. In one unusual case[132] it has been claimed that a bicyclo[3,1,0]hex-2-ene derivative is produced directly from a cyclohexa-1,3-diene without the intermediacy of a hexa-1,3,5-triene, but in general it would seem that the triene is a precursor.[129]

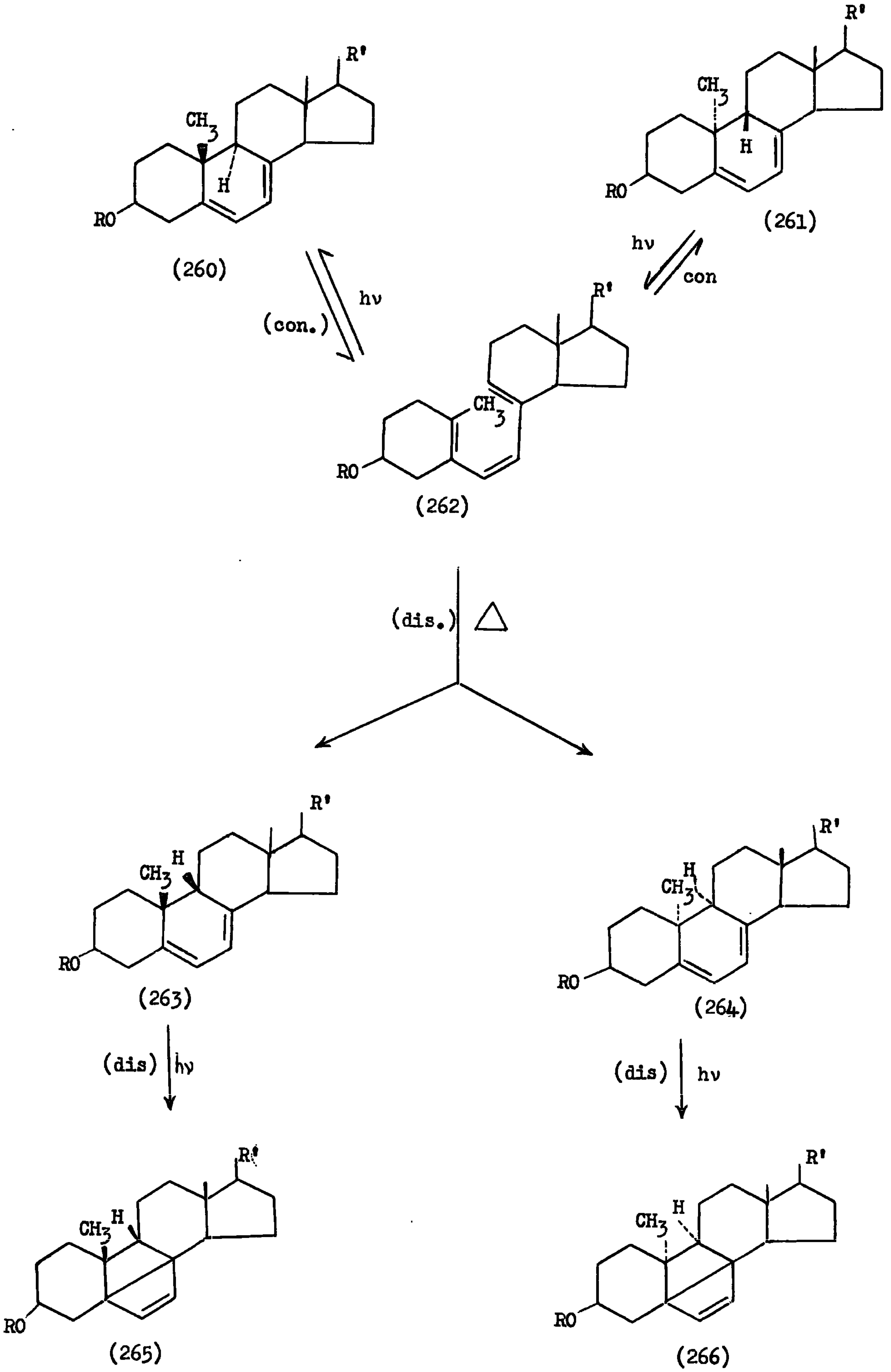
(ii) Photolyses of cyclohexa-1,3-dienes which give bicyclo[2,2,0]hex-2-enes

There is a single example in which photolysis of a cyclohexa-1,3-diene derivative gives both a ring-opened hexa-1,3,5-triene and a bicyclo-[2,2,0]hex-2-ene derivative. Thus short irradiation of (257) gives both the triene (258) and (259).[133] The structure of (259) was confirmed by heating to 150° whereupon it reverted to (257).



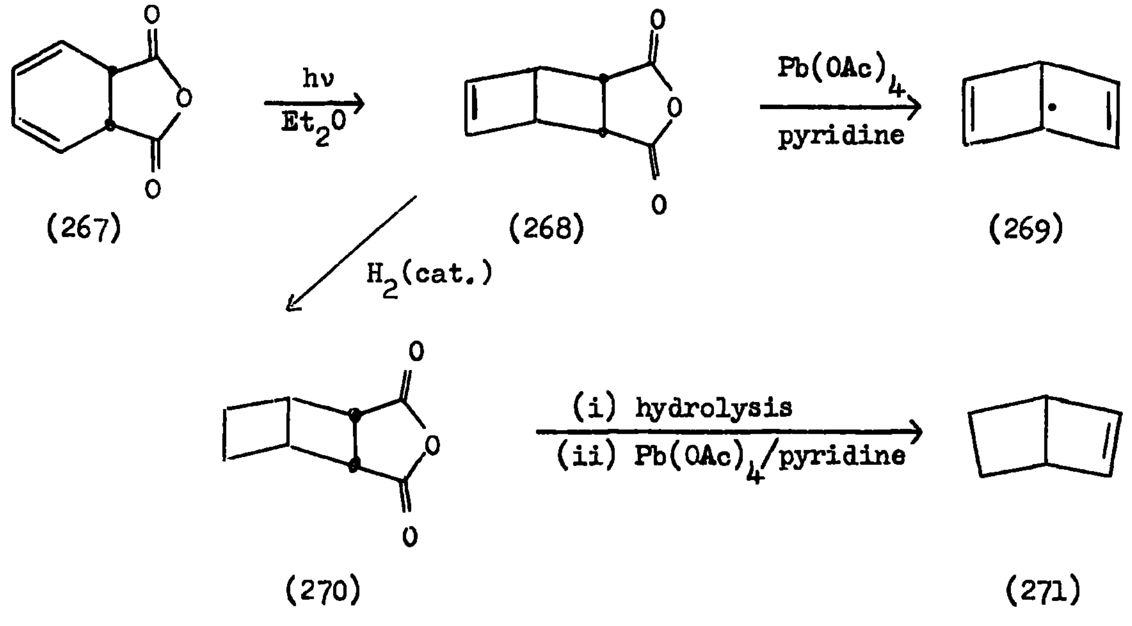
(259)

The effect of steric constraints on the cyclohexa-1,3-diene system in determining the course of photochemical reaction has been observed in the photochemical and thermal reactions of steroidal dienes.[27] The conversions (260)-(266) were all recognised in the course of studies in the vitamin D field and all steps are symmetry-allowed transformations[27] (conrotatory and disrotatory processes are marked "con" and "dis"). That the syn isomers (263) and (264) are isomerised to bicyclo[2,2,0]hex-2-enes (265) and (266) respectively, whilst the anti isomers (260) and (261) are isomerised to the triene (262) is explained by Woodward and Hoffmann[27] by the effect of

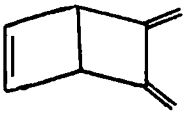

R'
CH3
H
RO
(260)
(261)
hν
con
(con.)
(262)
(dis.)
△
(263)
(264)
(dis)
(265)
(266)

insurmountable geometrical restraints in (263) and (264) which prevent them from undergoing the "normal" electrocyclic cleavage by conrotatory ring opening. Thus the photochemical cleavage of cyclohexa-1,3-diene is the preferred reaction except where this is energetically impossible, e.g. conrotatory ring opening of (246) or (247) would require the formation of a trans double bond in a six-membered ring in the products. In these cases the alternative symmetry allowed electrocyclic reaction course available is followed to give bicyclo 2,2,0 hex-2-ene derivatives (265) and (266).

One synthetically important example of photochemical cyclisation was observed in the photolysis of anhydride (267) which gives (268)[134] in unspecified yield. Photoisomer (268) has been used to prepare bicyclo[2,2,0]hexa-



2,5-diene (269),[134] known as "Dewar Benzene"; bicyclo[2,2,0]hex-2-ene (271)[135] and "Dewar o-xylylene" (272).[135a] Both the cis and trans isomers of diacid (273), unlike the anhydride (267), gave ring-opened trienes on photolysis.[134] Originally the behaviour of anhydride (267) was attributed[134] to an unfavourable steric crowding of the 3,8-hydrogen atoms in the supposed product (274). However (274) would have to arise by the photochemically forbidden



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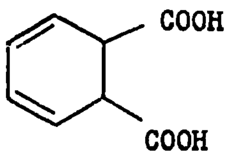

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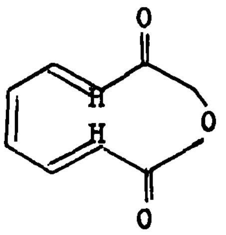

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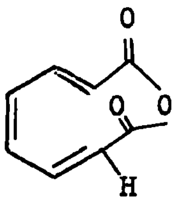
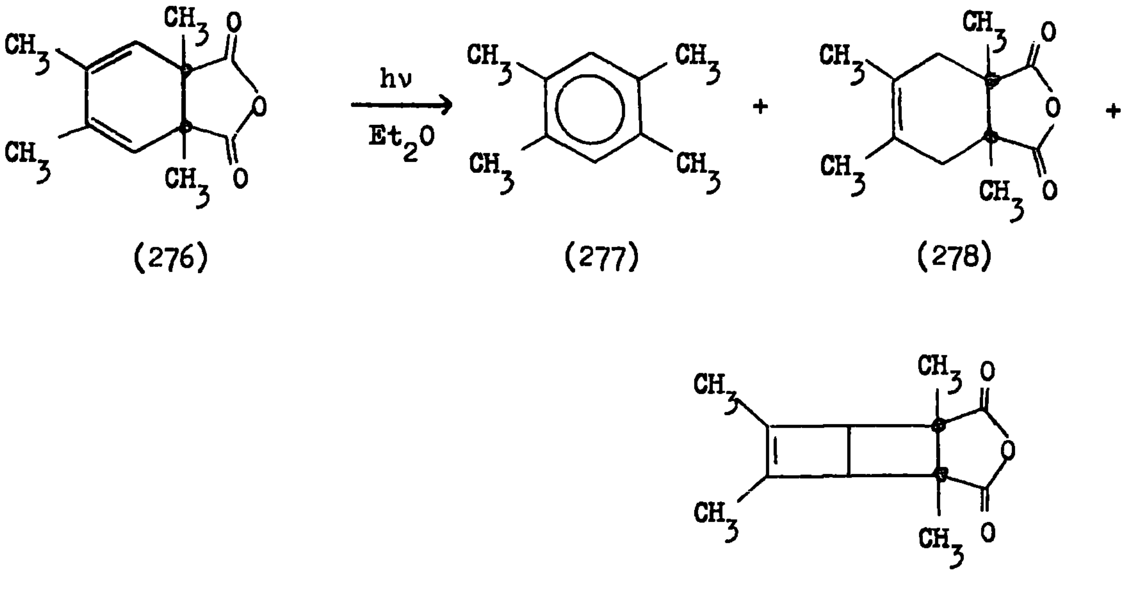


(275)

disrotatory ring opening of (267). The product which would hypothetically be formed by the photochemically allowed conrotatory process, (275) would be a highly strained structure. This reaction may be compared with the observed course of photolysis of diene (239) (Section 5.2e(i)) which ring opens to give triene (240). In the case of the hypothetical product (275) ring strain in the nine-membered ring would be increased by the further presence of two trigonally hybridised carbonyl carbons compared to (240). Thus in this case it is reasonable that disrotatory ring-closure of (267) to give (268) is energetically easier than ring-opening to triene (275).

Reexamination of the photolysis of (267) showed[136] that (268) was the exclusive photoproduct formed in 22% yield. However the behaviour of some substituted derivatives of (267) can be more complex. Thus irradiation of diene (276) gives[136] (277), (278) and (279), in respective yields up to 40%,



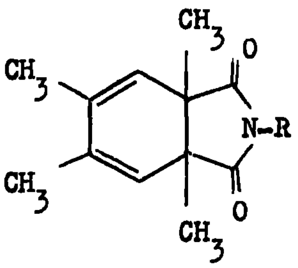
(276)

(277)

(278)

(279)

12% and 10%. Thus the products of ring closure, syn and anti isomers of (279), are only minor products from the reaction, the main process being aromatisation to durene, (277), carbon dioxide and carbon monoxide, in a process attributed to multicentre valence-electron redistribution of the excited diene rather than of the anhydride group itself. A curious photoreduction also occurs to give (278) in up to 12% yield. This product is photostable.



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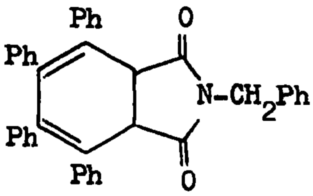
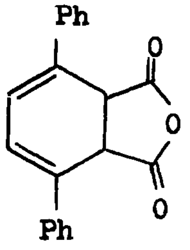


(281)

Bicyclo[2,2,0]hexene formation was also observed[138] on photolysis of the related imides (280) (R = H, Ph, Bu) and (281); for (280) (R = H) concommitant formation of durene was observed but not in the other cases.



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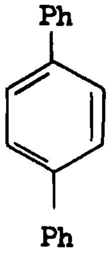

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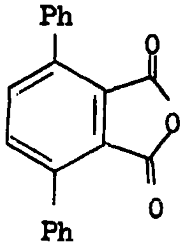

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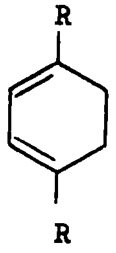
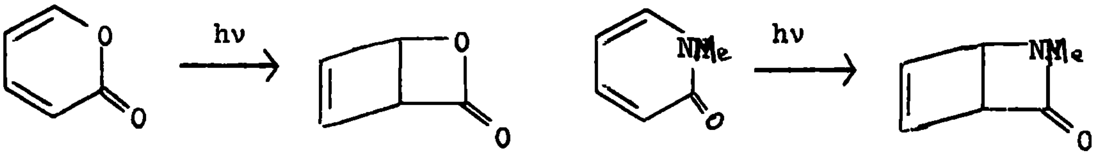


(285)

Irradiation of (282) at 254 nm. in 10^{-3}M ethereal solution gave[137] p-terphenyl (283) is 80-85% yield by loss of carbon monoxide and carbon dioxide. Irradiation at wavelengths greater than 310 nm. produced[137] dehydrogenation to give (284) and no formation of a bicyclo[2,2,0]hex-2-ene derivative was reported.

Claims[139] that sensitised irradiation of dienes (285) (R = $-CO_2CH_3$-CN) yielded bicyclo[2,2,0]hex-2-ene derivatives have since been placed in doubt.[140]

The highly conjugated molecule α-pyrone (286) (ν_{max} 291 nm., ε, 7500) on

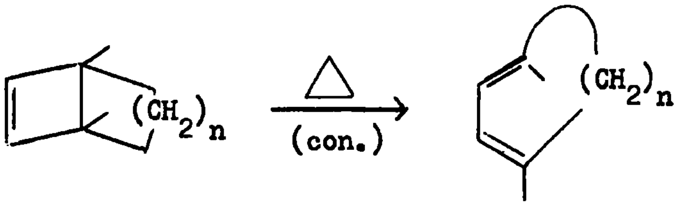


(286) (287) (288) (289)

irradiation at wavelengths below 250 nm. gives the bicyclic product (287) in virtually quantitative yield.[141] Molecule (287) is interesting in that it has the possibility of breaking down into highly unstable cyclobutadiene and carbon dioxide. It is in fact pyrophoric in air and can explode on warming. Similarly N-methylpyr[illegible]idone (288) is isomerised on irradiation to (289) in 20% yield.[141]

5.3 The factors which affect the thermal stability of bicyclo[2,2,0]hex-2-enes

The thermal ring opening of the bicyclo[n,2,0] derivatives (290) in the symmetry allowed conrotatory manner as shown leads to a cis-trans diene (291).



(290) (291)

Such a cis-trans diene becomes increasingly strained as the ring size diminishes. The trend is reflected in the temperatures, T, at which the half-life of compound (290) is 2 hours as n is varied; (from Reference 27, p.48):

n	1	2	3	4	5	6
T°C	<100°	195°	>380°	350°	335°	180°

As n decreases from 6 to 4 the ease of formation of the cis-trans diene (291) decreases and hence thermal stability (290) increases. For n = 3 it is no longer possible to produce cis-trans cycloheptadiene - the eight-membered ring is the smallest which can accommodate a cis-trans 1,3 diene and since (290) itself, for n = 3, is not very highly strained, thermal stability of bicyclo-[3,2,0]hept-2-ene is high. As n is decreased below 3, although the conrotatory ring opening is impossible, the compounds (290) are so highly strained that thermal stability falls rapidly and clearly for such highly strained molecules as bicyclo[2,1,0]pentene and bicyclo[2,2,0]hex-2-ene what stability they do possess is due to the fact that tranformations to the very much more stable molecules cyclopentadiene and cyclohexa-1,3-diene are symmetry forbidden by disrotatory ring opening.

The modes of thermal ring opening of compounds (290), n = 1,2,3,4 and related systems have been the subject of much speculation and the energetics of many systems have been studied in detail.[142] The decomposition of bicyclo [2,1,0] pentenes now seems to be a special case, where there is an alternative symmetry allowed pathway available as described earlier. The description of the process of ring opening in bicyclo[3,2,0]heptene[122] and in bicyclo[4,2,0] octene[143] has been given as disrotatory rather than via a diradical on energetic grounds, although bicyclo[4,2,0]octene could theoretically ring open to produce cis,trans cycloocta-1,3-diene.[143]

The energetics of ring-opening of bicyclo[2,2,0]hexene to cyclohexa-1,3-diene have not so far been investigated so that it is not yet possible to make an attempt at distinguishing between the possible biradical or disrotatory ring-opening mechanisms.

CHAPTER 5

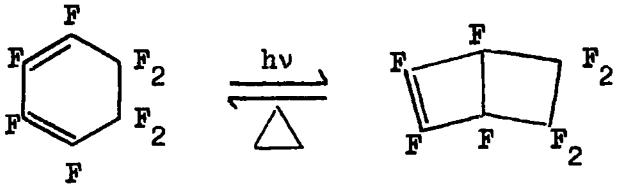
DISCUSSION

PHOTOCHEMICAL ISOMERISATION OF POLYFLUOROCYCLOHEXA-1,3-DIENES TO BICYCLO[2,2,0]HEX-2-ENES AND THE REVERSE THERMAL REACTION

5.4 Description of photolyses and pyrolyses

(a) Perfluorocyclohexa-1,3-diene (XIX)

Direct irradiation at 253.7 nm of perfluorocyclohexa-1,3-diene (XIX) (λ_{max} 256 nm., ϵ, 3.2×10^3)[19] in the vapour phase in a quartz ampoule gave a single photoproduct assigned as perfluorobicyclo[2,2,0]hex-2-ene (XX). With a sufficiently long irradiation time yields of (XX) were essentially quantitative. In runs where isomerisation was incomplete olefin (XX) was readily separated from unreacted (XIX) by preparative scale gas chromatography. Irradiations were carried out upon the vapour above the liquid diene (XIX), the liquid being shielded from the radiation by black paper. In this way quantities of (XX) of the order of 20 g. are readily prepared.



(XIX) b.p.63°

(XX) b.p.47°

The photoisomer (XX) showed the correct elemental analysis; its mass spectrum showed the same parent and fragment ions as that of perfluorocyclohexa-1,3-diene (XIX), however the relative abundances of the ions differed in the two cases (see Appendix B); the i.r. spectrum showed a single strong absorbtion at 1764 cm^{-1} (-CF=CF-); the ^{19}F spectrum (Table 5.1) fully confirmed the assigned symmetrical structure (XX), showing single resonances for the bridgehead fluorines (2F) and vinylic fluorines (2F) and a "pseudo" AB quartet pattern (4F) for the $-CF_2-CF_2-$ fluorines. This pseudo AB quartet pattern (Fig.5.1) is observed in many derived compounds (see Table 5.1 and Table 7.3) and is strictly an AA'BB' pattern showing further couplings to the other nuclei in the molecule. Thus the splitting pattern of limb 1 is not

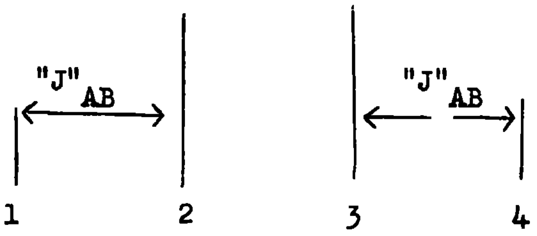
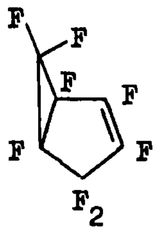


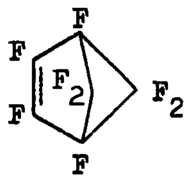
Fig.5.1

the same as in limb 2 and that of 3 is not identical to that of 4 as it should be in a true AB quartet pattern.

One of the two possible alternative structures for the photoisomer, bicyclo[3,1,0]hex-2-ene (292), is ruled out on symmetry grounds alone by the ^{19}F n.m.r. spectrum. However the other possible structure, perfluoro-



(292)



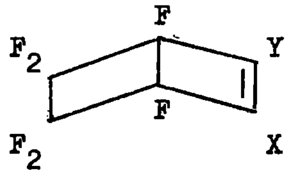
(293)

bicyclo[2,1,1] hex-2-ene (293), whilst being entirely unprecedented (see section 5.2e) might be expected to show a similar n.m.r. spectrum to (XX). However the photoisomer (XX) is readily and quantitatively isomerised thermally back to perfluorocyclohexa-1,3-diene (XIX) on pyrolysis in a flow system at 300°, 10^{-3}mm.Hg, a reaction only reasonable for isomer (XX).

The thermal stability of perfluorobicyclo[2,2,0]hex-2-ene (XX) is considerable. It can be stored indefinitely at room temperature without isomerisation or decomposition and pyrolysis in a flow system at 200°, 10^{-3} mm.Hg did not cause any isomerisation. It has been used in reactions in sealed tubes at 100° (see Chapter 7) without observation of any isomerisation.

TABLE 5.1

^{1}H and ^{19}F N.m.r. spectra and $\geq$C=C$\leq$ stretching frequencies and boiling points for 2,3-disubstituted hexafluorobicyclo[2,2,0]hex-2-enes



			^{19}F N.M.R. shifts in p.p.m. from CFCl$_3$				^{1}H N.M.R. (τ scale)				I.R.	m.p./b.p.
Compound Number	X	Y	-CF$_2$-CF$_2$- ("pseudo AB" pattern) $\vert\xleftrightarrow{"J"_{AB}}\vert\quad\vert\quad\vert$	$\succ$F	=CF-	^{19}F Ref.	=CH-,	-CH$_3$,	-OCH$_3$	^{1}H ref.	ν (C=C) cm^{-1}	b.p./m.p.
(XX)	F	F	117.0, 121.0, 128.3, 132.3 "J_{AB}" = 224 Hz	201.4	122.0	B	-	-	-		1764s	b.p. 47°
(XXXIX)	H	H	115.0, 118.9, 129.3, 133.1 "J_{AB}" = 218 Hz	191.4	-	A*	3.51	-	-	C*	-	m.p. 37°
(IV)	-CH$_3$	-CH$_3$	117.3, 121.2, 126.7, 130.5 "J_{AB}" = 220 Hz	194.6	-	B	-	8.15	-	D	-	b.p.127°

contd./

TABLE 5.1 contd.

		^{19}F N.M.R. shifts in p.p.m. from $CFCl_3$					^{1}H N.M.R. (τ scale)				I.R.	m.p./b.p.
Compound Number	X	Y	$-CF_2-CF_2-$ ("pseudo AB" pattern) $\vert\leftarrow$ "J"AB $\rightarrow\vert$	$\succ F$	=CF-	^{19}F Ref.	$=CH-, -CH_3, -OCH_3$			^{1}H ref.	ν(C=C) cm^{-1}	b.p./m.p.
(VII)	$-OCH_3$	$-OCH_3$	117.0, 120.7, 124.3, 128.1 "J_{AB}" = ca.210 Hz	190.4	-	A*	-	-	6.13	C"	1712ms	b.p.160°
(XII)	F	$-OCH_3$	117.7, 121.6, 126.7, 130.6 "J_{AB}" = 220 Hz	194.1 199.4	132.4	B	-	-	6.34	D	1733m	b.p.112°

N.M.R. References

A = measured in p.p.m. relative to internal $CFCl_3$

B = " " " external $CFCl_3$

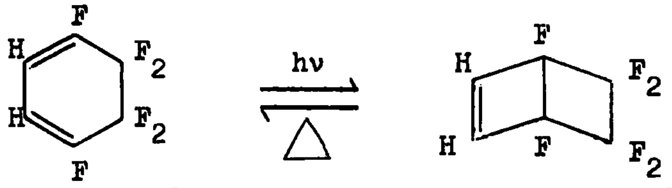
C = measured in p.p.m. relative to internal Me_4Si

D = " " " external Me_4Si

* CCl_4 solution (otherwise neat)

(b) 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII)

Photolysis of 2H,3H-hexafluorocyclohexa-1,3-diene (XXXXVIII) (λ_{max} 266.0, ε,3.3 x 10^{2})[7] in the vapour phase at 253.7 nm. gave 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene (XXXIX) as the sole photoproduct, which was obtained in 33% yield after preparative g.l.c. separation. Olefin (XXXIX) had the correct elemental analysis; the mass spectrum showed a strong parent peak and the



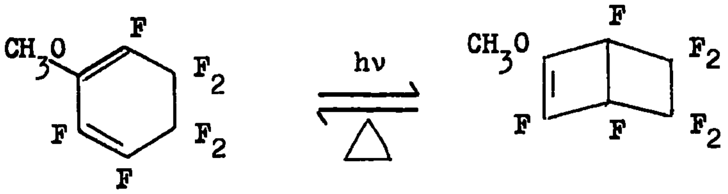
(XXXVIII) b.p.98°   (XXXIX) m.p.37°

same fragment peaks as for diene (XXXVIII) but the relative abundances of the ions differed (see Appendix B); the i.r. spectrum showed no strong absorbtions between 1600-1800 cm^{-1} in agreement with the presence of a symmetrically substituted -CH=CH- group; the ^{19}F and ^{1}H n.m.r. spectra (Table 5.1) were in full agreement with the proposed structure.

