A study of the reactions of fluorine containing olefins

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A STUDY OF THE REACTIONS OF FLUORINE CONTAINING OLEFINS

submitted by

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A candidate for the degree of Doctor of Philosophy

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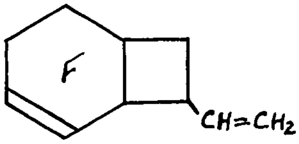
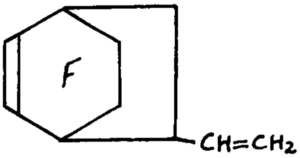
I should also like to thank Dr. J.W. Emsley for the recording and interpretation of nuclear magnetic resonance spectra; the Imperial Smelting Corpor-ation for a Research Studentship and gifts of Octafluorocyclohexa-1,3,-diene; Blackburn Education Committee for an Honorarium and the many Science Laboratory Technicians.

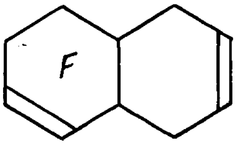
SUMMARY

Thermally initiated additions of some unsaturated organic compounds to octafluorocyclohexa-1,3-diene have been investigated.

The addition of buta-1,3-diene yielded three major compounds which have been shown, by oxidative degradation and fluorine nuclear magnetic resonance spectroscopy, to be 1,2,2,3,3,4,5,6-octafluoro-7(8)-vinyl-bicyclo-(4.2.0)-oct-4-ene, (I), 1,2,3,4,5,5,6,6-octafluoro-7-vinyl-bicyclo-(2.2.2)-oct-2-ene, (II) and 1,2,3,4,4,5,5,6-octafluoro-bicyclo-(4.4.0)-deca-2,8-diene, (III).







At 420° compounds I and II isomerise to produce III, which can be dehydrofluorinated/defluorinated to yield 1,2,3,4-tetrafluoronaphthalene. (X). This compound has been shown to undergo nucleophilic substitution in the fluoroaromatic ring at the α position, while electrophilic reagents substitute in the hydrocarbon ring, presumably at the α position. Oxidation of the naphthalene yielded phthalic anyhydride indicating the relative stability of the hydrocarbon aromatic ring towards conventional

oxidising agents.

Adducts prepared from substituted vinyl compounds and anthracene have been shown, by a combination of oxidative degradation, fluorine nuclear magnetic resonance spectroscopy and infrared absorption correlations to be Diels-Alder adducts of the fluorodiene.

Two charts showing the reaction scheme of the butadiene adducts and the structures of other adducts can be found inside the back cover.

INDEX

Reactions of octafluorocyclohexa-1,3-diene with

CHAPTER 1

INTRODUCTION

INTRODUCTION

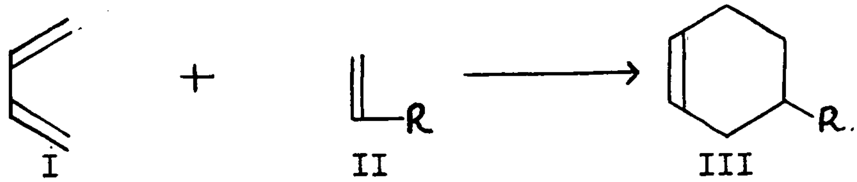
The aspects of organic chemistry pertinent to this thesis are the Diels-Alder reaction, the role of fluoroolefins therein and Cycloaddition Reactions. Tables 1 - 5 contain references to the important publications relating to polyfluorinated compounds in these reactions, though not all have been referred to in the text.

THE DIELS-ALDER REACTION

Since its discovery by Diels and Alder[1], this reaction has been shown to be most versatile and a large number of papers relating to its scope, stereochemistry and mechanism have been published[2-5].

A. SCOPE OF THE REACTION

The reaction can be represented, in the simplest terms, as the cyclisation of a conjugated diene(I) with a substituted olefin(II) yielding a substituted cyclohexene(III).

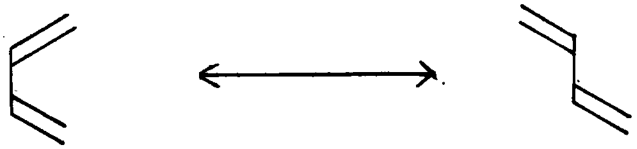


The diene may possess an open or a cyclic configuration and, with certain reservations, be substituted at any carbon atom. The dienophile is more variable, including mono- and disubstituted ethylenes, acetylenes and nitroso compounds.

B. INFLUENCE OF STRUCTURE ON REACTIVITY

i) The Diene

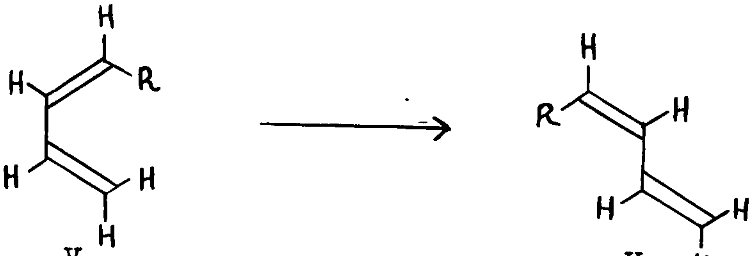
An alicyclic diene may exist in one of two extreme forms, cisoid(IV) or transoid(IVa), where rotation about



IV IVa

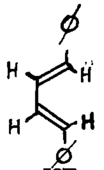
the single bond is prevented by conjugation between the $p\pi$ orbitals of the double bonds and a coplanar molecule ensures maximum overlap of those orbitals. If a diene possesses a planar cisoid conformation(IV) then it will participate in the reaction[6]. These conditions are reflected in the high reactivity of cyclopentadiene and, to a lesser extent, cyclohexa$^{-1,3-}$diene. Larger ring systems which possess a cisoid configuration may not participate in the reaction because they are not coplanar. Dienes with transoid configurations(IVa) are unreactive, an observation which has been employed in the chemistry of steroids to evaluate between cis and trans configurations[7].

Cis-Terminal substituents determine that the trans configuration of the diene(Va) is the more stable due to repulsive forces set up between the cis-1 substituent and the cis-4 hydrogen atom in the cisoid configuration of the diene(V).

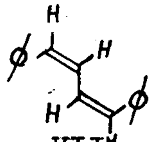


V Va

It has been shown by Inhoffen[8] that trans-1, trans-4-diphenylbuta-1,3-diene(VI) gives quantitative yields of Diels-Alder adducts with maleic anhydride while the corresponding cis, cis isomer(VII) does not react.



VI



VII

Similarly 2,3-dichloro and 2,3-di(t-butyl)-buta-1,3-dienes do not react with the most powerful dienophiles due to the repulsive forces, between the adjacent substituents, which stabilise the trans configuration of the diene[9,10].

Electron donating groups in the diene facilitate the reaction. Sauer and Weist[11] investigated the rates of reaction of a number of dienes and the following conclusions were drawn from the results.

a) Cyclic dienes are more reactive than acyclic dienes.

b) Electron donating groups at the 2 or 3 positions of the diene accelerate the reaction to a greater extent than at the 1 or 4 positions. The effectiveness of the electron donating groups was found to be $-OMe > -\phi > -Me$.

c) The change of influence, $-\mathrm{Me} > -\mathrm{OMe} > -\phi$, in 9 substituted anthracenes, though not explained in the above publication, must be due to steric interference outweighing the advantage of electron availability.

De Witt et al[12] have investigated 1-(p-x phenyl)buta-1,3-dienes in the Diels Alder Reaction and found that electron availability in the aromatic system is transmitted into the diene. The rates of reaction decreased in the order $-\mathrm{OMe} > -\mathrm{Me} > -\mathrm{H} > -\mathrm{Cl} > -\mathrm{NO}_2$, an order which is in agreement with Hammett σ_p values[13].

ii) <u>The Dienophile</u>

Steric effects are responsible for reduction of dienophilic activity[14]. Addition of a diene to an olefin of the type $\mathrm{RR'C{=}CHCOCH{=}CH_2}$ takes place exclusively at the unsubstituted vinyl group if the substituents R and R' are alkyl groups[15].

Cyclohexenones(VIII), although they resemble quinones, are poor dienophiles and this has been attributed to steric blocking by the methylene group at the 6 position[16].

VIII

Electron withdrawing groups in the dienophile produce an electron deficient double bond, and the following trends have been observed[3].

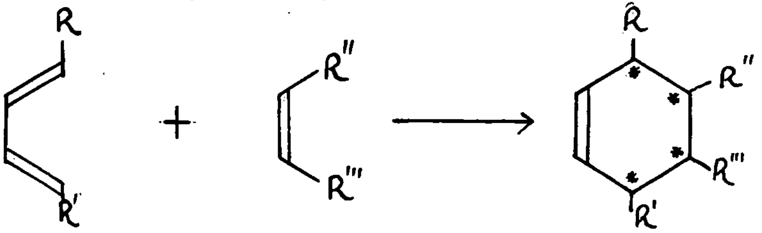
a) Bifunctional dienophiles possess greater activity than corresponding monosubstituted compounds.

b) Reactivity decreases in the following order: anhydride > dinitrile > dicarboxylic acid > dicarboxylic ester.

As the strength of the electron withdrawing group is increased in p-substituted phenylpyruvic acids so the rate of the reaction is increased[17], e.g. $-NO_2 > -Cl > H > CH_3 > OCH_3$.

C. STEREOCHEMISTRY OF THE DIELS-ALDER REACTION

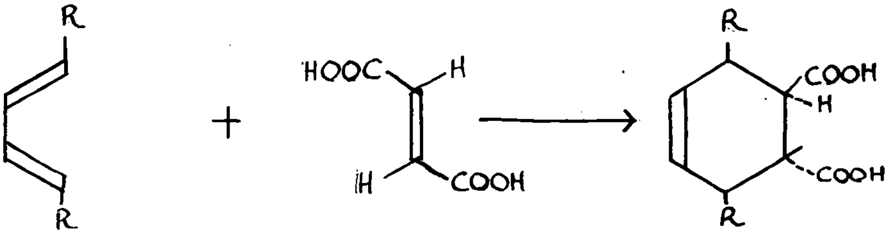
The reaction may be expressed in general terms



IX X XI

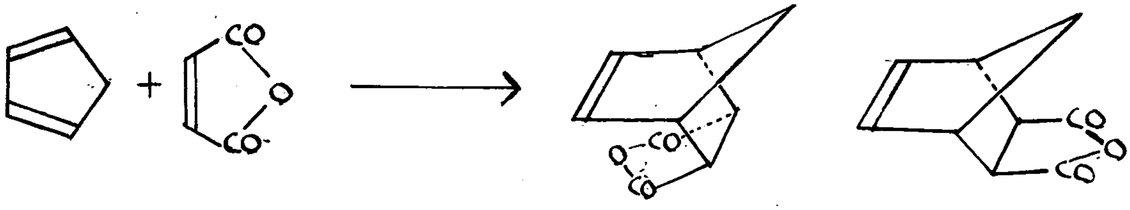
Because the adduct(XI) possesses 4 asymmetric carbon atoms, 16 stereoisomeric products are possible from such a reaction. Usually, only one stereoisomer is produced and this stereochemical reactivity is explained in Alder's "Cis Rule"[18,19].

1) The addition of a dienophile to a diene is purely cis, with the relative configurations of the substituents in the reactants retained in the adduct.

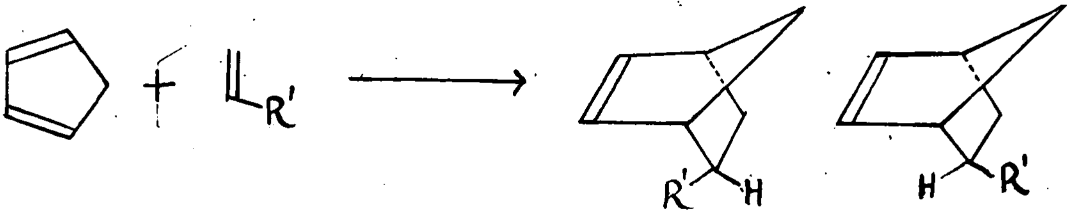


XII

2) In the reaction of cyclic dienes with dienophiles, two modes of addition are possible to give either endo(XIII, XV) or exo(XIV, XVI) adducts.



XIII XIV



XV XVI

D. EPIMERISATION OF ADDUCTS

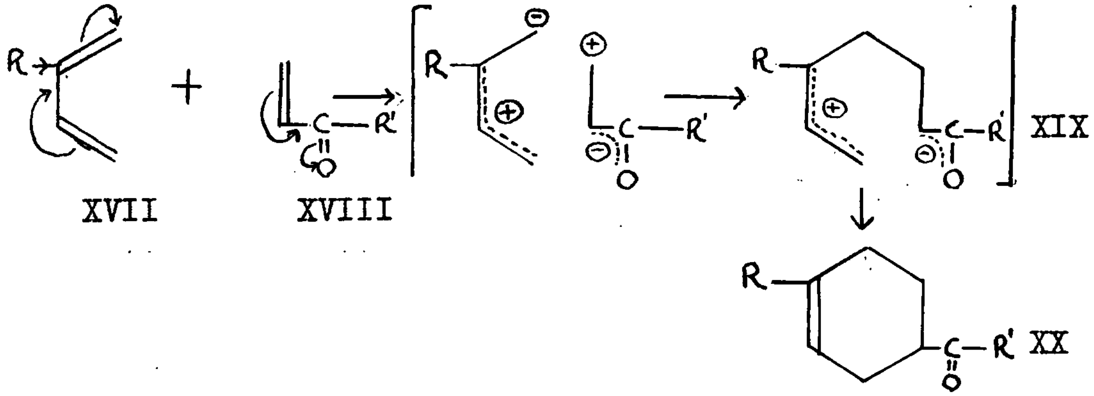
Reactions carried out above an optimum temperature (thermodynamic rather than kinetic control) produce an adduct which contravenes the Alder Rules. At room temperature the reaction of maleic esters with butadiene yields cis-1,2,3,6-tetrahydro-phthalic esters while in refluxing xylene the trans ester is formed exclusively[20]. Woodward and Baer[21] have interpreted this observation in terms of a retrogression reaction where the kinetic adduct dissociates readily to reform the stable thermodynamic adduct.

E. MECHANISM

Ionic and free radical intermediates have been postulated as intermediates in the Diels-Alder Reaction.

Experimental data is now being interpreted in terms of a concerted or four centre intermediate.

i) Ionic



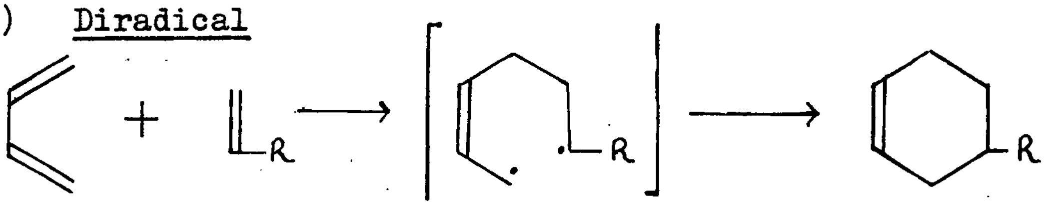
The reaction was thought to proceed in two distinct steps:

a) The slow combination of the reactants XVII and XVIII to form the charged intermediate XIX followed by

b) A fast cyclisation step.

Objections to this mode of reaction were based on the absence of pronounced solvent effects upon the rate of reaction and also that 1,2 disubstituted dienophiles reacted more readily than a monosubstituted dienophile, an effect which is not compatible with an easy polarisation.

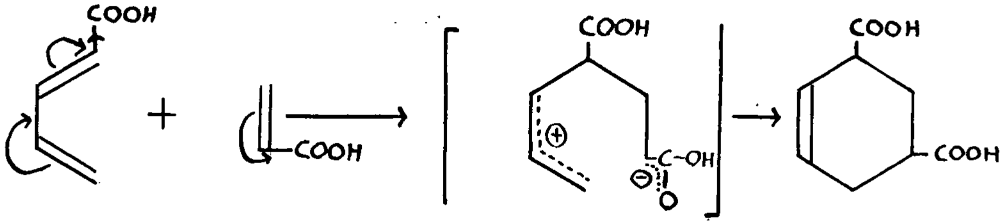
ii) Diradical



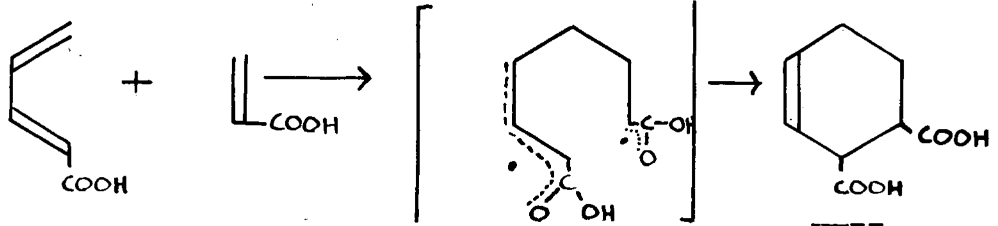
A number of arguments for and against this mode of reaction have been reviewed by Berson and Remanick[22]. One of those in favour is based on a calculation of the entropy

of activation of the diradical formed in the dimerisation of butadiene[23]. This calculation was later shown by Wasserman[24] to be incorrect due to errors in postulating the fundamental vibrational frequencies of the transition state.

Alder and co-workers[25] demonstrated that the "diradical intermediate theory" could be employed to explain the addition of vinylacrylic acid to acrylic acid in which two isomeric products, XXI and XXII, are theoretically possible.



XXI



XXII

The formation of the former can be explained in terms of an ionic mechanism and the latter in terms of a stable radical intermediate. They found that the product from such a reaction was 1,2,3,4-tetrahydro-phthalic acid(XXII), thus supporting the diradical intermediate. The formation of this isomer can also be explained in terms of a four centre mechanism, the most stable resonance hybrid leading to the formation of XXII[26].

iii) Concerted Mechanism

Woodward and Katz[27] envisage a two stage mechanism where one bond is formed and the stereospecific nature of the addition is maintained by "secondary attractive forces" between the diene and the dienophile substituent. Berson and Remanick[22] interpret the above postulation as a two step addition (two discrete bond forming processes) if it is considered that activation energy is required to convert the attractive forces to a covalent bond. If no activation energy is required, then a four centre mechanism must be operative.

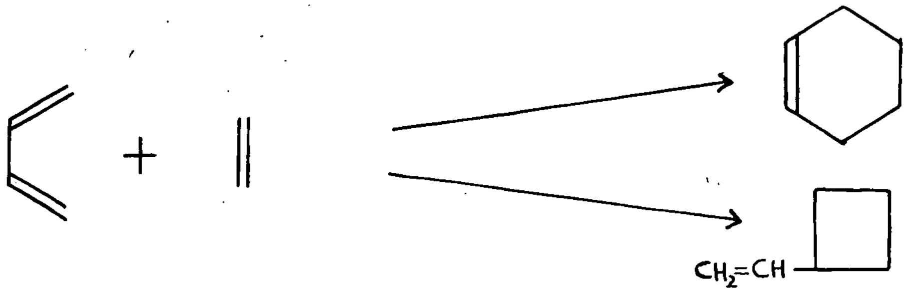
The same authors[22] then discuss the additions of methyl acrylate and methyl methacrylate to cyclopentadiene. It would be anticipated that the endo esters would be the predominant adducts under conditions of kinetic control, but the exo methyl methacrylate ester is the major product. Thus the carbonyl diene interaction cannot be a major contribution during the addition.

The results so far compiled indicate a four centre mechanism, but the authors are unable to state whether bond formation is simultaneous or whether there is a lag in bond order. They anticipate that no one mechanism will explain all Diels-Alder reactions.

FLUORINATED COMPOUNDS IN THE DIELS-ALDER REACTION

The role of unsaturated fluorine-containing compounds in the Diels-Alder Reaction has been investigated by a number of workers.

The reaction between any conjugated diene and an olefin can yield a cyclohexene(XXIII) or a vinyl-cyclobutane(XXIV).



XXIII

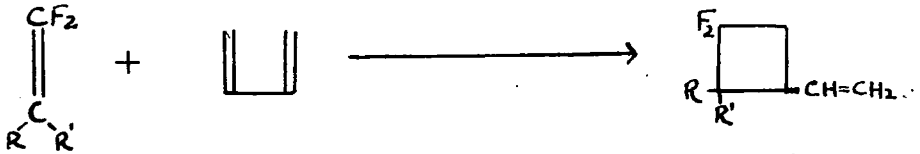
XXIV

The conventional Diels-Alder adduct is a cyclohexene(XXIII) though vinyl-cyclobutanes can be obtained when the dienophile is highly negatively substituted. Stewart and co-workers[28] observed that the reaction of 2-Methyl-penta-2,4-diene with tetracyanoethylene resulted in various mixtures of the two possible adducts, dependent upon the solvent media, and other investigators have obtained Diels-Alder adducts only using alternative dienes[28a,29,30].

Fluorinated dienophiles exhibit the same diversity of reaction.

FLUOROOLEFINS AS DIENOPHILES

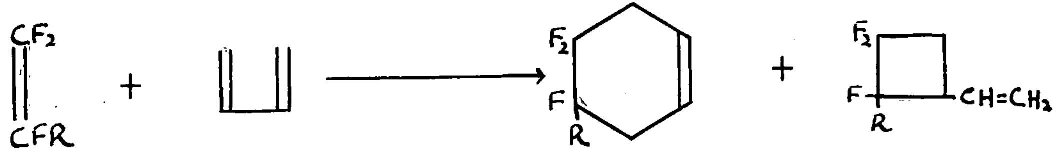
The reactions of fluoroolefins with butadiene have been investigated by Johnson[31]. It was observed that halotrifluoroethylenes(halogen=Cl,Br,I) yielded 2-halo-2,3,3-trifluoro-1-vinyl-cyclobutanes(XXVa,b,c) and 2,2-dichloro-3,3-difluoro-1-vinyl-cyclobutane from 1,1 dichlorodifluoroethylene(XXVa).



XXV

XXV a) R=F;R' =Cl b) R=F;R' =Br c) R=F;R' =I d) R=Cl=R'

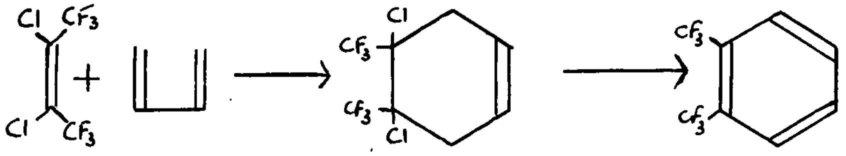
Perfluoropropene, perfluoroacrylonitrile and 4-bromo 1,1,2-trifluoro but-1-ene gave a mixture of the Diels-Alder adduct(XXVI) and vinyl cyclobutane(XXVII).



