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W I T H

C O M P O U N D S C O N T A I N I N G T R I P L E B O N D S

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A thesis submitted for the degree of Doctor of Philosophy

by

LEONARD PHILIP ANDERSON, B.Sc.

(GREY COLLEGE)

* * * * * * * * *

UNIVERSITY OF DURHAM

1969

S U M M A R Y

Diels-Alder reactions pf perfluorocyclohexa-1,3-diene with compounds containing triple bonds.

This work provides a synthetic route to a large number of new polyfluoro-aromatic and heteroaromatic compounds. The method depends upon the initial Diels-Alder reaction between perfluorocyclohexa-1,3-diene, a commercially available product, and the triple bond of an alkyne, nitrile or thiazyl chloride.

Heating the diene with alkynes in a sealed tube at 200° produces 1:1 Diels-Alder adducts. The yields are increased by electron-donating substituents, thus showing the "inverse electron demand" of perfluorocyclohexa-1,3-diene in Diels-Alder reactions with alkynes. Pyrolysis of the adducts in vacuo results in the elimination of tetrafluoroethylene and the formation of 1,2-disubstituted tetrafluoro-benzenes. These are the sole products, except in cases where the substituent groups can also undergo elimination reactions under the conditions used.

The reaction with nitriles is less versatile, and boron trifluoride added as a catalyst has no apparent effect. Adducts are formed only with nitriles containing highly electronegative substituents, and a reaction temperature of ca. 400° is required. These forcing conditions

cause the elimination of tetrafluoroethylene in situ, and hence the adducts are not normally isolated. The major difference between these and the alkyne adducts is that, on pyrolysis, there is competition between the required formation of a 2-substituted tetrafluoropyridine and the reverse Diels-Alder reaction, which merely reforms starting materials. At 400° perfluorocyclohexa-1,3-diene also forms a Diels-Alder dimer and a 1,2- cycloadduct with tetrafluoroethylene, both previously unreported compounds.

Heating the trimer of thiazyl chloride with perfluorocyclohexa-1,3-diene at 100° produces a compound which has properties consistent with the 1:1 Diels-Alder adduct of thiazyl chloride monomer and the diene. The evidence, however, is not conclusive, since structural data is not unambiguous.

A C K N O W L E D G E M E N T S

The author is indebted to Dr. W.J. Feast and Professor W.K.R. Musgrave for their continued help and encouragement during the supervision of this work, and to Dr. A.J. Banister for many consultations on sulphur-nitrogen chemistry. Assistance from the numerous technical and laboratory staff is greatly appreciated, and thanks are also due to the Science Research Council for the award of a maintenance grant.

M E M O R A N D U M

The work described in this thesis was carried out in the Chemistry Laboratories of the University of Durham between October 1966 and August 1969. This work has not been submitted for any other degree and is the original work of the author, except where acknowledged by reference.

Part of this work has been the subject of the following publications:-

L.P. Anderson, W.J. Feast and W.K.R. Musgrave, Chem. Comm., 1433 (1968); provisional B.P., 51554/68 (1968); J. Chem. Soc. (C), 211 (1969); J. Chem Soc. (C), accepted for publication.

C O N T E N T S

Page

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F O R E W O R D

This thesis describes the use of perfluorocyclohexa-1,3-diene, a commercially available starting material, in the preparation of a large number of highly fluorinated aromatic and alicyclic compounds.

Fluorocarbon compounds are unique in organic chemistry. They provide a completely different electronic environment for functional groups without significantly affecting the stereochemistry of their hydrocarbon analogues. A novel set of chemical and physical properties arise which are interesting both academically and industrially. At present, aromatic fluorocarbon compounds have not found any really important commercial outlets. Nevertheless, industrial research into these compounds is continuing because aliphatic and alicyclic fluorine compounds are already used in a wide variety of products, from aerosol propellants to thermally stable polymers.

However, most of the discussion is concerned with the synthetic aspects of the work, and the way in which the results correlate with presently held theories about the Diels-Alder reaction. A broad survey of this field is given in the Introduction, which consists of a chapter on cyclic dienes, followed by chapters on alkynes, nitriles, other dienophiles containing triple bonds, and possible mechanisms of Diels-

Alder reactions. Although applied studies are beyond the scope of the experimental work, there has been sufficient interest in some of the reaction products to warrant the application for a provisional patent. Another electron-deficient diene, perchlorocyclopentadiene, undergoes similar Diels-Alder reactions from which the powerful insecticides Dieldrin and Aldrin are derived. Many fluorocarbon compounds are biologically active and it is possible that some of the compounds prepared may also be potential insecticides or herbicides.

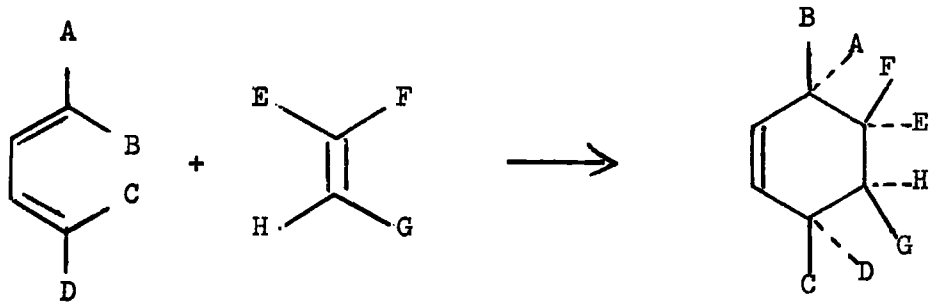
PART I

INTRODUCTION

CHAPTER 1. CYCLIC DIENES IN THE DIELS-ALDER REACTION.

1.1] Cis- principle and the effect of ring size.

The Diels-Alder reaction, in which a conjugated diene (I) reacts with an unsaturated compound, the dienophile (II), to yield a six membered ring is well-known and has proved very useful synthetically and interesting theoretically for many years.



I II

Early workers in the field soon recognized the high stereospecificity of the reaction and results led to the formulation of the "cis- principle".[1,2] This principle has two parts:

(i) the relative position of the substituents remains the same in the products as in the starting materials. Thus, in the general case above, substituents B and C in the diene and F and G in the dienophile remain cis to each other. There is no free rotation about the dienophile double bond - hence providing good evidence for a concerted one-step mechanism.

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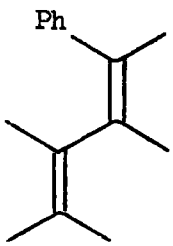
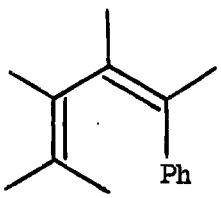
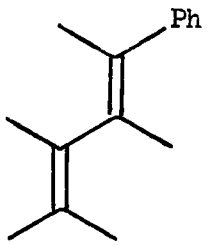
(ii) The conjugated double bonds in the diene must be cis-orientated. This can be illustrated by the addition of maleic anhydride to 1-phenylbuta-1,3-diene.[3] Butadienes may exist in transoid (a) and cisoid (b) conformations, which are shown below for cis- (III) and trans-1-phenylbuta-1,3-diene (IV).