Olefin (XXXIX) shows similar thermal stability to perfluorobicyclo[2,2,0]hex-2-ene (XX); it can be stored unchanged as a solid at room temperature for several months. Pyrolysis at 300°, 10^{-3}mm.Hg in a flow system gives diene (XXXVIII) quantitatively.

(c) 2-methoxyheptafluorocyclohexa-1,3-diene (XI)

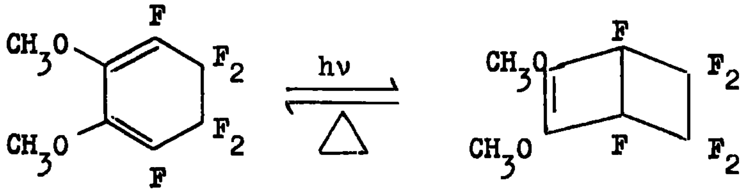
2-methoxyheptafluorobicyclo[2,2,0]hex-2-ene (XII) was initially prepared by nucleophilic substitution from perfluorobicyclo[2,2,0]hex-2-ene (XX) (see Chapter 6). Pyrolysis of olefin (XII) under the conditions used for



(XI) b.p.123°   (XII) b.p.112°

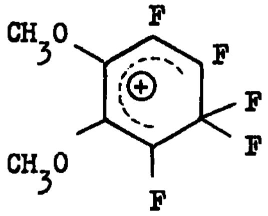
quantitative isomerisation of olefins (XX) and (XXXIX), i.e. 300°, 10^{-3}mm did not effect complete isomerisation of (XII) to diene (XI), there being about 20% of (XII) remaining. Pyrolysis at 400°, 10^{-3} mm. gave diene (XII) quantitatively with the correct i.r. spectrum. Thus the mono-methoxy derivative (XII) appears to be slightly more stable than the perfluoro and hexafluoro derivatives.

(d) 2,3-dimethoxyhexafluorocyclohexa-1,3-diene (VI)



(VI) b.p. 175°　　(VII) b.p.160°

2,3-dimethoxyhexafluorobicyclo[2,2,0]hex-2-ene (VII) was initially prepared by nucleophilic substitution from perfluorobicyclo[2,2,0]hex-2-ene (XX). Olefin (VII) is stable indefinitely at room temperature and does not decompose on heating at 100° in a sealed tube for several hours. Pyrolysis of (VII) at 400°, 10^{-3}mm.Hg in a flow system produced quantitative decomposition of (VII) giving the new diene (VI) (ca.90%), contaminated with other products, of slightly shorter retention time on analytical g.l.c. column A, which were not identified. Diene (VI) was obtained pure by preparative g.l.c. On standing diene (VI) decomposed over several days, the liquid became turbid and analytical g.l.c. indicated the presence of three new components which grew at the expense of diene (VI), until after 20 days diene (VI) was approximately 50% decomposed to the new compounds. In this department recent ^{19}F n.m.r. studies of diene (VI), carried out in liquid sulphur dioxide in the presence of antimony pentafluoride, indicate the ready formation of carbonium ion (294) by loss of fluoride ion.[144] This ease of carbonium ion formation may explain the instability of diene (VI), since a slightly alkaline surface of soda glass



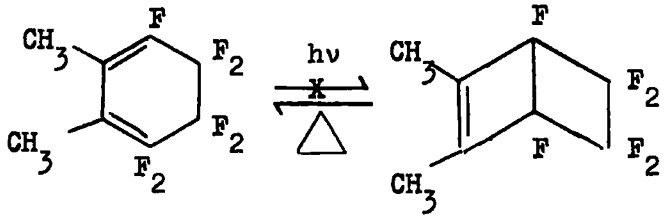
(294)

could cause facile elimination of hydrogen fluoride from (VI) leading to rearranged products and further decomposition, especially in the presence of traces of water. As mentioned in Chapter 2 diene (VI) decomposed completely when heated in a pyrex ampoule at 200° with ethylene.

Irradiation of the vapour of diene (VI) (λ_{max} 274.5 nm., ε, 1550) at 253.7 nm. for 66 hours gave olefin (VII) in low yield together with recovered starting materials and an involatile yellow oil.

(e) 2,3-dimethylhexafluorocyclohexa-1,3-diene (III) - attempted photolysis

2,3-dimethylhexafluorobicyclo[2,2,0]hex-2-ene (IV) was produced by nucleophilic substitution of perfluorobicyclo[2,2,0]hex-2-ene (XX) (see Chapter 6).



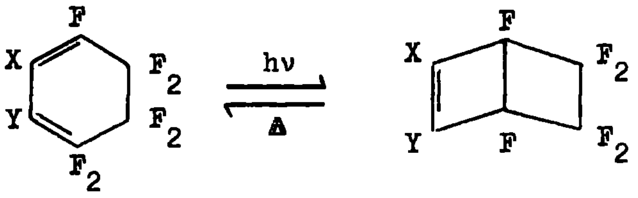
(III) (IV)

Pyrolysis of olefin (IV) at 300°, 10^{-3}mm.Hg gave diene (III) quantitatively.

Photolysis of diene (III) (λ_{max} 269.0 nm., ε, 2300) in the vapour phase at 253.7 nm. did not produce any of the expected photoisomer (IV) but gave a resin and only silicon tetrafluoride was detectable in the gas phase. This would seem to indicate that under the influence of ultraviolet light diene (III) eliminated hydrogen fluoride (which further reacted with the silica photolysis tube to give silicon tetrafluoride), since diene (III) and olefin (IV) can be stored unchanged for several weeks without decomposition in the absence of ultraviolet irradiation. Loss of hydrogen fluoride would yield a readily polymerisable triene accounting for the absence of tractable organic products.

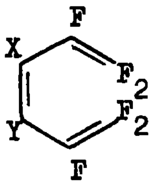
5.5 Comparison of the photochemical behaviour of polyfluorocyclohexa-1,3-dienes with that of hydrocarbon 1,3 dienes

From the foregoing work it appears that the interconversion $(295) \rightleftharpoons (296)$ has some generality.



(295) (296) (X and Y from F,H,OMe)

In the introduction section of this chapter it was shown that, in the absence of steric constraints, hydrocarbon dienes photoisomerise normally by conrotatory ring-opening to produce hexa-1,3,5-trienes; otherwise by disrotatory ring closure to give bicyclo[2,2,0]hex-2-enes. Since there are no steric constraints on dienes (VI), (XI), (XIX) and (XXXVIII) there can be no steric inhibition to the symmetry allowed conrotatory ring opening of these dienes to give the hypothetical triene (297). Nevertheless, photoisomerisation procceds via the alternative symmetry-allowed disrotatory ring closure reaction



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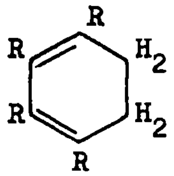


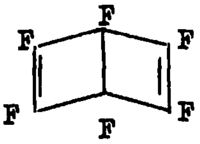
(298)

to give bicyclo[2,2,0]hex-2-enes and thus this pathway must be of lower activation energy in these cases.

A possible explanation of this behaviour may lie in the relative strengths of the C_5-C_6 bond in the dienes (296) compared to that of that in hydrocarbon cyclohexa-1,3-dienes. Substitution of hydrogen attached to aliphatic carbon by fluorine causes an increase in C-C σ bond strength.[101] The C-C bond of the $-CF_2-CF_2-$ group in dienes (295) will be stronger and consequently more difficult to break in a ring opening reaction than for instance in a hydrocarbon diene (298) having hydrogen substituents at C_5 and C_6.

5.6 The thermal stability of 2,3-disubstituted-hexafluorobicyclo[2,2,0]hex-2-enes

Octafluorobicyclo[2,2,0]hex-2-ene (XX) and its substituted derivatives (IV), (VII), (XIII), (XXXIX) possess remarkable thermal stability when compared to hexafluorobicyclo[2,2,0]hexa-2,5-diene (299), which is reported to be dangerously explosive in the liquid phase[145] and isomerises to hexafluorobenzene above 40°



(299)

in vapour phase.[146] Methyl-, trifluoromethyl-, methoxy- and hydrogen-substituted derivatives of (299)[145] are of similar thermal stability to (299) and their gas-phase decompositions have been studied.[147]

The greatly increased thermal stability of polyfluorobicyclo[2,2,0]hex-2-enes compared to the hexa-2,5-dienes reflects the lower angle strain of a structure containing only one double bond. The thermal stability of both these highly strained structures is explained by the symmetry-forbidden nature of the necessary disrotatory ring opening, as described for their hydrocarbon analogues in Section 5.3.

CHAPTER 5

EXPERIMENTAL

Photolyses were carried out in a silica tube, 40 cm. x 2.5 cm. diam. At its upper end it was connected by a graded seal to a pyrex constriction by means of which the tube could be sealed under vacuum. The pyrex seal was renewable. Irradiations were carried out in a Rayonet RPR 204 or 206 photochemical reactor fitted with low-pressure mercury lamps giving a narrow band centred at 253.7 nm. The reactor was placed over a powerful fan to maintain the temperature below 25°.

5.7 General Procedure for Photolyses

The diene to be photolysed was transferred from phosphoric oxide into the photolysis tube by vacuum transfer and the tube sealed under vacuum. The tube was maintained vertical and the diene allowed to warm to room temperature. The lower portion of the tube (ca. 8 cm.) was covered with black photographic paper to screen the liquid diene from the radiation, and the tube placed vertically in the photochemical reactor without splashing liquid diene up the sides of the tube onto the part of the walls exposed to the radiation. (Direct irradiation of the liquid diene can cause polymerisation). The liquid product was removed from the photolysis tube by vacuum transfer and where necessary separated by preparative g.l.c.

5.8 Photolyses

(a) Perfluorocyclohexa-1,3-diene (XIX)

Expt. 1. Irradiation of the diene (19.7 g.) for 220 hours gave (pure by analytical g.l.c.) octafluorobicyclo[2,2,0]hex-2-ene (XX) (19.5 g.) [Found: C,31.86; F,67.88%; M (mass spectrometry), 224. C_6F_8 requires C,32.16; F,67.84%; M 224], b.p. 47°, ν_{max} 1764 cm^{-1} (CF=CF).

If shorter irradiation times are used, separation of the unphotolysed diene may be readily accomplished by preparative g.l.c. and a greater rate of production of octafluorobicyclo[2,2,0]hex-2-ene obtained.

Exp.2. Irradiation of octafluorocyclohexa-1,3-diene (XIX) (26.43 g.)

was irradiated for 140 hrs. to give 26.21 g. of a liquid mixture which was separated by preparative g.l.c. (Column A, 100°) to give (i) octafluorobicyclo [2,2,0] hex-2-ene (XX) (13.2 g., 50%), (ii) octafluorocyclohexa-1,3-diene (XIX) (12.080 g.) with the correct i.r. (Total recovery 96%).

(b) 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII)

Irradiation of the diene (2.204 g.) for 88 hours gave a liquid mixture (1.98 g.) which was separated by preparative g.l.c. (Column B, 100°) to give (i) 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene (XXXIX) (0.718 g., 33%) [Found: C,38.39; H,1.01; F,60.7%, M (mass spectrometry), 188. $C_6H_2F_6$ requires C,38.31; H,1.07; F,60.61%; M, 188], m.p.37°; (ii) 2H,3H-hexafluorocyclohexa-1,3-diene (0.433 g.) with the correct i.r.

(c) 2-methoxy-heptafluorocyclohexa-1,3-diene (XI)

Irradiation of the diene (0.519 g.) for 50 hours gave a liquid product (0.354 g., 70%), shown by analytical g.l.c. and i.r. to be an approximately 95:5 mixture of 2-methoxy-heptafluorobicyclo[2,2,0]hex-2-ene (XII) and 2-methoxy-heptafluorocyclohexa-1,3-diene (XI). An involatile yellow oil remained in the photolysis tube.

(d) 2,3-dimethoxyhexafluorocyclohexa-1,3-diene (VI)

Irradiation of the diene (0.149 g.) for 66 hours gave a volatile liquid (0.026 g.), shown by analytical g.l.c. and i.r. to be an approximately equimolar mixture of (i) 2,3-dimethoxyhexafluorobicyclo[2,2,0]hex-2-ene (VII) and (ii) 2,3-dimethoxyhexafluorocyclohexa-1,3-diene (VI). An involatile yellow oil remained in the tube.

(e) 2,3-dimethylhexafluorocyclohexa-1,3-diene (III)

Photolysis of the diene (0.036 g.) for 27.5 hours gave (i) a small amount of gas, shown by i.r. to be predominantly silicon tetrafluoride, (ii) a brown film which remained on the walls of the photolysis tube.

5.9 Pyrolyses

The apparatus used was as described in the Experimental Section of Chapter 4.

(a) Octafluorobicyclo[2,2,0]hex-2-ene (XX)

The olefin (0.211 g.) was pyrolysed at 300°/10^{-3}mm.Hg to give octafluorocyclohexa-1,3-diene (XIX) (0.195 g., 92%) with the correct i.r. Analytical g.l.c. (Column A,100°) showed the complete absence of starting olefin.

(b) 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene (XXXIX)

The olefin (0.084 g.) was pyrolysed at 300°/10^{-3}mm.Hg to give 2H,3H-hexafluorocyclohexa-1,3-diene (XXXVIII) (0.062 g., 74%) with the correct i.r.

(c) 2-methoxy-heptafluorobicyclo[2,2,0]hex-2-ene (XII)

The olefin (1.195 g.) was pyrolysed at 400°/10^{-3}mm.Hg to give 2-methoxy-heptafluorocyclohexa-1,3-diene (XI) (1.124 g., 94%) with an i.r. spectrum identical to that of an authentic sample, supplied by Dr. R. Stephens, Birmingham University.

(d) 2,3-dimethoxyhexafluorobicyclo[2,2,0]hex-2-ene (VII)

The olefin (1.92 g.) was pyrolysed at 400°/10^{-3} mm.Hg to give a liquid mixture (1.74 g.) shown by analytical g.l.c. (Column A, 150°) to consist~~ing~~ of a major component contaminated with ca. 5% of two shorter retained components. Preparative g.l.c. (Column B, 100°) gave 2,3-dimethoxyhexafluorocyclohexa-1,3-diene (VI) (1.00 g., 52%) [Found: C,39.00; H,2.29; F,46.4%; M (mass spectrometry), 248. $C_8H_6F_6O_2$ requires C,38.72; H,2.44; F,45.94%; M, 248], b.p. 175°, ν_{max} 1718 and 1678 cm^{-1} (conjugated diene), λ_{max} 274.5 nm. (ε, 1550), ^{19}F and ^1H n.m.r. Table 1.2.

(e) 2,3-dimethyl-hexafluorobicyclo[2,2,0]hex-2-ene (IV)

The olefin (0.0643 g.) was pyrolysed at 300°/10^{-3}mm.Hg to give 2,3-dimethylhexafluorocyclohexa-1,3-diene (III) (0.053 g., 83%) with the correct i.r. spectrum.

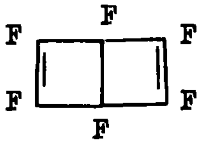
CHAPTER 6

NUCLEOPHILIC SUBSTITUTION REACTIONS OF PERFLUOROBICYCLO[2,2,0]HEX-2-ENE

INTRODUCTION

6.1 Nucleophilic substitution reactions of systems closely related to perfluorobicyclo[2,2,0]hex-2-ene

Nucleophilic substitutions have been carried out[145] on perfluorobicyclo [2,2,0]hexa-2-,5-diene (299) and on its bromine adduct (300), which is a 45:55



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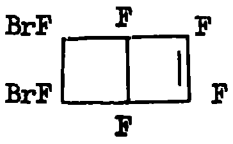

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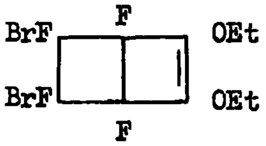
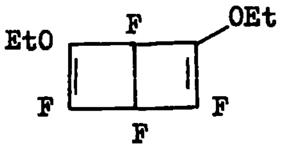


(301)

cis-trans mixture. When adduct (300) (1 mole) was reacted with sodium ethoxide (10 moles) in ethanol at 0° for 2 hours the diethoxy derivative (301) was obtained as a 1:1 cis-trans mixture in 83% yield after purification. No other products were reported from this reaction.

Reactions of perfluoro-Dewar Benzene (299) with nucleophiles are complicated by the possibility of aromatisation occurring during or after substitution. When diene (299) (1 mole) was reacted with sodium ethoxide (6 moles) in ethanol at 0° for 2 hours a 1:2 mixture of the diethoxy derivatives (302) and (303) was obtained in 65% yield. No other products were isolated



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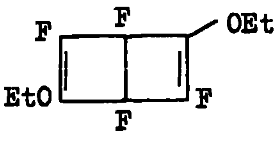
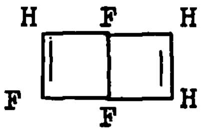


(303)

though small amounts of involatile materials were present.

Reaction of diene (299) (1 mole) with sodium borohydride (4 moles) in diglyme at 0° for 5 hours produced the trisubstituted derivative (304), together with aromatics (305) and (306) in the ratio 12:4:1. The aromatics were presumed to arise by thermal decomposition of (304) and (307) respectively, though (307) was not itself identified among the reaction products. The simple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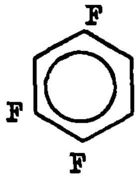
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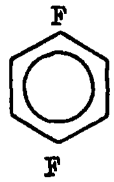
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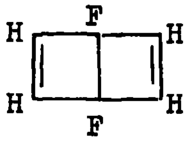
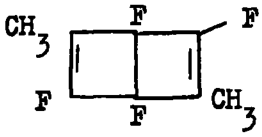

(307)

weight recovery of the liquid product before separation was only 36%.

Reaction of diene (299) (1 mole) with methyllithium (2 moles) in ether at -70° gave a 2:1 mixture of the dimethyl derivatives (308) and (309) in a combined yield of ca. 75%.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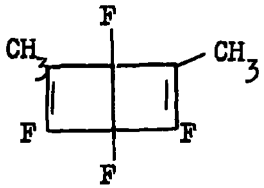
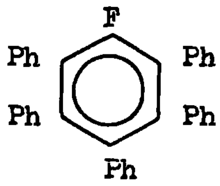

(309)

With phenylating agents, diene (299) gave only benzene derivatives. Thus the reaction of (299) (1 mole) with phenyllithium (4 moles) in ether at -70°, followed by warming to room temperature gave (310) and (311) in the ratio 1:4 in 71% combined yield. With phenyl magnesium bromide (a milder phenylating agent),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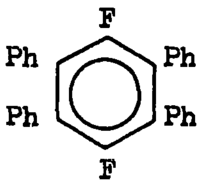
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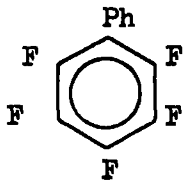
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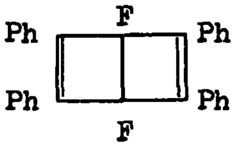
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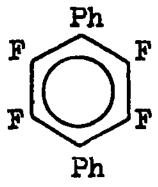
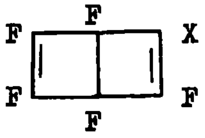

(314)

(299) gave the biphenyl (312). Control experiments with hexafluorobenzene indicated that the polyphenyl derivative (e.g. 313) was formed at low temperature and isomerised to (311) on warming to room temperature. Presumably (310) arose from (311) at room temperature. Hexafluorobenzene with phenyllithium under forcing conditions gave (314) as the major product.

Nucleophilic substitution of vinylic fluorine in (299) has also been observed using transition-metal complex ions, (X^-) to give the derivatives (315).[148]



(315)

$X^- = [Fe(CO)_2\pi(C_5H_5)]^-$

$[Re(CO)_5]^-$

$[Mn(CO)_5]^-$

CHAPTER 6

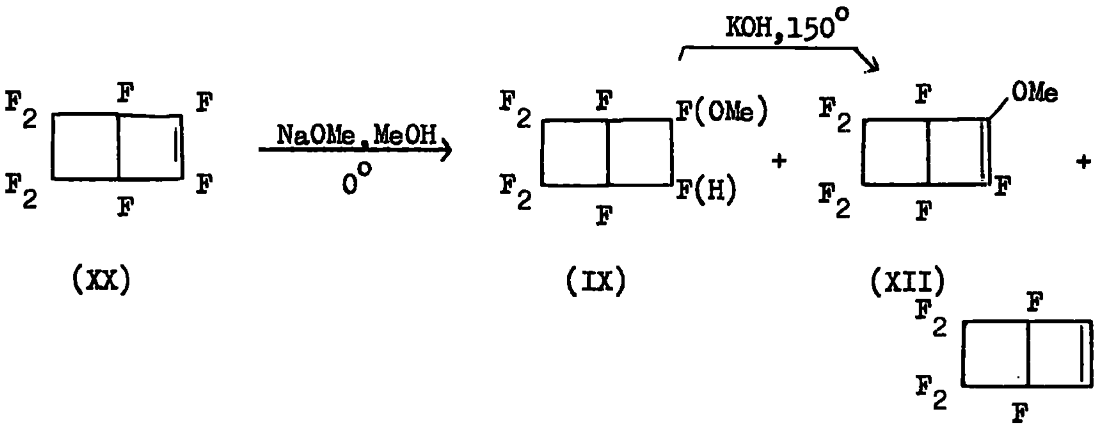
DISCUSSION

6.2 Nucleophilic substitution of perfluorobicyclo[2,2,0]hex-2-ene

Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with mildly nucleophilic reagents has been found to give products of substitution of one or both of the vinylic fluorine atoms, whilst more vigorous reagents give either high molecular weight materials of unknown structure or complex mixtures of polysubstitution products.

(a) Reaction with sodium methoxide in methanol

Olefin (XX) (1 mole) reacts with sodium methoxide (1 mole) in methanol at 0° over 2.5 hours to give a liquid product (ca.90% recovery) consisting of three components (IX), (XII) and (VII) in the approximate ratio (estimated by analytical g.l.c.) of 2:3:1. Using a molar ratio of olefin (XX):NaOMe of 1:1.4, when the reaction was run at 25° for 14 hours the same products were obtained in the approximate ratio of 2:3:8.



(XX)

(IX)

(XII)

(VII)

The products (IX), (XII) and (VII) were separated by preparative scale g.l.c. and characterised by elemental analysis and spectroscopy. Olefins (XII) and (VII) each showed a single strong infrared absorbtion in the carbon-carbon double bond stretching region at 1733 cm^{-1} (CF=C(OMe)) and 1712 cm^{-1} (C(OMe)=C(OMe)); their mass spectra (Appendix B) each showed a strong parent peak and a consistent breakdown pattern; and their ^{19}F and ^{1}H n.m.r. spectra (Table 5.1) were in full agreement with the assigned structures. Pyrolysis of

(XII) at 400°, 10^{-3}mm.Hg (Chapter 5) to give the known[10] 2-methoxyheptafluorocyclohexa-1,3-diene (XI) further confirmed the structure of (XII).

The methanol adduct (IX) showed no absorbtions between 1600-1800 cm^{-1} as expected for a saturated compound; in its mass spectrum (Appendix B) there was no parent peak and the highest mass peak was observed at m/e 224 (C_6F_8). The ^{19}F and ^{1}H n.m.r. spectra were in accordance with the proposed structure: the ^{1}H n.m.r. spectrum showed a sharp doublet centred at 6.60τ (with respect to external Me_4Si), ($-OCH_3$,3H) and a very broad doublet centred at 4.93τ (>CHF, J_{HF}(gem) 50 Hz, 1H); the ^{19}F n.m.r. spectrum showed: (a) two overlapping AB quartets (J_{AB} = 220 Hz in each) in the region 117.2-134.5 p.p.m. (relative to external $CFCl_3$), (two $-CF_2-$, 4F),(b) a complex multiplet at 134.5 p.p.m. (>C(OMe)F, 1F),(c) two complex resonances at 185.9 and 200.0 p.p.m. (>C-F, 1F each) and (d) a very broad complex multiplet at 201.4 p.p.m. (>CHF, 1F). The shift positions in this adduct of the H and F atoms in the -CHF-C(OMe)F-system of (IX) are similar to those in the related methanol adduct (VIII) obtained in the reaction of 1,2,3,4,5,5,6,6-hexafluorobicyclo[2,2,2]hex-2-ene with sodium methoxide in methanol - see Section 3.2a. As for adduct (VIII), the n.m.r. spectra of (IX) were consistent with the presence of a single isomer, however it was not possible to assign the relative stereochemistry of the -CFH- and -CF(OMe) groups.

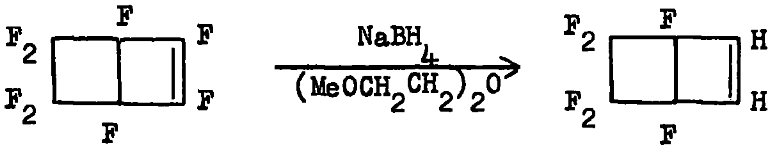
Dehydrofluorination of adduct (IX) in a flow system using potassium hydroxide at 150° gave (XII) as the sole product. This reaction is useful for removing (IX) from product mixtures of (IX), (XII) and (VII); the remaining products, (XII) and (VII) are then readily separated by preparative scale g.l.c.

The reaction of olefin (XX) with excess sodium methoxide in dry diglyme has recently been shown[144] to give the dimethoxy derivative (VII) as the sole product in a yield greater than 80%. No adduct (IX) was formed under these aprotic conditions.