XXVI XXVII

-R	XXVI	XXVII
$-CF_3$	25	75
-CN	50	50
$-CH_2CH_2Br$	50	50

The reaction with 2,3 dichlorohexafluorobut-2-ene gave the Diels-Alder adduct only (XXVIII) which, on dehydrochlorination, yielded the known σ-bis (trifluoromethyl) benzene XXIX.



XXVIII XXIX

The structures of the adducts have been determined by nuclear magnetic resonance spectroscopy and though no details have been published, it has been indicated by Tarrant and co-workers[32] that a paper will be devoted to this information.

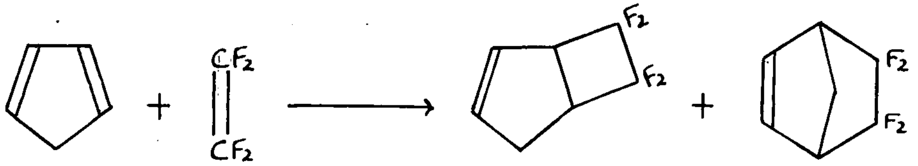
In contrast to Johnson's work, McBee and co-workers[33] report a 64% yield of the Diels-Alder adduct from perfluoropropene and butadiene while the former investigator quotes a 26% yield of both adducts. The discrepancies in reported yields and products cannot be accounted for in terms of different reaction conditions since both are similar (see Table 1). Further, McBee has proved that only the Diels-Alder adduct is formed[34].

McBee and co-workers[33] synthesised a number of Diels-Alder adducts from cyclopentadiene, butadiene, anthracene and a number of fluoroolefins. The reactivity of the olefins was found to decrease in the following order:

$$CF_3CF{=}CF_2 > CF_3CF_2CH{=}CH_2 > CF_3CH{=}CH_2 > CFH_2CH{=}CH_2 > CF_3(CH_3)C{=}CH_2$$

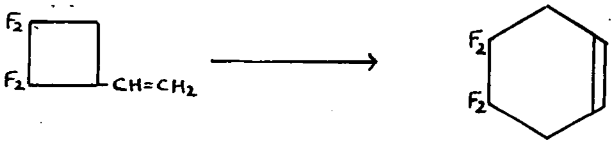
The assignment of structure was based on the infra-red spectra of the adducts and their dibromo derivatives. This proof was not accepted as "compelling evidence" by Roberts and Sharts[35] due to results obtained by Coffmann and Drysdale.

Coffmann and co-workers[36] obtained 6,6,7,7-tetrafluoro-bicyclo(3,2,0)hept-3-ene(XXX) from cyclopentadiene and tetrafluoroethylene at 190°C. Drysdale et al[37], using far more stringent conditions obtained the same adduct together with 5,5,6,6-tetra-fluoro-bicyclo-(2,2,1)-hept-3-ene(XXXI).



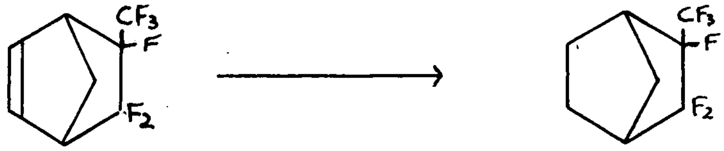
XXX XXXI

Roberts and Sharts postulate that thermodynamic control favours the formation of the Diels-Alder adduct and they quote further work by Drysdale[38], in which a Diels-Alder adduct(XXXIII) was obtained from a vinyl cyclobutane(XXXII), to support their argument.

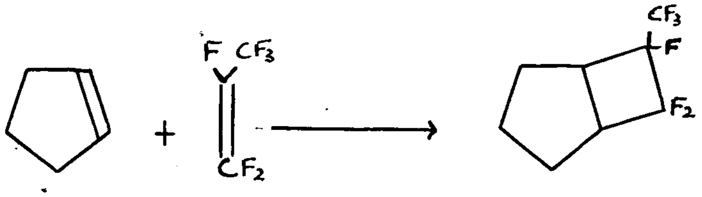


XXXII XXXIII

McBee has proved that the perfluoropropene/cyclopentadiene adduct is as originally postulated. The reduced adduct(XXXIV) did not produce the same compound formed from the addition of perfluoropropene to cyclopentene(XXXV).



XXXIV



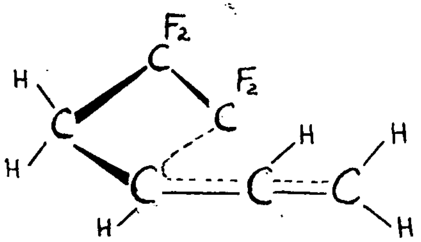
XXXV

Hexafluorocyclobutene, 1,2-dichlorotetrafluorocyclobut-1-ene and 1-ethyl-pentafluorocyclobut-1-ene do not participate in the Diels-Alder reaction[31,39], though 3,3,4,4-tetrafluorocyclobut-1-ene will react normally with butadiene, 2,3-dimethyl-butadiene and cyclopentadiene[40].

The reactivity of trans-4,4,4-trifluorocrotonic acid as a dienophile, has been demonstrated by McBee[41,42]. The carboxyl group in the dienophile is not a strong endo-directing group when reacted with cyclopentadiene but appears to be very strong when furan is the diene.

MECHANISM OF THE COMPETING CYCLOBUTANE REACTION

Butadiene and tetrafluoroethylene codimerise in the presence of polymerisation inhibitors more easily than they will homodimerise. Roberts and Sharts[35] put forward a tentative mechanism for this reaction. It was assumed that if tetrafluoroethylene adds to the trans form of the diene then an intermediate(XXXVI) will be produced.



XXXVI

Since rotation about the 2-3 carbon bond is not possible, a cyclobutane will be formed. The production of a cyclohexene requires the cis form of the diene to react. A similar argument cannot be applied to the reaction between cyclopentadiene and tetrafluoroethylene because the diene is in an enforced cis conformation. The authors stated that both possible adducts should be, and are, produced[37]. They omit to mention that the reaction conditions used by Drysdale were almost sufficient to effect isomerisation to a Diels-Alder adduct and that Coffmann and co-workers[36] obtained only the 1:2 addition product under normal reaction conditions.

It may be possible to interpret these observations in one of two ways.

a) If radical intermediates exist a highly reactive difluoromethylene radical would react at the first available site.

or b) If a concerted mechanism is operative, the most stable intermediate is that with attractive forces spread over the shortest possible distance.

The first interpretation explains the formation of adducts from acyclic dienes if it is assumed that the short life-time of the radical excludes rotation about the 2-3 bond. The cyclopentadiene adduct would be dependent upon the relative position of the $-CF_2$ group relative to C_2 and C_4 of cyclopentadiene.

The addition of perfluoropropene and perfluoroacrylonitrile to conjugated dienes yielding Diels-Alder adducts, must be assumed to proceed via radical intermediates of lower reactivity which allow bond rotation in the diene.

At the time of writing, the author does not feel competent to postulate a detailed mechanism for the following reasons:

a) Kinetic and thermodynamic control of adduct formation must be considered.

b) Activation energies and pre-exponential factors for such reactions are not available and it is not possible to assess whether the two products are found from the same transition state or via independent intermediates.

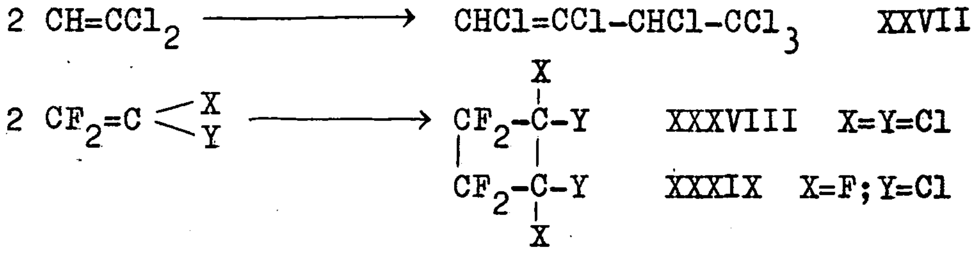
CYCLOALKYLATION REACTIONS OF FLUOROOLEFINS

The formation of polyfluorinated cyclobutanes may be effected by the interaction of a fluoroolefin with:-

a) itself - cyclic dimerisation or a second fluoroolefin, and b) an unsaturated hydrocarbon or vinyl compound-co-cyclisations.

CYCLIC DIMERISATION

Tetrafluoroethylene was the first fluoroolefin to be cyclised at elevated temperatures in the presence of a polymerisation inhibitor[43]. Henne and Ruh[44] demonstrated that two fluorine atoms are required, in an olefin, to produce cyclobutanes by comparing the products from the dimerisations of 1,1,3-trichloroethylene. The non-fluorinated olefin did not produce a cyclobutane as did the remaining two.



$$2\ CH{=}CCl_2 \longrightarrow CHCl{=}CCl{-}CHCl{-}CCl_3$$ XXVII

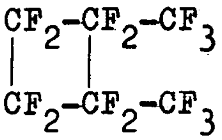
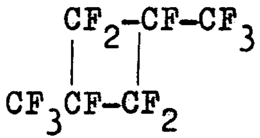
$$2\ CF_2{=}C{<}^{X}_{Y} \longrightarrow \begin{array}{l} CF_2{-}CXY \\ | \quad\quad | \\ CF_2{-}CXY \end{array}$$

XXXVIII X=Y=Cl

XXXIX X=F; Y=Cl

It has been demonstrated that a pre-requisite for reaction is the possession of a difluoromethylene group, in view of the fact that 1,2-dichlorodifluoroethylene will not form a cyclobutane[45].

While the dimerisation of most fluoroolefins is head to head/tail to tail, Hauptschein and co-workers[46] have shown that the dimerisation of perfluoropropene is temperature dependent: higher temperatures favouring the formation of 1,3-bis(trifluoromethyl)-hexafluorocyclobutane.

TEMP.			
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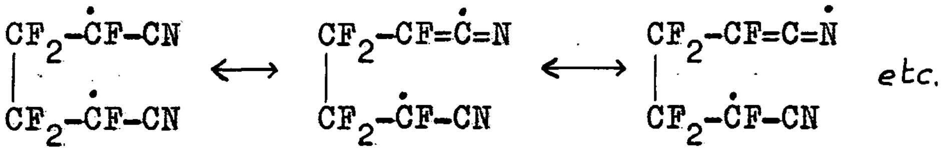
390	15	80	5
450	-	40	60

Perfluoroacrylonitrile has been dimerised to yield 1,2-dicyanohexafluorocyclobutane[31,47]. The specific nature of this reaction has been interpreted by Sharts and Roberts in terms of a highly stabilised radical transition state.



They propose such a mechanism in view of the preponderence of 1:2 adducts and they also propose that cis 1,2 adducts are the major products due to strong attractive force between the substituents in the transition state.

The fluoro-buta-1,3-dienes exhibit a 1:2 mode of addition rather than 1:4[48,49,50] and can be exemplified by the dimerisation of perfluorobutadiene, yielding 1,2-bis-(perfluorovinyl)-hexafluorocyclobutane.

The cyclisation reactions of fluoroolefins have no parallel in the hydrocarbon field, though it has been observed that a small amount of 1,2-divinyl-cyclobutane is produced during the dimerisation of butadiene[51].

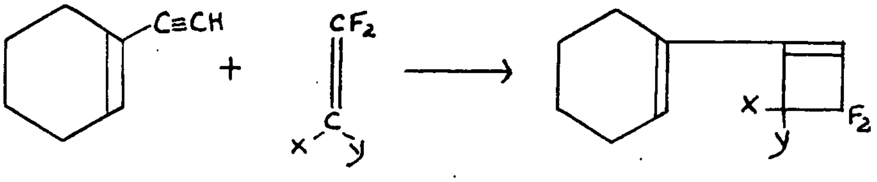
COCYCLISATION REACTIONS OF FLUOROOLEFINS

This type of reaction has been extensively studied and for the purpose of clarity this section will be divided into subsections considering addition of fluoroolefins to:-

i) Olefins and acetylenes,
ii) Simple halogenated olefins,
and iii) Nitrogen and oxygen substituted olefins.

i) Reactions of fluoroolefins with olefins and acetylenes

These reactions are rather difficult to achieve with simple aliphatic alkenes and alkynes, high temperatures and prolonged reaction times being necessary to effect low conversions. Terminal olefins react most readily[36,52] and the introduction of a second unsaturated group facilitates the reaction, e.g. vinyl-acetylene[36,52,53], divinyl-acetylene[54] and styrene[31,36,52,55]. Though the reactivity of ethylenic and acetylenic compounds are similar, the complete unreactivity of the double bond in 1-cyclohexenyl-acetylene is rather anomalous[56,57], producing substituted (1-cyclobutenyl)cyclohex-1-enes. (XL and XLI).



XL X=Y=Cl
XLI X=F; Y=Cl

Cyclisation reactions with styrene result in high yields of phenylcyclobutanes demonstrating the activating influence of the aromatic system and affording an assessment of the reactivity of fluoroolefins towards styrene. Tarrant and co-workers[32] observed that the ease of addition was similar to the ease of dimerisation of the fluoroolefins.

$CF_2{=}CF_2 > CF_2{=}CFCl > CF_2{=}CCl_2 > CF_2{=}CFCN > CF_2{=}CFBr > CF_2{=}CFI \gg CF_2{=}CFCF_3 \sim CF_2{=}CFH$

The very low reactivity of hexafluoropropene and trifluoroethylene cannot be explained in terms of adverse electronic or steric effects. The electron withdrawing power and the size of the $-CF_3$ and $-CN$ groups are rather similar though the reactivities of hexafluoropropene and perfluoroacrylonitrile are quite dissimilar.

The activating influence of the aromatic system is also apparent in phenyl acetylene[58-61].

ii) <u>Reactions of fluoroolefins with halogenated olefins</u>

These reactions have not been intensively studied and no correlations can be made concerning the factors influencing the decrease in reactivity, relative to the parent hydrocarbon.

Two observations can be made:

i) Removal of the halogen atom from the site of unsaturation results in higher yields on reaction with fluoroolefins, e.g. allyl chloride is a better addend to tetrafluoroethylene than vinyl chloride[36,52].

ii) The difference between the reactivities, as indicated by the yields of adducts, of compounds and their α-methyl homologues, is small by comparison with oxygen and nitrogen containing unsaturated compounds and their α-methyl homologues (see iii), e.g. allyl chloride and α-methallyl chloride, on reaction with tetrafluoroethylene, yield approximately the same amounts of the corresponding tetrafluorocyclobutanes.

iii) Reaction of fluoroolefins with Nitrogen and Oxygen containing unsaturated compounds

It is not possible to predict the reactivity of the hydrocarbon addend, but a number of observations may be made.

i) The removal of the activating group from the double bond decreases the reactivity of the hydrocarbon addend, e.g. $CH_2=CHCN \gg CH_2=CHCH_2CN$ under similar reaction conditions.

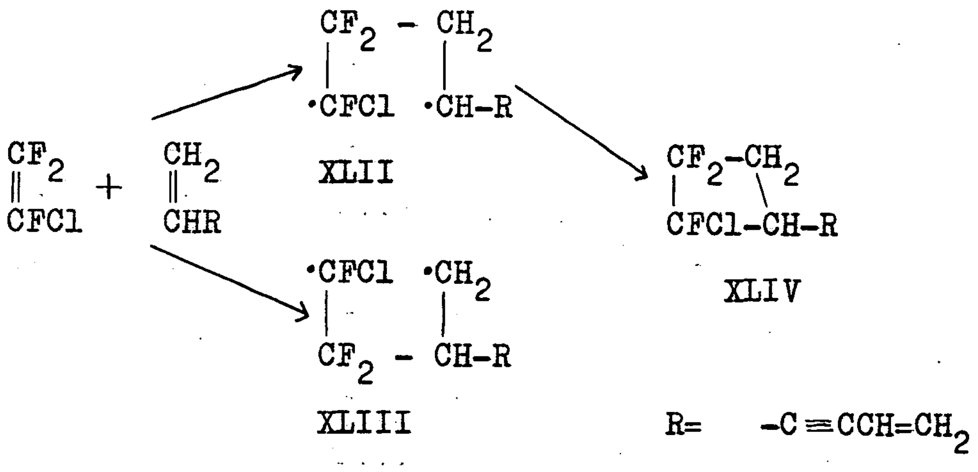
ii) The electronic effects of the substituents do not follow a definite trend related to electron withdrawing or donating power, e.g. $-CN > -CH_2OH \gg -COCH_3 \sim -OCH_3 \sim -CHO$

iii) The effect of an α-methyl group is anomalous in that it increases the reactivity of methacrolein relative to acrolein but decreases that methacrylonitrile relative to the parent compound.

iv) The reactivity of the fluoroolefins decreases in the order tetrafluoroethylene > monochlorotrifluoroethylene > 1,1-dichlorodifluoroethylene when reacted with acrylonitrile. Thus, it may be possible to predict the feasibility of a reaction of a fluoroolefin with an addend known to react with one fluoroolefin capable of forming cyclobutanes.

MECHANISM OF THE CYCLISATION REACTION

The structures of products from such reactions have, in many cases, been explained in terms of the most stable radical intermediates. Roberts and Sharts[35] explain 1:2 addition and the formation of cis adducts in such terms. In the addition of monochlorotrifluoroethylene to divinylacetylene Handy and Benson[54] state that since the intermediate (XLII) is more stable than (XLIII) they predict the structure of the product as (XLIV).



Kinetic studies of the dimerisations of tetrafluoroethylene, monochlorotrifluoroethylene and their co-dimerisation, were carried out by Lacher and co-workers[62]. It was observed that the activation energies were identical, indicating a common mechanism, but the pre-exponential factors were low and of the same order as those observed in Diels-Alder reactions. Thus, geometrical arrangement of the reactants is specific in the transition state.

As has been said of the Diels-Alder reaction more thermodynamic data are required of a wide range of reactions which will serve to elucidate the nature of the intermediates. The parallel between the Diels-Alder reaction and cyclobutane formation is striking in that some products can be explained in terms of free radicals and yet rigid intermediates are required to explain the dominant cis 1:2 addition. It may become apparent during further investigations that no one mechanism will satisfy all cyclisation reactions.

T A B L E 1

Reactions of Fluoroolefins with Conjugated Dienes

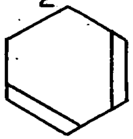
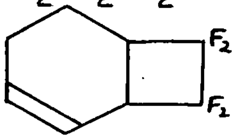
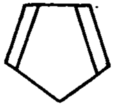
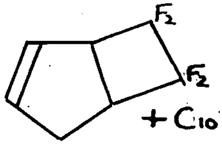
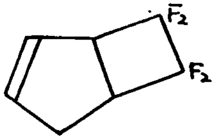
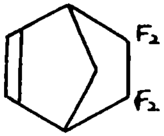
Fluoroolefin	Diene	Structures	Y^1	R^2	T^3	t^4	Refs.
$CF_2=CF_2$	$CH_2=CHCH=CH_2$	$\overline{CF_2CF_2CH_2C}HCH=CH_2$	90	0.43	125	8	36,52,53
	$CH_2=CHCF=CH_2$	$\overline{CF_2CF_2CH_2C}HCF=CH_2$	35	0.56	125	8	36
		$\overline{CF_2CF_2CH_2C}FCH=CH_2$	35				
	$CH_2=CHCCl=CH_2$	$\overline{CF_2CF_2CH_2C}ClCH=CH_2$	51	1.0	100	9.75	36,52,53
		$\overline{CF_2CF_2CH_2C}HCCl=CH_2$	10				
	$CH_2=CHCH=C(Me)$	$\overline{CF_2CF_2CH_2C}HCH=C(Me)$	68	1.0	100	9	36,52
	$CH_2=CHC(Me)=CH_2$	$\overline{CF_2CF_2CH_2C}(Me)CH=CH_2$	83	1.0	100	8	36,52,53
			50	2.0	100	8	36
		 + $C_{10}H_{12}\cdot C_2F_4$	23 9	2.0	190	8	36
		 	47 23	2.0	475	Flow	37

TABLE 1 (cont.)

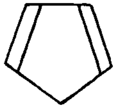
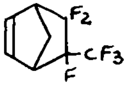
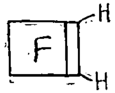
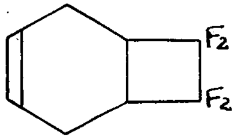
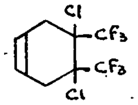
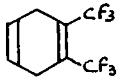
Fluoroolefin	Diene	Structures	Y[1]	R[2]	T[3]	t[4]	Refs.
$CF_2{=}CFCl$	$CH_2{=}CHCH{=}CH_2$	$CFClCF_2CH_2CHCH{=}CH_2$	92	0.8	100	20	31,39
$CF_2{=}CFBr$	$CH_2{=}CHCH{=}CH_2$	$CFBrCF_2CH_2CHCH{=}CH_2$	61	0.9	140	20	31
$CF_2{=}CFI$	$CH_2{=}CHCH{=}CH_2$	$CFICF_2CH_2CHCH{=}CH_2$	56	0.65	125	16	31
$CF_2{=}CCl_2$	$CH_2{=}CHCH{=}CH_2$	$CCl_2CF_2CH_2CHCH{=}CH_2$	76	0.88	125	16	31
	$CH_2{=}C(Me)C(Me){=}CH_2$	$CCl_2CF_2CH_2C(Me)C(Me){=}CH_2$	68	1.0	105	5.5	63
$CF_2{=}(CF_3)CF$	$CH_2{=}CHCH{=}CH_2$	$CF_3CFCF_2CH_2CHCH{=}CH_2$	20	0.8	175	16	31
		$CF_3CFCF_2CH_2CH{=}CHCH_2$	6				
		$CF_3CFCF_2CH_2CH{=}CHCH_2$	64	1.1	180	24	33
			69	1.0	135	60	33
$CF_2{=}(CN)CF$	$CH_2{=}CHCH{=}CH_2$	$CNCFCF_2CH_2CHCH{=}CH_2$	19	0.71	150	15	31
		$CNCFCF_2CH_2CH{=}CHCH_2$	19				
		Cyclobutane presumed	88	0.75	45	8	47
$CF_2{=}(BrCH_2CH_2)CF$		$BrCH_2CH_2CFCF_2CH_2CHCH{=}CH_2$	18	0.91	160	19	31
		$BrCH_2CH_2CFCF_2CH_2CH{=}CHCH_2$	18				

TABLE 1 (cont.)