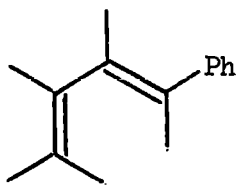
IIIa



IIIb



IVa



IVb

Steric interactions make IIIb energetically less favourable than IIIa and consequently conformer IIIb is present only as a small percentage of the equilibrium mixture; no such rotational restriction apply to IV. Under the same conditions, isomer IV gives a quantitative yield of adduct whereas III gives only a 5% yield.

All the alicyclic dienes under consideration in this Chapter have the cis- orientation of double bonds constrained upon them by their basic structures. In these cases, therefore, the distance between the termini of the conjugated system is a very important consideration. This is reflected by the second order rate constants (k_2, in $l.mole^{-1}sec.^{-1}$) in the addition of maleic anhydride (MA) and tetracyanoethylene (TCNE) to cyclopenta- and hexa-1,3-diene.[4] A greater activation energy (E) is

involved in going from reactants to transition state for hexadiene and the considerable reduction of rate can be seen in Table 1.1(i). When

TABLE 1.1(i). Effect of ring size on rates.

Diene	Interterminal Distance (Å)	TCNE (20°)	MA (30°)	
		k_2	k_2	E (kcal.mole^{-1})
Cyclopentadiene	2·44	$4·3 \times 10^{2}$	$9·2 \times 10^{-2}$	8·9
Cyclohexa-1,3-diene	3·04	$7·3 \times 10^{-2}$	$1·3 \times 10^{-4}$	12·6

1,1-dichlorodifluoroethylene ("1122") is the dienophile there is competition with the alternative 1,2-addition across one double bond. Since the bond length of the 1,1-dichlorodifluoroethylene is only 1·34Å 1,4-addition takes place more easily as the interterminal distance reduces [see Table 1.1(ii)].[5]

TABLE 1.1(ii). Effect of interterminal distance with "1122" addition.

Diene	Interterminal Distance (Å)	% 1,4-Addition
	3·35	< 1
	3·04	6
	3·04	30
	< 3·04	56
	2·44	84

The difference between the amounts of 1,4-addition between cyclohexadiene (6%) and 1,2-dimethylenepentane (30%) is large considering that both have the same interterminal distance (3·04Å). The lack of coplanarity of the former [Fig. 1.1(i)][6], with consequent loss of conjugation, is a possible explanation of this effect.

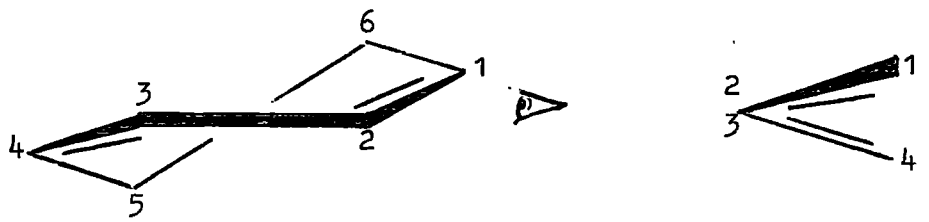
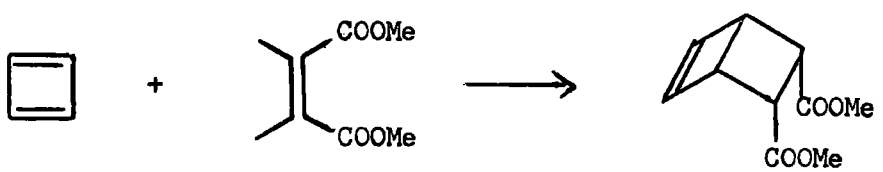
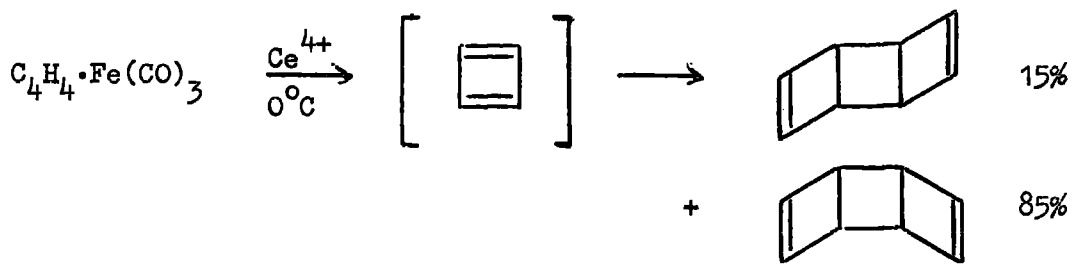


Fig. 1.1(i). Conformation of cyclohexa-1,3-diene.

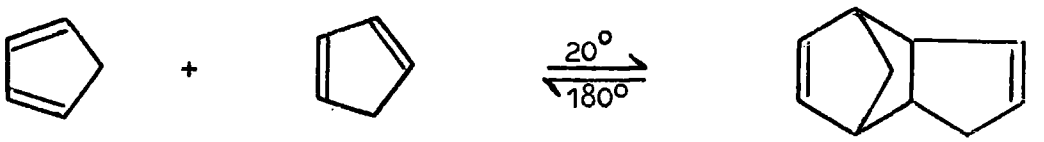
Cyclo-octa-1,3-diene has practically no ability to undergo 1,4-addition,[7,8] and it takes place again only with 14- and 15-membered ring dienes (and then under severe conditions).[9] Cyclobutadiene should be regarded as a special case. This highly strained rectangular molecule has the shortest possible distance for a dienophile to add across (calculated 1·514Å[10] or 1·498Å[10a]) but there is practically no conjugation (calculated 0·8 kcal.mole^{-1}).[10] It is difficult to distinguish Diels-Alder type addition from 1,2-addition but the stereospecific cis addition of dienophiles provides evidence for the former mode, i.e. the "cis- principle" holds.[11]



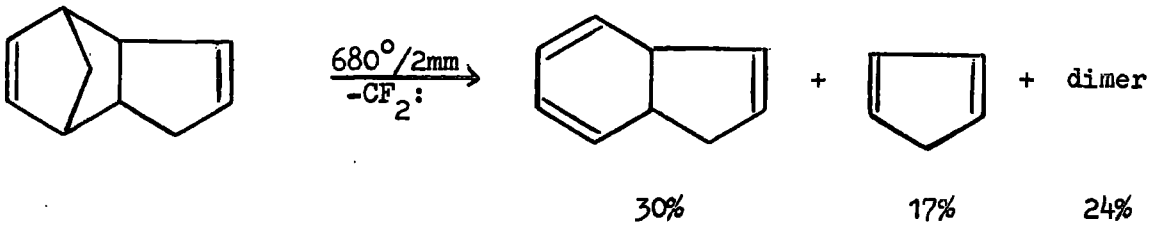
Another factor which is dependent on ring size is the ease of dimerization of certain cyclic dienes. Thus, cyclobutadiene undergoes dimerization at 0° and has not even been isolated as the monomer.[11]