These results are in full agreement with the usual addition-elimination mechanism for reactions of fluoroolefins as discussed previously in Chapter 3. In the light of these results it is surprising that Camaggi and Gozzo[145] obtained no ethanol adducts in the reactions of hexafluorobicyclo[2,2,0]hexa-2,5-diene (299) and its bromine adduct (300) with sodium ethoxide in ethanol.

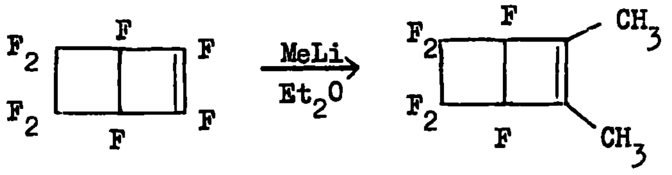
(b) Reaction with sodium borohydride in diglyme

When perfluorobicyclo[2,2,0]hex-2-ene (XX) (1 mole) was reacted with sodium borohydride (2.5 mole) in diglyme at 0° for 5 hours, the dihydro derivative (XXXIX) was produced in ca.29% yield as greater than 95% of the volatile product which distilled from the mixture after the reaction. Acidification of the involatile residue from the reaction gave a substantial amount of an organic liquid material which presumably formed in side reactions, thus reducing the yield of (XXXIX).



(XX) (XXXIX)

(c) Reaction with methyllithium in ether



(XX) (IV)

Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) (1 mole) with methyllithium (2 moles) in ether at -70° over 20 min. gave a solution whose analytical g.l.c. showed in addition to ether one major component (IV) and several shorter and longer retained materials in very small amount. The major component (IV) was obtained pure by fractional distillation and preparative scale chromatography in 19% yield. (This low yield probably reflects losses incurred in the separation procedure owing to the high volatility of (IV) rather than a low yield in the reaction itself).

2,3-dimethylhexafluorobicyclo[2,2,0]hex-2-ene (IV) was characterised by elemental analysis, spectroscopy and by pyrolysis (Chapter 5) to the previously prepared 2,3-dimethylcyclohexa-1,3-diene (III).[14] The ^{19}F and ^{1}H n.m.r. spectra (Table 5.1) were in full accord with the assigned structure and the mass spectrum (Appendix B) showed a strong parent (which was also the base peak) and a consistent fragmentation pattern.

(d) Reaction with lithium aluminium hydride

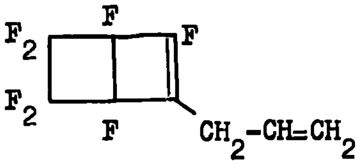
Perfluorobicyclo[2,2,0]hex-2-ene (XX) reacted violently with a suspension of lithium aluminium hydride in ether at -78°. On warming to room temperature a further exothermic reaction occurred. The product, a mixture of at least five components was shown by analytical g.l.c. to contain none of the expected disubstituted product (XXXIX). Two of the major components were separated pure by preparative g.l.c. with great difficulty and in very small amount. The mass spectrum of each showed a parent peak at m/e 134, indicating replacement of five fluorine atoms by hydrogen to give materials of composition $C_6F_3H_5$. The longer-retained material showed i.r. bands at 1700 cm^{-1} and 1745 cm^{-1} and the shorter-retained material showed bands at 1680 cm^{-1} and 1740 cm^{-1} in the C=C double bond stretching region and both dienes displayed ultraviolet absorbtions characteristic of conjugated dienes at 262 nm. and 260 nm. respectively. Thus it appears that the reaction proceeds by ring opening at some stage enabling further reduction to proceed, hence giving a complex mixture of products.

(e) Reaction with phenyllithium

Perfluorobicyclo[2,2,0]hex-2-ene (XX) reacted violently with phenyllithium in ether at -70° to give an intractable tar, concluded to be of very high molecular weight (see Experimental Section).

(f) Reaction with allyl magnesium bromide

In an attempt to synthesise ((316) and hence (317) by pyrolysis),



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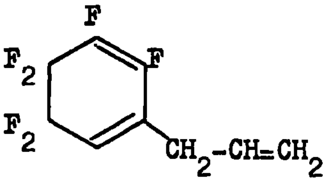

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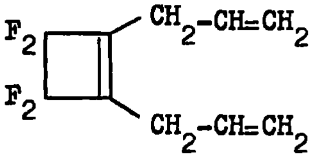


(318)

perfluorobicyclo[2,2,0]hex-2-ene (XX) was reacted with allyl magnesium bromide in ether at -78°. When the clear solution of allyl magnesium bromide was added to the precooled solution of (XX) in ether a dark brown resin formed immediately and no volatile products were detectable in the ether by analytical g.l.c.

Tarrant and Heyes[149] observed that replacement of vinylic fluorine by allyl groups in simple acyclic fluoroolefins could be accomplished in moderate yields, however in the reaction of perfluorocyclobutene with allyl magnesium bromide only polymer was obtained. They attributed this to facile polymerisation of (318), which was not isolated.

Possibly a similar explanation can be used to explain the reaction of olefin (XX) with allyl magnesium bromide, although polysubstitution may have also occurred.

CHAPTER 6

EXPERIMENTAL

6.3a Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with sodium methoxide in methanol

Reaction 1 (using equimolar quantities of the olefin (XX) and sodium methoxide)

To a solution of perfluorobicyclo[2,2,0]hex-2-ene (XX) (5.40 g., 24.2 mmoles) in dry methanol (20 ml.) at 0° was added dropwise a solution of sodium methoxide (1.30 g., 23.0 mmoles) in dry methanol (50 ml.) over a period of 0.5 hours and the mixture was stirred at 0° for 2.6 hours. The product was shaken with 2N hydrochloric acid (120 ml.). The lower organic layer (4.887 g.) was separated by preparative g.l.c. (Column B, 75 —— 100°) to give: (i) 2-methoxy-heptafluorobicyclo[2,2,0]hex-2-ene (XII) (1.39 g., 5.9 mmoles, 26%) [Found: C,35.81; H,1.45; F,56.6%; M (mass spectrometry), 236. $C_7H_3F_7O$ requires C,35.61; H,1.28; F,56.33%; M,236], b.p. 112°, ν_{max}, 1733 cm^{-1} (-C(OMe)=CF-), ^{19}F and ^{1}H n.m.r. (see Table 5.1); (ii) 1,2,3,4,5,5,6,6-octafluoro-2-methoxy-bicyclo[2,2,0]hexane (IX) (0.924 g., 3.6 mmoles, 15%) [Found: C,32.71; H,1.59; F,59.8%. $C_7H_4F_8O$ requires C,32.83; H,1.57; F,59.4%]; (iii) 2,3-dimethoxy-hexafluorobicyclo[2,2,0]hex-2-ene (VII) (0.295 g., 1.19 mmoles, 4.9%) [Found: C,38.58; H,2.28; F,46.1%; M (mass spectrometry), 248. $C_8H_6F_6O_2$ requires C,38.72; H,2.44; F,45.94%; M, 248], b.p. 160°, ν_{max} 1712 cm^{-1}, ^{19}F and ^{1}H n.m.r. see Table 5.1.

Reaction 2 (using olefin (XX) and sodium methoxide in the molar ratio 1:1.4 and the procedure as for Reaction 1).

Olefin (XX) (10.6 g., 47.4 mmoles) in methanol (40 ml.) and sodium methoxide (3.68 g., 68 mmoles) in methanol (100 ml.) stirred at 25° for 14 hours gave 10.5 g. of a liquid product. G.l.c. analysis (Column A, 150°) indicated the presence of (XII), (IX) and (VII) in the approximate ratio 3:2:8.

Dehydrofluorination of 1,2,3,4,5,5,6,6-octafluoro-2-methoxybicyclo[2,2,0] hexane (IX)

Using the procedure described in Chapter 1, 1,2,3,4,5,5,6,6-octafluoro-2-methoxybicyclo[2,2,0]hexane (IX) (0.10 g.) was passed through molten potassium hydroxide at 170° in a stream of nitrogen to give 2-methoxyheptafluorobicyclo[2,2,0]hex-2-ene (XII) (0.05 g.) with the correct i.r. spectrum. Analytical g.l.c. (Column A, 100°) showed that less than 1% of (IX) remained undehydrofluorinated in the product.

Dehydrofluorination of the product from Reaction 2

The liquid product (10.5 g.) was passed through molten potassium hydroxide at 195° in a stream of nitrogen to give a liquid mixture (5.91 g.) shown by analytical g.l.c. to consist of only (XII) and (VII) with no (IX) remaining. The mixture was separated by preparative scale g.l.c. (Column B, 120°) to give (i) 2-methoxyheptafluorobicyclo[2,2,0]hex-2-ene (XII) (1.225 g., 5.2 mmoles, 11% overall on perfluorobicyclo[2,2,0]hex-2-ene (XX)) and (ii) 2,3-dimethoxyhexafluorobicyclo[2,2,0]hex-2-ene (VII) (3.265 g., 13.2 mmoles, 28%).

6.3b Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with sodium borohydride in diglyme

To a suspension of sodium borohydride (1.89 g., 49.5 mmoles) in dry di(2-methoxyethyl)ether (diglyme) (50 ml.) at 0° was added a solution of perfluorobicyclo[2,2,0]hex-2-ene (XX) (4.54 g., 20.2 mmoles) dropwise over 25 minutes and stirring was continued at 0° for 5 hours. The volatile product together with some solvent was pumped off into a trap cooled in liquid air. The contents of the trap were shaken with NHCl (50 ml.) and the lower fluorocarbon layer (1.09 g.) run off. Analytical g.l.c. and i.r. showed it to be ca.95% 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene (XXXIX).

Destruction of the excess sodium borohydride by addition of 2N HCl (200ml.) to the residue gave an involatile oil (1.17 g.) as a lower layer.

6.3c Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with methyllithium in ether

To a solution of perfluorobicyclo[2,2,0]hex-2-ene (XX) (3.128 g., 14.0 mmoles) in ether (10 ml.) cooled to -78° was added dropwise a solution of methyllithium[150] in ether (21.6 ml. of a 1.3M solution, 28 mmoles) over 20 minutes. The mixture was allowed to warm to room temperature and shaken with 2N HCl (30 ml.). The ethereal layer was dried ($MgSO_4$) and distilled through a short column to give a residue (ca. 3 g.) which was separated by preparative scale g.l.c. (Column B, 130°, 9 injections) to give ether and 2,3-dimethylhexafluorobicyclo[2,2,0]hex-2-ene (IV) (0.57 g., 2.66 mmoles 19%) [Found: C,44.7; H,2.8; F,52.4%; M (mass spectrometry), 216. $C_8H_6F_6$ requires C,44.5; H,2.8; F,52.8%; M, 216], b.p. 127°, ^{19}F and ^{1}H n.m.r. spectra see Table 5.1.

6.3d Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with lithium aluminium hydride in ether

Using the procedure for lithium aluminium hydride reductions described in Chapter 3, a solution of perfluorobicyclo[2,2,0]hex-2-ene (XX) (10.3 g., 45.6 mmoles) in ether (10 ml.),was added dropwise to a suspension of lithium aluminium hydride (3.2 g., 89.2 mmoles) in ether (25 ml.) all at -78°. A violent reaction was observed on each addition. The mixture was allowed to warm to room temperature and worked up as before (Chapter 3), to give a colourless liquid mixture (7.075 g.) still containing some ether. Analytical g.l.c. (Column A, 60°) showed three components in addition to ether. Very small amounts (ca. 20 mg.) of the first 2 components were obtained pure by preparative scale g.l.c. (Column B, 25°). The spectroscopic examination is described in the Discussion (Section 6.2d).

6.3e Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with phenyl lithium in ether

To a stirred solution of phenyl lithium[151] (400 mmoles) in ether (100 ml.) precooled to -78°, was added dropwise perfluorobicyclo[2,2,0]hex-2-ene (4.75 g., 21.2 mmoles) in ether (7 ml.). A violent reaction took place on each addition. The mixture was allowed to attain room temperature. Water (100 ml.) was added and the ether layer separated, washed with water (3 x 50 ml.) and dried ($MgSO_4$). The ether was removed to give a red-brown oil. Sublimation ($70^o/10^{-3}$mm.) gave only biphenyl (1.003 g.) with the correct i.r. spectrum. Column chromatography of the residue on SilicAR using petrol (b.p. 40-60°) gave only biphenyl (0.11 g.). A brown residue remained at the top of the column.

6.3f Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with allyl magnesium bromide in ether

Allyl magnesium bromide was prepared according to reference 152 and was 1.02M by titrimetric analysis.

To a solution of perfluorobicyclo[2,2,0]hex-2-ene (XX) (1.775 g., 7.95 mmoles) in ether (20 ml.) cooled to -78° was added dropwise a clear ethereal solution of allyl magnesium bromide (8.1 ml. of a 1.02M solution, 8.1 mmoles). A dark brown resinous substance was formed immediately on each addition. After stirring at -78° for 1 hour, any volatile products and solvent were pumped off maintaining the temperature at ca. -10°. G.l.c. analysis of the volatiles showed only ether and a trace of allyl bromide. To the involatile residue was added 2N HCl (20 ml.) and ether (20 ml.). The ether layer was separated and the ether removed on a rotary evaporator to give a tar (0.806 g.).

CHAPTER 7

2,3-Disubstituted Polyfluorobicyclo[2,2,0]hex-2-enes as Dienophiles

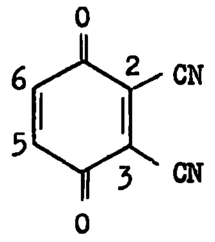
INTRODUCTION

The factors Affecting the Dienophilicity of Carbon-Carbon Double Bonds

Further to Section 2.2 a more detailed consideration will be given to the factors which affect the dienophilicity of carbon-carbon double bonds. Only reactions with electron-rich dienes are to be considered.

7.1 The effect of cross-conjugation

Cross conjugation of the C=C double bond with carbonyl or cyano groups very greatly increases its dienophilicity (see Section 2.4). Quinones additionally substituted with electron-attracting groups prove to be particularly reactive with respect to electron-rich dienes.[30] Where there are two dienophilic double bonds in a molecule, the reaction occurs at the most highly activated double bond rather than at the least sterically crowded one. Thus cyclopentadiene, 2,3-dimethylbuta-1,3-diene and 3,4-dimethylenecyclobutene add across the 2,3 rather than the 5,6 carbon atoms in (319) and (320) and across the 9,10 positions rather than the 2,3 positions in (321).



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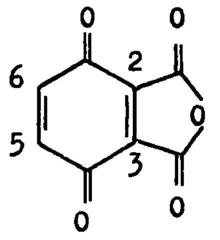

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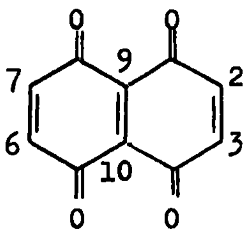


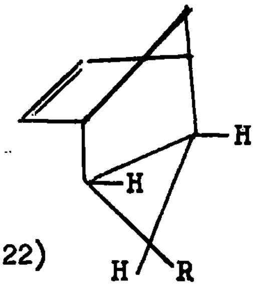
(321)

7.2 The effect of angle strain

Cyclic olefins (and acetylenes) with pronounced angular strain exhibit enhanced dienophilic reactivity. It has been argued[30] that the driving force for reaction is associated with a reduction of angular strain in the transition state leading to adduct formation.

(a) Cyclopropenes as dienophiles

Cyclopropene and 3-methylcyclopropene react[153,154] quantitatively and stereospecifically with cyclopentadiene at 0° to give the endo-anti adducts (322) (R = H,Me respectively). The effect of ring strain is apparent from the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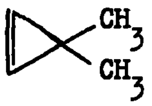
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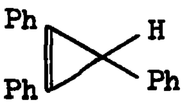
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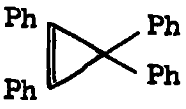
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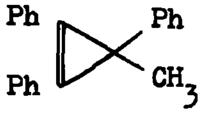
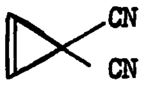

(326)

fact that ethylene only reacts with cyclopentadiene at 200° under high pressure.[155] The geminally disubstituted cyclopropene (323),[154] although stable at room temperature, is unreactive towards cyclopentadiene at room temperature. The 1,2,3-triphenyl derivative (324) reacts[156] with cyclopentadiene at room temperature in 85% yield to give the endo-anti adduct analogous to (322), whereas the tetrasubstituted derivatives (325) and (326) are unreactive in the Diels-Alder reaction even under forcing conditions. 3,3-Dicyanocyclopropene (327)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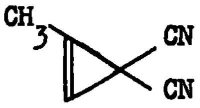
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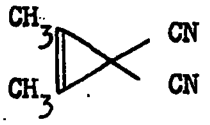
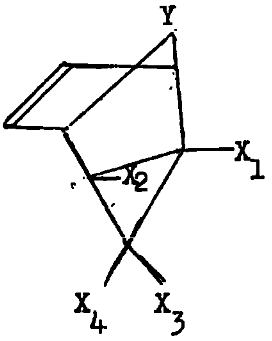

(329)

gave[157] a Diels-Alder adduct with 2,3-dimethylbuta-1,3-diene rapidly at 76° but its monomethyl derivative (328) reacted only at 120° and the dimethyl derivative (329) was unreactive even at 150°.

Several halogenated cyclopropenes are known. Tetrahalocyclopropenes have been found to undergo facile 1,4 addition to cyclopentadiene, furan and buta-1,3-diene. Competition reactions have shown[158] that although tetrahalocyclopropenes are less reactive than cyclopropene itself, tetrabromocyclopropene reacts more readily than tetrachlorocyclopropene and that both these cyclopropenes are more reactive than their counterparts having 3,3-difluoro-substituents. The observed relative rate-enhancing effect of halogen substituents in the 3 position upon cyclopropene reactivity towards furan is Br $>$ Cl $>$ F, an order inversely opposed to that predicted on steric grounds, and to that predicted by the Alder Rule. These observations have been rationalised[158] in terms of the thermodynamic stability of the cyclopropenes involved. It is argued that factors which stabilise the ground state energies of the cyclopropenes will decrease dienophilicity. The effect of replacement of chlorine or bromine at the methylene carbon atom by fluorine is postulated to change the bonding properties of the methylene carbon so that internal ring sigma bond strain is diminished and the overall cyclopropene thermodynamic ground state energy is lowered. (Closs et al.[154] suggest that replacement of hydrogen by alkyl at the 3 position has a similar stabilising effect on cyclopropenes). Preferential stabilisation by fluorine relative to chlorine has been observed elsewhere in three- and four-membered ring chemistry. Thus[162] perchlorocyclopropane ring opens at 250° whereas perfluorocyclopropane is stable up to 1000° and perfluorocyclobutene is thermodynamically favoured over perfluorobuta-1,3-diene at 200°, whereas for perchlorobuta-1,3-diene the equilibrium lies towards perchlorobuta-1,3-diene at this temperature.

The initial adducts of perhalocyclopropenes with cyclopentadiene and furan (330) (Y = CH$_2$ and O respectively) in some cases are unstable and



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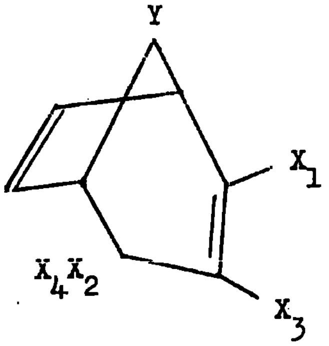

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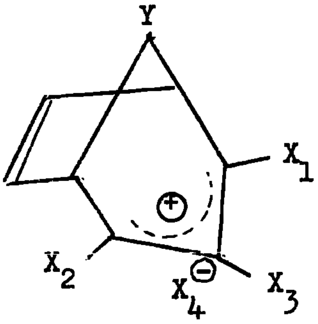
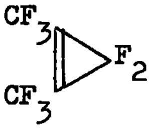


(332)

rearrange spontaneously by the cyclopropyl-allyl rearrangement to give[158] the isomer (331). This thermal reaction is a concerted disrotatory process with stereospecific loss of the endo-halogen (X_4) as X_4^- to give the intermediate ion pair (332) which collapses to (331). When X_4 is Cl or Br the rearrangement is very facile and the initial adducts are not observed and the adduct (331) is the observed product of the Diels-Alder reaction. When the endo halogen X_4 is fluorine the rearrangement occurs much less readily and the initial adduct (330) may be observed. Thus perfluorocyclopropene reacts[159] with furan at room temperature over several days to give (330) ($Y = O$, $X_1 = X_2 = X_3 = X_4 = F$) in 30% yield which appears to be stable, and with cyclopentadiene to give (330) ($Y = CH_2$, $X_1 = X_2 = X_3 = X_4 = F$) which takes 6 days to rearrange completely to (331). Other workers found[160] that perfluorocyclopropene gave the same product with furan in a reaction carried out at 80°.

1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene (333) is very much more



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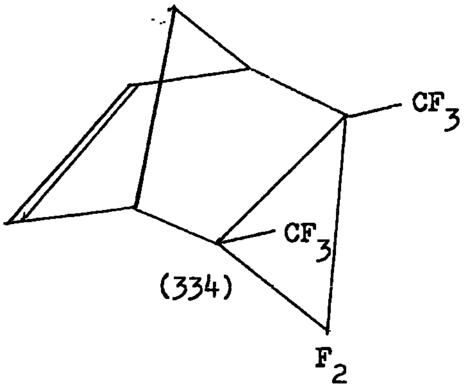

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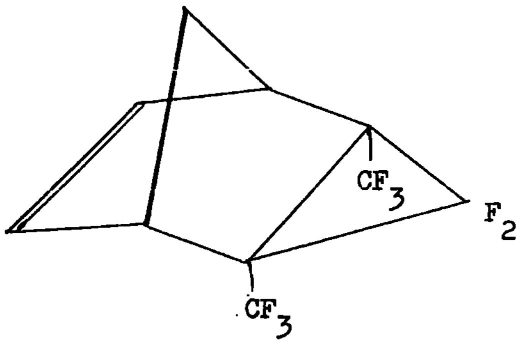

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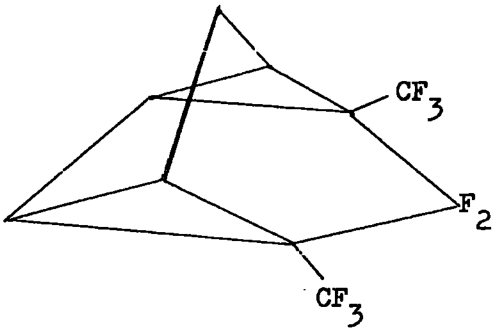
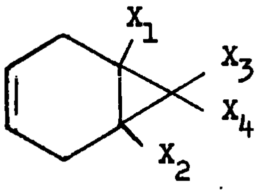


(336)

reactive than perfluorocyclopropene and reacts with cyclopentadiene at -78° to give the endo- and exo-adducts (334) and (335) in the ratio 31:69 in 90% yield.[159] At 65° (335) rearranged to (334). The cyclopropyl-allyl rearrangement did not occur but at 200° after 1 hour the tetracycle (336) was obtained quantitatively. Furan reacted with (333) instantaneously in quantitative yield.

The adducts (337) (a-f)[158] are formed smoothly at 80° from buta-1,3-diene



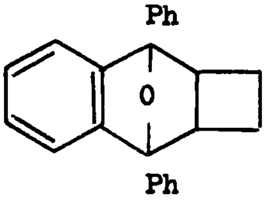
(337)(a-f)

	X_1	X_2	X_3	X_4
a)	Cl	Cl	F	Cl
b)	Cl	Cl	F	F
c)	Br	Br	F	F
d)	Cl	F	F	F
e)	Cl	Cl	Cl	Cl
f)	Br	Br	Br	Br
g)[161]	F	F	F	F

and the corresponding tetrahalocyclopropene and they are stable at 100°. None of these adducts (337) (a-g) were observed to undergo cyclopropyl-allyl rearrangement. The driving force for the rearrangement of the tricyclic adducts (330) must thus be relief of ring strain which is not so acute in adducts (337).

(b) Cyclobutenes as dienophiles

The only reported Diels-Alder reaction of cyclobutene itself appears to be that with the highly reactive diene 1,3-diphenylisobenzofuran to give[163] adduct (338) in 60% yield at room temperature from which it is not possible to assess its reactivity. The cis 3,4-dichlorocyclobutene (339) has however received considerable attention as a dienophile, but relatively high reaction temperatures appear to be required. Thus (339) gives Diels-Alder adducts with 1,3-diphenylisobenzofuran (rapid reaction at 100°, adduct formed in 86%



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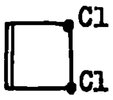
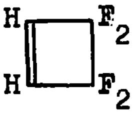


(339)

yield[164]), cyclopentadiene (140°, 73% yield[165]), furan (120°, 10% yield[165]), tetraphenylcyclopentadienone (140°, 80% yield), 1,4-dimethyl-2,3-diphenylcyclopenta-1,3-dien-5-one (60°, product a 4:1 mixture of anti-exo and anti-endo isomers, combined yield 85%[166]), hexachlorocyclopentadiene (140°, 33% yield[165]), anthracene (150°, 74% yield[167]) and 9,10-dimethylanthracene (150°, 90% yield[167]). From these data is would appear that (339) is only moderately dienophilic towards electron-rich and electron-poor dienes.

3,3,4,4-tetrafluorocyclobutene (340) reacted[168] to give 1:1 Diels-Alder



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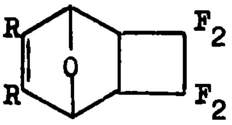

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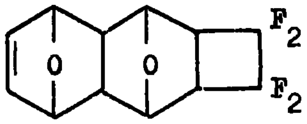


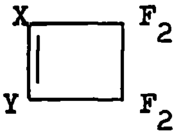
(342)

adducts with buta-1,3-diene (reaction temperature 150°, 75% yield), 2,3-dimethylbuta-1,3-diene (100°, 96%), cyclopentadiene (90°, 60%), furan (100°, 77%), 2,3-dimethylfuran (100°, 40%). With furan in addition to the 1:1 adduct (341) (R = H), a 2:1 adduct (342) was also formed, however with 2,5-dimethylfuran only the 1:1 adduct (341) (R = CH_3) was formed.