Fluoroolefin	Diene	Structures	Y^1	R^2	T^3	t^4	Refs.
	$CH_2=CHCH=CH_2$		75	1.8	140	40	40
$CF_3CCl=CClCF_3$	$CH_2=CHCH=CH_2$		22	0.84	150	24	31
$CF_3C\equiv CCF_3$	$CH_2=CHCH=CH_2$		96	0.62	28	48	64

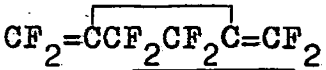
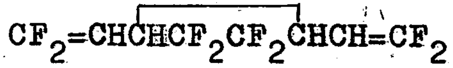
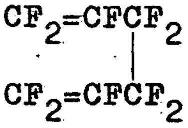
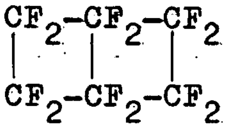
1. Yield - based on reactant in lowest molar concentration
2. Ratio - of fluoroolefin to diene
3. Temp. - °C.
4. Time - hours

T A B L E 2

Cyclic Dimerisation of Fluoroolefins

Fluoroolefin	Adduct Structure	Y^1	T^2	t^3	Refs.
$CF_2{=}CF_2$	$CF_2CF_2CF_2CF_2$	–	200	–	43
$CF_2{=}CFBr$	$BrCFCF_2CF_2CFBr$	72	200	5	39
$CF_2{=}CFCl$	$ClCFCF_2CF_2CFCl$	64	200	11	43,65
		85	200	12	44,66
$CF_2{=}CFH$	$HCFCF_2CF_2CFH$ $HCFCF_2CFHCF_2$		260	23	67
$CF_2{=}CFCF_3$	$CF_3CFCF_2CF_2CFCF_3$ $CF_3CFCF_2CF(CF_3)CF_2$ (C&T)	100	a	a	46
$CF_2{=}CFCN$	$CNCFCF_2CF_2CFCN$	100	230	72	47
		64	225	8	31
$CF_2{=}CF\text{Ø}$	$\text{Ø}CFCF_2CF_2CF\text{Ø}$	15			68
$CF_2{=}CFOMe$	$MeOCFCF_2CF_2CFOMe$	83	150	12	69
$CF_2{=}CBr_2$	$Br_2CCF_2CF_2CBr_2$	25	195	24	39
$CF_2{=}CCl_2$	$Cl_2CCF_2CF_2CCl_2$	90	200	5–6	45
		85	200	12	44

T A B L E 2 (cont.)

Fluoroolefin	Adduct Structure	Y[1]	T[2]	t[3]	Refs.
$CF_2=C=CF_2$	 $CF_2=CCF_2CF_2C=CF_2$	83	40	20	70
$CF_2=CFCF=CF_2$	 $CF_2=CFCFCF_2CF_2CFCF=CF_2$	-	150	44	48,49
	 $CF_2CFCFCF_2CF_2CFCFCF_2$	60	500	Flow	48,49
$CF_2=CHCH=CF_2$	 $CF_2=CHCHCF_2CF_2CHCH=CF_2$	59	175	16	50
 $CF_2=CFCF_2$ $CF_2=CFCF_2$	 $CF_2-CF_2-CF_2$ $CF_2-CF_2-CF_2$	70	450	Flow	71

1. Yield - based on reactant in lowest molar concentration

2. Temp. - °C.

3. Time - hours

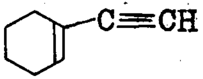
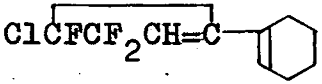
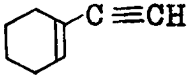
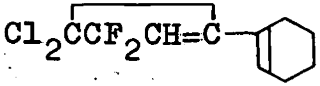
a - see text

TABLE 3

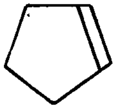
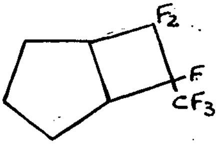
Reactions of Fluoroolefins with Olefins and Acetylenes

Fluoro-olefin	Addend	Structure	Y[1]	R[2]	T[3]	t[4]	Refs.
$CF_2=CF_2$	$CH_2=CH_2$	$CF_2CF_2CH_2CH_2$	40	0.13	200	7.5	36,52
	$CH_2=CHCH_3$	$CF_2CF_2CH_2CHCH_3$	72	0.17	225	9	31,36,52
	$CH_3CH=CHCH_2$	$CF_2CF_2CH(CH_3)CHCH_3$	5	0.22	175	7.75	36,52
	$CH_2=C(CH_3)_2$	$CF_2CF_2CH_2C(CH_3)_2$	30	0.22	225	8.25	31,36,52
	$CH_2=C=CH_2$	$CF_2CF_2CH_2C=CH_2$	17	1.00	150	14	31,36,53
	$CH_2=CH\emptyset$	$CF_2CF_2CH_2CH\emptyset$	85	0.42	175	13	36,52
	$CH_2=CHC\equiv CH$	$CF_2CF_2CH_2CHC\equiv CH$	35				36
		$CF_2CF_2CH=CCH=CH_2$	35	1.04	100	16	52
		$CF_2CF_2CH_2CHC=CHCF_2CF_2$	3.5				53
		$CF_2CF_2CH_2CH\emptyset$	3.5				
	$CH_2=CHC$ $\equiv$ $CH_2=CHC$	$CF_2CF_2CH_2CHC\equiv CCH=CH_2$	40	1.00	135	4	54
		$CF_2CF_2CH_2CHC\equiv CCHCH_2CF_2CF_2$	73	4.00	125	11	54
	$CH\equiv CH$	$CF_2CF_2CH=CH$	35	1.04	225	12	72
$CFCl=CF_2$	$CH_2=CH_2$	$ClCFCF_2CH_2CH_2$	19.5	13.1	200	9	39
	$CH_2=CHCH_3$	$ClCFCF_2CH_2CHCH_3$	35	1.28	275	18	31

TABLE 3 (cont.)

Fluoro-olefin	Addend	Structure	Y^1	R^2	T^3	t^4	Refs.
$CFCl=CF_2$	$CH_2=C(CH_3)_2$	$ClCFCF_2CH_2C(CH_3)_2$	20	1.12	310	3	31
	$CH_2=C=CH_2$	$ClCFCF_2CH_2C=CH_2$	26	0.82		12	31
	$CH_2=CH\emptyset$	$ClCFCF_2CH_2CH\emptyset$	71	1.14	120	23	31,55
	$CH_2=CHC$ $\equiv$ $CH_2=CH-C$	$ClCFCF_2CH_2CHC\equiv CCHCH_2CF_2CFCl$	67	3.00	150	6.5	54
	 C≡CH	 $ClCFCF_2CH=C-$	80	1.01	95	24	56,57
	$CH\equiv C\emptyset$	$ClCFCF_2CH=C-\emptyset$	70	1.01	120	24	58,59
$CF_2=CFBr$	$CH_2=CH\emptyset$	$BrCFCF_2CH_2CH\emptyset$	43	1.00	125	16	31
$CF_2=CFI$	$CH_2=CH\emptyset$	$ICFCF_2CH_2CH\emptyset$	33	0.5	125	16	31
$CF_2=CCl_2$	$CH_2=CHCH_3$	$Cl_2CCF_2CH_2CHCH_3$	17	1.04	255	16	31
	$CH_2=CH\emptyset$	$Cl_2CCF_2CH_2CH\emptyset$	58	1.01	130	3	55
	$CH_2=C(CH_3)C$ $\equiv$ CH_3C	$Cl_2CCF_2CH_2C(CH_3)C\equiv CCH_3$	63	0.92	140	70	60
	 C≡CH	 $Cl_2CCF_2CH=C-$	91	1.34	95	20	57

T A B L E 3 (cont.)

Fluoro-olefin	Addend	Structure	Y[1]	R[2]	T[3]	t[4]	Refs.
$CF_2=CCl_2$	$CH\equiv C\phi$	$Cl_2CCF_2CH=C\phi$	71	1.00	130	2	61
			58	0.88	95	48	60
$CF_2=CFCF_3$			68	1.00	30	12	34
	$CH_2=CH\phi$	$CF_3CFCF_2CH_2CH\phi$	?	0.613	125	14	31
$CF_2=CNCF$	$CH_2=CH\phi$	$CNCFCF_2CH_2CH\phi$	57	0.41	100	14	31

1. Yield - based on reactant in lowest molar concentration
2. Ratio - of fluoroolefin to diene
3. Temp. - °C.
4. Time - hours

TABLE 4

Reactions of Fluoroolefins with Simple Halogenated Olefins

Fluoroolefin	Addend	Structures	Y[1]	R[2]	T[3]	t[4]	Refs.
$CF_2=CF_2$	$CH_2=CHCl$	$\overline{CF_2CF_2CH_2C}HCl$	23	0.24	150	8	36,52
	$CH_2=CHBr$	$\overline{CF_2CF_2CH_2C}HBr$	12	1.44	200	8	39
	$CH_2=CCl_2$	$\overline{CF_2CF_2CH_2C}Cl_2$	46	0.39	150	8-12	36,52
	$CHCl=CCl_2$	$\overline{CF_2CF_2CHClC}Cl_2$	18	0.79	225	8	36
	$CH_2=CHCH_2Cl$	$\overline{CF_2CF_2CH_2C}HCH_2Cl$	42	0.3	150	8-9.5	36,52
	$CH_2=C(Me)CH_2Cl$	$\overline{CF_2CF_2CH_2C}(Me)CH_2Cl$	45	0.34	150	8 6.3	36,52
	$CF_2=CFCl$	$\overline{CF_2CF_2CF_2C}FCl$	46	0.84	150	13	73
$CF_2=(Cl)CF$	$CH_2=CHCH_2Cl$	$Cl\overline{CFCF_2CH_2C}HCH_2Cl$	7.8	1.2	240	2	31,39
	$CF_2=CCl_2$	$Cl\overline{CFCF_2CF_2C}Cl_2$	32	1.13	200	18.5	74,75
$CF_2=CCl_2$	$CH_2=CHCCl_3$	$\overline{CCl_2CF_2CH_2C}HCCl_3$	18	1.03	133	19	63

1. Yield – based on reactant in lowest molar concentration
2. Ratio – of fluoroolefin to diene
3. Temp. – °C.
4. Time – hours

TABLE 5

Reactions of Fluoroolefins with Nitrogen & Oxygen Substituted Olefins

Fluoro-olefin	Addend	Structures	Y[1]	R[2]	T[3]	t[4]	Refs.
$CF_2=CF_2$	$CH_2=CHOCH_3$	$\overline{CF_2CF_2CH_2C}HOCH_3$	13	0.23	150	8	36,52
	$CH_2=CHCH_2OH$	$\overline{CF_2CF_2CH_2C}HCH_2OH$	45	0.23	150	8	36
	$CH_2=CHCHO$	$\overline{CF_2CF_2CH_2C}HCHO$	12	0.22	150	8	36,52
	$CH_2=C(Me)CHO$	$\overline{CF_2CF_2CH_2C}(Me)CHO$	50	0.28	150	8	36,52
	$CH_2=CHCOCH_3$	$\overline{CF_2CF_2CH_2C}HCOCH_3$	18	0.28	150	8	36,52
	$CH_2=CHOCOCH_3$	$\overline{CF_2CF_2CH_2C}HOCOCH_3$	27	0.28	150	8	36,52
	$CH_2=CHCN$	$\overline{CF_2CF_2CH_2C}HCN$	84	0.34	150	8	31,36,52,76,77
	$CH_2=C(Cl)COOCH_3$	$\overline{CF_2CF_2CH_2C}ClCOOCH_3$	21	0.9	150	8	36
	$CH_2=CHCH_2CN$	$\overline{CF_2CF_2CH_2C}HCH_2CN$	15	0.27	150	8	36,52,77
	$CH_2C(Me)COOCH_3$	$\overline{CF_2CF_2CH_2C}(Me)COOCH_3$	84	0.8	150	8	36,52
	$CH_2=C(Me)CN$	$\overline{CF_2CF_2CH_2C}(Me)CN$			125	17	77
	$CF_2=CFOMe$	$\overline{CF_2CF_2CF_2C}FOMe$	65		175		78
$CF_2=(Cl)CF$	$CH_2=CHCOOCH_3$	$Cl\overline{CFCF_2CH_2C}HCOOCH_3$	47	1.2	140	18	31,79

T A B L E 5 (cont.)

Fluoro-olefin	Addend	Structures	Y[1]	R[2]	T[3]	t[4]	Refs.
$CF_2=(Cl)CF$	$CH_2=CHCN$	$ClCFCF_2CH_2CHCN$	65	1.17	155	18	31,80
	$CH_2=C(Me)CN$	$ClCFCF_2CH_2C(Me)CN$	31	0.67	140	16	31
	$HC \equiv CCOOET$	$ClCFCF_2CHCCOOET$	29	1	180	24	79
$CF_2=CCl_2$	$CH_2=CHCOOCH_3$	$Cl_2CCF_2CH_2CHCOOCH_3$	48	1.01	176	29	63
	$CH_2=CHCN$	$Cl_2CCF_2CH_2CHCN$	49	0.98	136	20	63
	$CH_2=C(Me)COOMe$	$Cl_2CCF_2GH_2CHCOOMe$	74	0.7	136	20.4	63

1. Yield – based on reactant in lowest molar concentration
2. Ratio – of fluoroolefin to diene
3. Temp. – °C.
4. Time – hours

CHAPTER 2

EXPERIMENTAL WORK

EXPERIMENTAL WORK

Cyclisation reactions were carried out in sealed carius tubes which were charged by vacuum transfer of volatile reagents, while solids, high boiling liquids and the polymerisation inhibitor (dipentene fraction) were weighed directly into the tubes which were cooled and evacuated. Oxygen was excluded from these systems by allowing the frozen material to melt, under vacuum, refreezing and removing entrained gases by further evacuation. The sealed tubes were heated in an oil bath, the temperature variation of which was less than ±1°C. of that quoted.

Purification of adducts was effected by vacuum distillation of the crude reaction mixture followed by distillation at atmospheric pressure, recrystallisation or large scale vapour phase chromatography.

Fluorine analyses were carried out according to the method of Johncock, Musgrave and Wiper[81].

INFRARED SPECTROSCOPY

Spectra were obtained from a Grubb-Parsons G.S. 2A and Grubb Parsons Spectromaster M2E1 infrared spectrophotometers, either as liquid contact films between KBr or as ground dispersions in KBr discs.

ULTRA-VIOLET SPECTROSCOPY

Spectra were recorded, using an Optika CF4 Ultra-Violet Spectrophotometer, of dilute solutions (10^{-4}-10^{-5}M) in Spectrosol methanol or cyclohexane. Wavelengths are given in A and extinction coefficients as (Ex10^{-3}).

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Spectra were recorded by means of an A.E.I., R.S.2 spectrometer, operating at 60 Mc/s. Samples were in the form of pure liquids or saturated solutions in a suitable solvent together with internal references ($CFCl_3$ and/or $(CH_3)_4Si$). Fluorine chemical shifts are calculated relative to trifluoroacetic acid, i.e. = (Shift from $CFCl_3$-4715)c/s. Most spectra were recorded at room temperature.

VAPOUR PHASE CHROMATOGRAPHY (V.P.C.)

i) Analytical Scale

Chromatograms were obtained using a Perkin-Elmer Fractometer Model 451. The stationary phases used were di-iso-decyl phthalate and silicone grease (20% w/w) on an inert support. Hydrogen was used as carrier gas flowing through a hot wire thermal conductivity detector.

ii) Large (Preparative) Scale

The apparatus employed was the same as that described by Kisby[82].

HYDROGENATIONS

Hydrogenations were carried out at atmospheric pressure + 1-2 cms Hg in a Towers HR 140 Hydrogenation apparatus. The catalyst, palladized charcoal, was prepared by the method of Linstead, Elvidge and Whalley.[83] Reactions are quoted as quantitative if the volume of Hydrogen absorbed was 98-102% of the theoretical amount as calculated by the following formula.

$$\text{Absorbtion } (\%) = \frac{V}{22.414} \times \frac{273}{T'} \times \frac{(P' - p)}{760} \times \frac{M}{W}$$

where V = Volume of hydrogen absorbed (L).

P' = Atmospheric Pressure (mmHg).

p = S.V.P. of water at room temperature (mmHg).

M = Molecular weight of compound.

T' = Room Temperature (^{o}K).

W = Weight of compound hydrogenated.

Reaction of Octafluorocyclohexa-1,3-diene with:

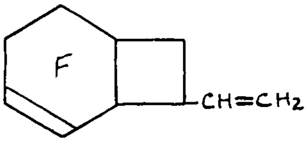
A) Buta-1,3-diene

a) Preparation

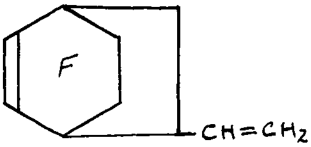
Octafluorocyclohexa-1,3,diene (22:4g, 0.1 mole), butadiene (5.4g, 0.1 mole) and dipentene (0.1 ml) were sealed in an evacuated Carius Tube and heated at 100^{o} for 8 hours. The volatile material (0.5g) was removed, under a vacuum at room temperature and the high boiling material (25g,90%) by vacuum distillation at 65^{o}C.

After distillation a polymeric material (2.0g) remained in the flask. Analytical scale vapour phase chromatography (di-n-decyl phthalate, 160°) indicated that the high boiling material contained five components I (18%); II (41%); IIa (3%); III (34%); IIIa (4%) (Percentages in the high boiling material were estimated by measuring areas of peaks, assuming equi-molar response).

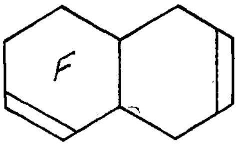
Compound I has been characterised as 1,2,2,3,3,4,5,6-Octafluoro-7(8)-vinylbicyclo-(4.2.0)-oct-4-ene. (Found: F,54.1; C,43.3; $C_{10}F_8H_6$ requires F,54.6; C.43.2). b.p. 158°/751mm; N_D^{20} 1.3770. Infrared spectrum 1.



Compound II has been characterised as 1,2,3,4,5,5,6,6-Octafluorobicyclo-(2.2.2.)-oct-2-ene. (Found: F,54.4; C,43.1. $C_{10}F_8H_6$ requires F,54.6; C,43.2.) b.p. 159°/751mm; N_D^{20} 1,3789. Infrared spectrum 2.



Compound III has been characterised as 1,2,3,3,4,4,9,10-Octfluorobicyclo-(4.4.0)-deca-1,6-diene. (Found: F,54.3; C,43.4. $C_{10}F_8H_6$ requires F,54.6; C,43.2). b.p 184/762 mm n_D^{20} 1.3961. Infrared spectrum 3.



b) Separation of I, II and III.

Distillation of the mixture of adducts (50g.), through a concentric tube (17-20 plates) column at atmospheric pressure (758 mm), yielded three main fractions.

Fraction 1 (b.p.160-164°)(37.5g) contained a mixture of I and II which was separated into the two components by preparative scale V.P.C. (tricresyl phosphate at 100°C; N_2 flow rate 12L/hr). Though the two components gave only one peak on analytical V.P.C. (di-n-decyl phthalate at 160°C) they were found to be contaminated by decomposition products from the stationary phase. The impure components were further purified by preparative scale V.P.C. (silicone elastomer at 135°; N_2 flow rate 8L/hr.).

Fraction 2 (b.p.164-181°)(1.5gm) contained four components (I, II, IIa, III).

Fraction 3(b.p. 181-184°)(9gm) gave only on peak on di-n-decyl phthalate and was of identical retention time to component III.

c) Reduction of I with one mole of hydrogen.

A solution of I (4.12g. 0.0148 mole) in aqueous ethanole (95% $^v/_v$, 40ml) containing a palladium on carboncatalyst (0.077g, 1.8%) was shaken in an atmosphere of hydrogen. The absorption of hydrogen (394ml) was quantitative for one double bond. The solution was filtered through a pad of Kreselguhr and water (150ml) was added to the filtrate. The resulting emulsion was extracted with ether (3x30ml), and the ethereal solution was washed with water (2x50ml). The ethereal solution was dried, by standing over anhydrous magnesium sulphate, and distilled yielding 7(8)-Ethyl-1,2,2,3,3,4,5,6-octafluorobicyclo-(4.2.0)-oct-4-ene (IV) (3.5g, 85%). b.p. 164-6°/753mm.
Infra Red Spectrum 4.

d) Attempted oxidation of IV.

Compound IV (1.3g,0.0046 mole) was added to a solution of potassium permanganate (1.0g, 0.0064 mole) in dry acetone 50 ml), and shaken at room temperature for half an hour. The brown suspension was acidified with dilute sulphuric acid (10ml) and diluted with water (50ml). The acetone was evaporated under reduced pressure and the aqueous solution was decolourised by passing a brisk stream of sulphur dioxide through it. The resulting solution was continuously extracted with ether for 24 hours.

The ethereal solution was dried by standing over anhydrous magnesium sulphate. The ether was evaporated under vacuum yielding a dark brown semi-solid (0.4g). Attempts to purify this material and obtain consistent molecular weights were unsuccessful.

e) Reduction of II.

i) with one mole of hydrogen.

A solution of II (5.00g, 0.018 mole) in aqueous ethanol (95% $^{v}/_{v}$, 30ml) containing a palladium on carbon catalyst (0.0866g, 1.7%) was shaken in an atmosphere of hydrogen. The absorption of hydrogen (450ml) was found to be quantitative for one double bond. The purification of the product was identical to that described under section (C). The distillate contained 7-Ethyl-1,2,2,3,3,4,5,6,-octafluorobicyclo-(2.2.2)-oct-5-ene. (V). (4.6g. 92%). b.p. 166-9°/769mm. Infra-red spectrum 5.

ii) with two moles of hydrogen.

A solution of II (2.06g. 0.0074 mole) in aqueous ethanol (95% $^{v}/_{v}$ 20ml) containing a palladised carbon catalyst (0.6g. 29%) was shaken in an atmosphere of hydrogen. The uptake of hydrogen (350ml) was found to be quantitative for the saturation of two double bonds. The solution was filtered through a pad of kieselguhr and water (100ml) was added to the filtrate. The precipitated solid was filtered and dried under reduced pressure at room temperature.

Recrystallisation from 40-60° petroleum ether yielded 7-Ethyl-1,2,2,3,3,4,5,6-octafluorobicyclo-(2.2.2)-octane (VI) (1.6g 78%). m.p. 60-60.5°. Infrared spectrum 6.

f) Oxidation of V

Compound V (6.96g. 0.0249mole) was added to a solution of potassium permanganate (4.0g. 0.0258 mole) in dry acetone (450ml) and shaken at room temperature for half an hour. To the brown suspension, water (450 ml) was added and dilute sulphuric acid (40 ml). The acetone was evaporated under reduced pressure and the aqueous suspension was decolourised with sulpur dioxide. The colourless solution was continuously ether extracted for 24 hours.