Cyclopentadienes are also rigidly cis-coplanar and have an ideal interterminal distance to undergo 1,4-addition [Table 1.1(ii)] and cyclopentadiene itself readily forms its Diels-Alder dimer at room temperature. The reverse reaction at higher temperatures allows the dimer to be used as a source of cyclopentadiene.[12] Perfluorocyclo-



pentadiene is even more susceptible to the same dimerization,[13,14,15] 80% when stored at room temperature for 14 days and 26% at -10° for 24 hrs. The monomer must be stored at -196° in vacuo. The reverse reaction to cleave the dimer does not quantitatively produce the monomer. It remains unchanged in a sealed glass tube at 475° for 45 min. and on flow pyrolysis the greatest yield is 17%. There is a greater tendency to lose the CF_2 bridge as difluorocarbene.[15]

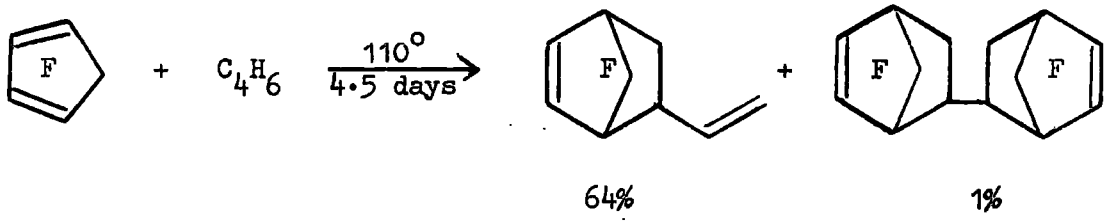


(all unmarked bonds to F)

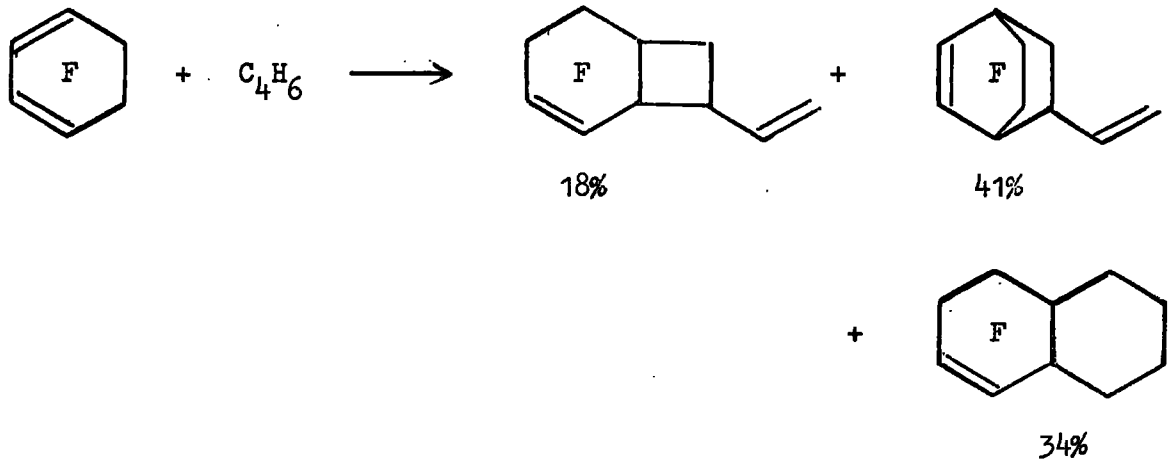
On the other hand, perchlorocyclopentadiene is perfectly stable as a monomer at room temperature. This failure to produce the Diels-Alder dimer directly is probably due to the steric effect of the chlorine atoms since Alder described it as "the diene with the highest possible addition ability".[7]

The geometry of cyclohexadienes is less favourable for 1,4-addition [Fig. 1.1(i)]. However, Diels-Alder reactions are well established, and cyclohexadiene does dimerize (180-200° for 24 hrs.), although yields are not quantitative (ca. 30-40%).[15a]

Perfluorocyclohexa-1,3-diene has been shown to act as the diene in Diels-Alder reactions.[16,17] Although no relative rates have been measured there are distinct product differences compared to the Diels-Alder additions with perfluorocyclopentadiene.[18] The latter may be classified as the "stronger" diene since it acts only as a diene with butadiene - giving only 1,4-addition products, which include a 2:1 adduct.[18]

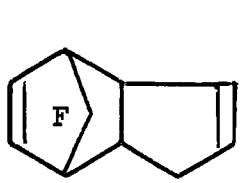


At a similar temperature perfluorocyclohexa-1,3-diene forms a mixture of 1,2-and 1,4-addition products and it also acts as a dienophile, by 1,4-addition to butadiene.[16,17]

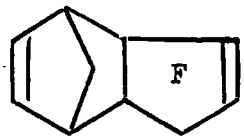


Again the simplest rationalization of these results is the size of the ring involved, as the electronic and steric effects of the fluorine atoms will be fairly similar.

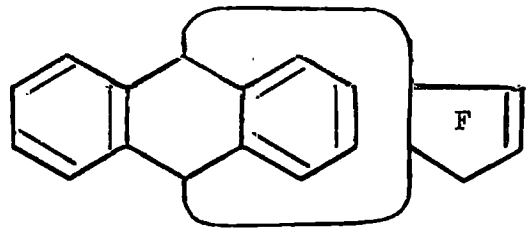
If another diene is sufficiently reactive perfluorocyclopentadiene can also react as a dienophile. Cyclopentadiene appears to have about equivalent "strength" and both possible adducts are obtained (compounds V and VI). As expected, with anthracene it behaves only as a dienophile to give VII.[18]



V

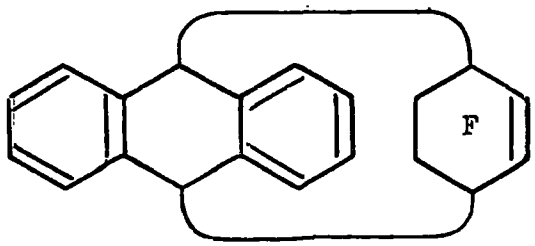


VI



VII

Pyke[16] reports that anthracene undergoes an unusual 4+4 addition[19] with perfluorocyclohexa-1,3-diene resulting in the formation of VIII (7% yield, 99° for 48 hr.). Although the i.r. absorption at 1753 $cm.^{-1}$



VIII

(CF=CF) correlates with that particular fluorinated ring system (1758 ± 6 $cm.^{-1}$) it is unlikely that such a symmetrical molecule should have nine separate ^{19}F n.m.r. resonances [at -45·1, -43·6, -40·8, -37·4, -32·6 (CF_2); -20·8, -8·2 (=CF-); -6·9, +2·5 (C-F) (shifts in p.p.m., with respect to hexafluorobenzene)]. These values would be expected by the straightforward 4+2 addition to anthracene - thus producing the adduct corresponding to VII.