Other halogenated cyclobutenes (343) have been reported[169] to display dienophilic behaviour towards butadiene, isoprene and 2,3-dimethylbutadiene to give 1:1 adducts as shown in Table 7.1.

Table 7.1

Yields of adducts of halogenated cyclobutenes (343) with (a) butadiene, (b) isoprene and (c) 2,3-dimethylbutadiene



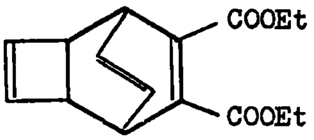
(343)

Compound	X	Y	(a)	(b)	(c)
(i)	F	F	-	-	77%
(ii)	F	Cl	3%	20%	89%
(iii)	H	Cl	28%	84%	88%

Unfortunately no reaction temperatures are given for the reactions. However it appears that 3,3,4,4-tetrafluorocyclobutene (340) is acting as an electron-poor diene, giving a higher yeild of adduct with 2,3-dimethylbuta-1,3-diene than with buta-1,3-diene and at a lower temperature.

(c) Fused cyclobutenes as dienophiles

Fusion of another small ring with the cyclobutene ring enhances dienophilicity by increasing ring strain. Thus compound (344) forms[166] a mixture of endo- and exo-adducts (345) at the most strained of its two



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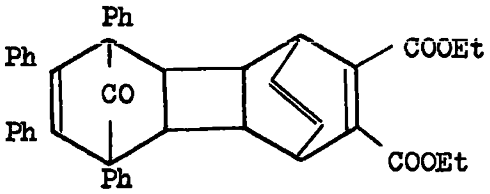

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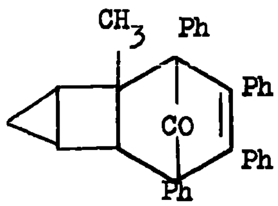
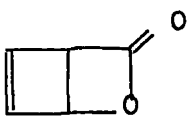


(346)

electron-rich double bonds, i.e. at the double bond in the fused cyclobutene system. The highly strained molecule 2-methylbicyclo[2,1,0]pentene (209) gives[116] adduct (346) quantitatively at room temperature, and the photoisomer of α-pyrone (287) reacts[141] quantitatively at 0° with 2,5-diphenylisobenzofuran to give adduct (347).



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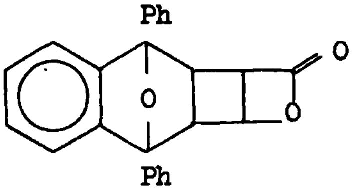

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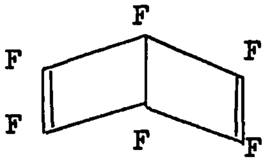
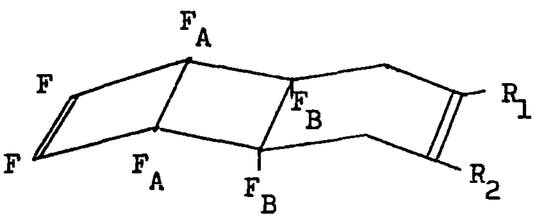
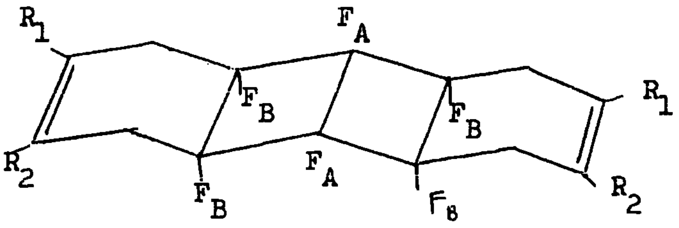


(299)

The structure of perfluorobicyclo[2,2,0]hexa-2,5-diene (299) has been shown by electron diffraction[170] to be bent, as expected from simple molecular models, into roughly an 'open-book' form with the angle between the 'covers' approximately 120°. Diene (299) is a reactive dienophile[171a and 171b] reacting at room temperature with electron-rich dienes to give 1:1 and, more slowly, 2:1 adducts as shown in Table 7.2. Prior to this work unsubstituted pyrrole had not been observed to react as a diene in the Diels-Alder reaction. Yields of adducts appear to be limited only by the slow aromatisation of (299) to hexafluorobenzene. ^{19}F n.m.r. measurements indicated[171b] that the 1:1 and 2:1 adducts with cyclic and acyclic dienes all had the cis-exo structures (347a)-(350).



(347a)



(348)

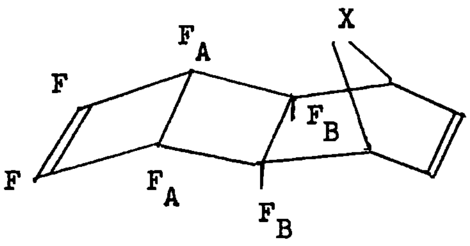
[R_1 and R_2 = Me,H]

TABLE 7.2

Diels-Alder Adducts of Perfluorobicyclo[2,2,0]hexa-2,5-diene[171]

	Diene	Reaction Time	Yield 1:1 adduct (%)	Yield 2:1 adduct (%)
(i)	cyclopentadiene	12 hours	70	15
(ii)	furan	19 hours	84[a]	8
(iii)	pyrrole	8 weeks	58[b]	-
		5 months	-	29[c]
(iv)	1,4-diphenylisobenzofuran	5 hours	100	-
		18 days	-	96[c]
(v)	ααdimethylfulvene	8 days	72[b]	4
(vi)	2,3-dimethylbuta-1,3-diene	60 days	54	-
		9 weeks	-	84[c]
(vii)	2-methylbuta-1,3-diene	7 months	43[b]	12
(viii)	buta-1,3-diene	6 months	51	-
(ix)	cyclohexa-1,3-diene	7 months	16	-

NOTES: a = yield on furan; b = yield on hexadiene converted; c = obtained by reaction of the 1:1 adduct with excess diene in ether solution.



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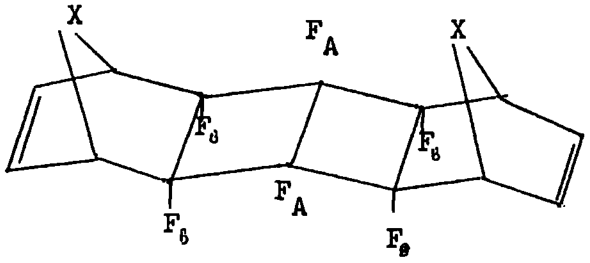


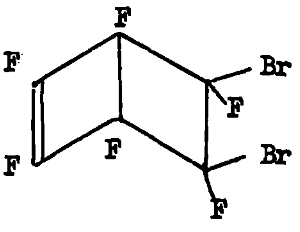
(350)

[X = CH_2,NH,O, C=CMe_2, $(CH_2)_2$]

In the 1:1 adducts (347a) and (349) the chemical shifts of fluorine F_A lay between +168·1 and +175·9 p.p.m. (relative to $CFCl_3$), whilst the shifts of F_B lay between +143·0 and +195·2 p.p.m. In the 2:1 adducts (348) and (350) the shifts of F_A lay between 149·2-173·5 p.p.m. and those of F_B lay between +162·9 and +173·9 p.p.m.

Perfluorobicyclo[2,2,0]hexa-2,5-diene (299) did not react with thiophen, cycloheptatriene, norbornadiene, tetramethylethylene, ethyl vinyl ether or diphenyl acetylene over several months[171b] but it is a reactive dipolarphile.[172] This property like dienophilicity is also association with ring-strain.

The exo-dibromide (351) is stated[171a and b] to be a good dienophile under comparable conditions to those used in the reactions of (299) but no data have yet been published.



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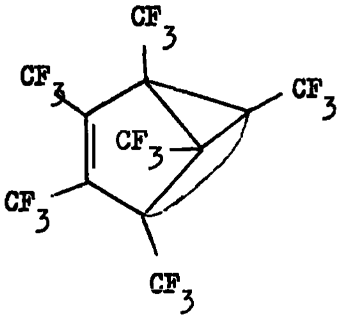


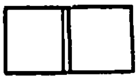
(352)

(d) Other strained olefins as dienophiles

It appears that the valence bond isomer (352) of hexakis(trifluoromethyl)benzene is a very reactive dienophile; it gives a quantitative yield of

1:1 adduct with cyclopentadiene in 2 minutes at 20°.[171a] From this observation and the very high observed dienophilicity of 1,2-bis(trifluoromethyl)cyclopropene (333) it would appear that trifluoromethyl substituents attached to ring-strained endocyclic double bonds enhance reactivity towards electron-rich double bonds, in spite of what may be presumed to be an unfavourable steric effect.

Under favourable conditions certain highly strained bridgehead olefins can be formed, and these are very reactive dienophiles. Thus for example $\Delta^{1,4}$-bicyclo[2,2,0]hexene (353)[173] was trapped as a Diels-Alder adduct of cyclopentadiene, and the olefin (354)[176] and its perfluoro-derivative (355)[174] have each been trapped as a Diels-Alder adduct with furan.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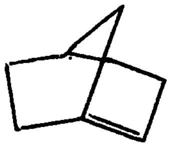
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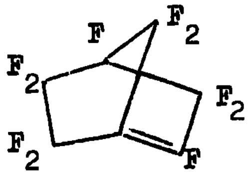


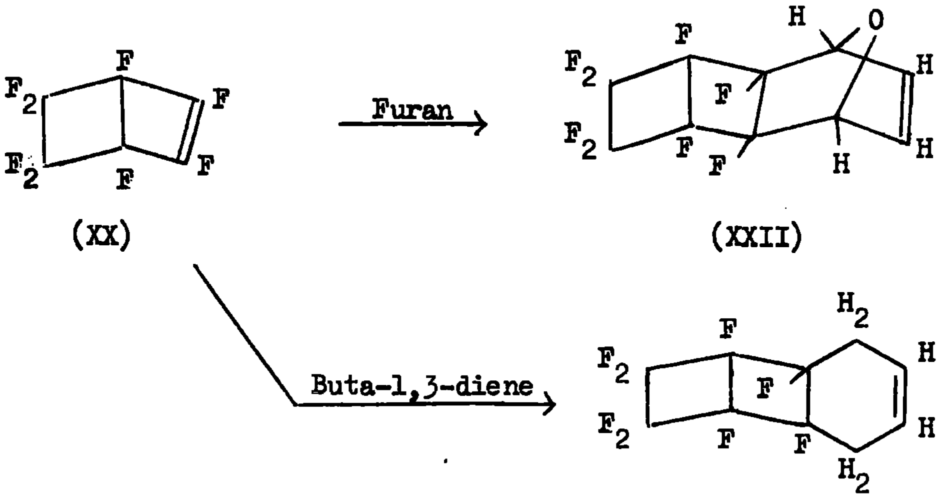
(355)

CHAPTER 7

DISCUSSION

7.3 The Effect of Double-Bond Substituents on the dienophilicity of 2,3-disubstituted-hexafluorobicyclo[2,2,0]hex-2-enes

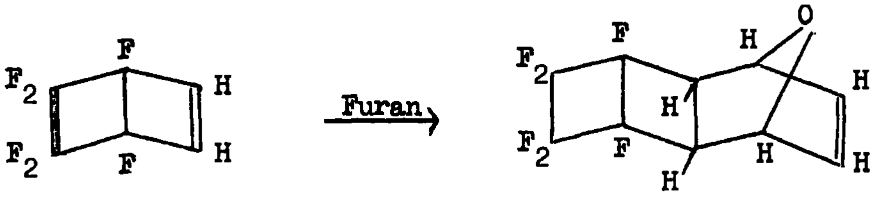
Perfluorobicyclo[2,2,0]hex-2-ene (XX), readily available by photolysis of perfluorocyclohexa-1,3-diene (Chapter 5) is a reactive dienophile as might be expected from thebehaviour of perfluorobicyclo[2,2,0]hexa-2,5-diene (299) and cis-exo-5,6-dibromohexafluorobicyclo[2,2,0]hex-2-ene (see Section 7.2c).



(XX) (XXII) (XXI)

Olefin (XX) reacted with an equimolar quantity of furan at 20° over 17 hours to give adduct (XXII) in 79% yield. With an equimolar quantity of buta-1,3-diene at 100° over 30 hours olefin (XX) gave the adduct (XXI) in 67% yield. The adducts were characterised by elemental analysis and by spectroscopy (see Section 7.4), and the stereochemistry was assigned by analogy with adducts of perfluorobicyclo[2,2,0]hexa-2,5-diene.[171a and b]

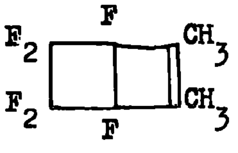
Nucleophilic substitution of olefin (XX) gives access to derivatives substituted at the vinylic positions (see Chapter 6). The dihydro derivative (XXXIX) reacted with excess furan in carbon tetrachloride quantitatively overnight at room temperature to give adduct (XXXX), which was characterised by elemental analysis and spectroscopy (Section 7.4). When a mixture of equimolar amounts of (XX) and (XXXIX) were reacted with excess furan in carbon tetrachloride at room temperature, g.l.c. analysis showed that olefin (XXXIX) was



(XXXIX) (XXXX)

consumed to the extent of ca.90% in 45 minutes, whereas less than 5% of (XX) had reacted. A true competition reaction indicated that the rate constant for the reaction of (XXXIX) with furan was at least 20 times that for the reaction of (XX) with furan.

Substitution of the vinylic fluorines of (XX) by methyl groups to give (IV) or by one or two methoxy groups to give (XII) and (VII) completely destroyed the dienophilicity of the double bond. Thus olefins (IV), (XII) and (VII) did not react with furan in carbon tetrachloride over several weeks. There was



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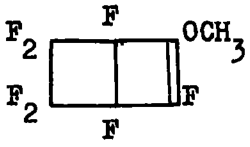
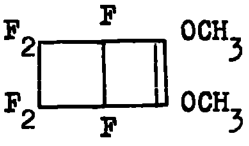


(XII)

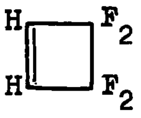


(VII)

no reaction when olefin (VII) was heated with furan at 100° for 19 hours.

The effect of substituents on the dienophilicity of 2,3-disubstituted-hexafluorobicyclo[2,2,0]hex-2-enes is a complex subject for rationalisation. An indication of some of the factors possibly governing the reactivity of ring-strained dienophiles was obtained from the reactions of substituted cyclopropenes (Section.2a), where it was seen that simple steric and electronic effects were insufficient to explain reactivity orders.[158] In particular the suggestion that α-substituents can effect hybridisation and hence the reactivity of double bonds in cyclopropenes, may possibly also be applied to fused ring systems such as bicyclo[2,2,0]hex-2-enes. Perhaps also the argument could be extended to include changes in hybridisation (and hence of ring strain and reactivity) with changes in vinylic substituents of angle-strained double bonds.

The explanation of the reactivity order towards furan, (XXXIX) $>$ (XX) $\ggg$ (IV), (XII) and (VII) may require an interplay of steric, electronic and hybridisation effects. Whilst angle-strain is clearly an importantfactor in the explanation of the high reactivity of (XXXIX) compared to (340) and of (XX)



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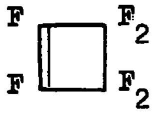


(343)(i)

compared to (343) (i), the extreme deactivating effect of the methyl group in (IV) is remarkable and surely not entirely attributable to steric effects. The deactivating effect of methyl groups on angle-strained double bonds has been observed in the dicyanocyclopropenes (327), (328) and (329) (Section 7.2a) and in the compounds (341), (Section 7.2b). The deactivating effect of methoxy substituents observed in (XXII) and (VII) has not been observed before in a strained olefin and may, at least in part, be attributed to the inductive effect of the methoxy group, tending to reduce the electron-deficient character of the double bond. The high dienophilicity of (XXXIX) relative to (XX) must in some degree be attributable to steric effects.

7.4 Spectroscopic characterisation of the adducts

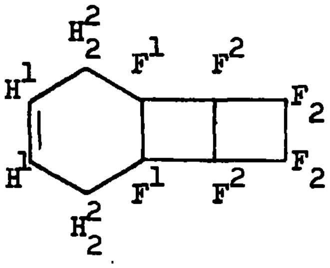
The mass spectra of the furan adducts (XXII) and (XXXX) (Appendix B) showed very weak parent peaks and the highest strong peak corresponded to loss of furan (C_4H_4O) from the parent ion. Both adducts showed a base peak at m/e 68 corresponding to furan (C_4H_4O). The mass spectrum of the butadiene adduct (XXI) showed a very strong parent peak, which was also the base peak of the spectrum.

The i.r. spectra of adducts (XXII), (XXI) and (XXXX) were transparent between 1500–1800 cm^{-1} as expected for compounds containing symmetrically substituted -CH=CH- double bonds.

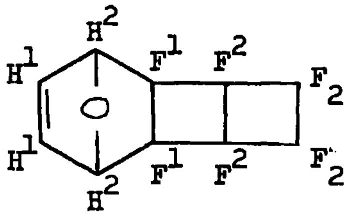
The ^{19}F and ^1H n.m.r. spectral parameters (Table 7.3) were consistent with the assigned structures. In the adducts as in the bicyclo[2,2,0]hex-2-ene precursors (XX) and (XXXIX), (table 5.1) the $-CF_2-CF_2-$ group resonates as a "pseudo AB quartet" (aABb) with "J_{AB}" = $(\delta_A-\delta_a)$ = $(\delta_b-\delta_B)$ = 226 Hz. In adducts (XXI) and (XXII) thetertiary fluorine showed a large splitting of 40 Hz also observed in the small and large (a and A) limbs of the $-CF_2-CF_2-$ AB quartet. This four-bond coupling is thus between F' and either the exo or endo fluorine atom of the neighbouring difluoromethylene group. The absence of this large coupling in adduct (XXX) is good evidence for the assignment of the tertiary fluorines as given in Table 7.3. In the ^1H spectrum of the butadiene adduct (XXI) the methylene hydrogens give two broad resonances centred at 7.16τ and 7.43τ in the ratio 3:1. This may be explained by assuming t hat one pair of methylene protons (syn or anti to F^1 gives a broad doublet (J = 18 Hz, centre 7.29τ) which overlap a broad singlet given by the other pair of methylene protons (anti or syn to F^1).

TABLE 7.3

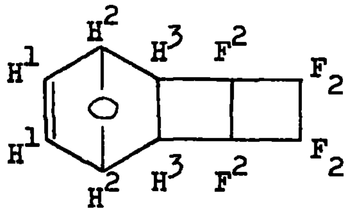
^{19}F and ^{1}H N.m.r. Spectral Parameters for Diels-Alder Adducts (XXI), (XXII) and (XXXX)



(XXI)



(XXII)



(XXXX)

	^{19}F			^{1}H		
Adduct	$-CF_2-CF_2-$ ^{c} δ_a δ_A δ_B δ_b	F^1	F^2	H^1	H^2	H^3
(XXI)	117·1,^{d} 121·1,^{d} 124·5, 128·5 (4F) "J"$_{AB}$ = 226 Hz	170·1^{d} (2F)	194·4 (2F)	4·11τ (2H)	7·16τ) 7·43τ)^{e} (2H)	-
(XXII)	116·2,^{d} 120·3,^{d} 124·6, 128·6 (4F) "J"$_{AB}$ = 226 Hz	187·0^{d} (2F)	194·4 (2F)	3·27τ (2H)	4·67τ (2H)	-
(XXXX)	121·2, 125·1, 133·4, 137·4 (4F) "J"$_{AB}$ = 226 Hz	-	193·1 (2F)	3·60τ (2H)	4·69τ (2H)	7·53τ (2H)

NOTES ^{19}F N.m.r. shifts are given in p.p.m. upfield from internal $CFCl_3$

^{1}H N.m.r. shifts are given on the scale relative to internal Me_4Si.

c, the $-CF_2-CF_2-$ group resonates as an apparent AB quartet weak, strong, strong, weak pattern, aABb

d, doublet, J = 40 Hz. e, see text.

CHAPTER 7

EXPERIMENTAL

7.5 Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with furan

A mixture of the olefin (XX) (3.09 g., 13.8 mmoles) and furan (0.904 g., 13.3 mmoles) was set aside in a sealed tube at 20° for 17 hours to give (i) a volatile fraction (0.857 g.) shown by analytical g.l.c. and i.r. to be a mixture of olefin (XX) and furan; (ii) a white solid which was sublimed in vacuo to give 11-oxa-2,3,4,4,5,5,6,7-octafluorotetracyclo[6,2,1,$0^{2,7}0^{3,6}$]undec-9-ene (XXII) (3.081 g., 10.5 mmoles, 79%) [Found: C,40.97; H,1.46; F,51.7%; M (mass spectrometry), 292. $C_{10}H_4F_8O$ requires C,41.11; H,1.38; F,52.03%; M, 292], m.p. 88-89° (from carbon tetrachloride).

7.6 Reaction of perfluorobicyclo[2,2,0]hex-2-ene (XX) with buta-1,3-diene

The olefin (XX) (2.59 g., 11.6 mmoles) and buta-1,3-diene (11.5 mmoles) were heated together in a sealed Pyrex ampoule (30 ml.) for 30 hours at 100° to give, after removal of volatiles, a white solid (2.27 g.) which was sublimed at 60°, 10^{-3} mm.Hg to give 1,2,3,3,4,4,5,6-octafluorotricyclo[4,4,0,$0^{2,5}$]dec-8-ene (XXI) (2.16 g., 7.8 mmoles, 67%) [Found: C,42.86; H,2.13; F,54.3%; M (mass spectrometry), 278. $C_{10}H_6F_8$ requires C,43.18; H,2.18; F,54.66%; M, 278], m.p. 65°.

7.7 Reaction of 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene (XXXIX) with furan

The olefin (XXXIX) (ca. 0.2 g., 1.1 mmole) in carbon tetrachloride (ca. 0.08 g.) was reacted with furan (0.12 g., 1.8 mmoles) at 20° for 14 hours. G.l.c. analysis indicated that (XXXIX) had reacted quantitatively. After removal of volatiles the residue (0.215 g.) was sublimed at 70°, 10^{-3}mm.Hg to give 11-oxa-3,4,4,5,5,6-hexafluorotetracyclo[6,2,1,$0^{2,7}$,$0^{3,6}$]undec-9-ene (XXXX) (0.184 g., 0.72 mmole, 68%) [Found: C,46.98; H,2.23; F,45.1%; M (mass spectrometry), 256. $C_{10}H_6F_6O$ requires C,46.89; H,2.36; F,45.1%; M,256], m.p. 96-97°.

7.8 Attempted reactions with furan

When the olefins 2,3-dimethylhexafluorobicyclo[2,2,0]hex-2-ene (IV), 2,3-dimethoxyhexafluorobicyclo[2,2,0]hex-2-ene (VII) and 2-methoxyheptafluorobicyclo[2,2,0]hex-2-ene (XII) were separately reacted with excess furan in carbon tetrachloride over several weeks g.l.c. analysis showed no diminution of the olefin relative to carbon tetrachloride as the inert internal marker. Heating olefin (XII) with furan in a sealed tube at 100° for 19 hours gave only recovered starting materials, with the production of no involatile residue.

7.9 Competition of perfluorobicyclo[2,2,0]hex-2-ene (XX) and 1,4,5,5,6,6-hexafluorobicyclo[2,2,0]hex-2-ene (XXXIX) for furan in carbon tetrachloride

Experiment (i). After addition of furan (0.04 g., 0.59 mmole) to a mixture of olefin (XX) (0.102 g., 0.457 mmole), olefin (XXXIX) (0.086, 0.459 g.) and carbon tetrachloride (0.159 g.), the amount of (XXXIX) estimated by g.l.c. relative to carbon tetrachloride as inert internal marker decreased rapidly. After 45 minutes it was estimated that (XXXIX) was consumed to the extent of ca. 90%, whilst less than 5% of (XX) had reacted.

Experiment (ii). A mixture of olefin (XX) (0.237 g., 1.06 mmoles), olefin (XXXIX) (0.201 g., 1.07 mmoles) in carbon tetrachloride (0.217 g.) was reacted with furan (0.021 g., 0.302 mmole) at 20° for 63 hours. The volatile materials were removed under reduced pressure to leave a solid which was dissolved in ether. The ^{19}F n.m.r. spectrum of this solution showed only resonances characteristic (Table 7.3) of 11-oxa-3,4,4,5,5,6-hexafluorotetracyclo[6,2,1,$0^{2,7}$,$0^{3,6}$]undec-9-ene (XXXX) and the resonances of the alternative adduct 11-oxa-2,3,4,4,5,5,6,7-octafluorotetracyclo[6,2,1,$0^{2,7}$,$0^{3,6}$]undec-9-ene (XXII) were below the level of detectability relative to (XXXX). From this observation it was deduced that the amount of (XXII) produced must have been at most 5% of the product. The ratio of the rate constants for the reaction of (XXXIX) and (XX) with furan (k_A/k_B) can be calculated from the relationship employed by Law and Tobey[158] for competition reactions of halogenated propenes with furan under similar conditions, viz.

$$\frac{k_A}{k_B} = \frac{p_A \, C_B}{p_B \, C_A}$$

where k_A and k_B are the rate constants for the reaction of (XXXIX) and (XX) with furan respectively.

p_A is the mole per cent of the product derived from (XXXIX)

p_B " " " " " (XX)

C_A is the initial mole per cent of reactant (XXXIX)

C_B " " " " (XX)

Now $C_A \doteqdot C_B$, $p_A \geqslant 20 \, p_B$

$\therefore \; k_A/k_B \geqslant 20.$

APPENDIX A

APPARATUS AND INSTRUMENTS

Vacuum System

Volatile compounds were handled in a conventional vacuum system incorporating a mercury diffusion pump and rotary oil pump, gas storage bulbs and two standard volume bulbs (623 ml. and 4240 ml.). Gases were measured by noting the pressure on a wide bore-manometer connected to one of the standard bulbs. The small bulb was used for quantities of gas less than 10 mmoles and the larger one for quantities up to 50 mmoles.

Mass Spectra were measured with an A.E.I. MS9 spectrometer at an ionising beam energy of 70 eV.

Infrared spectra were recorded with both a Perkin-Elmer 137 (sodium chloride) spectrometer and Grubb-Parsons Spectromaster.