The ethereal solution was dried by standing over anhydrous magnesium sulphate and after filtration, the solution was distilled yielding 1,4-Dicarboxy-5-ethyl-1,2,2,3,3,4-hexafluoro cyclohexane VII (4.2g,54%). M. (by titration with standard NaOH) 310 ($C_{10}F_6H_{10}O_4$ requires 308) Attempts to prepare dianilimium and S-benzylthiouronium salts, as described by Burdon and Tatlow[84] were unsuccessful, due to decomposition of the initial precipitate.

g) Reduction of III

A solution of III (4.82g. 0.0174 mole) in aqueous ethanol (95% $^{v}/_{v}$, 20 ml) containing a palladium on carbon catalyst (0·38g. 7.9%) was shaken in an atmosphere of hydrogen.

The uptake of hydrogen (410 ml) was found to be quantitative for one double bond. The solution was filtered through a pad of kieselguhr and water (100 ml) was added to the filtrate. The resulting emulsion was extracted with ether (3x20 ml) and the ethereal solution was washed with water (3x20 ml). The resulting solution was dried by standing over anhydrous magnesium sulphate and, after filtration, was distilled yielding 1,2,3,3,4,4,9,10-Octafluorobicyclo-(4.4.0)-dec-1-ene). VIII (3.25g. 67%) b.p. 193-195/769mm. Infrared spectrum 7.

h) Oxidation of VIII

Compound VIII (1.001g. 0.0036 mole) was added to a solution of potassium permanganate (0.6g. 0.0039 mole) in dry acetone (50 ml). The solution was warmed to 40°C for one hour, diluted with water (50 ml) and the acetone was removed under reduced pressure. The brown suspension was acidified with dilute sulphuric acid (5 ml) and decolourised by sulphur dioxide. The colourless solution was continuously extracted with ether for 24 hours.

The ethereal solution was dried by standing over anhydrous magnesium sulphate and, after filtration, the ether was evapourated under reduced pressure yielding β-(2-Carboxy-1,2-difluoro-cyclohex-1-yl)-perfluoroprionic acid IX (15g. 45%) M. 302 (by titration with standardised NaOH) $C_{10}F_{6}H_{10}04$ requires 308.

i) Determination of Vinyl groups.[85]

About 12 drops of the material to be tested were added to the solvent (5 ml 1:1 $^v/_v$ ethyl acetate: glacial acetic acid). A stream of ozonised oxygen (5-7% ozone) was passed through the cooled solution for 15 minutes. A portion of the ozonised solution (2 ml) was added to a modified Schiffs Reagent (90 ml) (Reagent:- Schiff's Reagent 300 ml, concentrated hydrochloric acid 150 ml, water 450 ml).

The development of a magenta colouration indicated the presence of formaldehyde and hence the presence of a vinyl group in the compound under investigation.

j) Defluorinations.

i) with iron powder

The original defluorinations of compounds I, II, III and V were carried out in the improved apparatus described by Heyes.[86] All reactions yielded three compounds from which could be isolated tetrafluoronaphthalene. X.

Typical Run:- Compound V (13g. 0.047 mole) was passed through the defluorinator (310°C), over a period of half an hour, in a stream of nitrogen (70cc/min). The resulting solid was sublimed from carbonaceous material and recrystallised from hexane yielding a mixture of aromatic compounds, as shown by A.S.V.P.C. (Silicone grease, 160°, 80ccH_2/min) (5.9gm, 62%) m.p. 105-107°.

Pure tetrafluoronaphthalene X. was obtained by repeated recrystallisation from ether and hexane. (Found: F, 37.6; C, 60.2. $C_{10}F_4H_4$ requires F, 37.9; C, 60.0) m.p. 109-110 Lit. 110-111[87]. Infrared spectrum 8. Lit. 1515, 1610, 1665. λmax ($\varepsilon x10^{-3}$). 2,585 (6,68); 2691 (9.45) 2767 (10.04); 2855 (7.55); 3038 (1.31); 3076 (.87); 3123 (.86) 3177 (1.1). Lit.[87] 2670 (2.3) 2750 (2.4) 3020 (2.96) 3170 (2.58).

ii) with steel wool

The defluorination consisted of a pyrex tube (27mm o.d. x 93 cm) packed with degreased steel wool. A concentric stainless steel tube (32mm i.d. x 88 cm), warmed with nichrome wire enabled temperatures up to 520°C to be attained. Samples were introduced and collected as described by Heyes.

Typical Run:- The adduct mixture (4.82 g. 0.0174 mole) was added to the vapouriser (220°) over a period of 45 minutes, and passed through the defluorinator (425°) in a stream of nitrogen (100cc/min). After 90 mins the solid material which had collected in the cold trap was dissolved in benzene and the solution was washed with water. The benzene solution was dried by standing over anhydrous magnesium sulphate, filtered and the solvent evaporated under reduced pressure. The resulting solid was sublimed and recrystallised from hexane yielding tetrafluoronaphthalene X. (2.56g. 73%) m.p. 109-110°.

k) Reaction of tetrafluoronaphthalene with sodium methoxide

Tetrafluoronaphthalene (2.0g. 0.01 mole) was added to a solution of sodium (.25g 0.011 mole) in dry methanol (8 ml). The solution was gently refluxed for three hours. To the cold solution, water (40 ml) was added and the precipitated solid was filtered and recrystallised from aqueous alcohol and dried under vacuum yielding 1,2,3-Trifluoro-4-methoxynaphthalene XI (1.65g 80%).

(Found: C,62.44;H,3.4; $C_{10}F_3H_7O$ requires: C,62.4;H,3.3:) m.p. 34.5-35.5° Infrared spectrum 9. λmax (ε x10^{-3}). 2624 (2.46); 2713 (3.94); 2794 (4.24); 2892 (3.22).

l) Nitration of tetrafluoronaphthalene

Tetrafluoronaphthalene (2.14g 0.01 mole) was added slowly to a stirred mixture of concentrated sulphuric and nitric acids (5 ml 50% $^{v}/_{v}$) at 0°. The temperature was then raised to 70-75° for 1 hour. To the cool reaction mixture water (15 ml) was added slowly. The precipitate was filtered then stirred with water while molten. On cooling the solid was dried sublimed and recrystallised from bezene/hexane yielding 1,2,3,4-Tetrafluoro-5-nitro naphthalene XII (1,4g 53%) (Found: F,30.9; C,38.7. $C_{10}F_4H_3NO_2$ requires: F,31.0; C,39.0) m.p. 84-84.5°. Infrared spectrum 10. λmax (εx10^{-3}) 2170 (4.16); 2370 (1.07) 2848 (.41).

m) Oxidation of tetrafluoronaphthalene

i) by potassium permanganate acetone

Tetrafluoronaphthalene (1g, 0.005 mole) was added to a solution of potassium permanganate (1.75g, 0.011 mole) in dry acetone (200 ml). There was no reaction until the solution had been refluxed for 2½ hours. The work-up of the product was carried out as in sections d,f and l.

The solid product (.8g) was sublimed under a 'sticking' vacuum at 160° yielding phthalic anhydride, m.p. 127-129°, identified by comparison with an infrared spectrum of an authentic sample and by mixed melting point. 129-131°

νmax 1870,$^{(vs)}$ 1765,$^{(vs)}$ 1599,$^{(m)}$ 1470,$^{(s)}$ 1350,$^{(s)}$ 1250.$^{(vs)}$

ii) by chromium trioxide in acetic acid[88]

A solution of chromium trioxide (10g, 0.1 mole) in acetic acid (50% $^{v}/_{v}$ 14 ml) was added to a solution of tetrafluoronaphthalene (2g, 0.01 mole) in glacial acetic acid (15 ml) at such a rate as to maintain the temperature at 60°C.

The orange solution was heated on a water bath at 85° for 2 hours. The cool solution was continuously ether extracted for 12 hours and the ethereal solution was dried by standing over anhydrous magnesium sulphate. Ether+acetic acid were evaporated under vacuum and the remaining solid (.17g) was sublimed under a 'sticking' vacuum at 170° yielding phthalic anhydride, m.p. 127-128° identified by comparison with an infrared spectrum of an authentic sample and by mixed melting point. 129-131°.

iii) by vanadium pentoxide[89]

The apparatus consisted of a small diameter glass tube (10 ml volume) containing the catalyst of vanadium pentoxide on silica gel (16-30 mesh). Air, metered by means of a rotameter flowmeter, and tetrafluoronaphthalene were passed upwards through the catalyst bed and the products were collected in a cold trap (-82°). The whole unit was heated in a 3" diameter oven packed with asbestos wool, the temperature being determined by means of a chrome/Alumel thermocouple.

Typical Run:- Tetrafluoronaphthalene (1.0g, 0.005 mole) was slowly sublimed at 95° in a stream of air (500 ml/min) and passed through the catalyst bed (5ml) which was heated to 450°. The cold trap was allowed to warm to room temperature (hydrogen fluoride was evolved) and the solid material was sublimed yielding phthalic anhydride (0.42g. 67%) m. 129-131°, and mixed melting point with an authentic sample 129.5-131°.

B) Methyl Vinyl Ketone

a) Preparation

Octafluorocyclohexa-1,3-diene (15.5g. 0.069 mole), methyl vinyl ketone (3.1g, 0.044 mole) and dipentene (0.1 ml) were heated in an evacuated Carius Tube at 114° for 2½ hours.

The crude reaction mixture was distilled under vacuum. The distillate was pumped dry and the colourless solid was sublimed under a sticking vacuum at 45° yielding impure 1,2,3,4,5,5,6,6-Octafluorobicyclo-(2.2.2)-oct-2-en-8-yl methyl ketone XIII (11g. 85%). Recrystallisation from heptane gave pure ketone (9.5g. 73%) (Found: F,51.1; C,40.9. $C_{10}F_8H_6O$ requires: F,51.7; C,40.8) m.p. 52.52° Infrared spectrum 11.

Derivatives a) 2:4-dinitrophenylhydrazone. (Found: F,33.0; $C_{16}H_9F_8$N404 requires: F,33.1) m. 191-195°.

b) Dithioketal derivative from propane-1,3-dithol[91] XIIIa (Found F,39.7; C,40.7. $C_{13}H_8H_{12}$ S_2 requires: F,39.5; C,40.6) m.p. 109.5-110.5°. Infrared spectrum 12.

b) Oxidation of the derived ketone

The ketone (1g. 0.0034 mole) was added to a solution of potassium permanganate (0.6gm 0.0038 mole) in dry acetone (100 ml). The solution was shaken at room temperature for half an hour. Water (100 ml) was added and the acetone was removed under vacuum. Dilute sulphuric acid (10 ml) was added to the brown suspension which was decolourised with sulphur dioxide. The solution was continuously ether extracted for 24 hours and the ethereal solution was dried and evaporated yielding 2.5-Dicarboxy-2,3,3,4,4,5-hexafluorocyclohexyl methyl ketone XIV (0.5g. 45%) (Found: E.Wt(by titration with standardised NaOH) 161.5. $C_{10}F_6H_8O_5$ requires 161) m.p. 150°d.

c) Attempted Oxidation of the side chain by the Haloform Reaction

Gaseous chlorine (11g. 0.155 mole) was bubbled through a cooled solution of sodium hydroxide (15g. 01375 mole) in water (21 ml) and ice (85g). To this a solution of sodium hydroxide (2.3g. in 3.5 ml of water) was added. The ketone (10g. 0.034 mole) was added to the vigorously stirred solution and warmed to 55°. There was no exothermic reaction, therefore the reaction mixture was heated to 92° for two hours. The mixture was cooled and a solution of sodium bisulphite (3.4g in 13.5 ml of water) was added to the stirred suspension which was then acidified by the careful addition of concentrated hydrochloric acid (10 ml). The acidic solution was continuously ether extracted for 24 hours. The ethereal layer was dried, by standing over anhydrous magnesium sulphate and distilled yielding a complex mixture (5g) b.160-185°/750mm. This material contained chlorine, formed a 2,4-Dinitrophenylhydrazone,m.188, which showed no CF=CF absorbtion in the 1754 cm^{-1} region of the spectrum. Infrared spectrum 12a.

d) Attempted Clemmensen Reduction

Granulated zinc (6.2g) was washed, for five minutes, with a solution of mercuric chloride (0.8g in 20 ml of water containing 1 ml of concentrated hydrochloric acid). After decantation water (30 ml) concentrated hydrochloric acid (30 ml) and the ketone (5g. 0.017 mole) were added to the activated zinc. The suspension was boiled for 5½ hours, with the addition of acid (½ ml) every half an hour. The reaction mixture was extracted with ether and the ethereal layer was washed with water (2 x 30 ml). The ethereal layer was dried, by standing over anhydrous magnesium sulphate, and distilled yielding starting material only (4g. 80%).

e) Attempted reduction of the Di-thioketal

The dithioketal (3.95g. 0.00104 mole) was added to a suspension of Raney Nickel (W2-3) in rectified spirit (350 ml) and refluxed for 23 hours. The reaction mixture was filtered through a sintered funnel and the residue washed with ether. The combined filtrates were combined and distilled through a Vigreux column (18"), to a final volume of 15 ml. The concentrated solution was diluted with water (40 ml) and extracted with ether. The ethereal solution was dried, by standing over anhydrous magnesium sulphate, and distilled yielding an unidentified compound (2.2g. 56%) containing no CF=CF or C=O unsaturation in its infrared spectrum. 12b.

C) Ethyl Vinyl Ether

a) Preparation

Octafluorocyclohexa-1,3-diene (15g, 0.071 mole) ethyl vinyl ether (7.2g, 0.100 mole) and dipentene (0.1 ml) were heated in an evacuated Carius tube at 114° for 2½ hours. The crude reaction product was distilled under vacuum at 60°C and the distillate redistilled through a 12" Vigreux column at atmospheric pressure yielding 8-Ethoxy-1,2,3,4,5,5,6,6-octafluorobicyclo-(2.2.2.)-oct-2-ene $\overline{\text{XV}}$ (16.3gm. 78%). (Found: F,50.8; C,40.9. $C_{10}H_8F_8O$ requires: F,51.3; C,40.6). b.p. 169°/757mm; n_D^{20} 1.3704. Infrared spectrum 13.

b) Oxidation of the derived ether

The ether (1.7g, 0.007 mole) was added to a solution of potassium permanganate (1.1g, 0.007 mole) in dry acetone (200 ml). The resulting solution was shaken at room temperature for half an hour, after which water (200 ml) was added and the acetone was removed under reduced pressure. The aqueous solution was acidified with dilute sulphuric acid (20 ml), decolourised with sulphur dioxide and continuously ether extracted over night. The ethereal solution was dried by standing over anhydrous magnesium sulphate, and evaporated yielding 2,5-Dicarboxy-1-ethoxy-2,3,3,4,4,5-hexafluorocyclohexane $\overline{\text{XVI}}$ (1.2g, 64%). E.wt, 160.6 (by titration with standardised NaOH).

$C_{10}H_{10}F_6O_5$ requires, 162. m.p. 209°d.

D) Acrylonitrile

a) Preparation

Octafluorocyclohexa-1,3-diene (14.6g, 0.0653 mole), acrylonitrile (4g, 0.01 mole) and dipentene (0.1 ml) were heated in a sealed Carius tube for 5¼ hours at 170°. The dark reaction mixture was distilled under reduced pressure at 100° and the volatile material was distilled under reduced pressure at 50°C. The solid residue was sublimed and recrystallised from 40-60° petroleum ether yielding 7-cyano-1,2,3,4,5,5,6,6-Octafluorobicyclo-(2.2.2.)-oct-2-ene XVII (11.8g, 65%) m.p. 81.5-83.5. (sealed tube) Infrared spectrum 14.

Consistent analysis could not be obtained for this compound though it gave only one peak on A.S.V.P.C. (di-isodecyl phthalate 160°C; silicone grease 160° 220°C).

b) Hydrolysis of the above nitrile

The nitrile (5g, 0.018 mole) was heated in sulphuric acid (40 mls 80% $^{v}/_{v}$) at 99°C for 24 hours. The mixture was diluted with water (200 mls) and continuously ether extracted for 3 hours. The ethereal layer was dried by standing over anhydrous magnesium sulphate, and evaporated. The resulting solid was recrystallised from chloroform/benzene and dried yielding 1,2,3,4,5,5,6,6-Octafluorobicyclo-(2.2.2.)-oct-2-en-7-oic acid XVIII. (3.2g, 60%) (Found: F,52; C,36.5; E.wt 288 $C_9F_8H_4O_2$ requires F,52.0; C,36.5; E.wt 296) m.p. 117.5-119° Infrared spectrum 15.

E) Styrene

Octafluorocyclohexa-1,3-diene (3.5g, 0.016 mole) and styrene (1.5g, 0.011 mole) were heated in an evacuated Carius tube for 7 hours at 98°. Distillation at atmospheric pressure yielded 1,2,3,4,5,5,6,6-octafluoro-7-phenyl-bicyclo-(2.2.2.)-oct-2-ene XIX (3.4g, 94%) b.p. 196°/750 mm. m.p. 41-42 (after recrystallisation from 40-60° petroleum ether). (Found: F,45.2; C,51.5: $C_{14}F_8H_8$ requires F,46.3; C,51.3). Infrared spectrum 16.

F) Methyl Acrylate

Octafluorocyclohexa-1,3-diene (13g, 0.058 mole), methyl acrylate (7g. 0.081) and dipentene (0.1 ml) were heated in an evacuated Carius tube, for 6 hours at 100°C. After vacuum distillation at 90° the volatile materials were evaporated under vacuum at room temperature. Recrystallisation of the remaining solid from 40-60° petroleum ether at 0°yielded the methyl ester 1,2,3,4,5,5,6,6-octafluorobicyclo-(2.2.2.)-oct-2-enoicacid XX (6g, 34%) m.p. 22-24°. Infrared spectrum 17.

No satisfactory analysis have been obtained though the product gives only one peak on A.S.V.P.C. (Di-iso-decyl phthalate and silicone grease 160°).

G) Maleic Anhydride

Octafluorocyclohexa-1,3-diene (15.1g, 0.067 mole), maleic anhydride (6.7g, 0.069 mole) and benzene (25 ml) were heated in a sealed Carius tube at 190° for 7 hours. The solid was filtered yielding 1,2,3,4,5,5,6,6-octafluorobicyclo-(2.2.2.)-oct-2-ene-7,8-dicarboxyanhydride XXI (14.8g, 6 %). m.p. 199-203°. Recrystallisation from benzene afforded the pure adduct (10g, 46%) (Found: F,47.0; C,36.9. $C_{10}F_8H_2O_3$ requires: F,47.2; C,37.3) m.p. 194-195°. Infrared spectrum 18. E.wt 161 (by hydrolysis and titration with standardised NaOH) $C_{10}F_8H_2O_3$ requires 160.

H) Anthracene

Octafluorocyclohexa-1,3-diene (9.2g, 0.041 mole), anthracene (7g, 0.039 mole) and benzene (25 ml) were heated in a sealed tube at 99° for 48 hours. On cooling the contents of the tube were filtered yielding anthracene (6.1g) m215-7 and from mothers liquors, on evaporation a solid (2.5g) 130-180°. Two recrystallisations from 70% methylated spirits yielded a 1:1 adduct XXII (1.2g, 7%). (Found: F,37.1; C,60.1. $C_{20}F_8H_{10}$ requires F,37.7; C,59.7). Infrared spectrum 19. λmax in methanol. 2530 (7.9) 2640(.69) 274 (.6)

CHAPTER 3

DISCUSSION

DISCUSSION

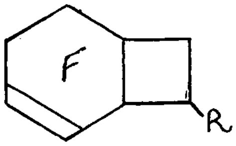
Copolymerisation reactions of Octafluorocyclohexa-1,3-diene with vinyl compounds, butadiene and substituted butadienes have been investigated by Hopkin and Barbour,[92] and, to a lesser extent, by Plimmer.[93] The former workers found in the investigation of this diene, and the corresponding 1,4 isomer, that copolymers approaching a 1:1 constitution were more easily formed with unsaturated hydrocarbons than with unsaturated fluorine containing compounds.

Model compounds (1:1 adducts) of some of these copolymers have been prepared and this work demonstrates that octafluorocyclohexa-1,3-diene can behave as a diene or a dienophile in the Diels-Alder reaction, depending upon the nature of the hydrocarbon addend.

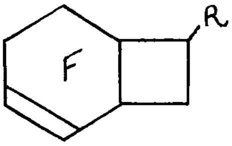
This is the first example of a fluorinated diene taking part in the Diels-Alder reaction as the diene component. Perfluorobutadiene does not form Diels-Alder adducts with maleic anhydride or 1,4-naphthaquinone,[94] a fact which may be partially explained in terms of the more stable transoid configuration of the diene,[95] which is in the contrast to the diene under investigation which is in an enforced cisoid configuration

General Determination of the Structure of Initial Adducts

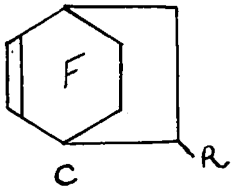
The three possible structures of adducts arising from the reaction between Octafluorocyclohexa-1,3-diene and a substituted ethylene ($CH_2 = CHR$) are:-



A

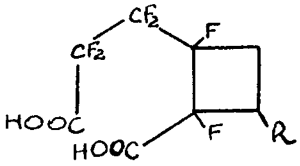


B

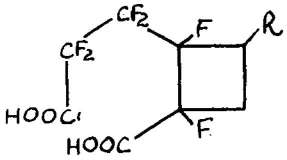


C

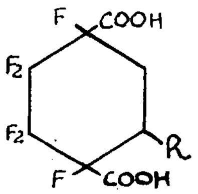
Due to the fact that no similar compounds have previously been synthesised no correlation of the spectral data of the derived compounds was possible. Similarly no compounds have been synthesised which could be obtained from unambiguous degradation of A, B or C. Therefore, the only route available for the identification of the adducts produced was to obtain one compound, by a known degradation route, which might then be differentiated from the other two possibilities by instrumental analysis. The method chosen was the oxidation of the remaining fluorinated carbon-carbon double bond, by the method of Burdon and Tatlow,[84] to give one of the following compounds



E



F



G

Essentially the problem then reduces to differentiation of a cyclobutane containing two difluoromethylene groups in the side chain (E and F) from a fluorinated cyclohexane (G).