1.2] Electronic effects.

The "Alder Rule"[7] states that the rate of addition generally increases with electron donating substituents in the diene e.g. $N(Me)_2$, OMe, Me and with electron withdrawing substituents in the dienophile e.g. CN, COOMe, CHO, NO_2. This is illustrated by the results in Tables 1.2(i)[4] and 1.2(ii).[20] The fact that the only authenticated 1,4-additions of

TABLE 1.2(i). Effect of substitution in the diene.

Diene	Rel. rate TCNE : diene addition
2-Chlorobutadiene	1·0
Butadiene	$5{\cdot}2 \times 10^2$
2-Methylbutadiene	$1{\cdot}1 \times 10^3$
2,3-Dimethylbutadiene	$2{\cdot}4 \times 10^4$
1-Methoxybutadiene	$6{\cdot}0 \times 10^5$
Perchlorocyclopentadiene	0
Cyclopentadiene	$4{\cdot}3 \times 10^7$

highly fluorinated butadienes are those of trifluoronitrosomethane with 2,3-dihydro- and perfluorobutadiene[21,22] is also consistent with this rule. Here the products were accompanied by considerable amounts of resin, whereas it reacts quantitatively with hydrocarbon butadiene at -78°.[23]

TABLE 1.2(ii). Effect of electron withdrawal from dienophile.

Dienophile	Rel. rate cyclopentadiene : dienophile
Acrylonitrile	1
Cis-1,2-dicyanoethylene	91
Trans-1,2-dicyanoethylene	81
1,1-Dicyanoethylene	4.5×10^4
Tricyanoethylene	4.8×10^5
Tetracyanoethylene (TCNE)	4.3×10^7

Since, as in Table 1.2(i), the presence of halogen atoms markedly reduces the rate of addition, polyhalocyclic dienes might be expected not to undergo the Diels-Alder reaction readily. This is not the case. A review catalogues about a hundred such reactions of perchlorocyclopentadiene.[24] In such cases, however, the order of reactivity with the dienophile is often inverted compared to its addition to an electron rich diene. Table 1.2(iii)[25] shows how the rates are affected by electron withdrawal from the dienophile. The results with perchlorocyclopentadiene are the opposite to those expected by using the "Alder Rule" and they illustrate a particular example of reactions with "inverse electron demand"[26,27] i.e. the rate of addition increases with electron withdrawing substituents in the diene and electron donating substituents in the dienophile. No satisfactory explanation has been given for these effects.

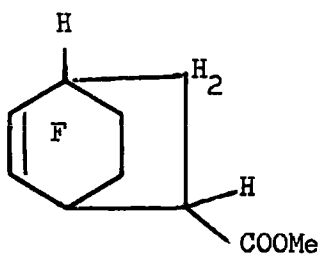
TABLE 1.2(iii). Inverse electron demand.

Dienophile	$10^6 k_2$ (l.mole^{-1}sec.$^{-1}$)	
	Perchlorocyclopentadiene	9,10-Dimethylanthracene
p-Methoxystyrene	1.6×10^3	50
Styrene	7.9×10^2	70
p-Nitrostyrene	5.4×10^2	6.0×10^2
Cyclopentadiene	1.5×10^4	0
Cyclopentene	59	78
Maleic anhydride (MA)	29	1.4×10^6

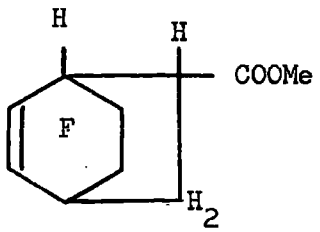
Nevertheless, from this it can be predicted that perfluorocyclohexa-1,3-diene and other highly fluorinated dienes will take part in Diels-Alder reactions with "inverse electron demand" and probably with electron rich dienophiles.

At present, working from the above principles, it is not possible to explain the effect of introducing a proton into a fluorinated diene system. 2H-Pentafluorocyclopentadiene dimerizes irreversibly, too fast for it to be used in a Diels-Alder reaction.[28] This irreversibility is in contrast to dicyclopentadiene, but nearer the properties of perfluorodicyclopentadiene. The 1H- isomer, which dimerizes slowly (1 month at 10-15°), does not react with either TCNE (predictable by the "inverse electron demand") or ethyl vinyl ether.[28]

Orientation problems also arise when dealing with unsymmetrical compounds. The reaction of methyl acrylate with 1H-perfluorocyclohexa-1,3-diene gives both of the possible adducts (compounds IX and X), but the yield of each isomer was not quoted.[29]



IX



X

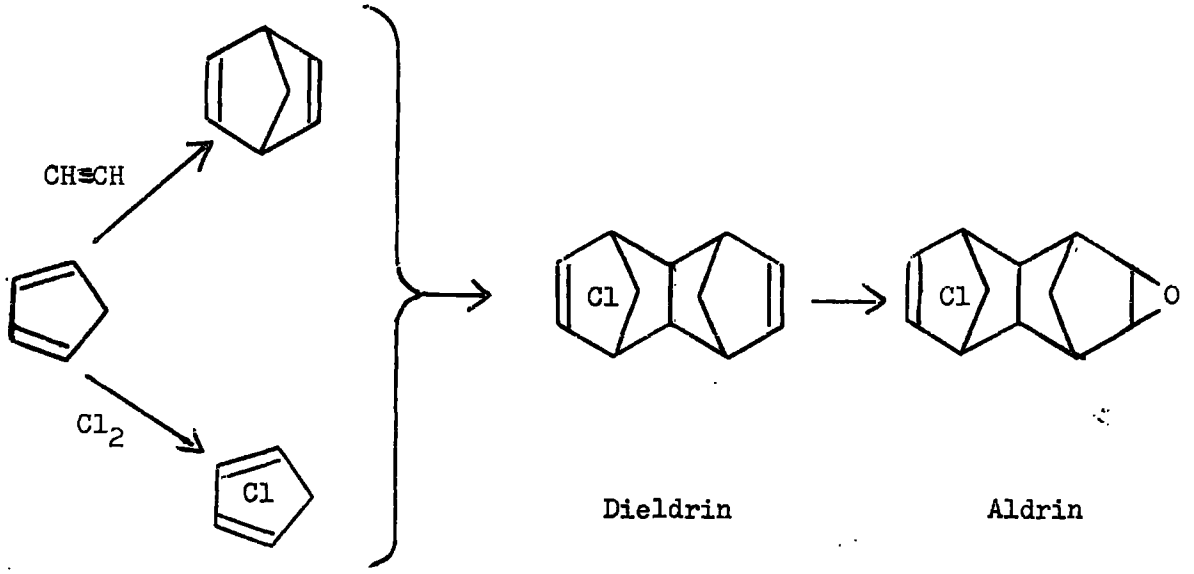
The only other fluorinated cyclic diene which is reported to undergo Diels-Alder reaction is 5,5-difluorotetrachloropentadiene.[30,32] This dimerizes at room temperature and reacts with both electron-rich and electron-deficient dienophiles e.g. pentadiene, p-benzoquinone, p-chlorostyrene and maleic anhydride. However, no relative rates were published. More data needs to be accumulated before accurate predictions of reactivities can be made for this type of compound.