Ultraviolet Spectra were recorded with a Unicam SP800 spectrophotometer

N.M.R. Spectra were measured with either a Perkin-Elmer R10 spectrometer (operating at 56.46 MHz for ^{19}F and 60.0 MHz for ^{1}H spectra, operating temperature 33.5°) or a Varian A56/60 spectrometer (operating at 56.40 MHz for ^{19}F and 60.0 MHz for ^{1}H, operating temperature 40°); unless otherwise stated. ^{19}F chemical shifts are in p.p.m. from external fluorotrichloromethane (positive upfield) and ^{1}H shifts are measured on the τ scale relative to external tetramethylsilane. Where necessary integrations were refined with the aid of a Digiac computer of average transients interfaced to the R10 instrument.

Analytical Gas Liquid Chromatography (g.l.c.)

A Perkin-Elmer 452 using hydrogen as carrier gas and a hot wire detector was used for analytical work.

Column designations were:

Column A: 2.2 m x 7 mm diam., di-n-decylphthalate/Celite

Column O: 2.2 m x 7 mm diam., silicone grease/Celite.

Peak areas were measured by a Honeywell Integrator Model 5530000.

Preparative g.l.c. - All instruments used nitrogen as the carrier gas.

Column A: 4.9 m x 75 mm. diam., dinonylphthalate-Celite 1:2, ca. 60 l./hr.

Column B: Perkin-Elmer F.21. Praparative Gaschomatograph, 4.5 m x 0.95 cm. diam., di-n-decylphthalate-Chromosorb P (1:4); N_2 carrier (ca. 1.0-2.0 atmos.)

Column C: As for Column B but with silicone oil, Chromosorb P (1:4) as stationary phase.

Column D: Varian "Autoprep". 6.1 m x 13 mm. diam., silicone elastomer-Celite (1:2); ca. 10 l./hr.

Column E: As for D but with di-n-decylphthalate-Celite, (1:2);

Carbon and Hydrogen Analyses were carried out with a Perkin-Elmer 240 CHN Analyser.

Melting Points and Boiling Points are uncorrected. The boiling points were measured by Sivoloboff's method.

APPENDIX B

MASS SPECTRA

The mass spectra of compounds obtained in the course of this work are tabulated below. Compounds marked with an asterisk, e.g. (XXXVIII)*, have been prepared previously but, except in the case of (XXXVIII),[175] their mass spectra have not been reported previously. Ions are tabulated in the form:

147(70%, $C_7H_6F_3$, P-CF_3)

In this example the ion has has mass number 147, its intensity is 70% of the intensity of the base peak of the spectrum, it has been provisionally assigned the formula $C_7H_6F_3^+$ (the + being understood), and its supposed origin is loss of a trifluoromethyl group from the parent ion (P). The base peak is designated B.

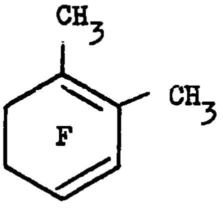
Metastable ion peaks, where observed, are tabulated underneath the main spectrum in the form $M^*(M_1 \xrightarrow{-F_r} M_2)$, where the metastable ion is understood to have been observed at

$$M^* = \frac{M_2^2}{M_1}$$

for the loss of neutral fragment F_r, from ion M_1^+ to give M_2^+.

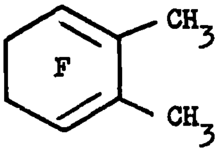
a) Polyfluorocyclohexa-1,3-dienes

(I)



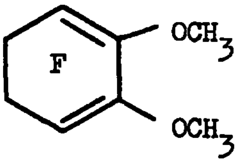
217(11%, P + 1), 216(100%, $C_8F_6H_6$, P and B), 201(40%, $C_7F_6H_3$, P-CH_3), 197(26%, $C_8F_5H_6$, P-F), 196(8%), 195(9%), 181(19%, $C_7F_5H_2$, P-CH_3-HF), 166(26%, $C_7F_4H_6$, P-CF_2), 165(18%), 163(19%), 151(19%, $C_6F_4H_3$, P-CH_3-CF_2), 147(70%, $C_7F_3H_6$, P-CF_3), 146(19%), 145(48%), 132(22%, $C_6F_3H_3$, P-CF_3-CH_3), 127(46.0%, $C_7F_2H_5$, P-CF_3-HF), 119(11%), 116(23%, $C_6F_2H_6$, P-C_2F_4), 115(16%), 114(8.7%), 113(12%), 101(17%).

(III)



217(11%, P + 1), 216(100%, $C_8F_6H_6$, P and B), 201(37%, $C_7F_6H_3$, P-CH_3), 197(37%, $C_8F_5H_6$, P-F), 196(25%), 195(18%), 181(25%, $C_7F_5H_2$, P-CH_3-F), 166(34%, $C_7F_4H_6$, P-CF_2), 165(16%), 163(24%), 151(20%, $C_6F_4H_3$, P-CH_3-CF_2), 147(60%, $C_7F_3H_6$, P-CF_3), 146(19%), 145(62%), 132(46%, $C_6F_3H_3$, P-CF_3-CH_3), 127(46%, $C_7F_2H_5$, P-CF_3-HF), 119(23·6%), 116(24%, $C_6F_2H_6$, P-C_2F_4), 115(21%), 114(14%), 113(12%), 101(19%).

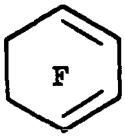
(VI)



248(100%, $C_8F_6H_6O_2$, PARENT and BASE), 233(40%, $C_7F_6H_3O_2$, P-CH_3), 229(20%, $C_8F_5H_6O_2$, P-F), 217(9%, $C_7F_6H_3O$, P-OCH_3), 214(4%, $C_7F_5H_3O_2$, P-CH_3-F), 210(4%, $C_8F_4H_6O_2$, P-F_2), 205(51%, $C_6F_6H_3O$, P-$COCH_3$), 198(11%, $C_7F_4H_6O_2$, P-CF_2), 190(11%, C_5F_6O, P-$COCH_3$-CH_3), 183(11%, $C_6F_4O_2H_3$, P-CF_2-CH_3), 175(9%), 171(13%, C_5F_5O, P-$COCH_3$-CH_3-F), 162(9%, C_4F_6), 155(16%, C_5F_5), 143(51%, P-$(COCH_3)_2$-F), 124(13%), 109(36%), 105(9%), 93(24%), 81(36%).

Metastable ions: 233 → 205 (-CO), 171 → 143 (-CO).

(XIX)[≠*]

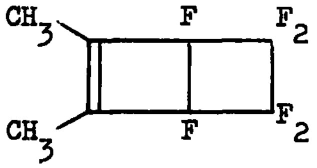


224(46%, C_6F_8, PARENT), 205(40%, C_6F_7, P-F), 186(12%, C_6F_6, P-F_2), 174(31%, C_5F_6, P-CF_2), 155(100%, C_5F_5, P-CF_3, BASE), 124(46%, C_4F_4, P-C_2F_4), 117(21%, C_5F_3), 105(13%, C_4F_3).

[≠] This spectrum was run under identical conditions to the spectrum of its photoisomer (XX).

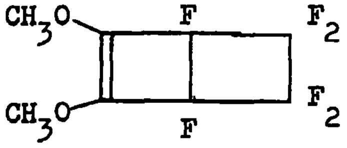
b) Polyfluorobicyclo[2,2,0]hex-2-enes, etc.

(IV)



217(13%, P + 1), 216(100%, $C_8F_6H_6$, PARENT and BASE), 201(48%, $C_7F_6H_3$, P-CH_3), 197(17%, $C_8F_5H_6$, P-F), 196(9%, $C_8F_5H_5$, P-HF), 195(9%), 181(17%, $C_7F_5H_2$, P-CH_3-HF), 166(43%, $C_7F_4H_6$, P-CF_2), 165(22%), 164(9%), 163(13%), 151(30%, $C_6F_4H_3$, P-CH_3-CF_2), 147(87%, $C_7F_3H_6$, P-CF_3), 146(17%), 145(43%), 132(35%, $C_6F_3H_3$, P-CH_3-CF_3), 128(13%, $C_7F_2H_6$, P-CF_4), 127(52%), 119(9%), 116(43%), 115(52%), 114(13%), 113(13%), 101(30%) ...... 69(48%, CF_3).

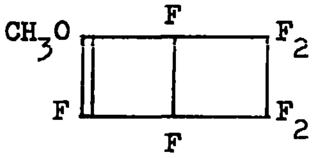
(VII)



248(50%, $C_8F_6H_6O_2$, PARENT), 233(50%, $C_7F_6H_3O_2$, P-CH_3), 229(17%, $C_8F_5H_6O_2$, P-F), 220(8%, P-CO or P-C_2H_4), 218(8%, $C_7F_4H_6O_2$, P-CF_2), 214(8%, $C_7F_5H_3O_2$, P-F-CH_3), 205(58%, $C_6F_6H_3O$, P-$COCH_3$), 198(17%), 190(17%), 183(17%), 179(8%, $C_7F_3H_6O_2$, P-CF_3), 176(17%), 171(17%), 162(17%, C_4F_6, P-2($COCH_3$)), 155(25%), 143(100%, C_4F_5, BASE PEAK = P-$(COCH_3)_2$-F), 137(25%), 133(33%), 131(8%), 125(33%), 124(33%), 112(17%), 109(67%), 105(58%), 94(75%), 82(58%) ......

Metastable ion: 233 ⟶ 205 (-CO).

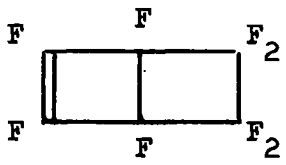
(XII)



236(43%, $C_7F_7H_3O$, PARENT), 221(14%, C_6F_7O, P-CH_3), 219(7%, $C_7F_7H_3$, P-O), 217(21%, $C_7F_6H_3O$, P-F), 205(14%, C_6F_7, P-OCH_3), 202(11%, C_6F_6O, P-CH_3-F), 193(64%, C_5F_7, P-$COCH_3$), 186 (21%, $C_6F_5H_3O$), P-CF_2), 183(21%, C_6F_5O, P-CH_3-F_2), 174(24%, $C_5F_5H_3O$, P-C_2F_2), 171(7%, C_5F_5O, P-CH_3-CF_2), 167(21%, $C_6F_4H_3O$, P-CF_3), 155(29%, $C_5F_4H_3O$, P-C_2F_3), 143(100%, C_4F_5, BASE PEAK = P-$COCH_3$-CF_2), 137(14%), 136(14%, $C_5F_3H_3O$, P-C_2F_4), 124(36%), 122(36%), 117(21%), 112(14%), 93(93%).

Metastable ion: 236 ⟶ 193 (-$COCH_3$), 221 ⟶ 193 (-CO), 205 ⟶ 186 (-F).

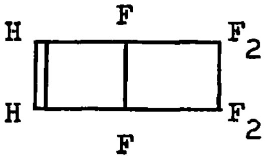
(XX)≠



224(23.5%, C_6F_8, PARENT), 205(18%, C_6F_7, P-F), 186(4%, C_6F_6, P-F_2), 174(27%, C_5F_6, P-CF_2), 155(100%, C_5F_5, BASE PEAK = P-CF_3), 124(71%, C_4F_4, P-C_2F_4, 117(12%), 105(12%, C_4F_3).

≠ run under exactly the same conditions as the perfluorocyclohexa-1,3-diene spectrum.

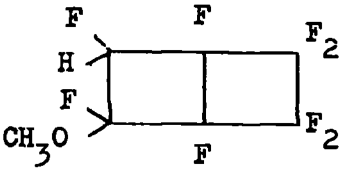
(XXXIX)



188(16%, $C_6F_6H_2$ PARENT), 169(8%, $C_6F_5H_2$, P-F), 168(5%, C_6F_5H, P-HF), 150(5%, $C_6F_4H_2$, P-F_2), 138(16%, $C_5F_4H_2$, P-CF_2), 137(8%, C_5F_4H, P-CF_2H), 120(5%), 119(100%, $C_5F_3H_2$, BASE PEAK = P-CF_3), 88(32%, $C_4F_2H_2$, P-C_2F_4), 75(8%), 69(19%, CF_3).

Metastable ion: 188 ⟶ 119 (-CF_3).

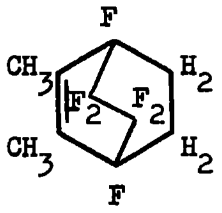
(IX)



256(Absent, $C_7F_8H_4O$, PARENT), 224(less than 1%, C_6F_8, P-CH_3OH), 163(20%), 143(3%), 131(77%, $C_2F_4OCH_3$), 125(6%), 119(6%, C_2F_5), 113(11%), 101(17%), 97(83%), 94(9%), 88(9%), 82(100%, BASE PEAK), 81(23%), 75(31%).

c) Polyfluorobicyclo[2,2,2]oct-2-enes

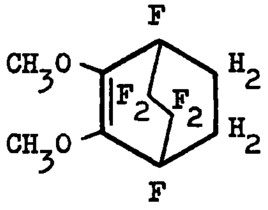
(II)



245(9%, P + 1), 244(47%, $C_{10}H_{10}F_6$, PARENT), 225(7%, $C_{10}H_{10}F_5$, P-F), 216(7%, $C_8H_6F_6$, P-C_2H_4), 145(14%), 144(100%, $C_8H_{10}F_2$, BASE PEAK = P-C_2F_4), 143(58%, $C_8H_9F_2$, B-H), 141(6·7%), 130(4%), 129(40%, $C_7H_7F_2$, B-CH_3), 128(7%), 127(13%), 123(4%), 109(9%) ....

Metastable ions: 244 ⟶ 144 (-C_2F_4), 144 ⟶ 129 (-CH_3).

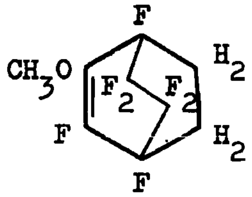
(V)



276(100%, $C_{10}F_6H_{10}O_2$ PARENT and BASE), 261(19%, $C_9F_6H_7O_2$, P-CH_3), 257(10%, $C_{10}F_5H_{10}O_2$, P-F), 248 (10%, $C_8F_6H_6O_2$, P-C_2H_4, 233(43%, $C_8F_6H_7O$, P-$COCH_3$), 205(10%), 176(76%, $C_8F_4H_{10}O_2$, P-C_2F_4), 175(57%, $C_8F_4H_9O_2$), 171(10%), 164(14%), 163(14%), 161(24%, $C_7F_4H_7O_2$, P-C_2F_4-CH_3), 151(19%), 133 (24%, $C_6F_4H_7O$, P-C_2F_4-CH_3-CO), 95(71%), 81(52%), 69(24%, CF_3).

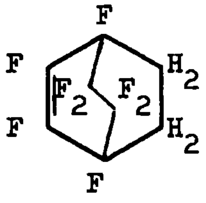
Metatsbale ion: 276 ⟶ 261 (-CH_3), 261 ⟶ 233 (-CO), 276 ⟶ 176 (-C_2F_4), 176 ⟶ 161 (-CH_3).

(X)



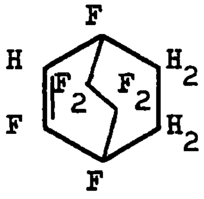
264(31%, $C_9H_7F_7O$, PARENT), 249(13%, $C_8H_4F_7$, P-CH_3), 245(11%, $C_8H_7F_6$, P-F), 165(12·5%), 164(100%, $C_7H_7F_3O$, BASE PEAK = P-C_2F_4), 163(62%, $C_7H_2F_7O$, B-H), 149(12%, C_6F_7O, B-CH_3), 133(19%, C_6F_7, B-OCH_3), 121(12·5%) ....

(XVIII)



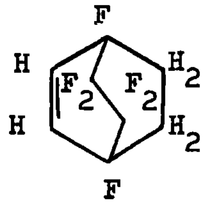
253(5%, P + 1), 252(21%, $C_8F_8H_4$, PARENT), 233(8%, $C_8F_7H_4$, P-F), 224(8%, C_6F_8, P-C_2H_4), 205(8%, C_6F_7, P-C_2H_4-F), 187(8%), 152(100%, $C_6F_4H_4$, BASE PEAK = P-C_2F_4), 151(28%, $C_6F_4H_3$, B-H), 134(13%, $C_6F_3H_4$, B-F), 102(15%), 101(18%).....

(XXVII)



235(3%, P + 1), 234(20%, $C_8F_7H_5$, PARENT), 215(6%, $C_8F_6H_5$, P-F), 206(8%, C_6F_7H, P-C_2H_4), 195(3%), 186(6%, C_6F_6, P-C_2H_4-HF), 137(14%), 135(8%), 134(100%, $C_6F_3H_5$, BASE PEAK = P-C_2F_4), 133(53%, $C_6F_3H_4$, B-H), 132(6%), 115(11%, $C_6F_2H_5$, B-F), 114(11%), 113(8%), 69(8%, CF_3).

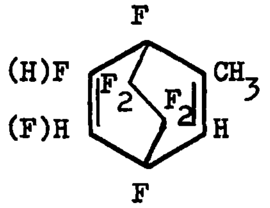
(XXXVII)



216(12%, $C_8F_6H_6$, PARENT), 188(6%, $C_6F_6H_2$, P-C_2H_4), 121(6%), 119(16%), 117(8%), 116(100%, $C_6F_2H_6$, BASE PEAK = P-C_2F_4), 115(38%, $C_6F_2H_5$, B-H), 97(8%, C_6FH_6, B-F), 96(8%, C_6FH_5, B-HF), 95(8%), 69(8%, CF_3).

d) Polyfluorobicyclo[2,2,2]octa-2,5-dienes

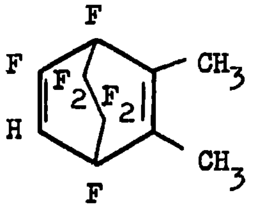
(XXV)



246(5%, $C_9F_7H_5$, PARENT), 227(5%, $C_9F_6H_5$, P-F), 177(10%, $C_8F_4H_5$, P-CF_3), 147(12.5%), 146(100%, $C_7F_3H_5$, BASE PEAK = P-C_2F_4), 145(53%, $C_7F_3H_4$, B-H), 100(5%, C_2F_4), 69(8%, CF_3).

Metastable ion: 146 ⟶ 145 (-H).

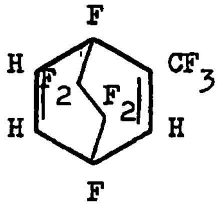
(XXVI)



260(8%, $C_{10}F_7H_7$, PARENT), 241(5%, $C_{10}F_6H_7$, P-F), 191(8%, $C_9F_4H_7$, P-CF_3), 160(100%, $C_8F_3H_7$, BASE PEAK = P-C_2F_4, 159(29%, $C_8F_3H_6$, B-H), 158(5%), 157(3%), 141(5%), 140(3%) ...... 119(8%).

Metastable ions: 160 ⟶ 145 (-CH_3).

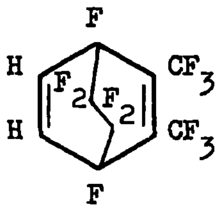
(XXXI)



282(v. weak, $C_9F_9H_3$, PARENT), 263(16%, $C_9F_8H_3$, P-F), 213(16%, $C_8F_6H_3$, P-CF_3), 182(100%, $C_7F_5H_3$, BASE PEAK = P-C_2F_4, 163(32%, $C_7F_4H_3$, B-F), 132(21%, $C_6F_3H_2$, B-CF_2), 100(11%, C_2F_4), 69(11%, CF_3).

Metastable ions: 182 ⟶ 163 (-F).

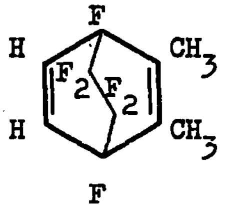
(XXXII)



350(v. weak, $C_{10}F_{12}H_2$, PARENT), 331(19% $C_{10}F_{11}H_2$, P-F), 281(4%, $C_9F_9H_2$, P-CF_3), 251(11%), 250(100%, $C_8F_8H_2$, BASE PEAK = P-C_2F_4), 231(37%, $C_8F_7H_2$, B-F), 212(4%, $C_8F_6H_2$, B-F_2), 201(2·4%), 200(18%, $C_7F_6H_2$, B-CF_2), 181(37%, $C_7F_5H_2$, B-CF_3), 100(22%, C_2F_4),

Metastable ions: 331 → 312 (-F), 331 → 281(-CF_3), 331 → 231 (-C_2F_4), 250 → 231 (-F), 250 → 181 (-CF_3), 231 → 181 (-CF_2), 200 → 181 (-F).

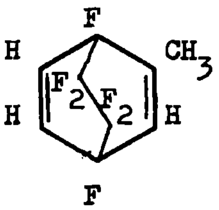
(XXXIII)



296(v. weak, $C_{10}F_9H_5$, PARENT), 277(11%, $C_{10}F_8H_5$, P-F), 257(4%, $C_{10}F_7H_4$, P-HF_2), 227(5%, $C_9F_6H_5$, P-CF_3), 196(100%, $C_8F_5H_5$, BASE PEAK = P-C_2F_4), 177(21%, $C_8F_4H_4$, B-HF), 145(11%, $C_7F_3H_4$, B-HF_2), 128(16%), 127(93%, $C_7F_2H_5$, B-CF_3), 126(5%), 125(9%), 100(7%, C_2F_4), 84(13%), 69(7%, CF_3).

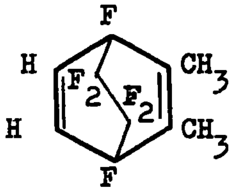
Metastable ions: 196 → 127 (-CF_3), 196 → 176 (-HF)

(XXXIV)



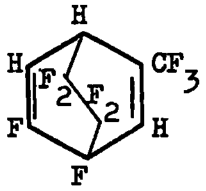
228(5%, $C_9F_6H_6$, PARENT), 209(5%, $C_9F_5H_6$, P-F), 196(5%, $C_8F_5H_5$, P-CFH), 159(11%, $C_8F_3H_6$, P-CF_3), 129(13·2%), 128(100%, $C_7F_2H_6$, BASE PEAK = P-C_2F_4), 127(61%, $C_7F_2H_5$, B-H), 119(11%, C_2F_4), 109(8%, C_7FH_5, B-F), 108(5%), 107(8%), 101(8%), 99(5%), 98(5%).

(XXXV)



243(3%, P + 1), 242(15%, $C_{10}F_6H_8$, PARENT), 223(4%, $C_{10}F_5H_8$, P-F), 203(2%, $C_{10}F_4H_7$, P-HF_2), 173(4%), 142(100%, $C_8F_2H_8$, BASE PEAK = P-C_2F_4), 127(55%, $C_7F_2H_5$, B-CH_3), 119(4%, C_2F_5), 114(4%), 101(8%).

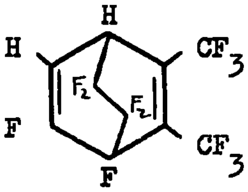
(XXXXI)



282(3%, $C_9F_9H_3$, PARENT), 263(7%, $C_9F_8H_3$, P-F), 213(10%, $C_8F_5H_3$, P-CF_3), 183(10%), 182(100%, $C_7F_5H_3$, BASE PEAK = P-C_2F_4), 181(9%, $C_7F_5H_2$, B-H), 164(14%), 163(50%, $C_7F_4H_2$, B-F), 143(4%, C_7F_3H, B-HF_2), 132(30%, $C_6F_3H_3$, B-CF_2), 120(3%), 119(3%), 107(14%), 106(17%),

Metastable ions: 182 ⟶ 163 (-F), 182 ⟶ 132 (-CF_2).

(XXXXII)

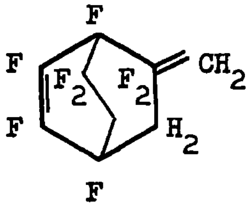


350(weak, $C_{10}F_{12}H_2$, PARENT), 331(17%, $C_{10}F_{11}H_2$, P-F), 312(4%, $C_{10}F_{10}H_2$, P-2F), 218(4%, $C_9F_9H_2$, P-CF_3), 251(13%), 250(100%, $C_8F_8H_2$, BASE PEAK = P-C_2F_4), 231(46%, $C_8F_7H_2$, B-F), 200(25%, $C_7F_6H_2$, B-CF_2), 181(33%, $C_7F_5H_2$, B-CF_3), 100(46%, C_2F_4), 69(25%, CF_3).

Metastable ions: 250 ⟶ 231 (-F), 250 ⟶ 181 (-CF_3).

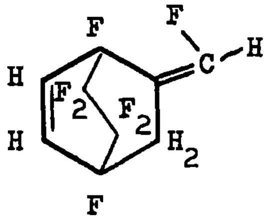
e) Polyfluoro-5-methylene-bicyclo[2,2,2]oct-2-enes

(XIII)



264(30%, $C_9F_8H_4$, PARENT), 250(4%, $C_8F_8H_2$, P-CH_2), 245(5%, $C_9F_7H_4$, P-F), 231(12%, $C_8F_7H_2$, P-CH_2-F), 229(12%), 219(10%, $C_7F_7H_2$, P-CFH_2), 200(17%, $C_7F_6H_2$, P-CF_2H_2), 195(7%, $C_8F_5H_4$, P-CF_3), 181(6%, $C_7F_5H_2$), 165(9·5%), 164(100%, $C_7F_4H_4$, BASE PEAK = P-C_2F_4), 163(61%, $C_7F_4H_3$ (B-H), 155(6%), 150(8%, $C_6F_4H_2$, B-CH_2), 145(32%, $C_7F_3H_4$, B-F), 131(8%, $C_6F_3H_2$, B-CH_2F), 114(22%, $C_6F_2H_4$, B-CF_2), 104(31%), 103(20%), 100(11%, C_2F_4), 93(7%), 81(5%), 69(38%, CF_3).

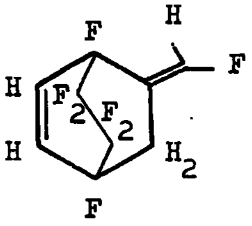
(XXIII)



246(8%, $C_9F_7H_5$, PARENT), 227(2%, $C_9F_6H_5$, P-F), 207(5·2%, $C_9F_5H_4$, P-HF_2), 177(5%, $C_8F_4H_5$, P-CF_3), 163(5%, $C_7F_4H_3$, P-CF_3-CH_2), 146(81%, $C_7F_3H_5$, P-C_2F_4), 145(100%, $C_7F_3H_4$, BASE PEAK = P-C_2F_4-H), 127(36%, $C_7F_2H_5$, P-C_2F_4-F), 126(5%, $C_7F_2H_4$), 125(12%, $C_7F_2H_3$), 119(10%).