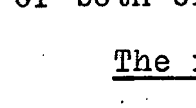
Fluorine nuclear magnetic resonance is capable of differentiating between these two types of structure. The spectrum of E or F would be expected to yield a complex AA' BB' type of spectrum in the CF_2 region of the spectrum (1,200-3,000 c/s). The complexity of this type of spectrum is due to the presence of both geminal and vicinal spin-spin coupling. By comparison the spectrum derived from a compound of type G would be expected to exhibit only eight lines in this region of the spectrum. The eight times can be analysed as two AB quartets, each quartet arising from one of the difluoromethylene groups. The relative simplicity of this type of spectrum is due to the absence of vicinal spin-spin coupling in fluorinated cyclohexanes.

The magnitude of the geminal coupling constants has been shown to lie within the range 250-350 c/s in fluorinated cyclohexanes.[96] The coupling constants of the non-cyclic difluoro-methylene groups have been shown to lie within the range 150-175 c/s.[97] Higher values have been observed in some hexafluoro-propyl compounds, but their significance has not yet been interpreted.[82] The assignment of structures to the dicarboxylic acids has been based on the type of spectrum rather than on the value of the coupling constants, Of the four dicarboxylic acids (VII; IX; XIV;XVI) prepared and investigated by fluorine nuclear magnetic resonance IX was found not to be a fluorinated cyclohexane dicarboxylic acid. The precursors of the other acids (V XIII and XV) were thus shown to be Diels-Alder adducts of the fluorodiene - structure type C.

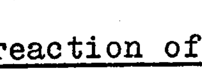
The adduct XV exhibited an eight line (two AB quartets) CF_2 spectrum with coupling constants of 234 and 175 c/s and it was thought that this may have been indicative of 1,2 addition to the fluorodiene. However the derived dicarboxylic acid (XVI) was shown, by fluorine nuclear magnetic resonance to be a fluorinated cyclohexane-1,4-dicarboxylic acid (structure G, R = OEt) and hence the original adduct was a Diels-Alder adduct (structure C, R = OEt). The occurrence of AB quartets in the spectra of some of the primary adducts may be due to interaction between the substituent R and one, or both of, the difluoromethylene groups.[98]

The reaction of octafluorocyclohexa-1,3-dien with buta-1,3-diene

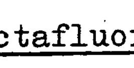
The reaction between these two conjugated dienes can give rise to five isomers, (H to M).



H



J



K

L

M

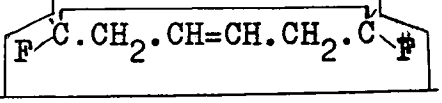
The structures H, J and K represent 1:2 addition to the fluorodiene by butadiene which, though anomalous for a hydrocarbon diene, is a normal mode of addition of fluorodienes, (see Table 2). Structures L and M represent the corresponding 1:4 addition products to the fluorodiene. The normal 1:4 addition of butadiene to the fluorodiene results in structures K and M while H, J and L show the anomalous 1:2 addition to butadiene which is known to occur readily with fluoroolefins. (see Table 1).

The reactions were carried out in metal autoclaves and evacuated Carius tubes, using 1:1 molar proportions of the reactants together with a trace of dipentene, to prevent homopolymerisation of butadiene. Even though a polymerisation inhibitor was used small amounts of copolymer (4%) were produced in all reactions. Analytical scale vapour phase chromatography, using tricresyl phosphate or di-isodecyl phthalate as stationary phase, showed that five compounds (I, II, IIa, III and IIIa) were formed during the reaction. Compounds IIa and IIIa, produced in very small amounts, were not investigated. The main components, I, II and III were separated by a combination of fractional distillation and large scale vapour phase chromatography.

The initial step in the elucidation of the structures of the compounds was to find in which of them vinyl groups were present. This was carried out by ozonolysis[31] of the three individual adducts and then testing the hydrolysed product specifically for formaldehyde. Schiff's reagent, containing about 30% concentrated hydrochloric acid is sensitive only to formaldehyde. Both compounds I and II were found to contain vinyl groups and must therefore possess structures H, J or L, while compound III, containing no vinyl group, must be K or M.

This chemical evidence also confirms spectroscopic correlations.

TABLE 6

	OBSERVED		LITERATURE		ASSIGNMENT
	I.R.	^{1}H N.M.R.	I.R.[99]	^{1}H N.M.R.[100]	
I	3.23	299-352	3.23-3.25	276-363	$-CH = CH_2$
II	3.227	303-356	3.23-3.25	276-363	$-CH = CH_2$
III	3.273	159.6-342	3.29-3.32	117-334	 $F\text{-}C.CH_2.CH{=}CH.CH_2.C\text{-}F$

The complex proton magnetic resonance spectrum of I and II within the limits quoted confirm a vinyl group while the simple absorbtions of vinylic and allylic protons in III confirm the 1:4 addition of the butadiene, i.e. no vinyl group.

The remaining problem was to determine the mode of addition of the fluorodiene, and thus determine the overall structure of the individual adducts. This was performed as described under "General Determination of Structure" (page 54) and attempts were made to obtain dicarboxylic acids. Initial attempts to carry out this oxidation were complicated by the simultaneous exidation of the hydrocarbon double bond.

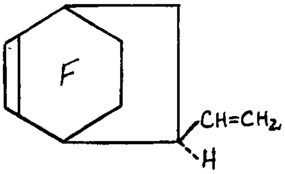
Hydrogenation at atmospheric pressure using a palladised charcoal catalyst[83] enable the hydrocarbon double bond to be specifically reduced. If large amounts of catalyst were employed (20-25%) then both sites of unsaturation were reduced (II → VI), but the fluorocarbon double bond was not saturated until after the hydrocarbon double bond, and then at a greatly reduced rate. The reduced adducts, IV, V and VIII were oxidised by potassium permanganate in dry acetone.

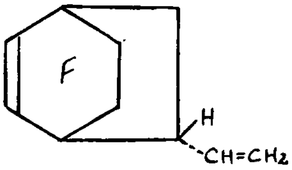
Compound IV did not give an identifiable dicarboxylic acid. The small amount of product obtained decomposed and hence purification was not possible.

Compound V gave a product which was characterised as a dicarboxylic acid by its equivalent weight, and its fluorine nuclear magnetic resonance showed that it was a fluorinated cyclohexane-1,4-dicarboxylic acid of structure G (R=Et). Hence V was of structure C (R=Et) and the original adduct, II also of structure C ($R=CH=CH_2$), a Diels-Alder adduct with respect to the fluorodiene.

Compound VIII, on oxidation, yielded a compound which was characterised as a dicarboxylic acid containing the two difluoromethylene groups in the side chain, and the dicarboxylic acid was therefore assigned structure IX. Hence the structure of the original adduct was III, a Diels-Alder adduct with respect to butadiene with the fluorodiene acting as the dienophile. The methylene group absorbtion at 3.43μ is also in agreement with a hexacyclic hydrocarbon ring.[100]

The structure of Compound I was not elucidated by direct proof, but by elimination of other possible structures. Since it contains a vinyl group it can only possess structures H, J or be a second geometric isomer of L. (exo or endo with respect to the fluorocarbon double bond).





If it is a second isomeric form of K, and hence of II, its reduction product should give, after oxidation, a dicarboxylic acid very similar to VII. No pure product was obtained, indicating some instability of the dicarboxylic acid which must have been produced. If I is structurally similar to II its isomerisation (see p 68) to III should be equally as difficult as the isomerisation of II to III, but I isomerises very easily at a temperature 150° less than that required to isomerise II. The structure of I must therefore be H or J, containing a cyclobutane ring system fused to a six membered ring system. The structure of I must therefore be H since on the basis stable intermediates proposed in this type of reaction it is not possible to obtain a compound of structure J.

The only confirmatory evidence for the existence of a four membered ring is from the infrared methylene absorbtion at 3.34μ, but compound II also exhibits a methylene absorbtion band at 3.336μ again indicating a four membered ring.[101] In view of the fact that the correlations are taken from monosubstituted cycloalkanes it is felt that assignments cannot be valid because of the extra strain due to bridging shifts the absorbtions to lower wavelengths.

Attempts to elucidate the structures of the adducts by dehydrofluorination resulted in complex mixtures and decomposition. Only in certain cases of reaction with ethanolic potash and resin dehydrofluorination[102] were mixtures obtained that could have been investigated, but since mixtures were obtained this approach was not pursued in favour of the more straightforward route already described.

As indicated previously the fluorine nuclear magnetic resonance spectra of the initial adducts gave no clear indication of their structures. However the spectra, in the CF_2 region at temperatures other than room temperature, do give some qualitative indication that the structural assignments are correct.

The spectra of both I and II did not change when investigated at 100° and -60°, indicating that only one conformation of the molecule was present over a temperature range of 160°. This phenomenum is to be expected where structures are prevented from interconverting. The cyclobutane ring in I and the bridged structure of II are structural factors which prevent the existence of more than one conformer.

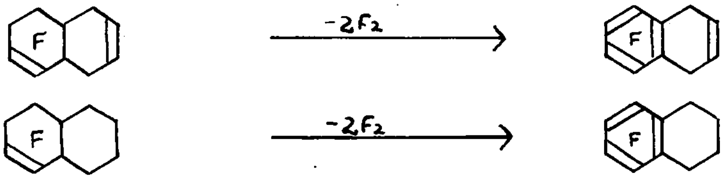
On the other hand the spectrum of III changed considerably on being cooled to -80°. The spectrum changed from two broad bands at room temperature to a fine multiline spectrum at -80°. The broad absorbtions in the room temperature spectrum showed that the compound was interconverting and that the spectrum was "averaged" for all conformations. At-80° the very complex absorbtions were attributed to one or more conformations which were not interconverting.

The fact that the broad spectrum of II could not be changed by cooling showed that, at room temperature, the observed spectrum was that of one conformation, and not of a number of interconverting conformers.

Defluorination reactions

Defluorinations of compounds III and VIII were attempted in order to prepare 1,2,3,4-tetrafluoro-5,8-dihydro naphthalene and 1,2,3,4-tetrafluoro-5,6,7,8-

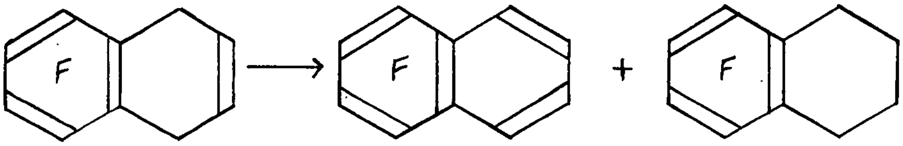
tetrahydronaphthalene respectively



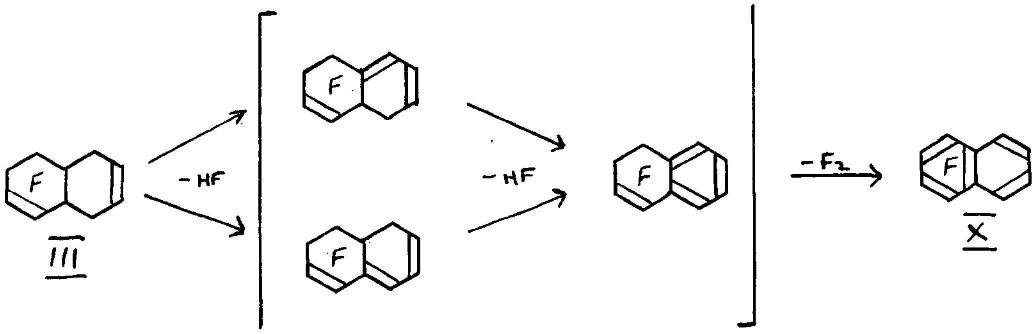
III

VIII

The products from these reactions, carried out over iron powder, were shown to contain three products, in about equal proportions, one or two of which contained chlorine. From the mixture there was obtained 1,2,3,4-tetrafluoronaphthalene ($\underline{X}$) and the total mixture was shown to be completely aromatic by its fluorine and hydrogen nuclear magnetic resonance spectrum. The reactions should have produced di-and tetrahydro-naphthalenes, but the products were aromatic and this observation eliminated the possibility of disproportionation



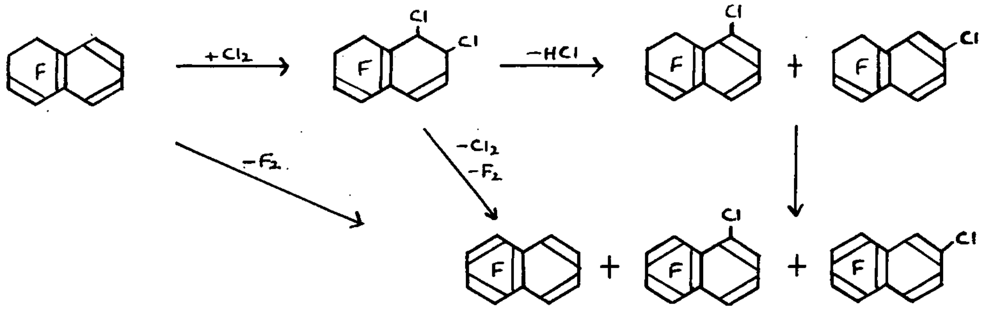
Therefore the reaction must involve the loss of hydrogen fluoride as a route to aromatising the hydrocarbon ring



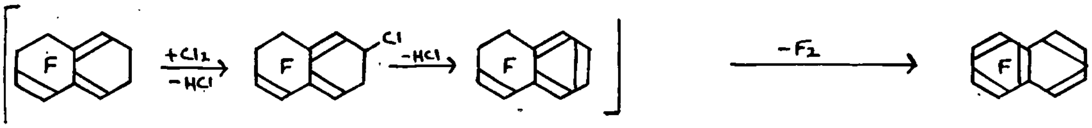
III

X

The initial defluorinations were performed in a system which had previously been used for dechlorofluorinations and thus the extra products may be postulated as chlorotetrafluoronaphthalenes, obtained by the following route.



In the case of VIII where a dehydrogenation step must be postulated it is possible to account for the presence of tetrafluoronaphthalene and chlorinated products by allylic substitution by chlorine and subsequent elimination of hydrogen chloride.

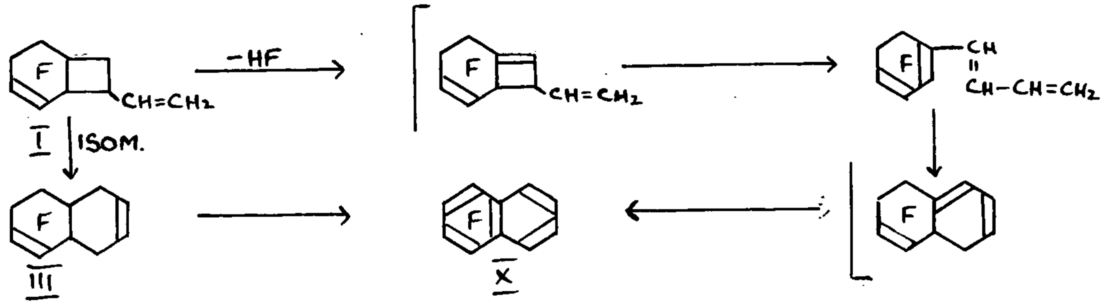


Defluorination of III over steel wool yields pure X, indicating that chlorine, molecular or as ferric chloride, was, in some way responsible for the extra products from the initial defluorinations.

A mixture of I and II was passed through the steel wool defluorination in an attempt to form more easily separable products, but at 325°, the same temperature used for the defluorinations of III and VIII, a small yield of

1,2,3,4-tetrafluoronaphthalene was obtained. The amount corresponded to about 60% of compound I present in the original mixture of I and II, and in addition compound II was recovered unchanged. This method was used for the purification of II.

In this reaction compound I must have isomerised before, or after, loss of hydrogen or fluorine to give a compound capable of producing compound X.



On increasing ~~the temperature~~ the defluorination temperature to 425° it was possible to obtain a total conversion of a mixture of I and II or of the vacuum distilled adduct mixture to the naphthalene. In this case the high temperature must effect the isomerisation of II to III as shown by later results.

Isomerisation of Adducts

Isomerisation of the adducts was performed in evacuated sealed tubes at various temperatures for three minutes. In this instance there is no reason to postulate the elimination of hydrogen fluoride, prior to isomerisation as there was in the case of I. The composition of the adduct mixture, which was enriched in I and still containing unidentified IIa and IIIa, before and after heat treatment is given in the following table and was evaluated by analytical scale vapour phase chromatography.

	I	II	IIa	III	IIIa
START. MAT.	18.9	64.5	4.6	12.1	-
250°C	.4	60.2	3.7	15.3	20.3
350	.4	42.7	2.9	34.1	19.9
400	0	8.3	4.1	72.6	11.8

The results show that the initial adduct mixture contains a high proportion of the fluorocarbon Diels-Alder adduct (II) and that above 350° its thermal stability is very low, relative to the hydrocarbon Diels-Alder adduct (III). The most unstable adduct is I which readily isomerises at 250°.

These results are in agreement with Drysdales observations that hydrocarbon Diels-Alder adducts are thermodynamically more stable;[38] and are formed only at high temperatures (p.13). While the systems compared are different in that compounds II and III are formed from two dienes, the basic principle, that isomerisation from a butadiene 1:2 adduct (II) to a thermodynamically more stable 1:4 adduct (III) takes place, is upheld.

Reactions of 1,2,3,4-tetrafluoronaphthalene (X)

Naphthalene is more easily substituted at the α position, relative to the β position, by electrophilic reagents due to the lower energy of the transition states involved during the reaction.

Octafluoronaphthalene is easily substituted at the β position by nucleophilic reagents[103] and this fact is interpreted by the authors in terms of the greater electron deficiency at the β position, rendering that position most susceptible to nucleophilic attack, irrespective of the fact that the compound is poly-fluorinated. This statement is borne out by the fact that 2-naphthyl halides react with piperidiene more rapidly (25-70%) than the 1-naphthyl halides.[104] However cases can be quoted where nucleophilic attack at the α position is preferential. Amination of naphthalene, naphthols and naphthylamines, by sodamide, takes place at the α position [104] and reduction of reduction of α and β bromonaphthalenes, with lithium aluminium hydride, is easiest at the α position.[105]

It has been found that nucleophilic substitution of tetrafluoronaphthalene gives 1,2,3-tetrafluoro-4-methoxynaphthalene (XI). The assignment of structure is based on its fluorine nuclear magnetic resonance spectrum which contained two doublets and one triplet with the appropriate σ- and m- coupling constants of 15 and 4c/s respectively, but no p-coupling constant ~10c/s. The spectrum obtained was the type to be expected from an aromatic compound containing three adjacent fluorine atoms.

No satisfactory explanation has been found to account for this specific α substitution in terms of relative stabilities of the transition state. Indeed relative to octafluoronaphthalene this reactivity cannot be explained, as in the case of the variation in the site of nucleophilic attack on naphthalene itself.

Electrophilic attack yields one product which has been presumed to be 1,2,3,4-tetrafluoro-5-nitronaphthalene (XII), in view of the specific nature of electrophilic attack on naphthalenes as a whole. The proton magnetic resonance spectrum of the nitro naphthalene showed that substitution had taken place in the hydrocarbon ring, but the position of attack (α or β) was not apparent due to the complexity of the spectrum.

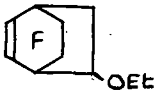
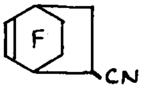
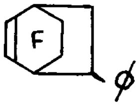
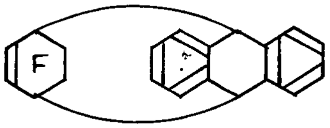
The oxidation of the naphthalene by a variety of reagents yielded phthalic acid or anhydride. The potassium permanganate/acetone reagent, known to react by initial nucleophilic addition,[84] was expected to produce phthalic acid, however other reagents; chromium trioxide in glacial acetic acid and a vanadium pentoxide catalyst for aerial vapour phase oxidation also gave phthalic acid, instead of the desired 3,4,5,6-tetrafluoro phthalic acid.

Oxidations using peroxytrifluoro acetic acid and diacetyl orthonitric acid[106] ($(CH_3 COO)_2N (OH)_3$) gave intermediate products, which were not characterised, which did not yield tetrafluorophthalic acid on further treatment with acidic permanganate solution.

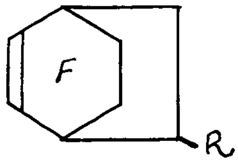
Reactions of octafluorocyclohexa-1,3-diene with unsaturated compounds

Octafluorocyclohexa-1,3-dienes was reacted with mono- and disubstituted ethylenes and anthracene. Table 8 shows reaction times, temperatures and yields of adduct based on the reactant in lowest molar concentration.

TABLE 8

	COMPOUND	TEMP. °C 6	TIME hrs. 6	YIELD %. 7
XIII		114	$2\frac{1}{2}$	73
XV		114	$2\frac{1}{2}$	78
XVII		170	$5\frac{1}{4}$	65
XIX		98	7	94
XX		100	6	34
XXI		190	7	68
XXII		99	48	7

The structures of the adducts were determined by two methods. Adducts XIII and XV were degraded, as previously described on page 57 to give the corresponding dicarboxylic acids. Both acids XIV and XVI were shown by their fluorine nuclear magnetic resonance spectra to be cyclohexan-1,4 dicarboxylic acids. Thus the structures of the original adducts were found to be of type C (page 57), Diels-Alder adducts of the fluorodiene.



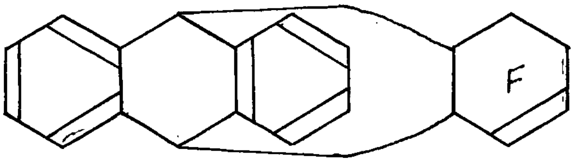
The structures of the XVII and XIX - XXII can be deduced from the fluorinated carbon-carbon double bond stretching frequency at about 1754 cm^{-1}. The butadiene adducts (I, II and III) exhibited absorptions at 1738; 1757 and 1744 cm^{-1}, respectively and their reduced products (IV, V and VIII) at 1739; 1758 and 1738 cm^{-1}. The small changes show that the fluorinated carbon-carbon double bond was not affected by reduction of the hydrocarbon double bond.

Compounds I, III, IV and VIII result from 1,2 addition to the fluorodiene and their absorptions are low, relative to compounds II and V which are the corresponding 1,4 adducts. The absorption frequency of the Diels-Alder type of structure would be expected to be a little higher due to the rigid form of the bicyclic ring system.