1.3] Synthetic applications.

Diels-Alder reactions of cyclic dienes always produce alicyclic polycyclic compounds, often stereospecifically and in good yield.

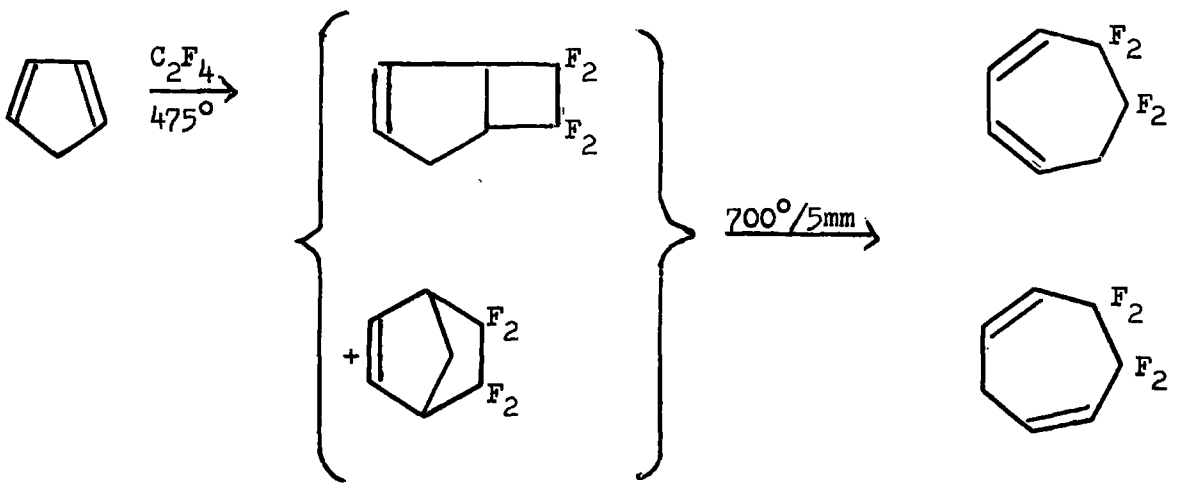
Perchlorocyclopentadiene adducts have many industrial uses. That with maleic anhydride is used in fire resistant paints[24] and that with

bicyclo[2,2,1]hepta-2,5-diene gives the insecticides Dieldrin and Aldrin.[9]

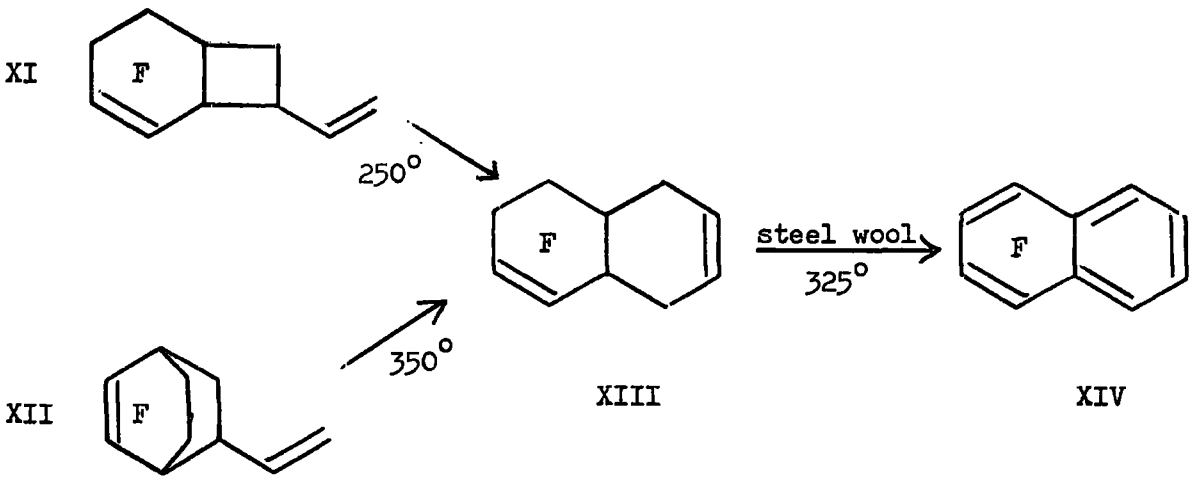


Dieldrin Aldrin

Bicyclic adducts can often be isomerized or pyrolyzed to produce new ring systems - particularly when the dienophile has been an acetylene (see Chapter 2). An interesting example, since it also involves the only known 1,4-addition of tetrafluoroethylene, is the ring expansion by pyrolysis of tetrafluorobicyclo[3,2,0]- and [2,2,1]heptenes into tetrafluoroheptadienes.[33]



The only product obtained by passing over steel wool Pyke's butadiene to perfluorocyclohexa-1,3-diene adducts was 1,2,3,4-tetrafluoronaphthalene (XIV). This is because, under the conditions of these reactions isomerization of the adducts takes place and there is dehydrofluorination as well as defluorination. The [4,4,0]deca-2,8-diene (XIII) is the most thermodynamically stable form, the [4,2,0]octene (XI)



isomerizes at 250° and the [2,2,2]octene (XII) at 350°. This explains why the naphthalene (XIV), formed from all isomers at 425°, is not formed from XII at 325°.[16,17]

Finally there are reactions which retain the basic ring structure. A recent example, involving addition to the double bond in the 6-membered ring, is the cobalt trifluoride fluorination of the adducts of methyl acrylate and 1H-perfluorocyclohexa-1,3-diene (IX and X). Many products are obtained, including perfluorobicyclo[2,2,2]octane.[29]

CHAPTER 2. ALKYNES IN THE DIELS-ALDER REACTION.

2.1] Reactivity.