Metastable ion: 146 ⟶ 145 (-H).

(XXIV)

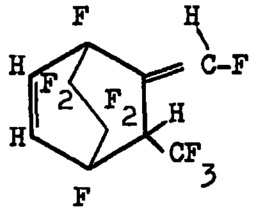


246(9%, $C_9F_7H_5$, PARENT), 227(2%, $C_9F_6H_5$, P-F), 207(5%, $C_9F_5H_4$, P-HF_2), 177(4%, $C_8F_4H_5$, P-CF_3), 163(5%, $C_7F_4H_3$, P-CF_3-CH_2), 147(9%), 146(88%, $C_7F_3H_5$, P-C_2F_4),

145(100%, $C_7F_3H_4$, BASE PEAK = P-C_2F_4-H), 127(36%, $C_7F_2H_5$, P-C_2F_4-F), 126(5%, $C_7F_2H_4$), 125(13%, $C_7F_2H_3$), 119(10%, C_2F_5), ... 96(19%),

Metastable ion: 146 ⟶ 145 (-H).

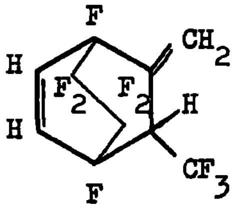
(XXVIII)



314(30%, $C_{10}F_{10}H_4$, PARENT), 295(12%, $C_{10}F_9H_4$, P-F), 275(6%, $C_{10}F_8H_3$, P-HF_2), 246(6%), 245(47%, $C_9F_7H_4$, P-CF_3), 226(5%, $C_9F_6H_4$, P-CF_3-F), 225(5%, $C_9F_6H_3$, P-CF_3-HF), 214(12%, $C_8F_6H_4$, P-C_2F_4), 195(9%, $C_8F_5H_4$, P-C_2F_4-F), 194(3%), 176(9%, $C_8F_4H_3$, P-C_2F_4-HF_2, 163(6%), 146(9%), 145(100%, $C_7F_3H_4$, BASE PEAK = P-C_2F_4-CF_3), 126(3%), 125(6%), 119(8%), 113(5%) ..... 69(11%, CF_3).

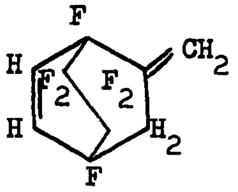
Metastable ions: 314 ⟶ 245 (-CF_3), 295 ⟶ 275 (-HF), 214 ⟶ 145 (-CF_3).

(XXIX)



296(47%, $C_{10}F_9H_5$, PARENT), 277(15%, $C_{10}F_8H_5$, P-F), 227(21%, $C_9F_6H_5$, P-CF_3), 196(34%, $C_8F_5H_5$, P-C_2F_4), 177(9%, $C_8F_4H_5$, P-C_2F_5), 176(9%, $C_8F_4H_4$, P-C_2F_5H), 163(9%), 145(13%), 128(11%), 127(100%, $C_7F_2H_5$, BASE PEAK = P-C_2F_4-CF_3), 119(9%), 69(11%, CF_3).

(XXX)

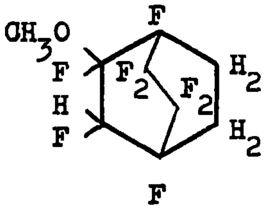


229(7%, P + 1), 228(27%, $C_9F_6H_6$, PARENT), 209(5%, $C_9F_5H_6$, P-F), 159(7%, $C_8F_3H_6$, P-CF_3), 145(5%, $C_7F_3H_4$, P-CF_3-CH_2, 129(12%, B + 1), 128(100%, $C_7F_2H_6$, BASE PEAK =

P-C_2F_4), 127(80%, $C_7F_2H_5$, B-H), 119(12%), 114(5%, $C_6F_2H_6$, B-CH_2), 109(12%, $C_7F_2H_5$, B-F), 107(7%), 104(7%), 101(7%), 100(6%).

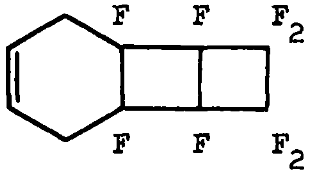
f) Miscellaneous Polyfluoropolycyclic Compounds

(VIII)



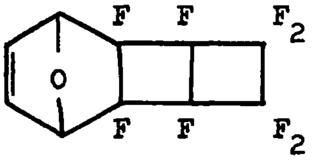
284(2%, $C_9F_8H_8O$, PARENT), 281(1%, $C_9F_8H_7O$), 264(7%, $C_9F_7H_7O$, P-HF), 233(2%, $C_8F_6H_7O$, P-CF_2H), 225(2%), 213(2%), 200(2%), 190(4%), 183(4%), 171(21%), 164(6%), 163(9%), 151(57%), 126(42%), 95(15%), 94(42%), 81(100%, C_2F_5, BASE PEAK), 76(11%), 69(21%, CF_3).

(XXI)



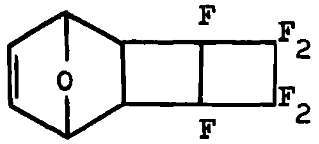
278(100%, $C_{10}F_8H_6$, PARENT AND BASE PEAK), 263(18%, $C_9F_8H_3$, P-CH_3), 258(18%, $C_{10}F_7H_5$, P-HF), 243(18%), 227(27%), 214(27%), 209(27%, $C_9F_5H_6$, P-CF_3), 207(27%), 201(27%), 194(18%), 189(18%), 178(27%, $C_8F_4H_6$, P-C_2F_4), 177(27%, $C_8F_4H_5$, P-C_2F_4H), 169(27%), 165(64%), 145(82%), 116(64%), 115(91%).

(XXII)



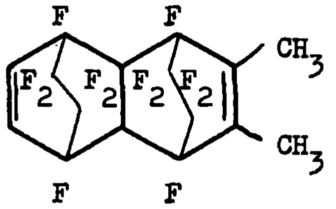
292(v. weak, $C_{10}F_8H_4O$, PARENT), 224(16%, C_6F_8, P-C_4H_4O), 205(10%, C_6F_7), 194(3%), 174(10%, C_6F_6), 163(6%), 155(32%, C_6F_5), 124(19%), 117(6%), 114(3%), 113(3%), 112(3%), 105(6%), 101(6%), 100(3%), 93(13%), 69(16%, CF_3), 68(100%, C_4H_4O (furan), BASE PEAK), 39(29%, C_3H_3, furan-CHO).

(XXXX)



256(v. weak, $C_{10}F_6H_6O$, PARENT), 206(2%, $C_9F_4H_6O$, P-CF_2), 188(8%, $C_6F_6H_2$, P-C_4H_4O), 169(7%, $C_6F_5H_2$), 150(4%, $C_6F_4H_2$), 150(4%, $C_6F_4H_2$), 139(8%), 138(4%), 127(4%), 119(37%, C_2F_5), 69(12%, CF_3), 68(100%, C_4H_4O, (furan), BASE PEAK).

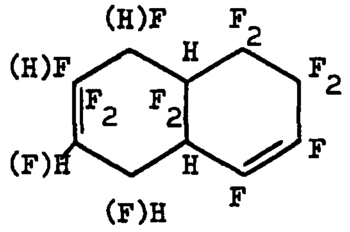
(XXXVI)



430(31%, $C_{16}H_{10}F_{12}$, PARENT), 391(3%, $C_{16}H_9F_{10}$, P-HF_2), 330(5%, $C_{14}H_{10}F_8$, P-C_2F_4), 329(3%, $C_{14}H_9F_8$, P-C_2F_4H), 242(3%, $C_8H_8F_6$, P-$C_6F_6H_2$), 241(2%), 216(13%), 201(3%), 195(3%), 169(3%), 163(3%), 143(10%), 142(100%, $C_8H_8F_2$, BASE PEAK = P-$C_6F_6H_2$-C_2F_4 i.e. $Me_2C_6F_2H_2$ aromatic ion), 141(9%), 128(7·5%), 127(17%, B-CH_3), 114(12%, $C_6H_4F_2$, B-C_2H_4)

Metastable ion: 142 ⟶ 127 (-CH_3).

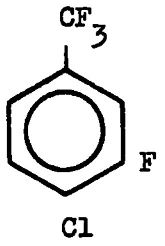
(XXXXIV)



376(9%, $C_{12}F_{12}H_4$, PARENT), 357(6%, $C_{12}F_{11}H_4$, P-F), 337(3%, $C_{12}F_{10}H_4$, P-HF_2), 189(9%), 188(100%, $C_6F_6H_2$, BASE PEAK = P-$C_6F_6H_2$, i.e. arises by Retrodiene reaction), 187(6%, C_6F_6H), 169(15%, $C_6F_5H_2$, B-F), 150(6%, $C_6F_4H_2$, B-F_2), 138(6%, $C_6F_3H_2$, B-CF_2), 137(3%, $C_5F_3H_2$, B-CF_2H), 120(5·9%), 119(56%, $C_5F_3H_3$, P-CF_3), 69(9%, CF_3).

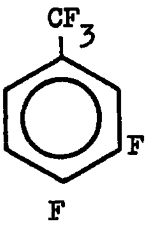
g) <u>Fluoroaromatics</u>

(XXXXVII)



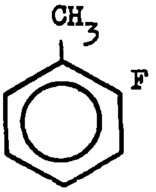
200(50%, $C_7H_3F_4Cl^{37}$, P + 2), 199(12%, P + 1), 198(100%, $C_7H_3F_4Cl^{35}$, PARENT AND BASE PEAK), 163(57%, $C_7H_3F_4$, P-Cl), 150(30%, $C_6H_3F_2Cl^{37}$, (P + 2)-CF_2), 148(84%, $C_6H_3F_2Cl^{35}$), 143(30%, $C_7H_2F_3$, P-HFCl), 131(10%, $C_6H_3FCl^{37}$, (P + 2)-CF_3), 129(20%, $C_6H_3FCl^{35}$, P-CF_3).

(XXXXVIII)



183(10%, P + 1), 182(100%, $C_7F_5H_3$, PARENT AND BASE PEAK), 181(15%, $C_7F_5H_2$, P-H), 164(8%), 163(79%, $C_7F_4H_3$, P-F), 143(5%, $C_7F_3H_2$, P-HF_2), 132(61%, $C_6F_3H_3$, P-CF_2), 119(5%), 113(15%, $C_6F_2H_3$, P-CF_3).

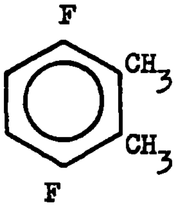
(IL)*



129(7%, P + 1), 128(62%, $C_7F_2H_6$, PARENT), 127(100%, $C_7F_2H_5$, BASE PEAK = P-H), 126(7%), 125(7%), 109(9%, C_7FH_6, P-F), 108(4%, C_7FH_5, P-HF), 107(7%, C_7FH_4, P-HF_2), 101(9%, $C_5F_2H_3$ P-C_2H_3), 83(4%), 81(6%).

Metastable ions: 128 ⟶ 127 (-H), 127 ⟶ 101 (-C_2H_2).

(L)*



143(12%, P + 1), 142(66%, $C_8F_2H_8$, PARENT), 141(39%, $C_8F_2H_7$, P-H), 140(12%), 139(8%), 138(4%), 128(15%), 127(100%, $C_7F_2H_5$, BASE PEAK = P-CH_3), 125(4%, $C_7F_2H_3$), 123(4%, C_8FH_8, P-F), 122(4%), 121(4%), 120(4%), 119(4%), 109(4%, C_7FH_6, P-CFH_2), 107(4%), 101(19%, $C_5F_2H_3$, P-C_3H_5), 99(4%), 95(4%), 94(8%), 81(8%), 76(8%), 74(8%), 69(8%), 68(8%).

Metastable ion: 142 ⟶ 127 (-CH_3).

APPENDIX C

INFRARED SPECTRA

Infrared spectra are given in the order (I), (II) ...... (L) and structures are given in the Summary Reaction Scheme. All spectra were measured using KBr cells, and were run under conditions designated by

(A) - KBr disc

(B) - Nujol mull; Nujol bands are marked 'n' on the spectra

(C) - thin liquid film

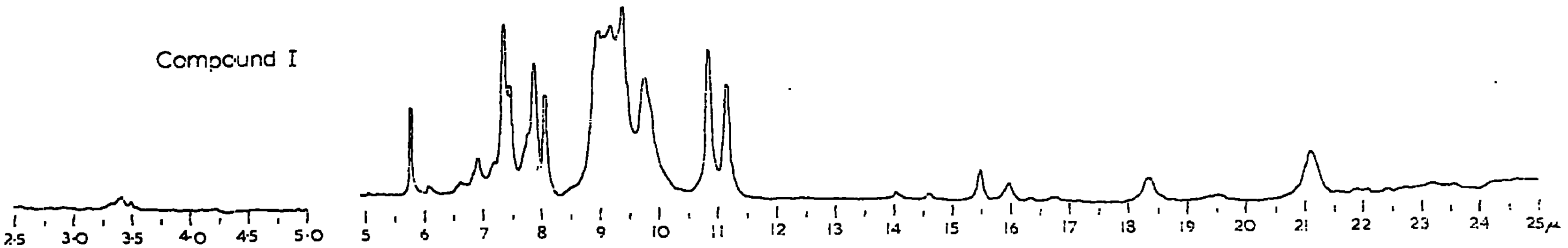
(D) - gas phase.

Compounds which have been reported previously are marked with an asterisk, e.g. (XI)*.

Compound Number	Name of Compound
(I)	1,2-Dimethylhexafluorocyclohexa-1,3-diene, (C)
(II)	2,3-Dimethyl-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene, (A)
(III)	2,3-Dimethylhexafluorocyclohexa-1,3-diene, (C)
(IV)	2,3-Dimethylhexafluorobicyclo[2,2,0]hex-2-ene, (C)
(V)	2,3-Dimethoxy-1,4,5,5,6,6-hexafluorobicyclo[2,2,2]oct-2-ene, (C)
(VI)	2,3-Dimethoxyhexafluorocyclohexa-1,3-diene, (C)
(VII)	2,3-Dimethoxyhexafluorobicyclo[2,2,0]hex-2-ene, (C)
(VIII)	2-Methoxy-1,2,3,4,5,5,6,6-octafluorobicyclo[2,2,2]octane, (C)
(IX)	1,2,3,4,5,5,6,6-Octafluoro-2-methoxybicyclo[2,2,0]hexane, (C)
(X)*	2-Methoxy-1,3,4,5,5,6,6-heptafluorobicyclo[2,2,2]oct-2-ene, (C)
(XI)*	2-Methoxyheptafluorocyclohexa-1,3-diene, (C)
(XII)	2-Methoxyheptafluorobicyclo[2,2,0]hex-2-ene, (C)
(XIII)	2-Methylene-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]oct-5-ene, (C)
(XVIII)	1,2,3,4,5,5,6,6-Octafluorobicyclo[2,2,2]oct-2-ene, (A)
(XX)	Octafluorobicyclo[2,2,0]hex-2-ene, (D)
(XXI)	1,2,3,3,4,4,5,6-Octafluorotricyclo[4,4,0,$0^{2,5}$]dec-8-ene, (B)

Compound Number	Name of Compound
(XXII)	11-Oxa-2,3,4,4,5,5,6,7-octafluorotetracyclo[6,2,1,$0^{2,7}0^{3,6}$]undec-9-ene, (A)
(XXIII)	2-Fluoromethylene(Z)-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene, (C)
(XXIV)	2-Fluoromethylene(E)-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene, (C)
(XXVa and b)	Mixture of 2-methyl-1,4,5,7,7,8,8- and 1,4,6,7,7,8,8-heptafluorobicyclo[2,2,2]octa-2,5-dienes, (C)
(XXVI)	2,3-Dimethyl-1,4,5,7,7,8,8-heptafluorobicyclo[2,2,2]octa-2,5-diene, (C)
(XXVII)	1,2,4,5,5,6,6-Heptafluorobicyclo[2,2,2]oct-2-ene, (B)
(XXVIII)	2-Monofluoromethylene(E)-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene, (C)
(XXIX)	2-Methylene-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene, (C)
(XXX)	2-Methylene-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]oct-5-ene, (C)
(XXXI)	2-Trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene, (C)
(XXXII)	2,3-Bis(trifluoromethyl)-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene, (C)
(XXXIII)	2-Methyl-3-trifluoromethyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene, (C)
(XXXIV)	2-Methyl-1,4,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene, (C)
(XXXV)	2,3-Dimethylhexafluorobicyclo[2,2,2]octa-2,5-diene, (C)
(XXXVI)	4,5-Dimethyl-1,3,6,8,11,11,12,12,13,13,14,14-dodecafluorotetracyclo[6,2,2,$2^{3,6}$,$0^{2,7}$]tetradeca-4,9-diene, (A)
(XXXVII)	1,4,5,5,6,6-Hexafluorobicyclo[2,2,2]oct-2-ene, (B)
(XXXIX)	1,4,5,5,6,6-Hexafluorobicyclo[2,2,0]hex-2-ene, (D)
(XXXX)	11-Oxa-3,4,4,5,5,6-hexafluorotetracyclo[6,2,1,$0^{2,7}$,$0^{3,6}$]undec-9-ene, (A).

Compound Number	Name of Compound
(XXXXI)	2-Trifluoromethyl-4,5,7,7,8,8-hexafluorobicyclo[2,2,2]octa-2,5-diene, (C)
(XXXXII)	2,3-Bis(trifluoromethyl)-4,5,7,7,8,8-hexafluorobicyclo[2,2,2]-octa-2,5-diene, (C)
(XXXXIV)	1H,2H,7H,10H-Dodecafluorotricyclo[6,2,2,$0^{2,7}$]dodeca-3,-9 (or 5,9)-diene, (A)
(XXXXVII)	4-Chloro-3-fluorobenzotrifluoride, (C)
(XXXXVIII)	3,4-Difluorobenzotrifluoride, (C)
(IL)*	2,5-Difluorotoluene, (C)
(L)*	1,4-Difluoro-2,3-dimethylbenzene, (C)



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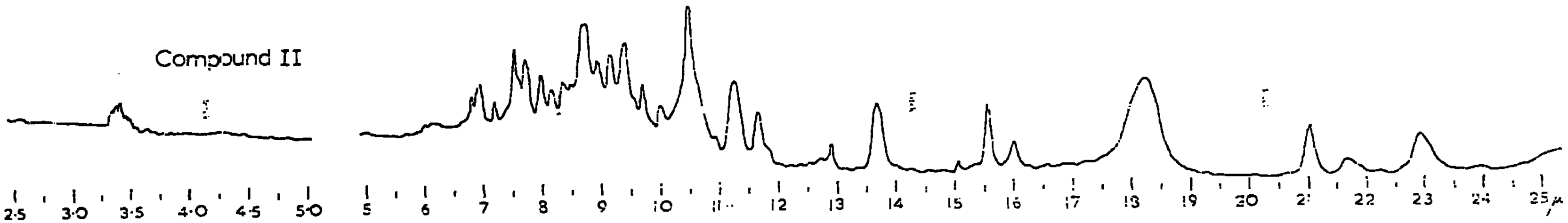

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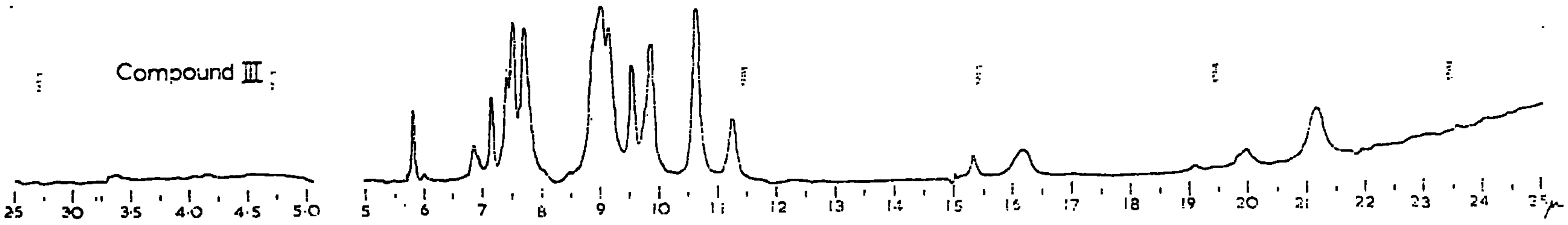

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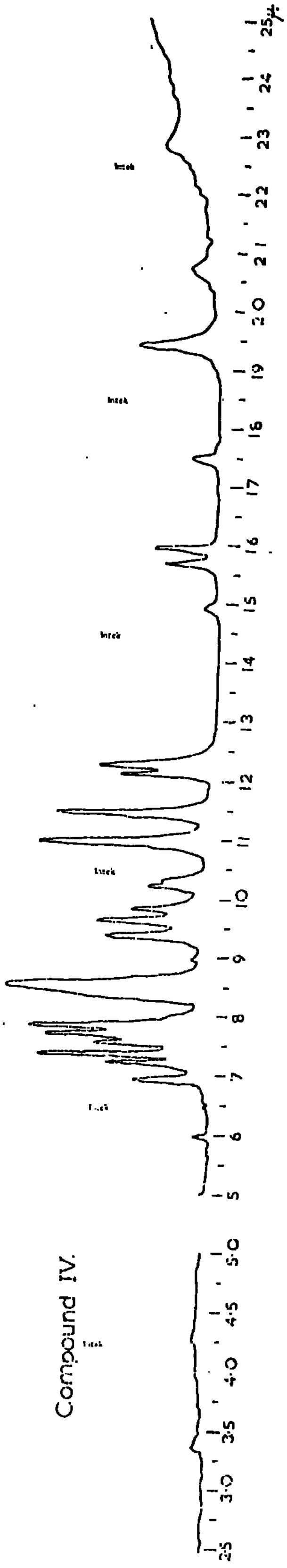
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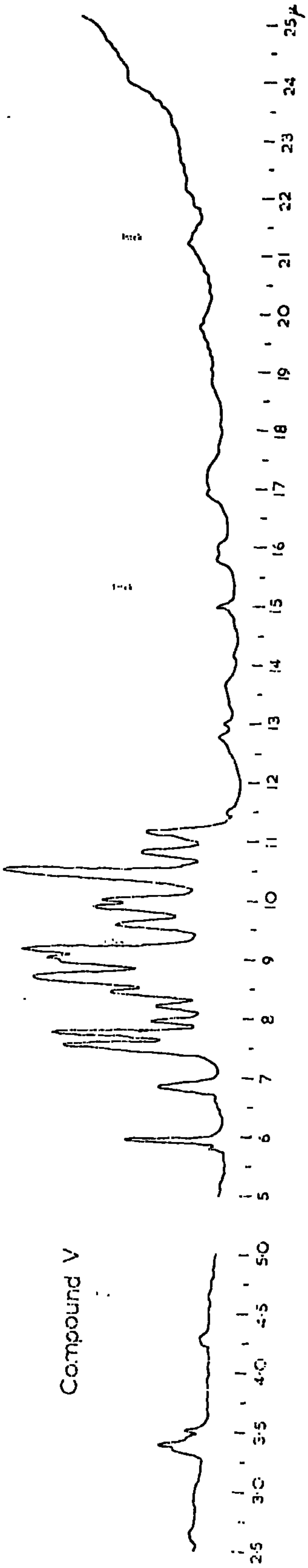
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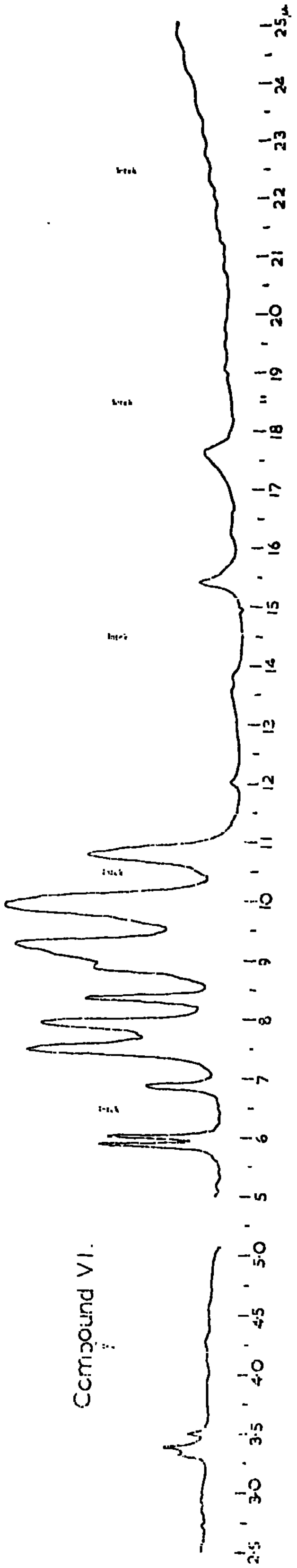
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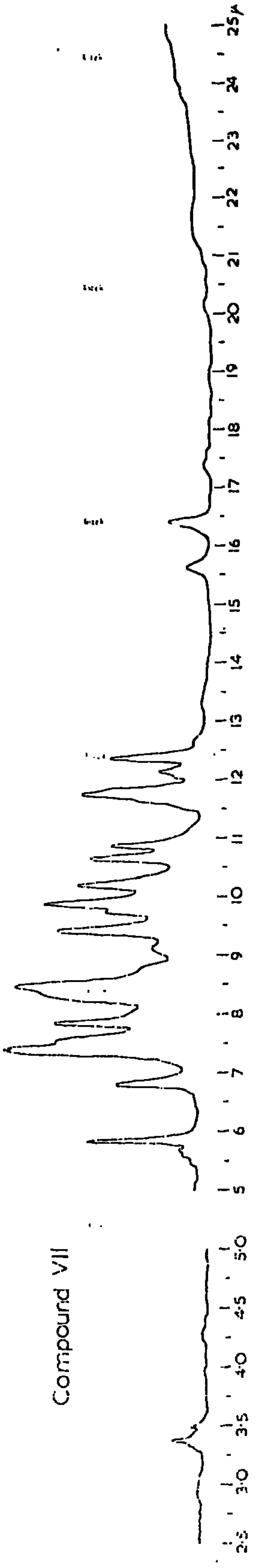