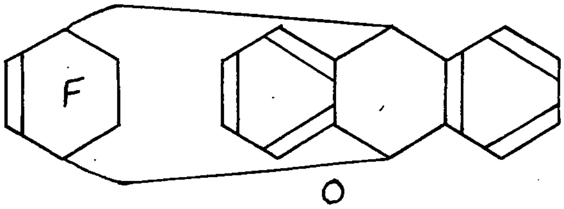
All adducts, except I, III, IV and VIII, including XIII and XV whose structures have already been confirmed by the standard method, exhibit absorptions between 1764 and 1751 cm^{-1} (1758 ± 6 cm^{-1}) and their absorptions in this region are listed in Table 9.

The absorbtions are higher than that quoted for perfluorocyclohexene, 1746 cm,$^{-1}$ or the averaged value for hydrogen substituted polyfluorocyclohexenes, 1749 cm.$^{-1}$ [107] However the average value of the adducts, 1758 cm,$^{-1}$ compares sufficiently well with that of perfluorocyclopentene, 1754 cm,$^{-1}$ all systems being fairly rigidly confirmed to one conformation.

All the addends, except anthracene, could be expected to form Diels-Alder adducts, but in the case of anthracene two possible structures could exist. (N or O).



N



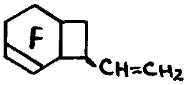
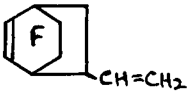
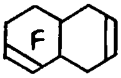
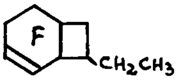
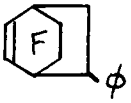
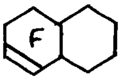
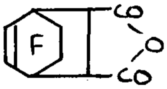
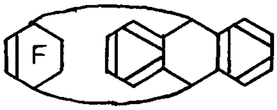
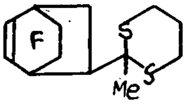
O

From the infrared correlations made, it was assigned structure O, 1,4 addition to the fluorodiene and the ultraviolet spectrum also showed it to be a 9,10 anthracene adduct, since the absorptions were characteristic of isolated phenyl groups.[33] Thus the structure is a double 1,4 adduct.

Attempts were made to interelate some of the adducts by carrying out specific reactions on the methyl vinyl ketone adduct (XIII). A Clemmensen reduction was attempted

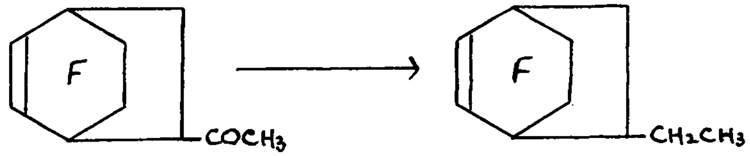
TABLE 9

INFRARED ABSORPTIONS OF ADDUCTS AND DERIVED COMPOUNDS

CMPD.	STRUCTURE	MAX cm^{-1}	CMPD.	STRUCTURE	MAX cm^{-1}
I		1738	XV		1756
II		1757	XVII		1762
III		1744	XVIII		1764
IV		1739	XIX		1754
V		1758	XX		OBSC.
VIII		1738	XXI		1753
XIII		1760	XXII		1753
XIIIA		1751			

in order to obtain compound V,

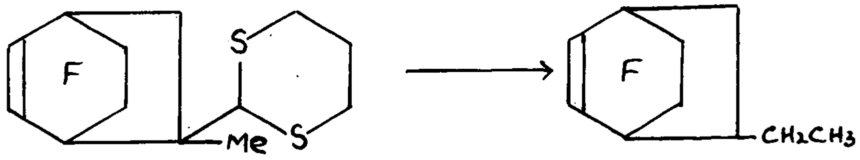
XIII



V

but no product was formed during the reaction. A Wolff-Kishner reduction of the hydrazone or a substituted hydrazone was not attempted since the second stage of the reaction, reductive cleavage with base, would have resulted in side reactions and nucleophilic attack in the fluorine ring system. Similarly reduction or desulphurisation of the dithioketal of the ketone (XIIIA) was not realised, unchanged ketal and hydrolysed ketal were recovered.

XIIIA



V

The Haloform reaction was performed on the ketone in an attempt to isolate a monocarboxylic acid similar to that derived from the nitrile XVIII. However addition to the double bond had taken place as shown by the absence of an absorption band at about 1754 $cm.^{-1}$

From a comparison of Tables 3 and 5 it is apparent that the reactions of octafluorocyclohexa-1,3-diene with methyl vinyl ketone, ethyl vinyl ether and styrene are far easier than their additions to tetrafluoroethylene or any other highly fluorinated olefin. Reaction temperatures are

considerably reduced and the yields are increased.
The reaction with acrylonitrile does not appear to be so facile and may be attributed to the negatively substituted hydrocarbon olefin.

Overall the increase in reactivity may be due to the relative ease of formation of a bicyclic system containing two fused six membered rings as compared with a bicyclic system having a four membered ring fused to a six membered ring.

Reactions of octafluorocyclohexa-1,3-diene with fluoro-olefins

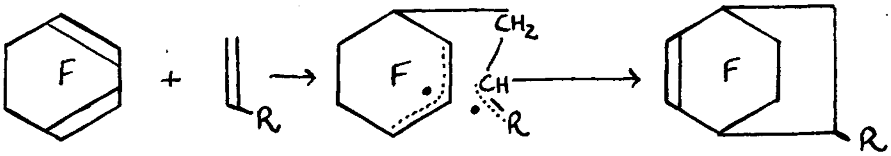
The following fluoro-olefins could not be made to cyclise with the fluorodiene:- C_2F_4; $CF_2 = CFCl$; $CF_2 = CF.CF_3$; $CF_3.C = C.CF_3$; $CF_2 = CH_2$. The reaction temperatures were as high as 250° and reaction times as long as 36 hours. In all cases quantitative recovery ($> 95\%$) of the reactants was achieved. Hopkin[108] observed that no copolymers could be obtained from $CF_2 = CF_2$; $CF_2 = CFCl$; $CF_2 = CFH$; $CF_2 = CF.CF_3$ and $CFH = CH_2$. Small yields of copolymer were obtained from $CF_2 = CH_2$ containing less than 25% of the diene. This lack of reactivity of the mono-unsaturated fluoro-olefins was also observed with the corresponding 1.4 diene.
The unreactivity of fluoro-olefins with the 1.3 diene will

be discussed in the following section.

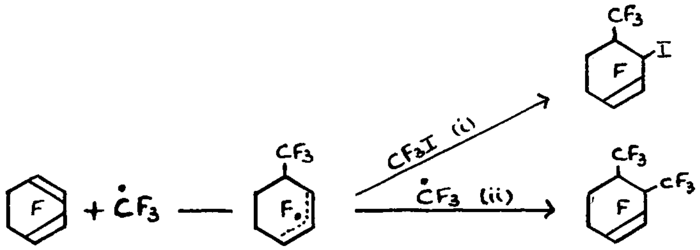
Mechanism of the Cyclisation Reactions

It is proposed that in these reactions a free radical mechanism is operative. Reactions of octafluorocyclohexa-1,3 diene and butadiene were carried out in solutions of cyclohexane and nitro-methane at room temperature and there was found to be no significant change in the extent of the reaction or of the isomer ratio. Thus the reaction mechanism is independent of solvent, indicating a free radical mechanism.

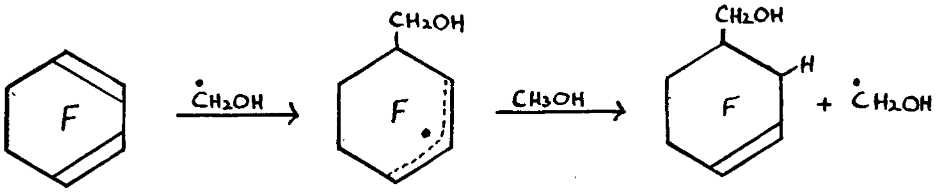
The addition of substituted vinyl compounds to the diene is exclusively 1,4 and the reaction path may be envisaged as follows



It has been found by Kisby[82] that this diene is more susceptible to attack by perfluoromethyl radicals than the corresponding 1,4 isomer, and that the intermediate radical is of low reactivity. Resonance stabilisation prevents the formation of product by a chain of transfer steps (i), but it will react preferentially with a second perfluoromethyl radical, since they were in excess, as shown in the chain termination step (ii).



However in the case of the free radical addition of methanol to the diene conversions are extremely low due to the very low concentrations of free radicals, which take part in initiation rather than in chain termination



Therefore the only route to the above product is by a chain transfer step which is known to be poor due to the resonance stabilisation of the intermediate radical.

Returning to the case of addition of vinyl compounds to the diene it can therefore be presumed that the efficiency of the reaction is determined by the reactivity of the hydrocarbon. Its subsequent attack on the fluoro-olefin will be easy in all reactions. It is not possible to assess the ease of formation of radicals by the hydrocarbon addend since their reactivity is only given qualitatively.[109]

The specific 1,4 mode of addition can be accounted for in two ways. Either a) the formation of a fused six-membered ring is energetically more favourable than the formation of a four membered ring

or b) some interaction or "secondary attractive forces"[24] fix the geometry of the intermediate, and hence the structure of the adduct.

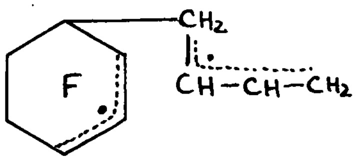
The former explanation is rather vague in view of the strong tendency of fluoro-olefins to form four membered rings, even with conjugated dienes (Table 1). The only observed case of this diene forming a four membered ring is in the formation of I, which is apparently a kinetic isomer since this readily isomerises to the more stable hydrocarbon Diels-Alder adduct (III).

The latter explanation is more in accordance with current thoughts on the Diels-Alder reaction.[22.24] The conformation of the intermediate may be fixed by Vander Waal's forces, partial bonds or by simultaneous bond formation but this problem applies to most cyclisation reactions and is unanswerable at the present time.

Isomers in the butadiene reaction

The variety of the butadiene adduct structures is interesting, in that almost every combination of type of addition is observed the only omission being the 1,4/1,4 addition to both dienes. Whether these adducts are formed from one complex transition state or whether each compound is formed from its own transition state, it is not possible to discern between the two possibilities. If one complex intermediate cyclised in three different ways then this process might be expected to be temperature dependent. As indicated earlier, at room temperature the isomer ratio is the same as the normal reaction at 100°. Thus either the compounds are formed from discrete transition states whose formation are not temperature dependent or the final cyclisation step from one transition state is not significantly affected by a temperature change of 80°.

The structure of I was found to be H or J, and it is proposed that the intermediate radical is most likely to be



Since initial attack is more liable to be at the 1 position, than at the 2 position. This argument must hold whether there is a discrete transition state leading to the formation of I and in the case of a complex transition state the former intermediate structure is the only one that is tenable. Since this is the only cyclisation reaction involving two dienes very little can be said concerning the factors influencing the isomer ratio.

The complete lack of reactivity of fluoro-olefins with octafluorocyclohexa-1,3-diene must be explicable in one of two ways. Either a) The reaction between two highly negatively substituted olefins reduces, in some way, the reactivity of the fluoro-ethylene radical.

or b) steric hinderance must inhibit the reaction completely.

NUCLEAR MAGNETIC RESONANCE SPECTRA OF ADDUCTS AND DERIVED COMPOUNDS

A). BUTADIENE ADDUCTS and derived compounds.

I

from [illegible]

^{19}F	1294; 1462; 1730; 2463; 2707;	
	2853; 3116; 3417; 3512; 3764;	$(>CF_2)$
	J_{ab} 265; 252	
	4571; 4821;	$(=CF)$
	7153	$(-\!\!\!>CF)$
$^{19}F_{60^\circ}$	1468; 1758; 2513; 2762; 2938;	
	3213; 3507; 3623; 3869;	$(>CF_2)$
	J_{ab} 283; 248	
^{1}H	119.7; 129.8; 135.0; 146.6; 157.2	
	163.9	$(>CH_2)$
	225.0 (Broad)	$(-\!\!\!>CH)$
	299.5; 311.6; 317.4; 320.2; 352.0 (Broad)	$(-CH=CH_2)$

II

^{19}F	2947; 2966; 2994; 3013;	$(>CF_2)$
	4269; 4466	$(=CF)$
	7176; 7297	$(-\!\!\!>CF)$

$^{19}F_{-40}$	2942; 2955; 2979; 2993; 3006 3017	($>CF_2$)
^{1}H	118; 149	($>CH_2$)
	178	($>\!\!-CH$)
	303; 305; 315; 316; 323; 331; 338; 346; 350; 356;	$(-CH=CH_2)$

<u>III</u>

^{19}F	2205; 2345; 2967; 3985	($>CF_2$)
	4845	($=CF$)
	5548	($>\!\!-CF$)
$^{19}F_{-80}$	Very Complex	
^{1}H	159.1; 180	($>CH_2$)
	342	($=CH$)

<u>IV</u>

^{19}F	Similar Spectrum to <u>I</u> in $>CF_2$ region J_{ab} 286 c/s.	
^{1}H	Three main peaks with undetermined structure 49.8; 56.4; 63.6	

<u>V</u>

^{1}H	39.7 (Complex)	($-CH_3$)
	66.2 (Broad)	($>CH_2$)

VI

^{19}F 2839; 3067 ($>CF_2$)

6632; 7274 ($>CFH$)

7958; 8518 ($>CF$)

VII

^{19}F 2186; 2455; 2908; 3051; 3181;

3327 ($>CF_2$)

J_{ab} 272

5478; 5646

VIII

^{1}H 105.0; 135.6 ($>CH_2$)

IX

^{19}F Very Complex

X

^{19}F 4365; 4372; 4377; 4383; 4896;

4903; 4908; 4913; (Aromatic F)

^{1}H 447.7; 451.7; 453.3; 459.7; 475.3;

477.7; 481.3; 484.7; (Aromatic H)

XI

^{19}F 4067; 4082 ($-F_3$)

4463; 4479; 4481; 4497 ($-F_2$)

4554; 4558; 4572; 4576 ($-F_1$)

^{1}H 241.7; 242.2; 243.4; 243.9 ($-OM_e$)

433.7; 437.0; 440.4; 443.4; 447.0 (Aromatic H)

465 (Aromatic H_s)

XII

^{19}F 3829; 4158; 4519; 4617 (Aromatic F)

^{1}H 446.5; 455.6; 459.1; 461.7; 491.5 (Broad (Aromatic H)

XIII

^{19}F 2975 (Broad) ($>CF_2$)

4405 (=CF)

7600 ($>\!\!-CF$)

^{1}H 139.2 ($-CH_3$)

139.4

XIV

^{19}F 2244; 2503; 3047; 3124; 3301; 3398 ($>CF_2$)

J_{ab} 257; 274

5350; 5688

XV

^{19}F 2646; 2783; 2885; 2947; 3000;

3082; 3187; 3311 ($>CF_2$)

J_{ab} 175; 234

^{1}H 77.4 ($-CH_3$)

216 ($>CH_2$)

231 (Complex)

XVI

^{19}F 2059; 2198; 2329; 2468; 2772;

3047; 3104; 3374 ($>CF_2$)

J_{ab} 270; 274

5580; 5646 ($>\!-CF$)

XVII

^{19}F 3017 ($>CF_2$)

4248 (=CF)

7165 ($>\!-CF$)

XVIII

^{19}F 3012 ($>CF_2$)

4282; 4546 (=CF)

7338; 7416 ($>\!-CF$)

XIX

^{19}F 2962; 2966; 2981; 2992; 3006 ($>CF_2$)

4215; 4488 (=CF)

7359 ($>\!-CF$)

XXI

^{19}F 2908 ($>CF_2$)

4355 (=CF)

6925 ($>\!-CF$)