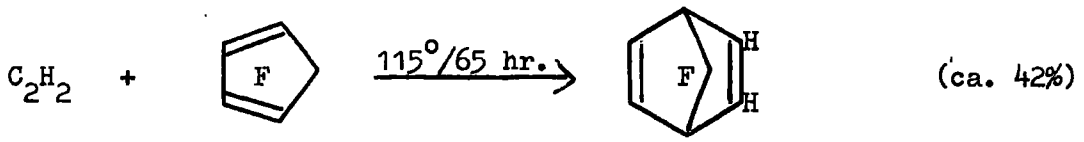
Alkynes readily react with dienes in the Diels-Alder reaction.[9] Their triple bonds have a greater electron density than the corresponding olefins and, as expected from the Alder rule (Chapter 1.2), react at a slower rate [Table 2.1(i)].[34] The Alder rule also predicts the increases in rate obtained by increasing the degree of substitution of electronegative groups [Table 2.1(i)].

TABLE 2.1(i). Application of Alder rule to alkynes and olefins.

Dienophile	Relative rates. Dienophile with 9,10-dimethylanthracene.
H·C≡C·COOMe	1·00
H_2·C=CH·COOMe	6·35
MeCOO·C≡C·COOMe	12·4
MeCOO·CH=CH·COOMe	19·0

Acetylene itself has no electron withdrawing groups and is thus expected to react with electron-rich dienes only under forcing conditions. It is, therefore, for synthetic purposes, considerably safer to react the diene with vinyl bromide and obtain the same product by elimination of HBr in a later reaction.[35] In spite of the danger a good yield of 1,2,3,4,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene was successfully obtained

by heating acetylene with perfluorobicyclopentadiene in a steel autoclave.[18] This is likely to be a case of "inverse electron demand"



applying.

However, the Alder rule does apply to the addition of cyclone to methyl arylpropiolates with substituents of increasing electron withdrawing power. Table 2.1(ii) shows the small increase in rate (k), but fairly constant activation energies (E), and A factors of the Arrhenius rate equation.[36]

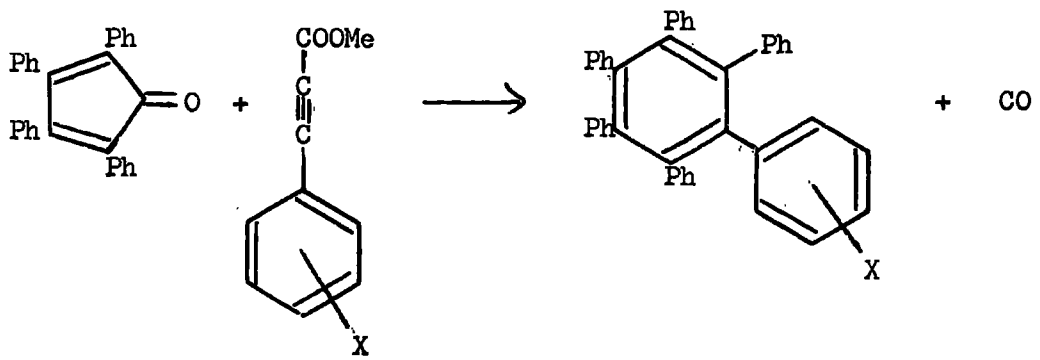
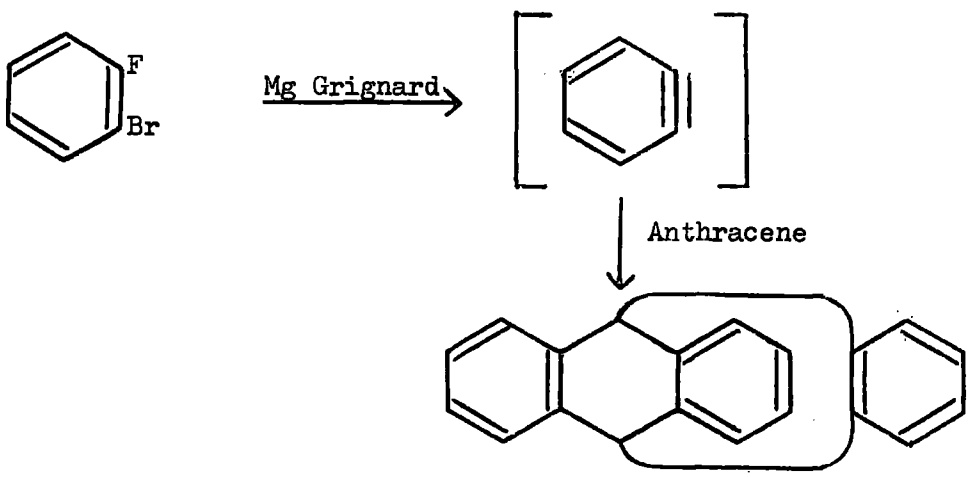


TABLE 2.1(ii). Application of Alder rule in methyl arylpropiolates.

X	10^3 k (175·6°)	E (kcal.mole^{-1})	log A
p-MeO	1·19	20·0	6·8
p-Me	1·26	20·2	6·9
p-H	1·48	20·0	6·8
p-Cl	2·25	18·9	6·6
p-NO_2	7·75	18·4	6·9

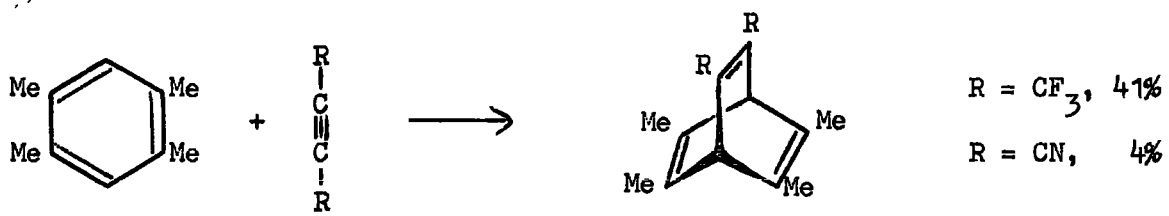
There is a good correlation of these figures with the Hammett "σ^-" parameters obtained from the ionization of phenols. Chapter 5 gives reasons for these pieces of evidence supporting a concerted reaction mechanism.[36]

The most reactive triple bond would appear to be in the highly strained arynes - a classical example being the formation of triptycene when o-bromofluorobenzene is treated with magnesium in the presence of anthracene.[37]