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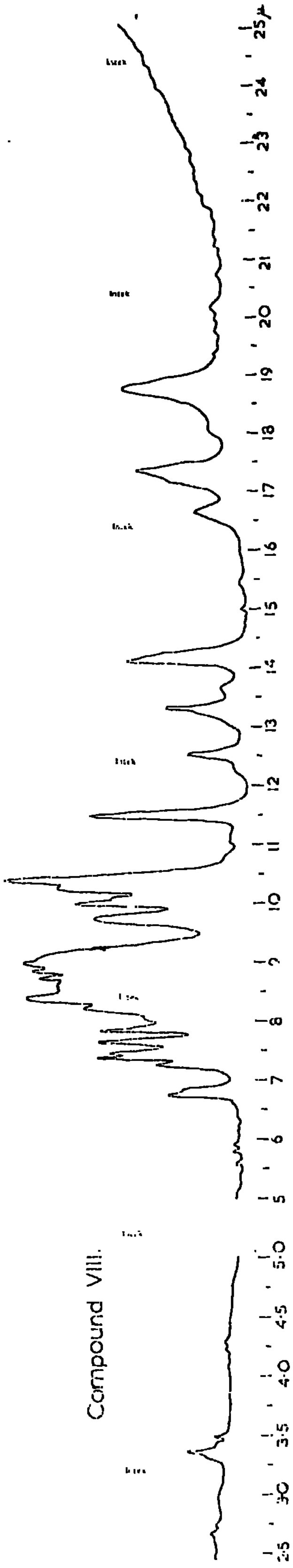

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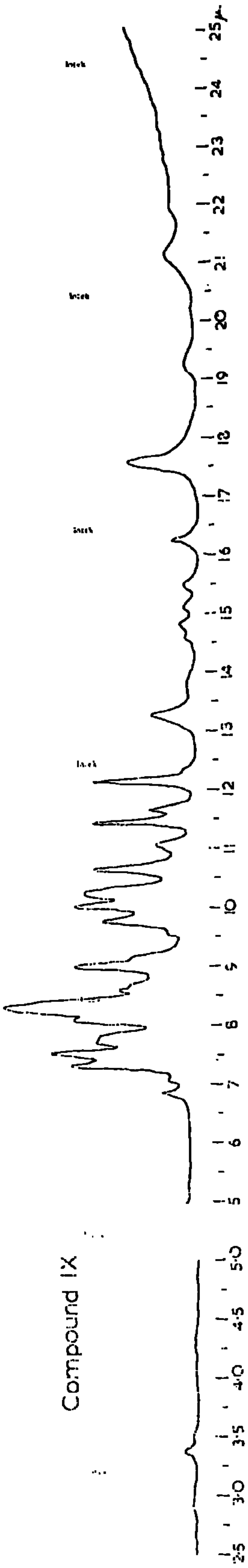
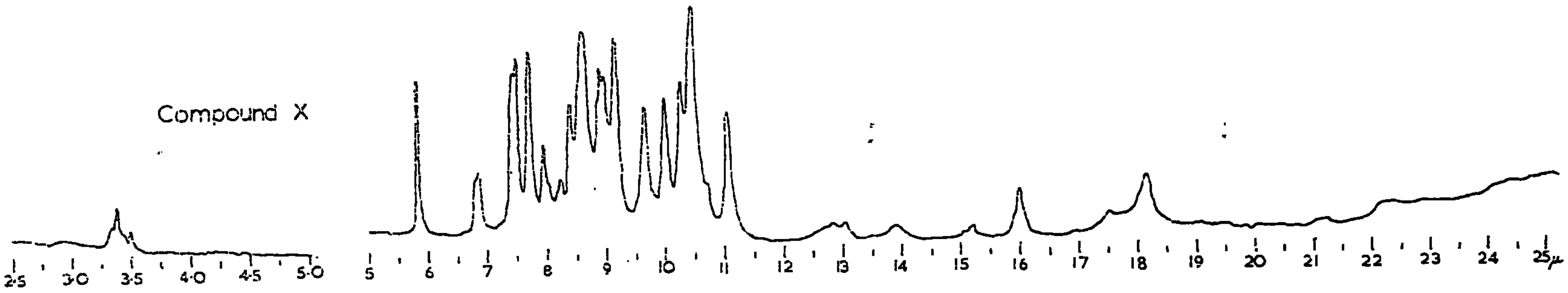


Compound IX

Compound X



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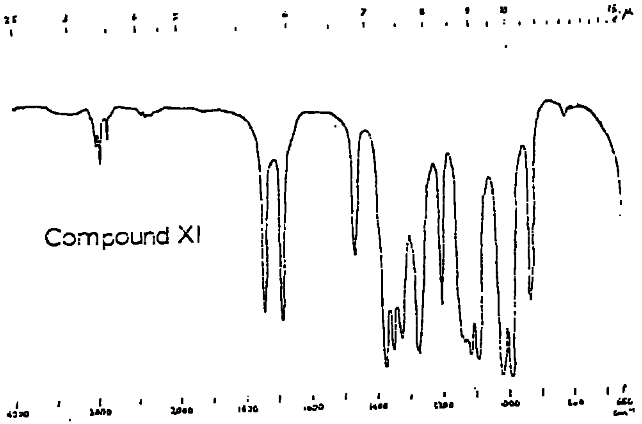

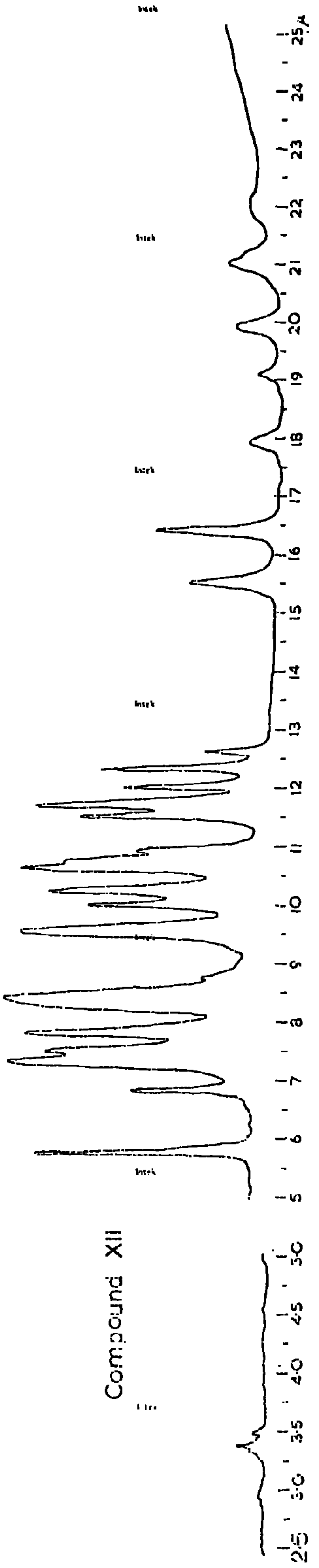

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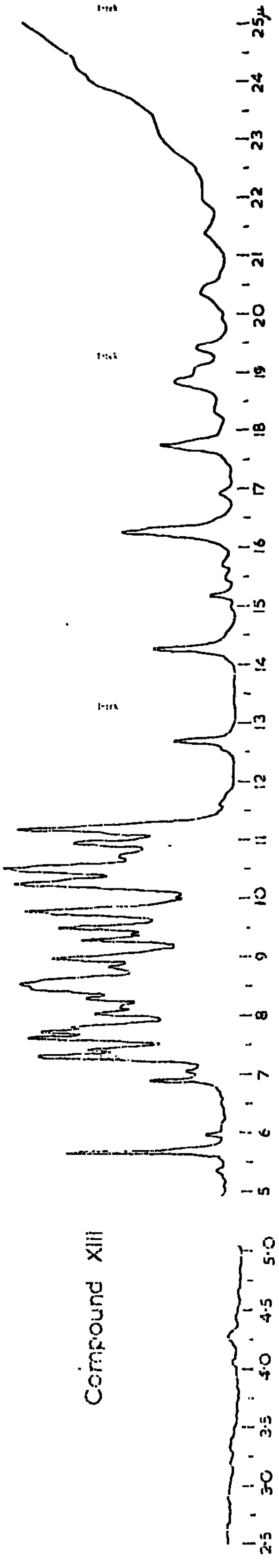

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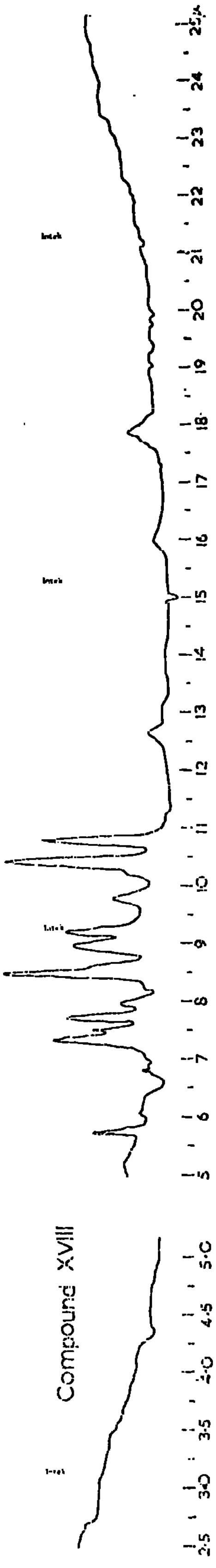

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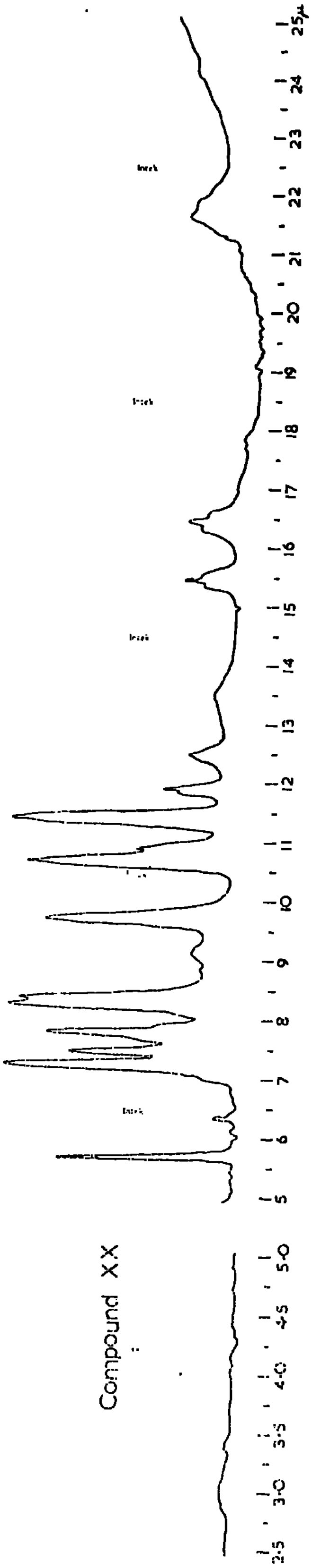

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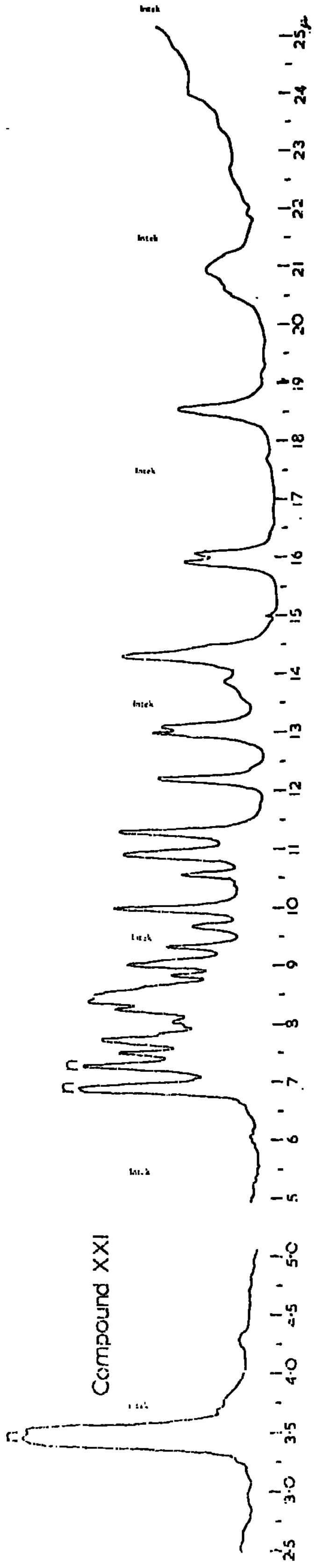

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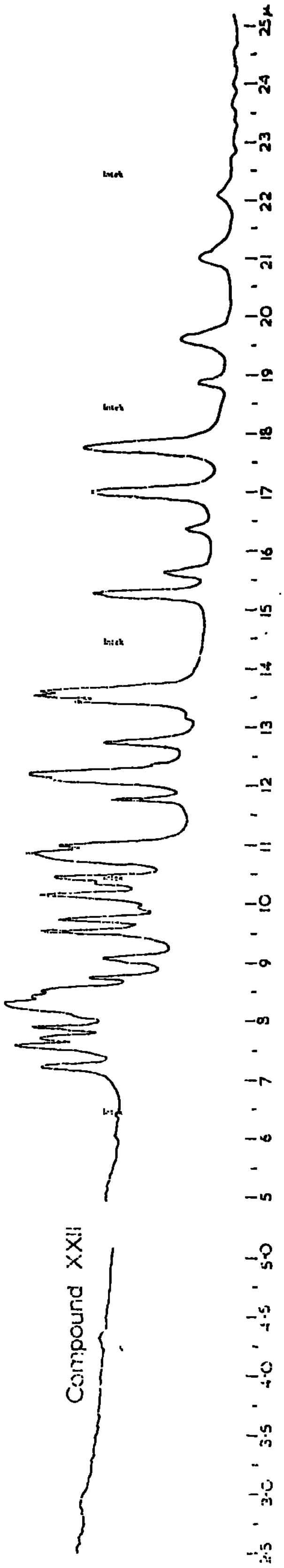

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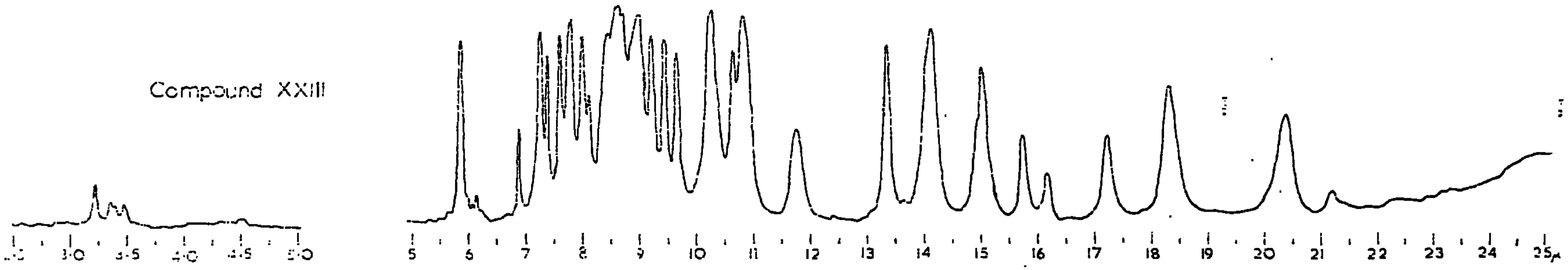
Compound XXIII



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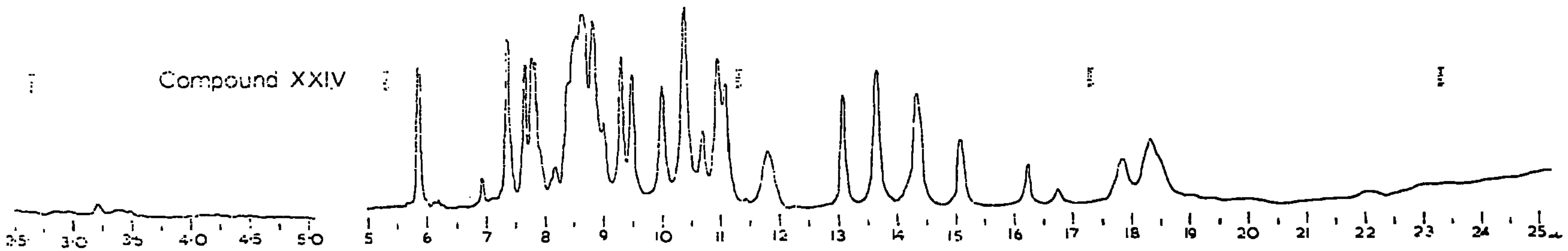

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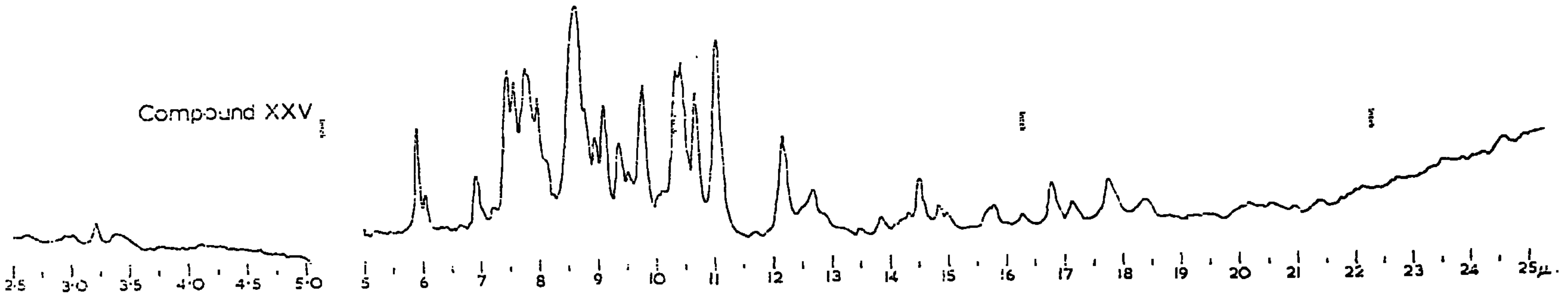

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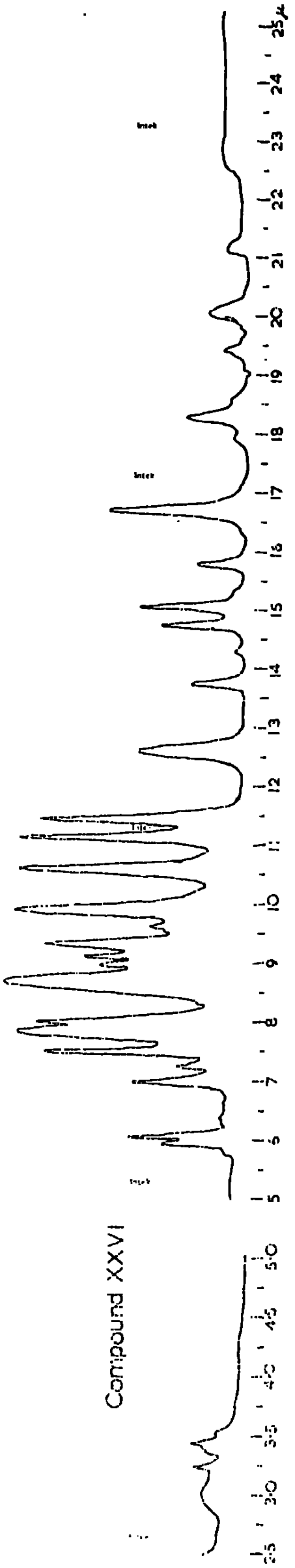

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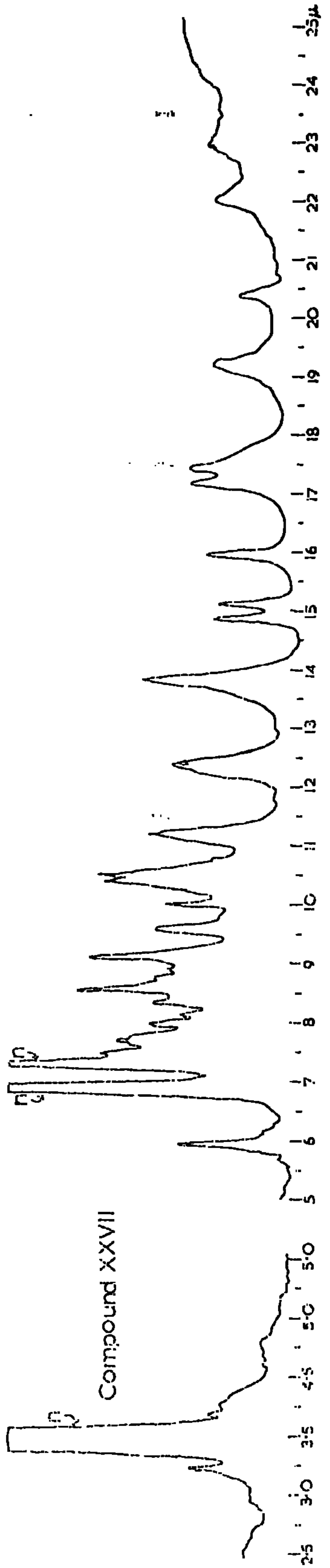

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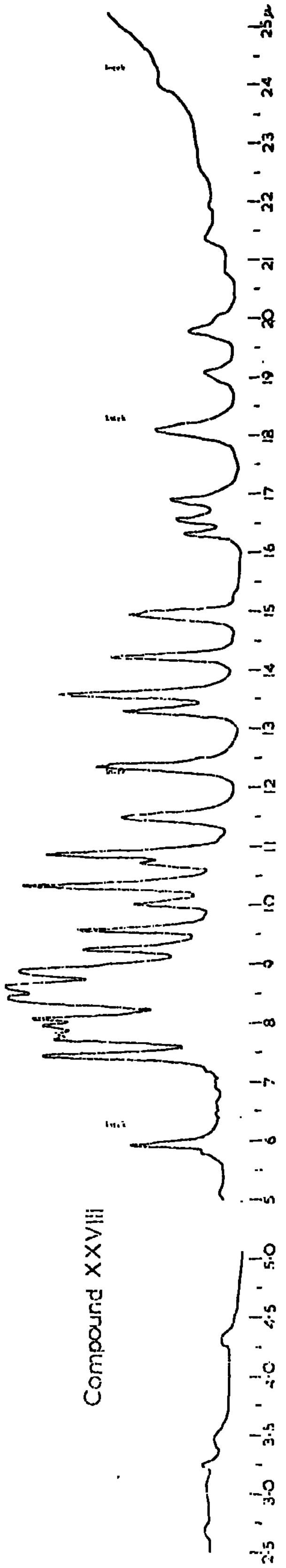

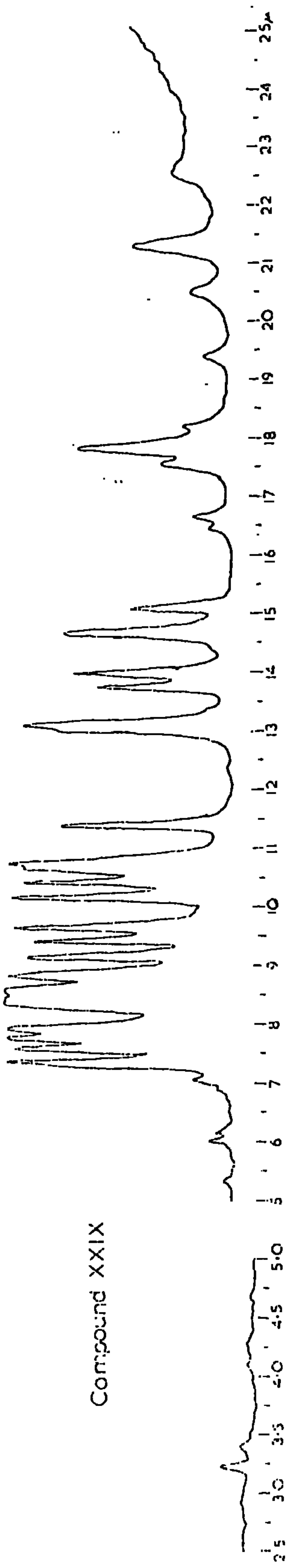

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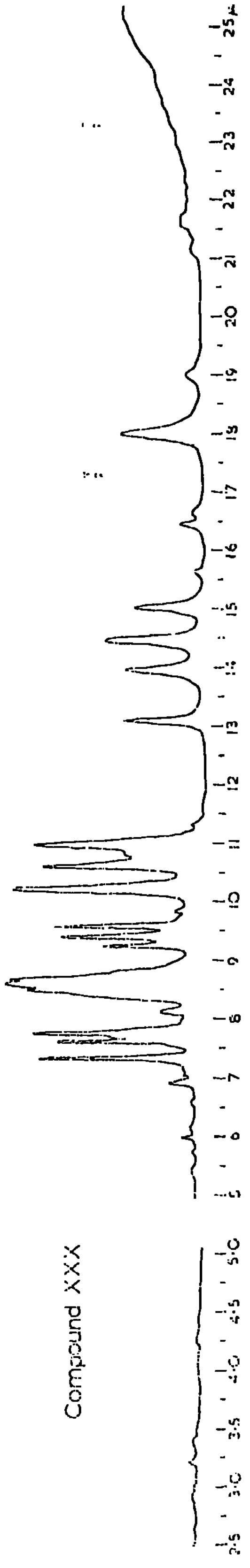