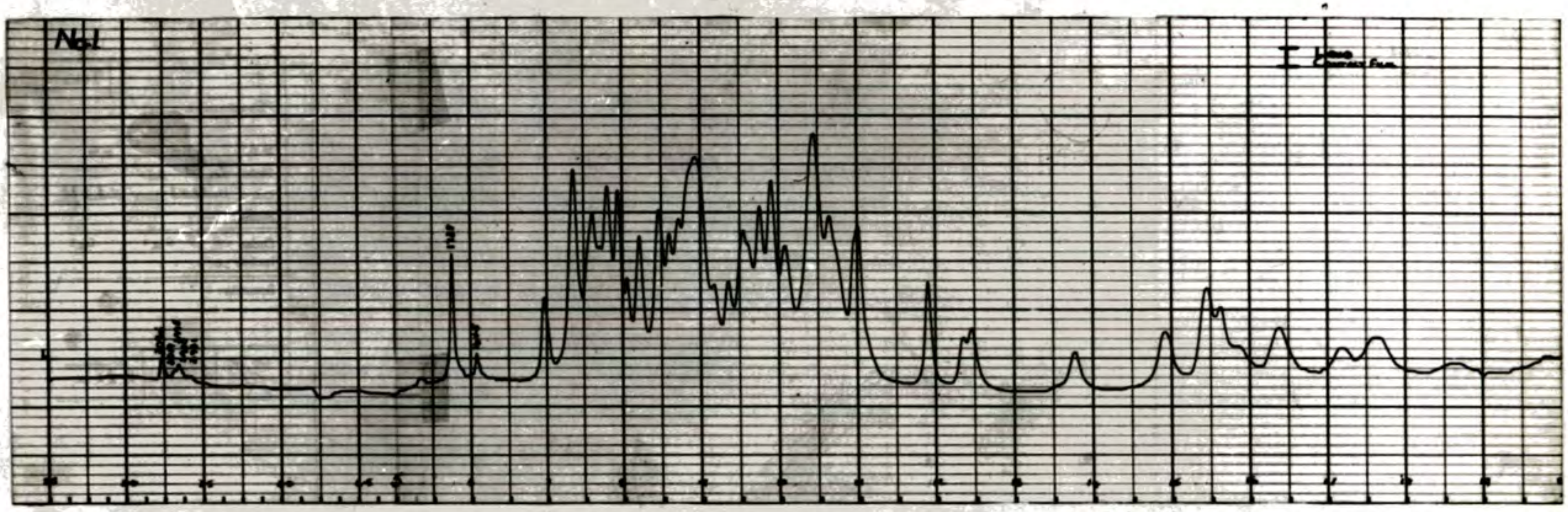
XXII

^{19}F 2319; 2405; 2577; 2779; 3065

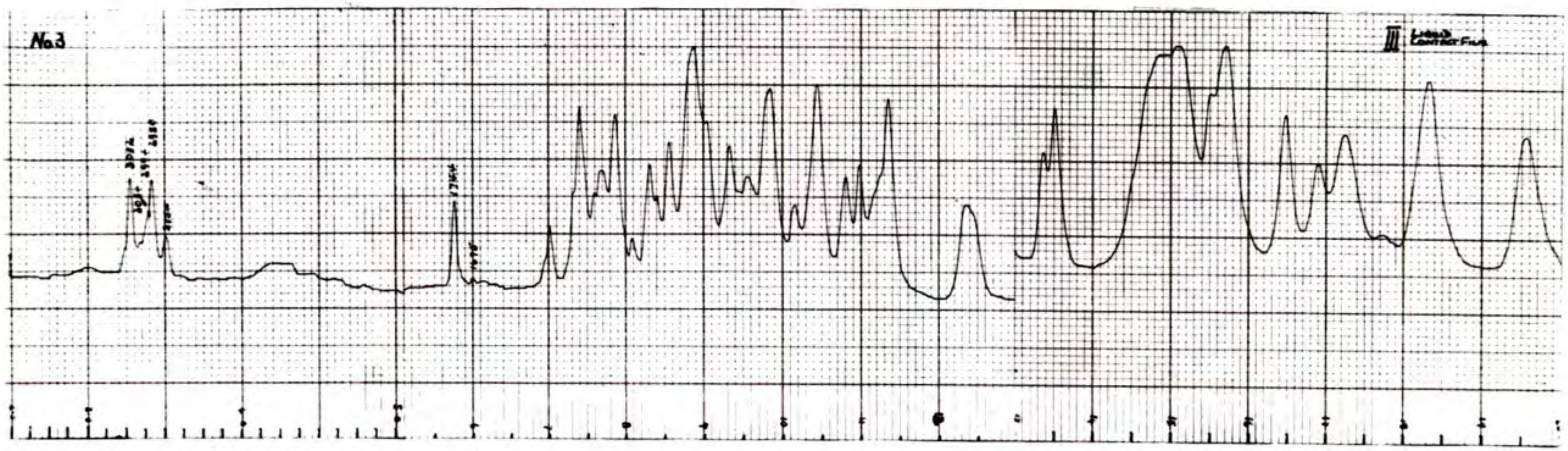
J_{ab} 267 $(>CF_2)$

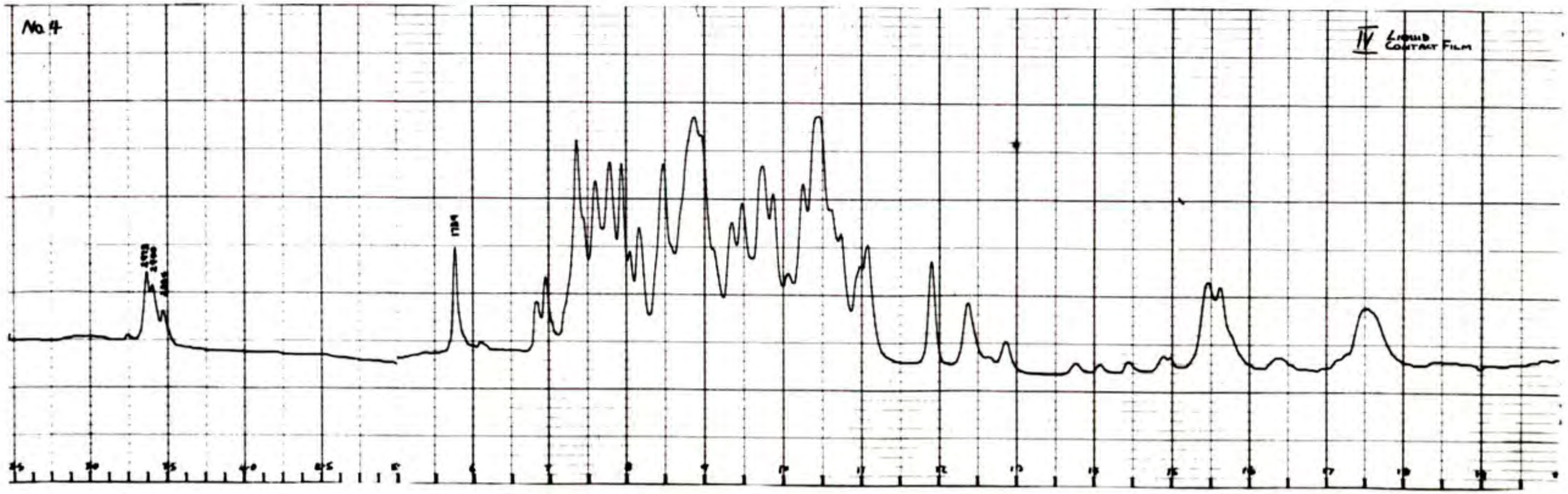
3775; 4529 $(=CF)$

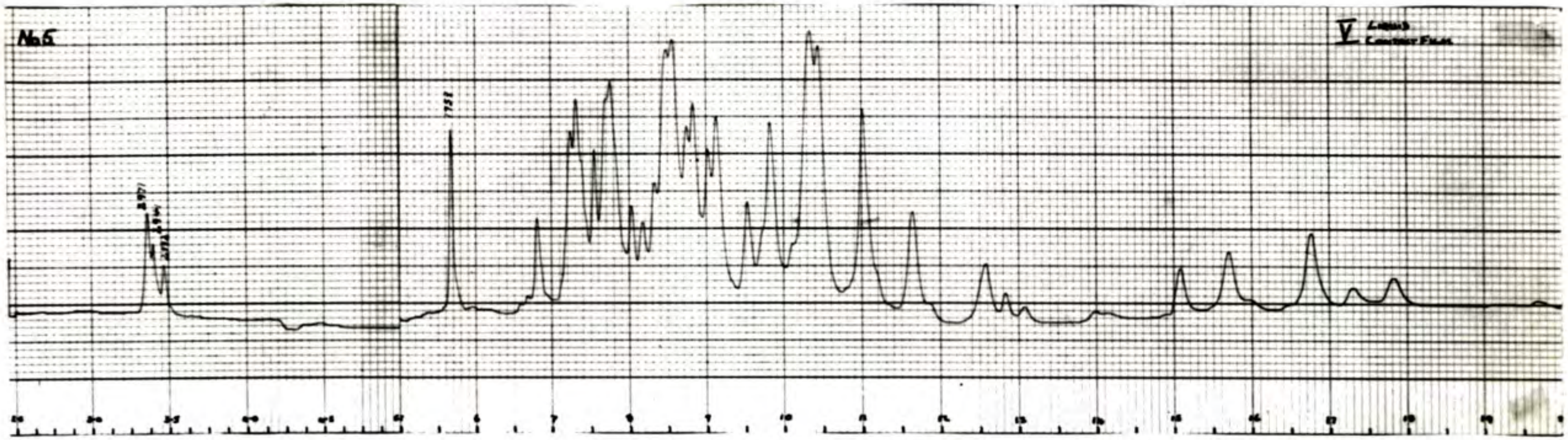
4605; 5175 $({-}\!\!>CF)$

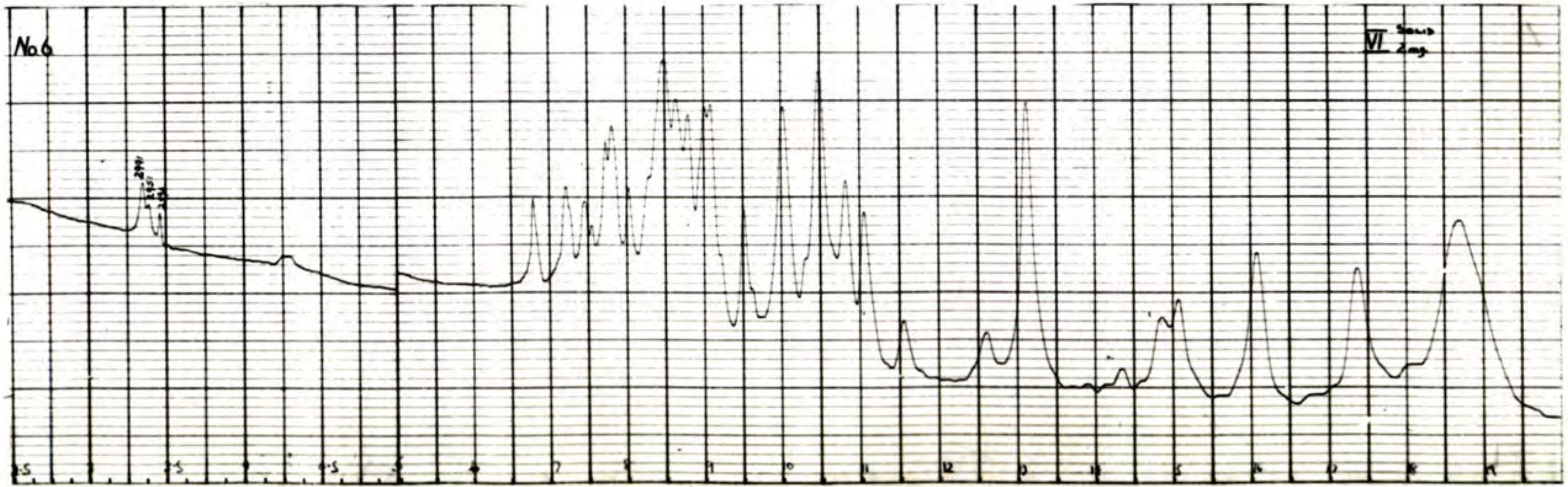

No.1
I

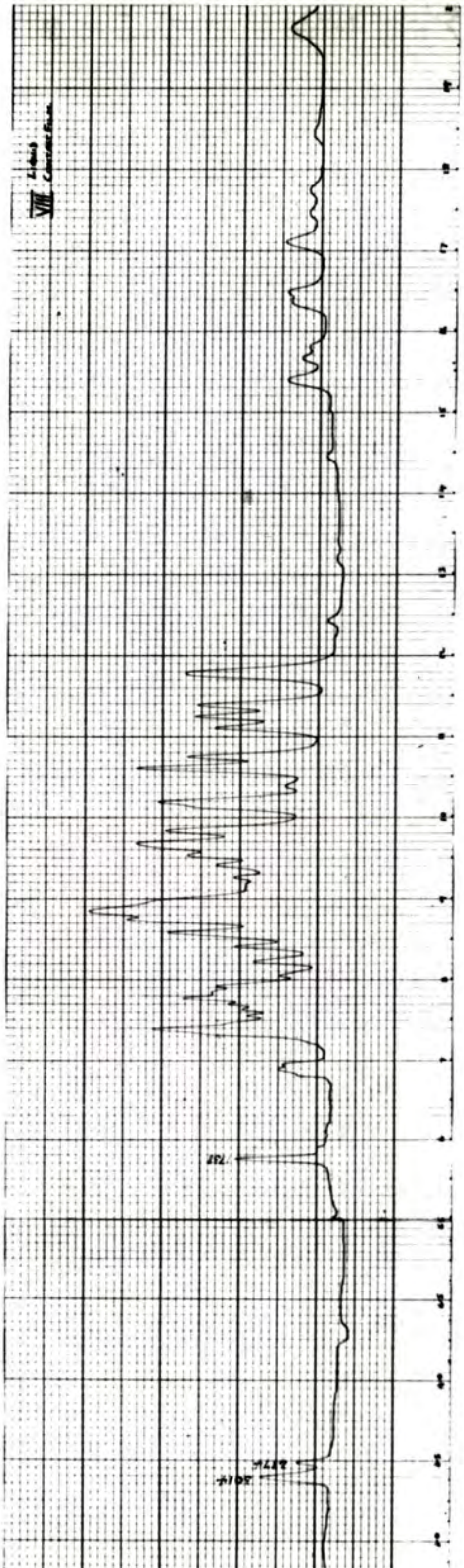

No.2
II

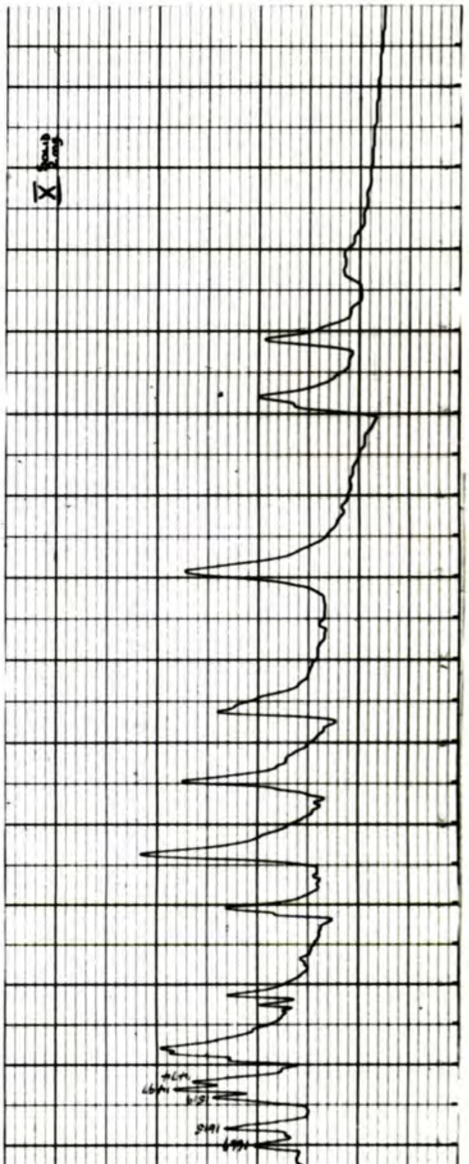

No.3
III Liquid Contact Film
3072
2880
1736

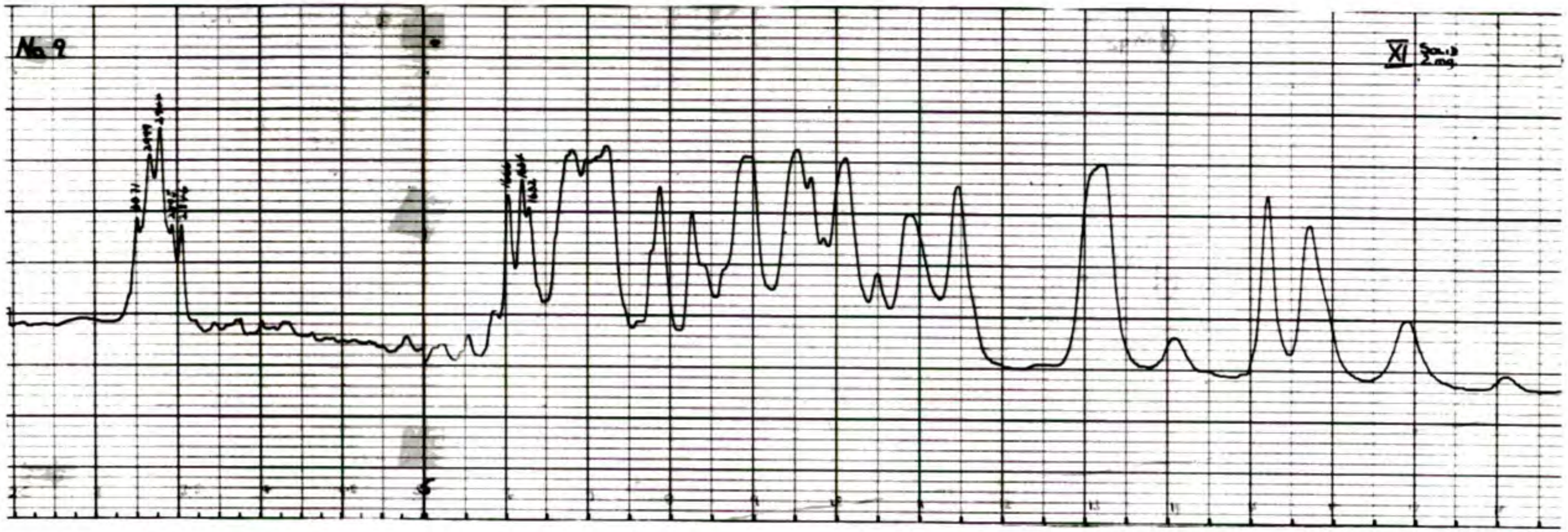

No.4
IV Liquid Contact Film
2973
2940
1734
2.5
3.0
3.5
4.0
4.5
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19


No.5
V Liquid Capillary Film
2971
2941
2872
1738


No.6
VI Solid 2mg

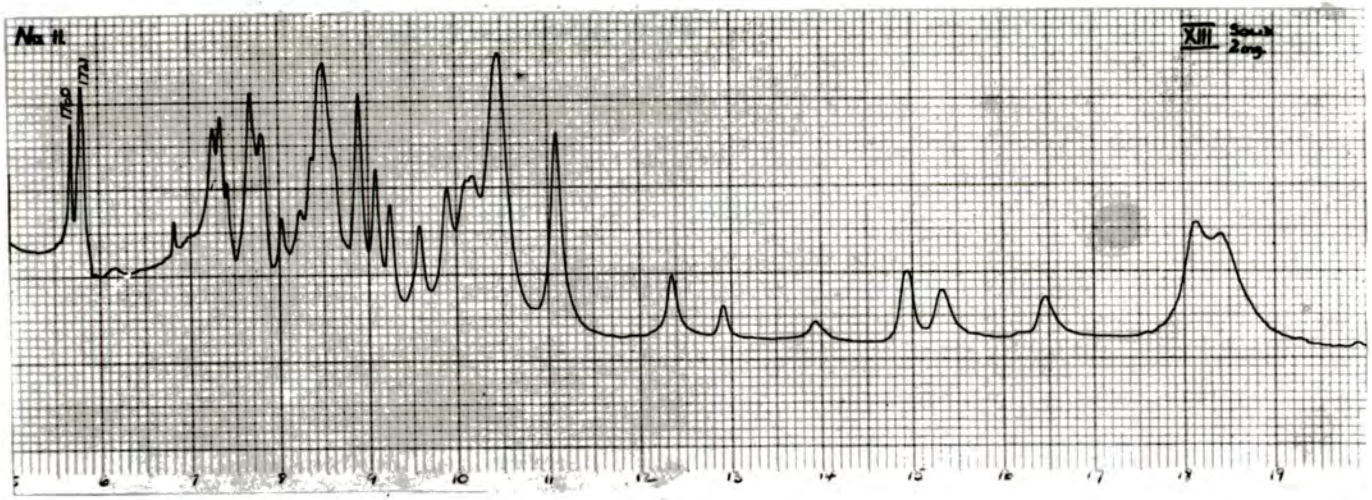

No.7
VIII Liquid Capillary Film
3014
2874
1738


No.8
X Solid Disc
1474
1497
1514
1615
1667

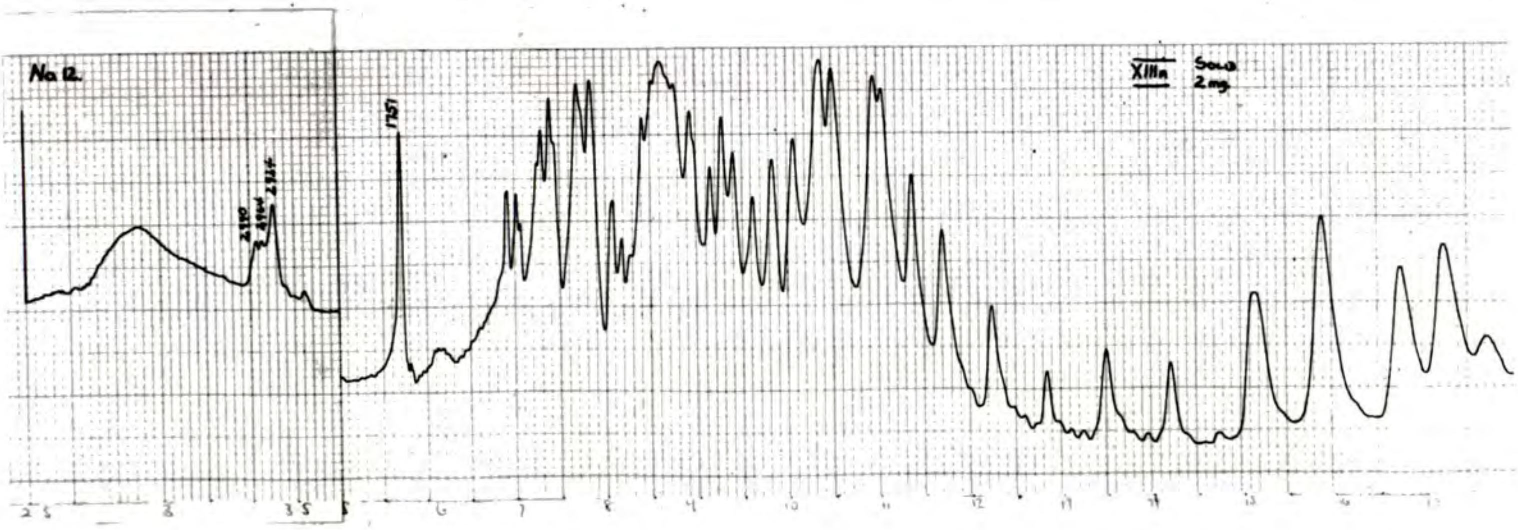

No. 9
XI
Solid
2 mg

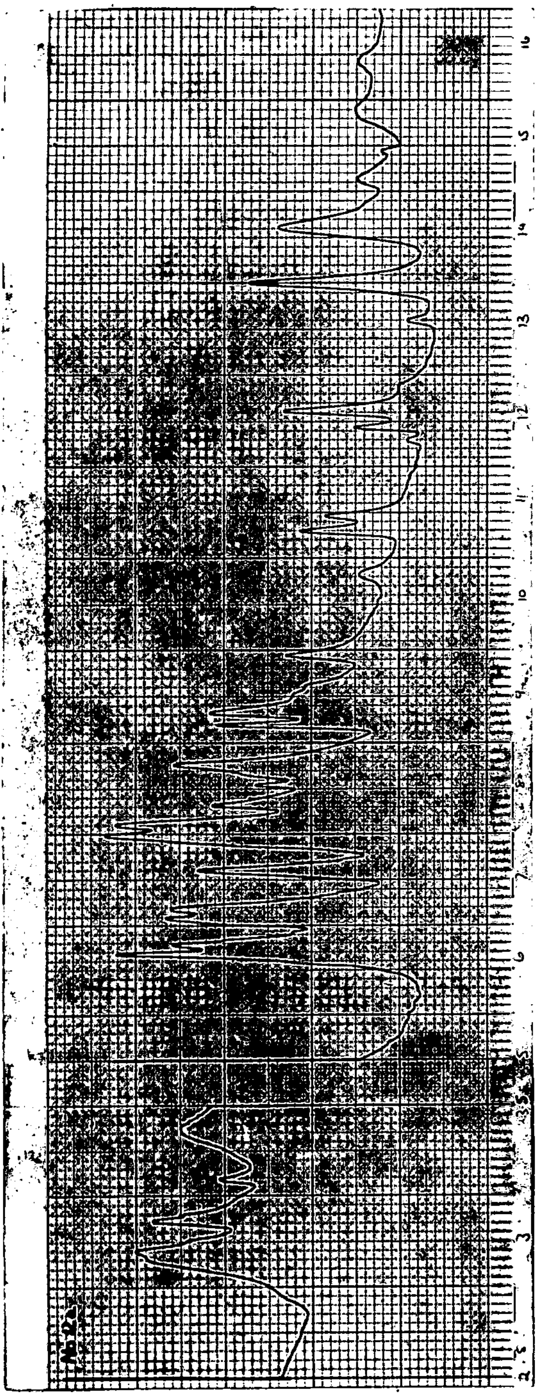

No. 10
XII
Solid
2 mg
1677
1620

No. 11


1760
1721
XIII Soln 2 mg
6
7
8
9
10
11
12
13
14
15
16
17
18
19

No. 12


2880
2904
2934
1751
XIIIa Soln 2 mg
2.5
3
3.5
6
7
8
9
10
11
12
13
14
15


No.12a
3
6
9
10
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14
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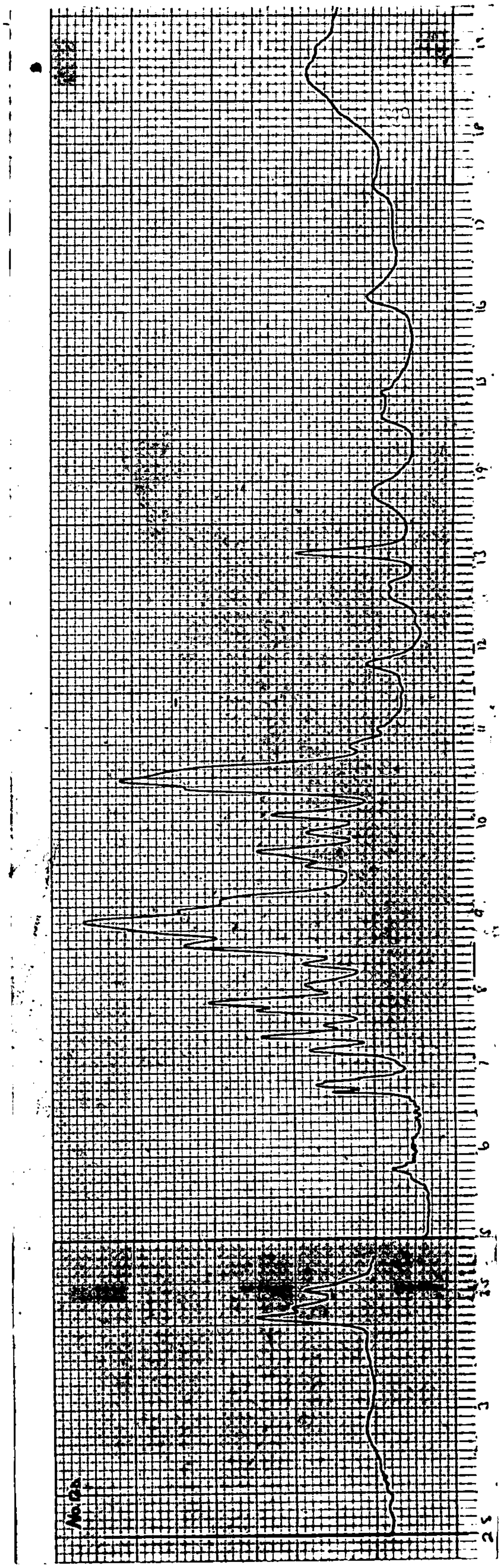
16