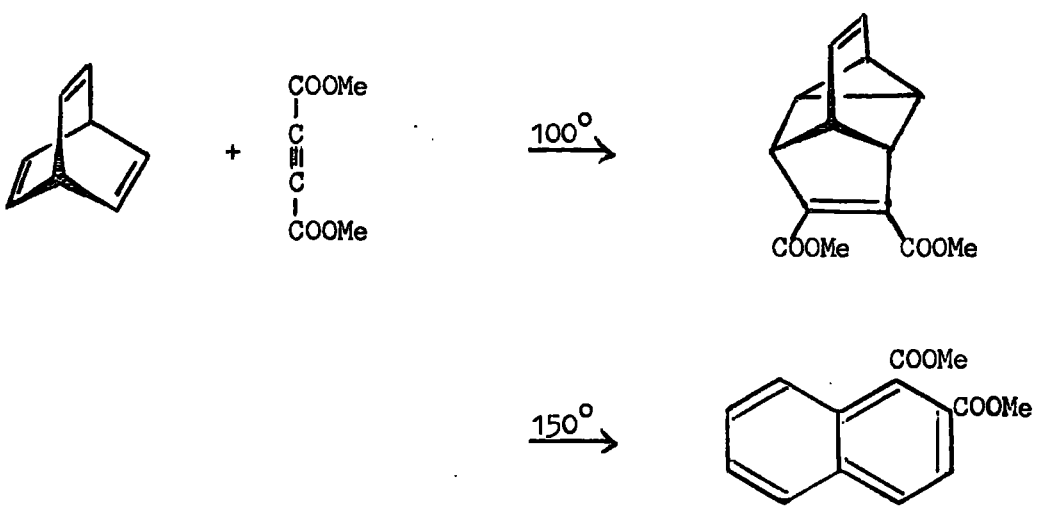


Perfluorobenzyne is particularly reactive and is trapped by a wide range of dienes. It even forms an isolable 1:1 adduct with benzene.[38,39] Very high activation energies must be involved to account for the loss of aromaticity of benzene in the transition state and the formation of a highly strained ring compound. Benzene itself also adds to the electron deficient perfluorobut-2-yne. The adduct has been isolated,[40] but in only 8% yield, and it readily eliminates acetylene to give 1,2-bis(tri-

fluoromethyl)benzene.[40,41] 1,2,4,5-Tetramethylbenzene, a more efficient diene than benzene, reacts with alkynes to give highly substituted derivatives of bicyclo[2,2,2]octa-2,5,7-triene, the so-called barrelenes. These are more stable adducts.[41,42]

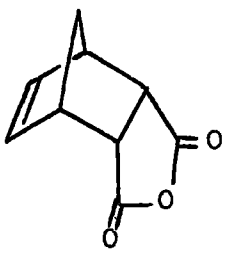


Certain alkynes also take part in what has become known as the "homo Diels-Alder" reaction.[43] The diene component is not conjugated, the double bonds are separated by a tetrahedral centre, and 3σ bonds are formed at the expense of 3π bonds - in the normal Diels-Alder reaction 2π bonds give 2σ bonds. The example given also illustrates the ease of rearrangement of the tetracyclic adduct.[44]

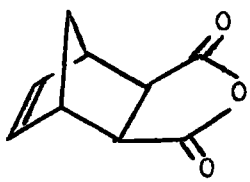


2.2] Preparative aspects.

In comparing the reactions of alkynes and alkenes with cyclic dienes one immediate difference is in the simplicity of the stereochemistry. The products of alkene addition have the possibility of exhibiting endo/exo isomerism e.g.



endo-

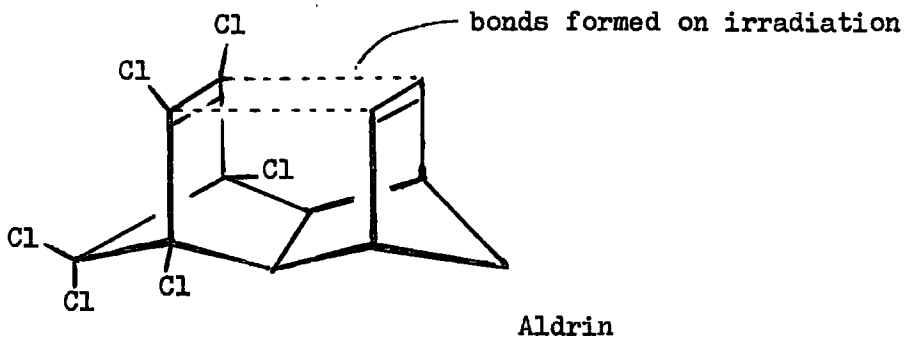


exo-

The relative amounts of endo- and exo- isomers which are formed, vary. From purely experimental observations of the proportions the Alder "endo" rule has been derived.[1] This states that the formation of the endo- adduct is favoured, accompanied by the "maximum concentration of unsaturated centres" in the transition state. This has generally been taken to imply that there are "secondary attractive forces" between the addends in the transition state, but recent theoretical considerations (Chapter 5) show that such forces need not be invoked. Although there are exceptions, the endo- adducts are usually the less thermodynamically stable by about 5 kcal.mole^{-1}, probably owing to steric crowding. Thus, there is kinetic control of the ratio of the reaction products.

Absolute configurations are usually difficult to determine by chemical means. Aldrin can be shown to have completely endo configuration

by the formation of a cage compound on irradiation.[46]

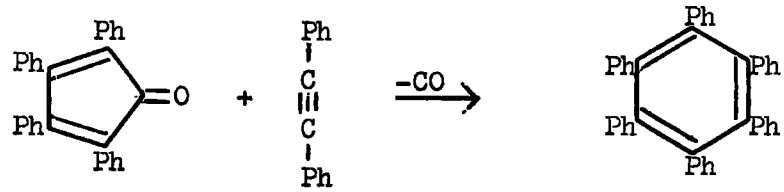


Aldrin

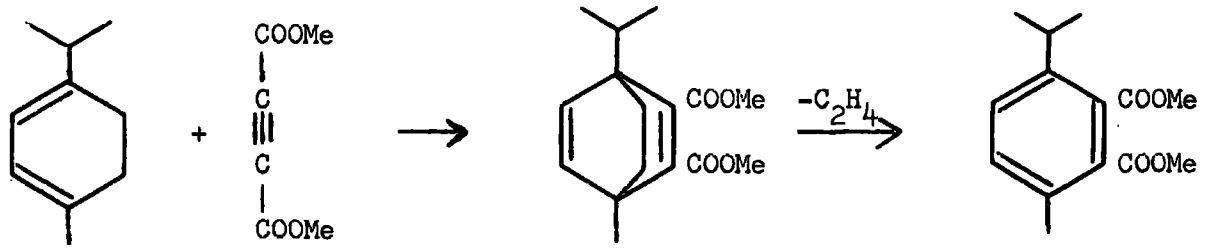
However, the equivalent adduct of norbornadiene and perfluorocyclopentadiene has two isomers formed in the ratio 68:32, but it was not possible to assign their structures.[18]

Acetylenes produce a planar ring junction containing a double bond and hence there can be no endo/exo isomerism.