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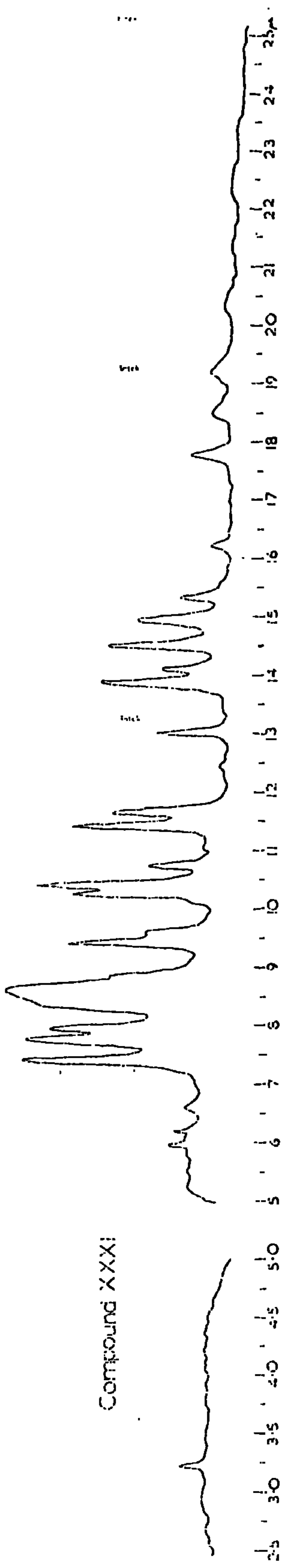
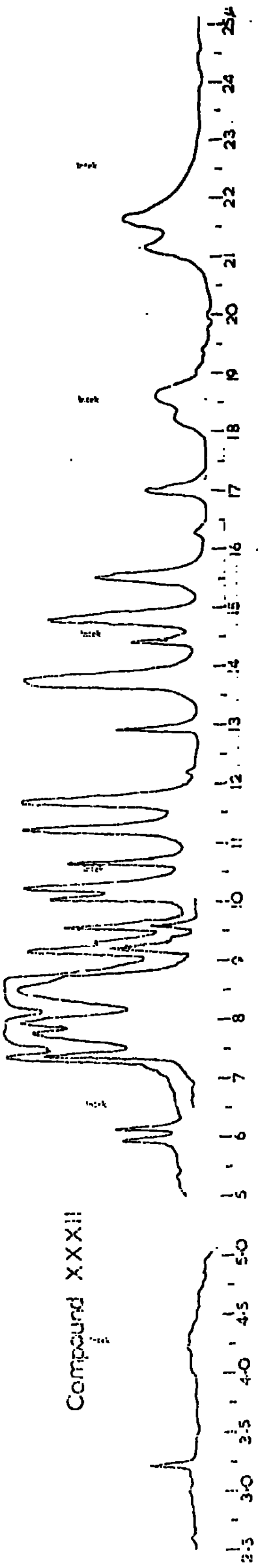


Compound XXXI

Compound XXXII



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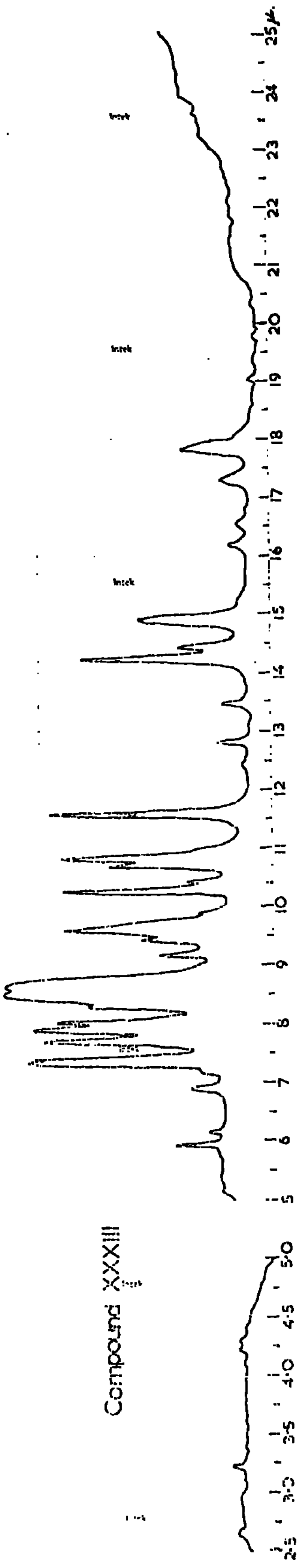

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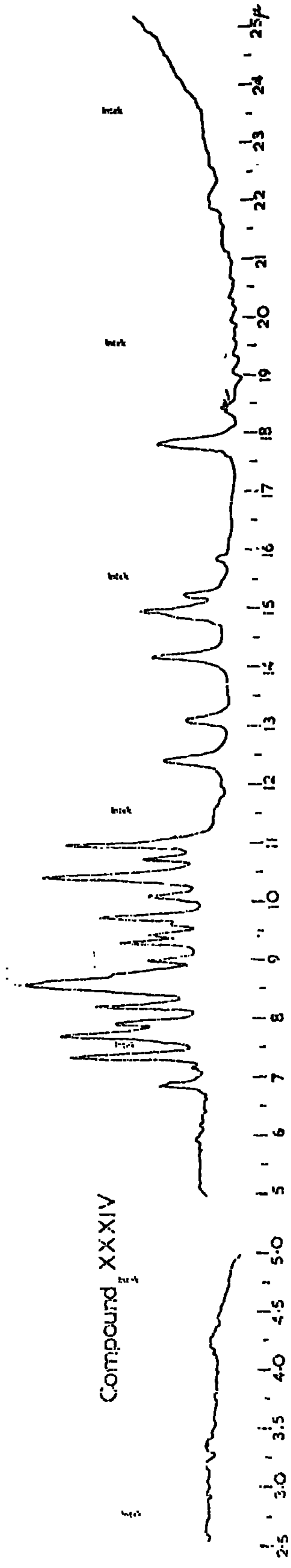

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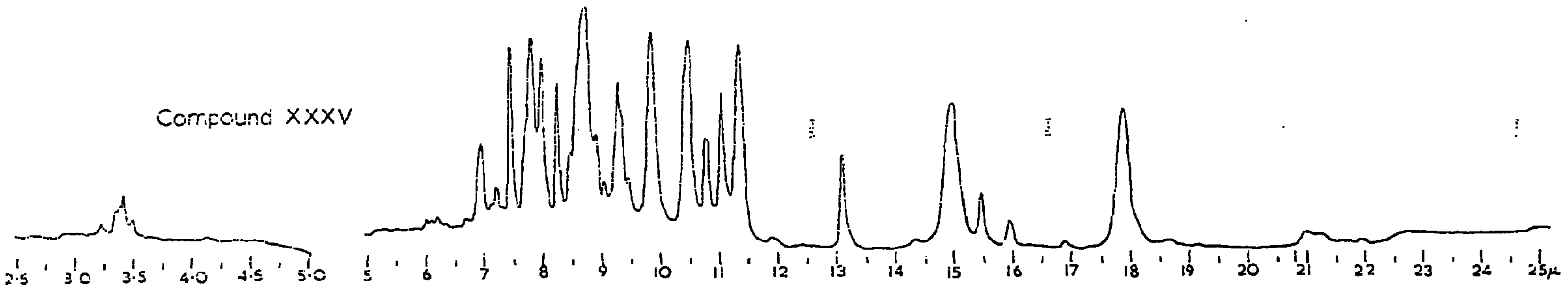

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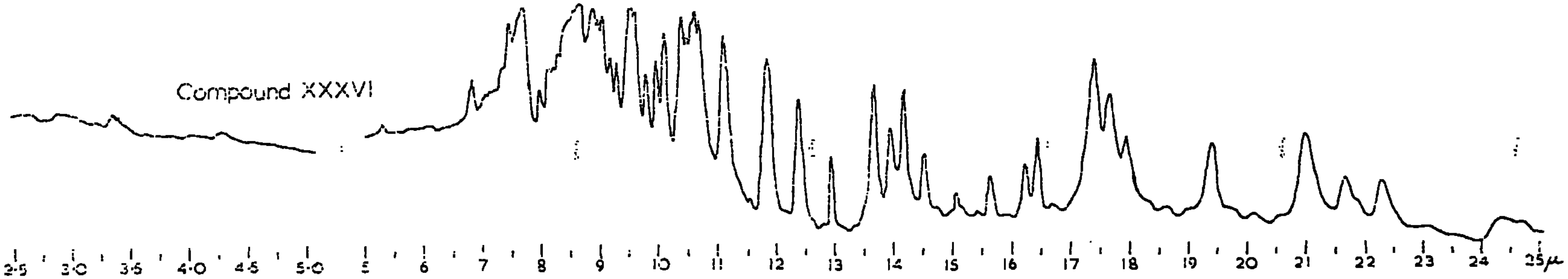
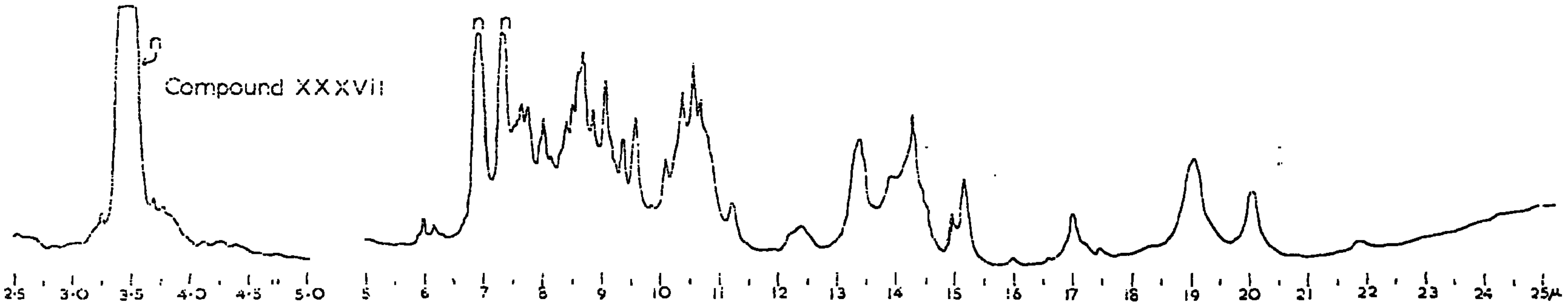
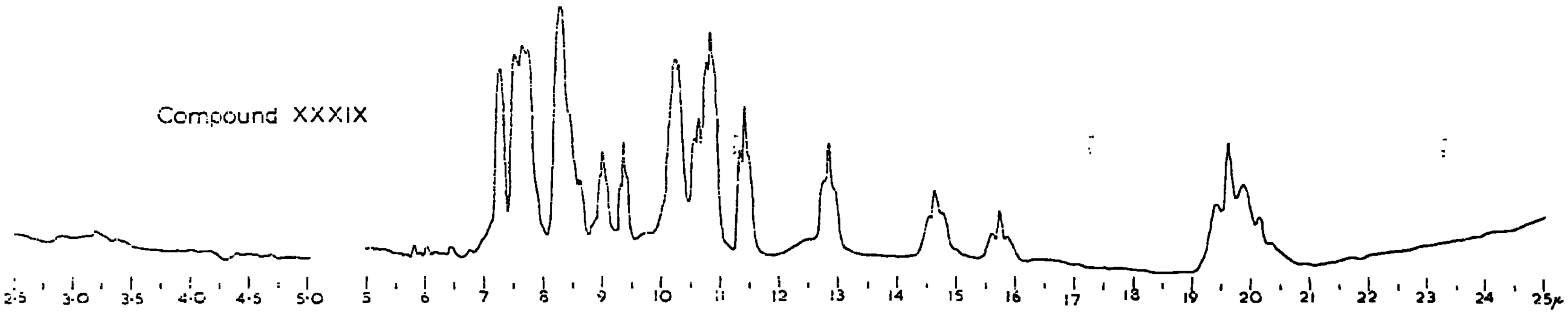


Compound XXXVII

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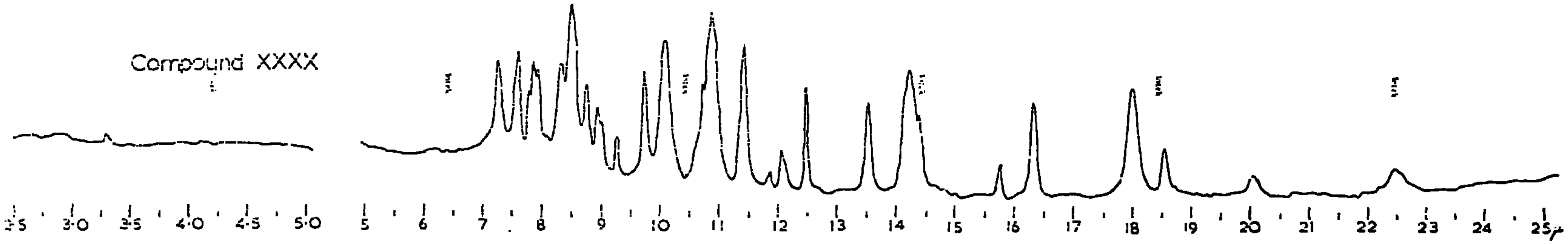
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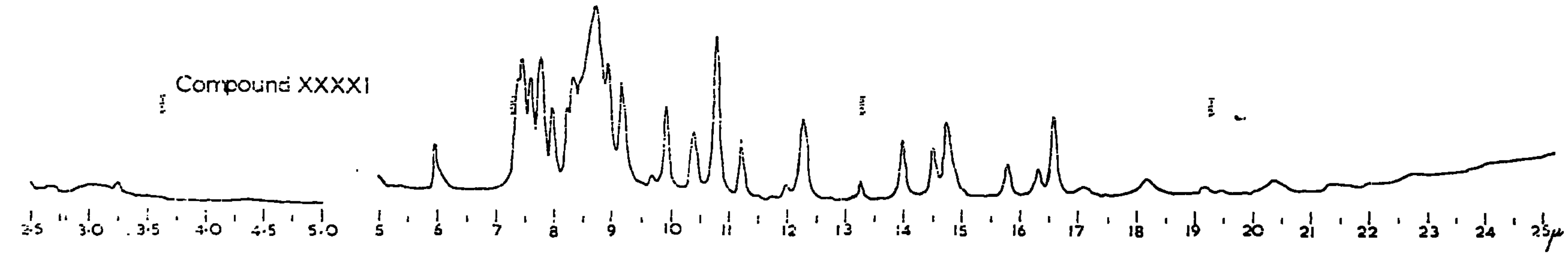
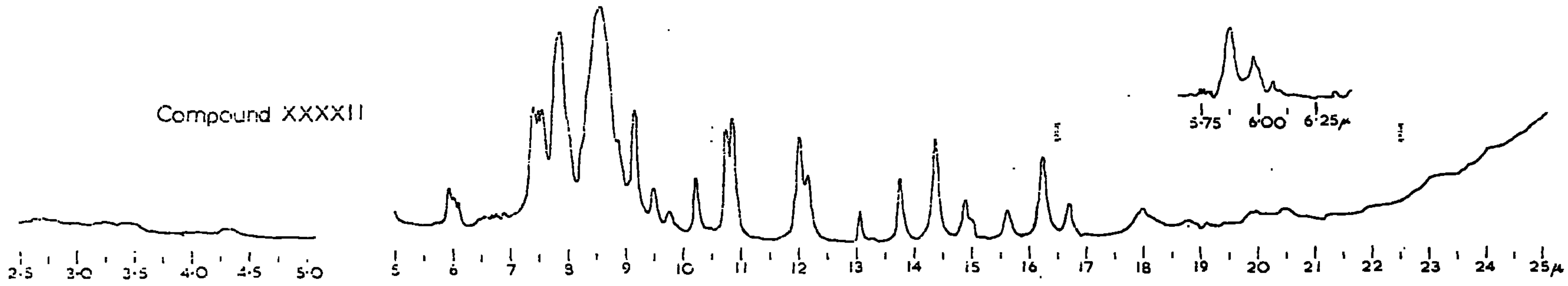

Compound XXXXI

Compound XXXXII



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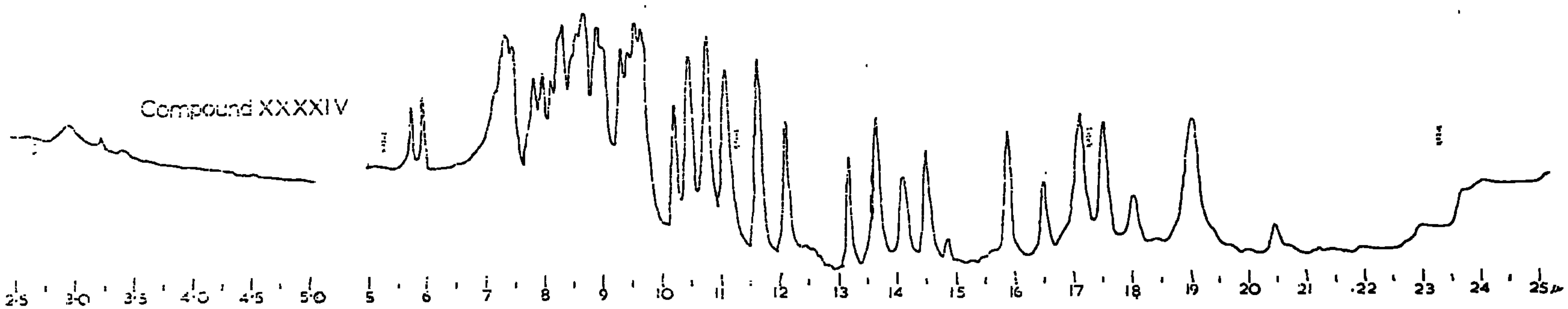
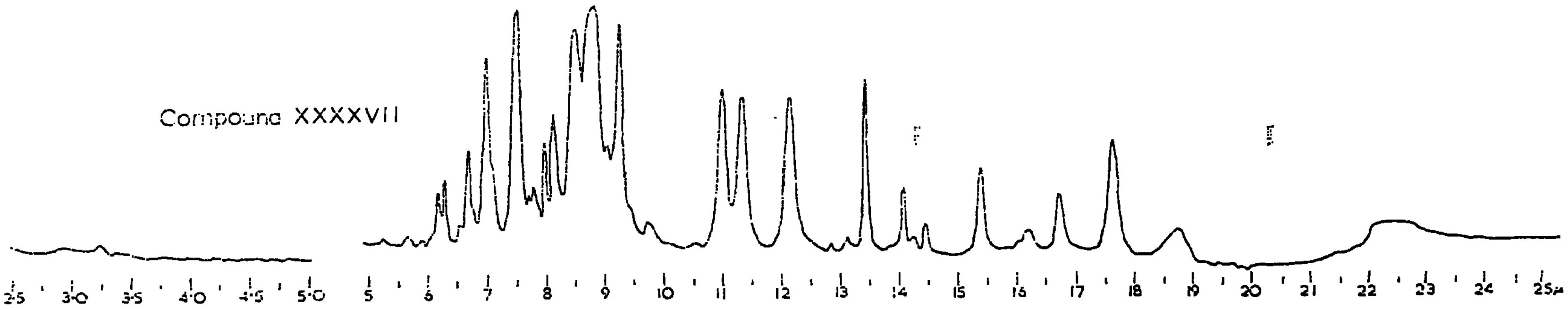
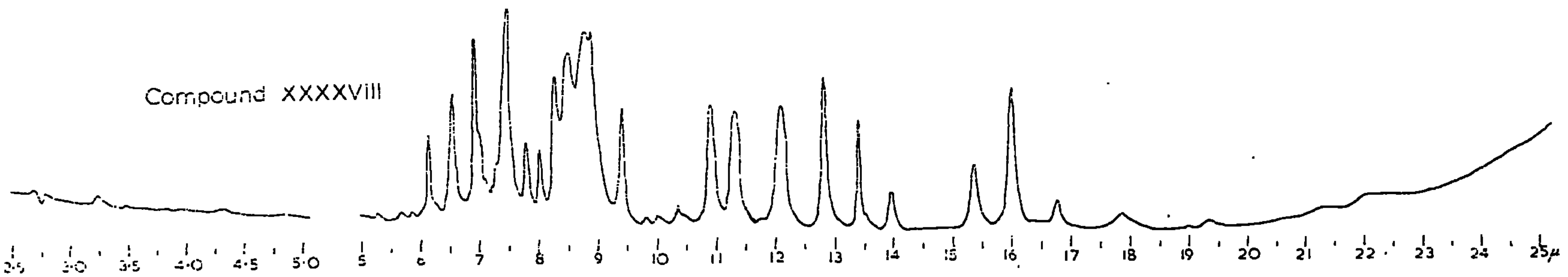


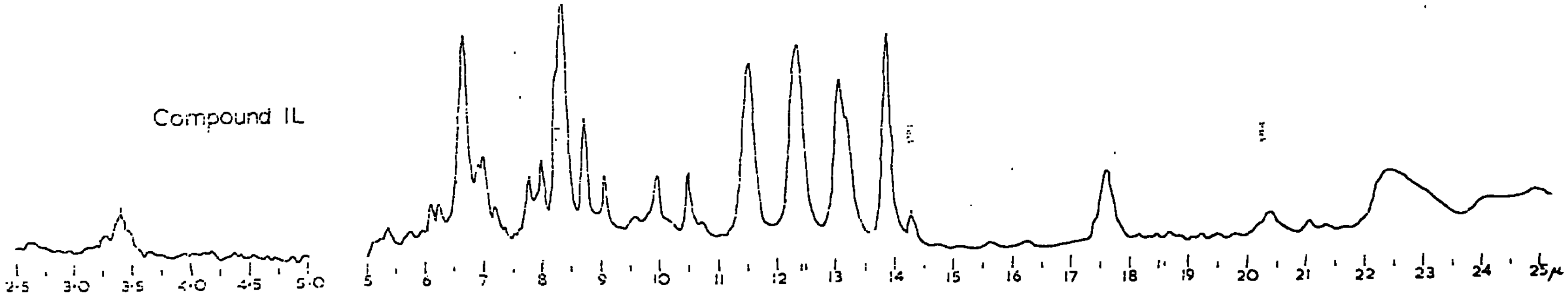
Compound XXXXVII



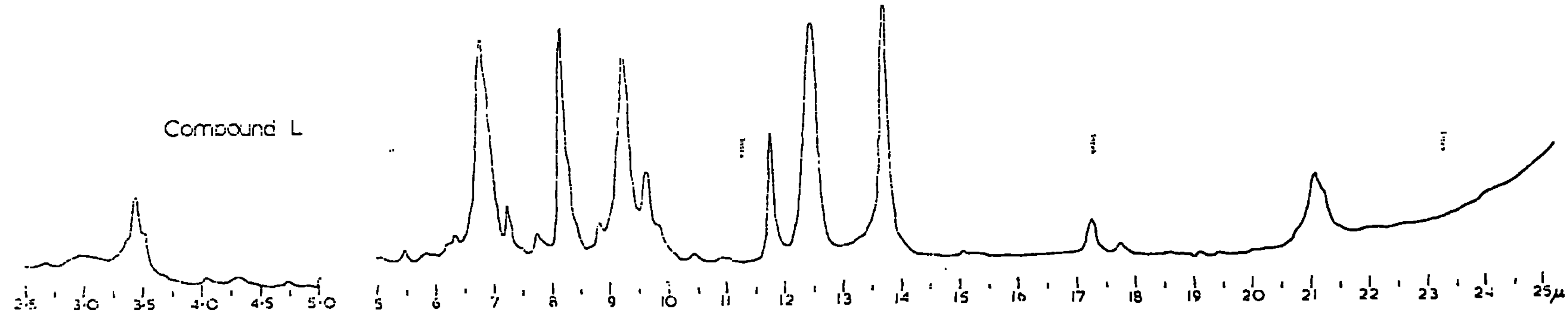
Compound XXXXVIII



Compound IL



Compound L



APPENDIX D

INDEX OF SYNTHESES,(S),N.M.R. SPECTRA (NMR) and MASS SPECTRA (MS)

Compound Number	Page Numbers			Compound Number	Page Numbers		
	S	NMR	MS		S	NMR	MS
(I)	101	17	166	(XXVI)	87	45	172
(II)	85,67	43	170	(XXVII)	86	44	86
(III)	101,133	17	167	(XXVIII)	87,133	49	176
(IV)	144	124	168	(XXIX)	87	49	176
(V)	85	43	170	(XXX)	62	48	176
(VI)	133	17	167	(XXXI)	64	46	172
(VII)	142,132	125	168	(XXXII)	63	46	173
(VIII)	84	76	177	(XXXIII)	64	46	173
(IX)	142	138	169	(XXXIV)	63,87	46	173
(X)†	84	43	170	(XXXV)	62,87	46	174
(XI)*	133,142	17	-	(XXXVI)	63	54	178
(XII)	142,132	125	168	(XXXVII)	62,86	44	171
(XIII)	61	48	175	(XXXVIII)*	20	16	
(XIV)*	See Ref.72			(XXXIX)	132,143	124	169
(XV)*				(XXXX)	161	160	178
(XVI)*				(XXXXI)	65	57	174
(XVII)*				(XXXXII)	65	56	174
(XVIII)	61	43	171	(XXXXIII)*	20	15	
(XIX)*	-	15	167	(XXXXIV)	64	55	178
(XX)	131	124	169	(XXXXV)	-	-	-
(XXI)	161	160	177	(XXXXVI)	66	-	-
(XXII)	161	160	177	(XXXXVII)	66	66	179
(XXIII)	88	48	175	(XXXXVIII)	65,66	66	179
(XXIV)	88	49	175	(IL)*	100	100	179
(XXV)	87	45	172	(L)*	99	99	180

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SUMMARY REACTION SCHEME

(Note: All unmarked bonds are attached to fluorine)

KEY TO REAGENTS

(i) ethylene	(ix) $CH_3 \cdot C \colon C \cdot CH_3$
(ii) LiMe in Et_2O	(x) $LiAlH_4$ in Et_2O
(iii) NaOMe in MeOH	(xi) buta-1,3-diene
(iv) KOH, 180°	(xii) furan
(v) allene	(xiii) $NaBH_4$ in diglyme
(vi) $CF_3 \cdot C \colon C \cdot H$	(xiv) $CF_3 \cdot C \colon C \cdot CH_3$
(vii) $CF_3 \cdot C \colon C \cdot CF_3$	(xv)
(viii) $CH_3 \cdot C \colon C \cdot H$	(xvi) a) diazotise, b) $NaBF_4$