No.12b
2.5
3
3.5
5
6
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14
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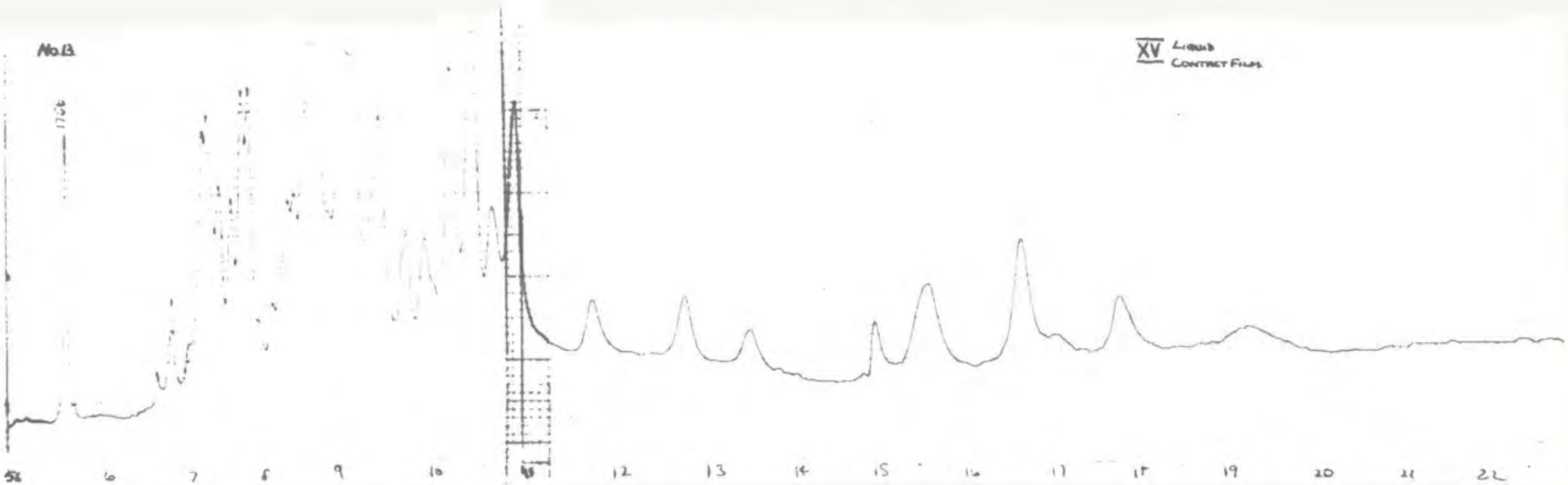
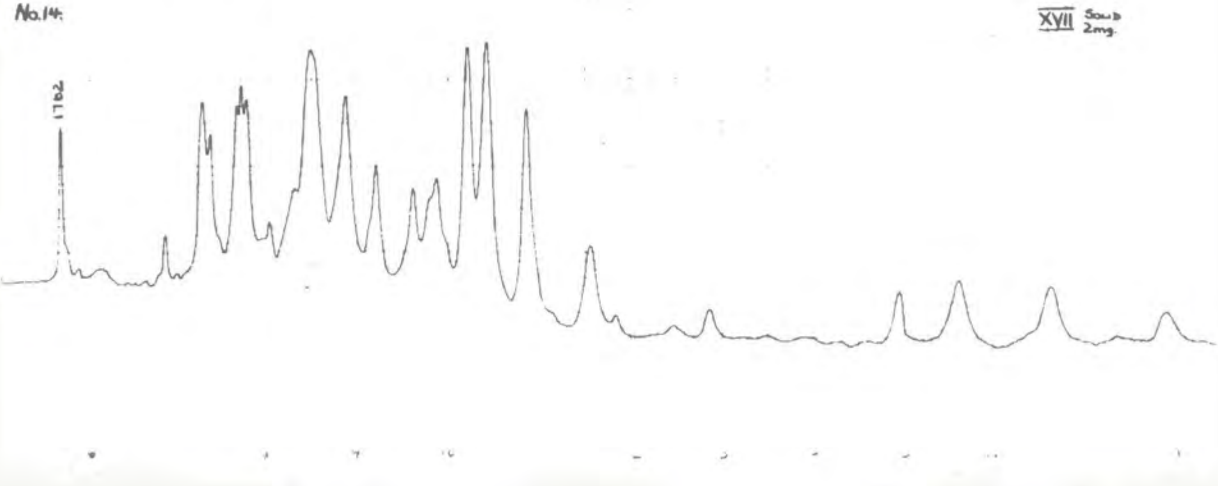
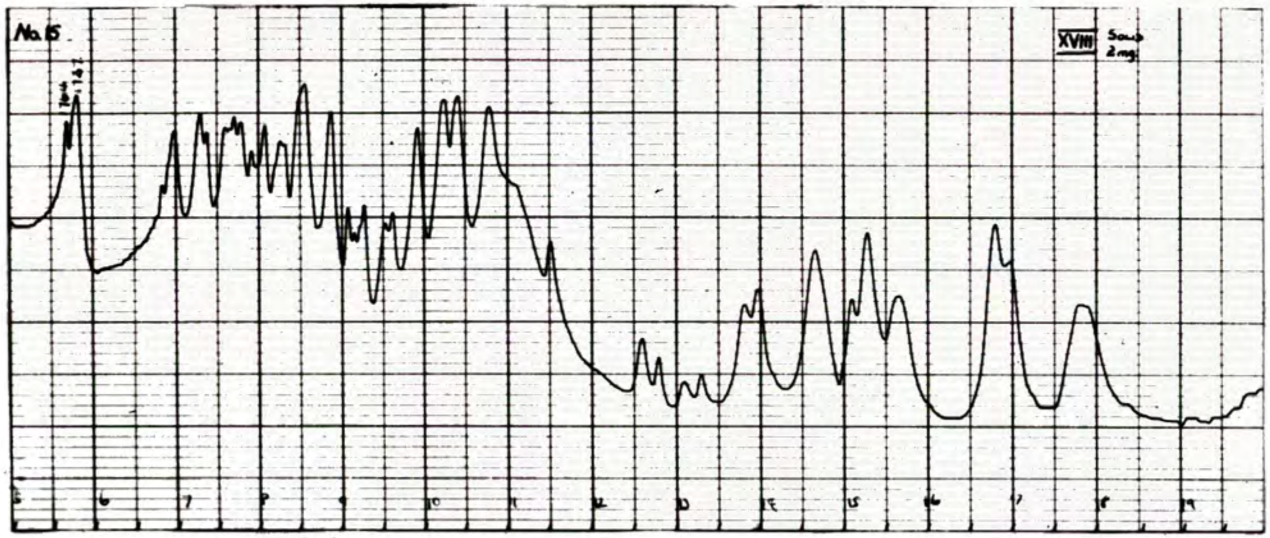
17
18

No.13


1736
XV Liquid
Contact Film
56
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

No.14

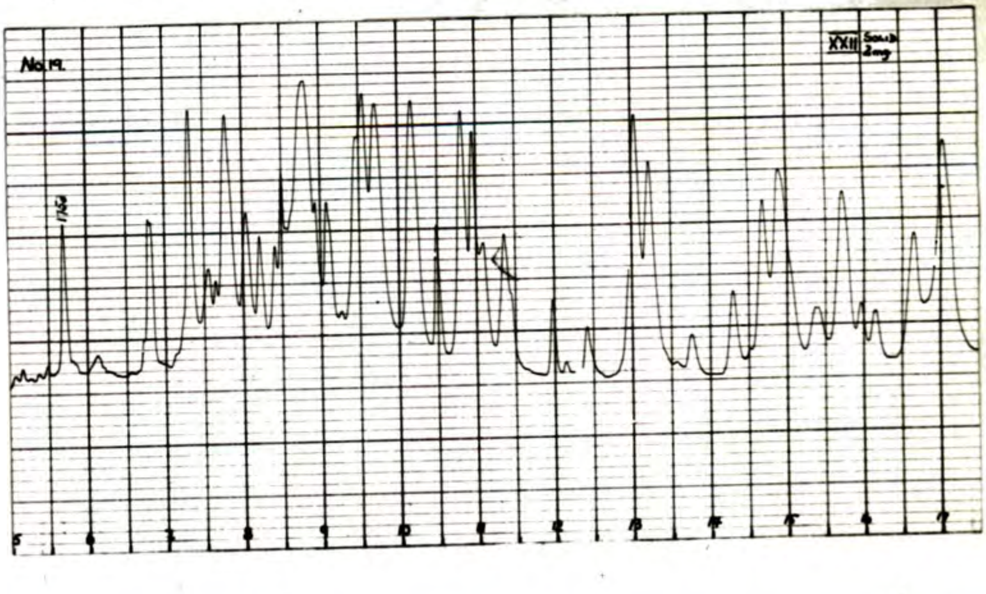

1762
XVII Solid
2mg.


No.15
1742
XVIII
2 mg
6
7
8
9
10
11
12
13
14
15
16
17
18
19


No.16
XIX
2 mg


No.17
XX Liquid Capillary Film
3086
3010
2959
1769
2.5
3
3.5
5
6
7
8
9
10
11


No.18
XXI Solid 2mg
1821
1807
1780
5
6
7
8
9
10
11
12
13
14
15
16
17
18


No.19
XXII Solid 2mg
1760
5
6
7
8
9
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12
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FIGURE 3. Weather conditions in the Durham area during the study period, November 1965 to August 1966.

Monthly mean temperature (deg. C.) - - - - - - - - - -

Monthly mean maximum temperature (deg.C.) o————o————o

Monthly mean minimum temperature (deg.C.) x————x————x

Hours of sunshine per month. —·—·—·—·—

Rainfall (inches per month). •————•————•————•

WEATHER CONDITIONS

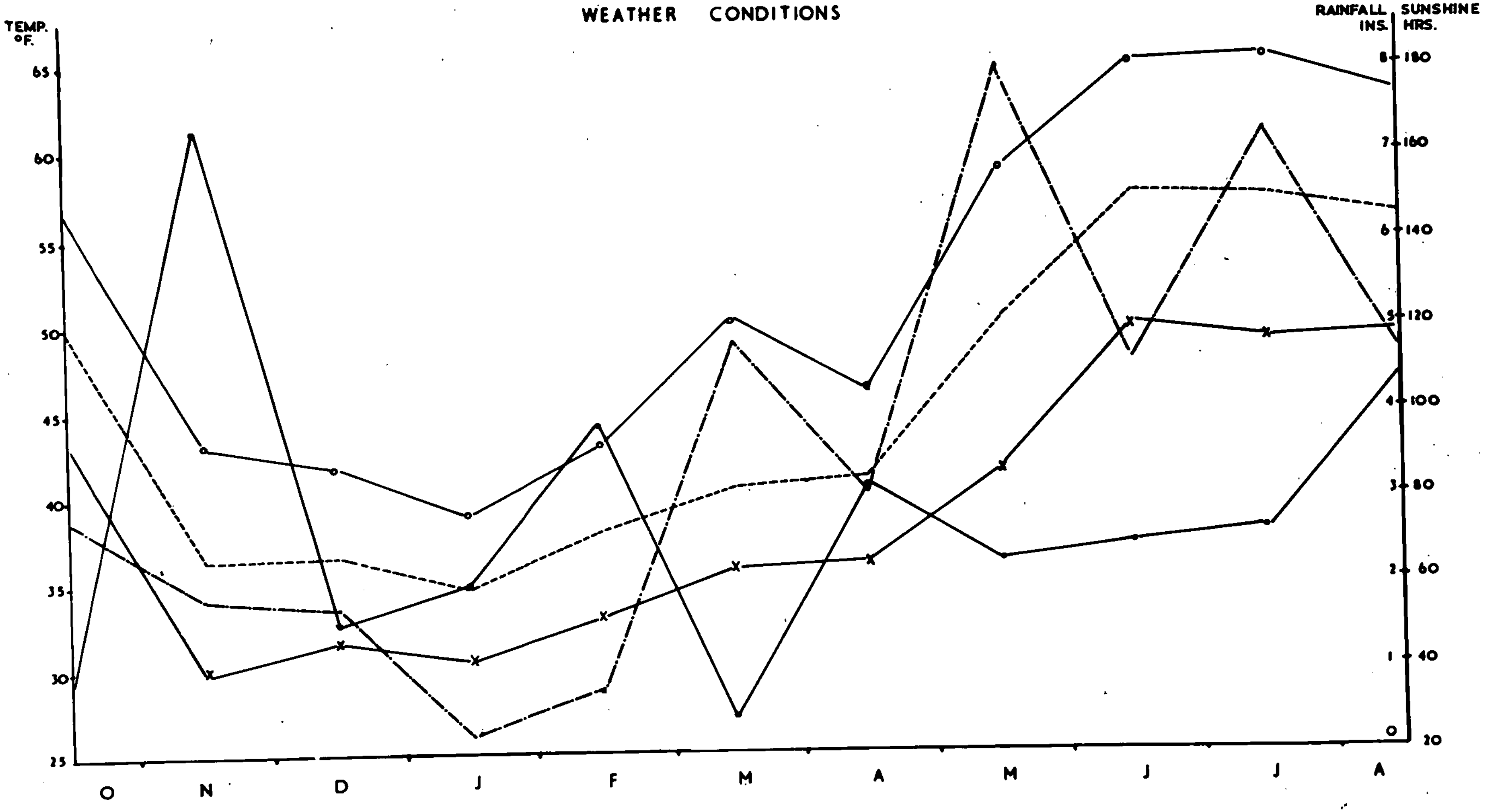


FIGURE 4. Pond A chemical data.

pH ------

Conductivity (mhos). ....

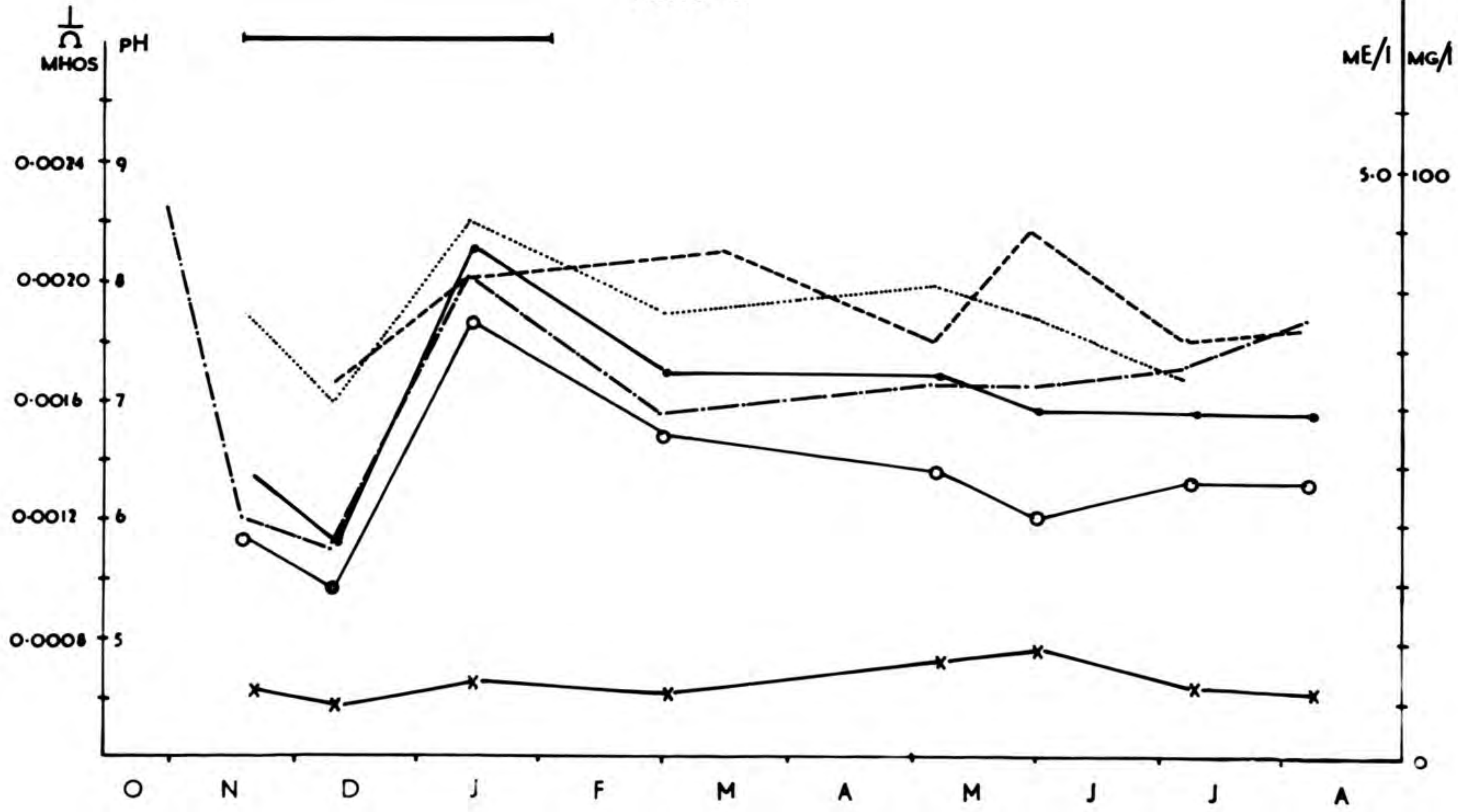
Alkalinity (mE/l.). —·—·—·—

Total Hardness (mg./l.). •——•——•

Calcium concentration (mg./l.). o——o——o

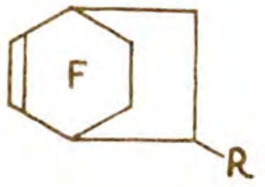
Magnesium concentration (mg./l.). x——x——x

POND A



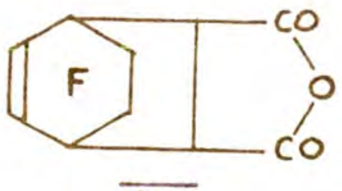
$\frac{1}{\Omega}$ MHOS
PH
0·0024
9
0·0020
8
0·0016
7
0·0012
6
0·0008
5
ME/l
MG/l
5·0
100
0
O
N
D
J
F
M
A
M
J
J
A

STRUCTURES of ADDUCTS and DERIVED COMPOUNDS

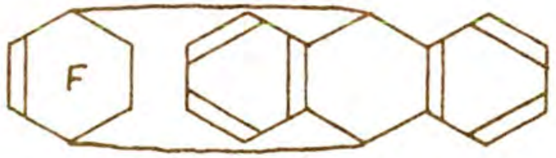


XIII	$-COCH_3$
XV	$-OCH_2CH_3$
XVII	$-CN$
XVIII	$-COOH$
XIX	$-C_6H_5$
XX	$-COOCH_3$

XIV	$-COCH_3$
XVI	$-OCH_2CH_3$

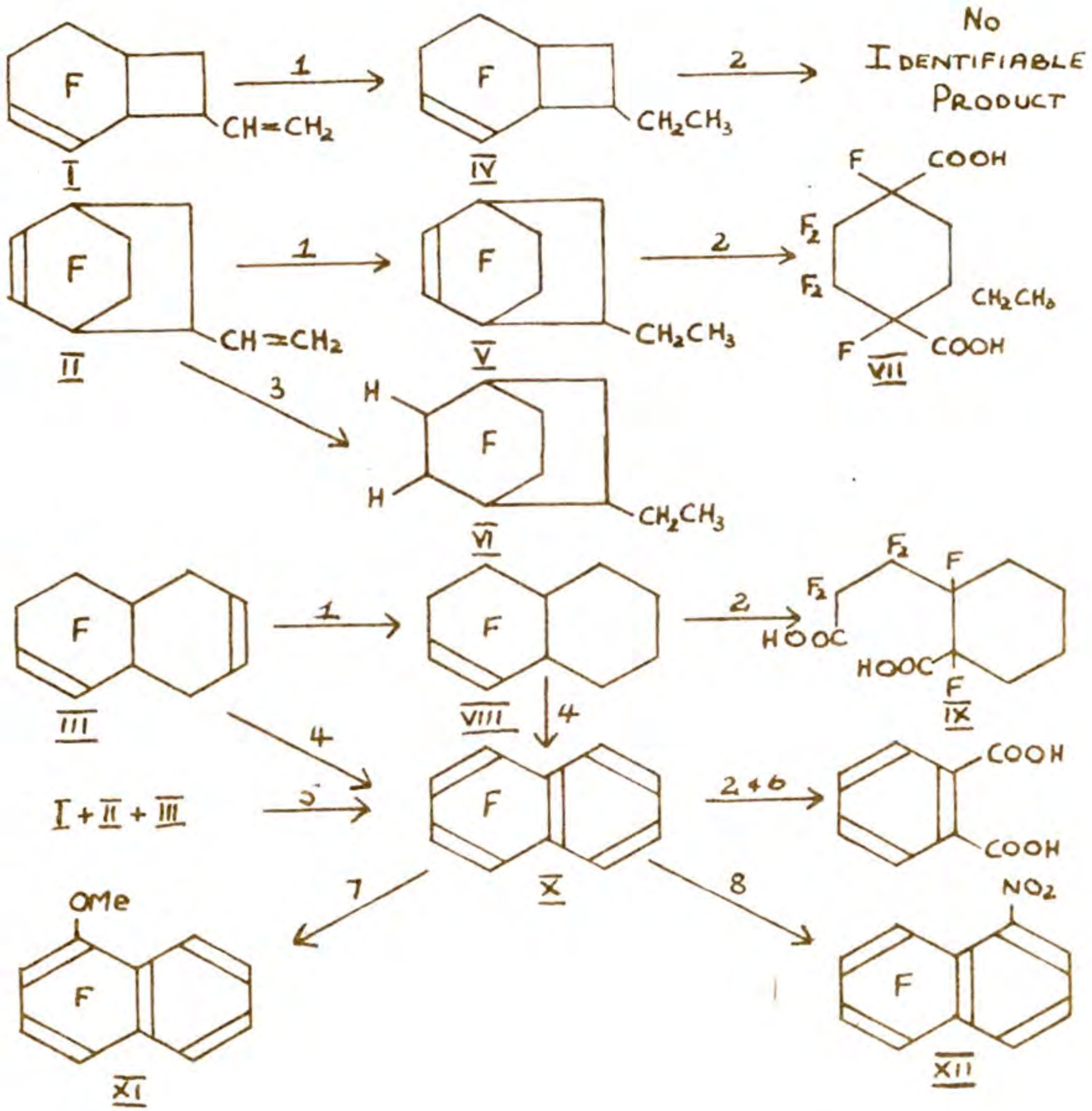


XXI



XXII

REACTIONS of BUTADIENE ADDUCTS.



1. $H_2/Pd/C$
2. $KMnO_4$/ACETONE
3. $2H_2/Pd/C$
4. Fe POWDER 310°
5. STEEL WOOL 425°
6. CrO_3/CH_3COOH or AIR/V_2O_5
7. Na/MeOH
8. HNO_3/H_2SO_4