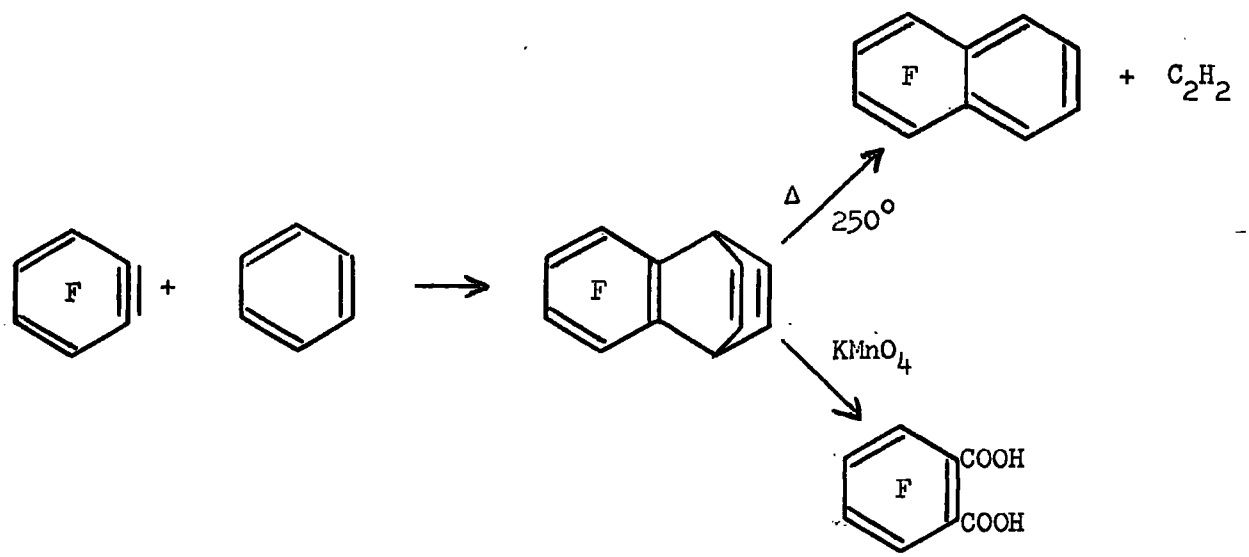
Strained bicyclic dienes are produced when acetylenes add to cyclic dienes such as cyclopentadiene and cyclohexadiene. Thus, in order to release this strain, there is a driving force to produce either an aromatic compound and/or eliminate a gas of low free energy such as nitrogen or carbon monoxide. This effect has been used in the synthesis of hexaphenyl benzene,[47]



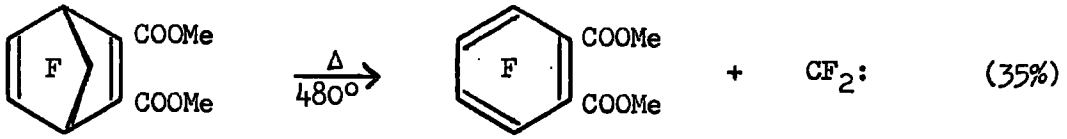
and for the structure determination of certain cyclohexadienes e.g. α-terpinene.[48]



Examples in fluorine chemistry of this kind of synthetic use of the Diels-Alder reaction are still somewhat limited. 1,2,3,4-Tetrafluoronaphthalene is produced by the pyrolytic elimination of acetylene from the adduct of tetrafluorobenzyne and benzene.[38,39] Oxidation of the adduct with permanganate produces tetrafluorophthalic acid.[39]

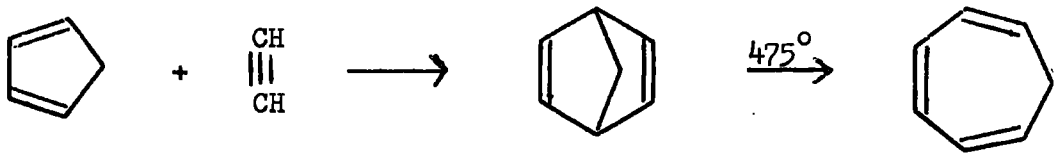


Difluorocarbene is the entity lost when dimethyl 1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene-2,3-dicarboxylate is pyrolyzed.



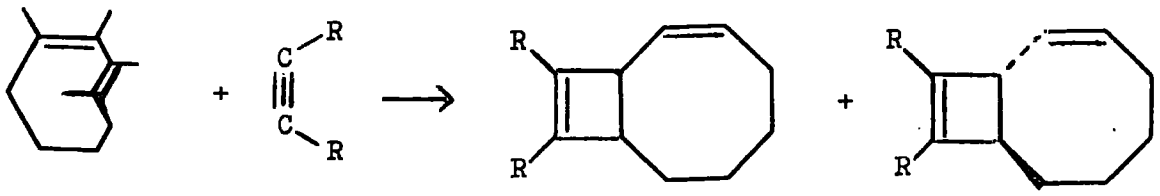
Again it is only an aromatic system which is stable under such drastic conditions.[18]

The ring strain may also be released by ring expansion, as in the pyrolysis of norbornadiene.[49]



This sort of case is uncommon, where there is no possibility of aromatic resonance stabilization. However, in the example given on page 18, a naphthalene is readily formed by the rearrangement of a tetracyclic diene.[44]

Little has been published about the Diels-Alder addition of alkynes to larger ring dienes. Attempts to add alkynes (including benzyne) to cis,trans-cycloocta-1,3-diene succeeded in forming only the 1,2 addition products by a non-concerted mechanism.[8]



R = COOMe (17%)

CHAPTER 3. NITRILES IN THE DIELS-ALDER REACTION.

3.1] Reactivity of nitriles.

From the large amount of work by Janz[50] it is clear that nitriles undergo Diels-Alder addition in an analogous fashion to alkynes. However, there are three major differences in the mode of reaction:

(i) Reactions must be carried out at higher temperatures. Although these reactions can be predicted to be thermodynamically feasible between 25 and 550° by the negative value of the free energy change (ΔG°), a temperature in the order of 400°C is required before a reasonable rate of reaction is obtained.[50] Some values of ΔG° at 327°, together with their associated equilibrium constants (K_p), are given in Table 3.1(i) (page 24).[51] As temperature increases both these values decrease and the rate of reaction increases. The lack of correlation with yields simply shows that many other kinetic factors have to be considered when attempting to predict the outcome of a reaction, such as activation energies, stability of reactants, alternative reaction paths, etc.

(ii) Prior to the work reported in this thesis, the primary Diels-Alder adduct has not been stable at the elevated temperatures required for its formation. In the case of the nitrile additions to butadiene [Table 3.1(i)], it is postulated that there is spontaneous elimination of hydrogen from the dihydropyridine formed in the addition step, thus accounting for the 2-substituted pyridines being the observed products.

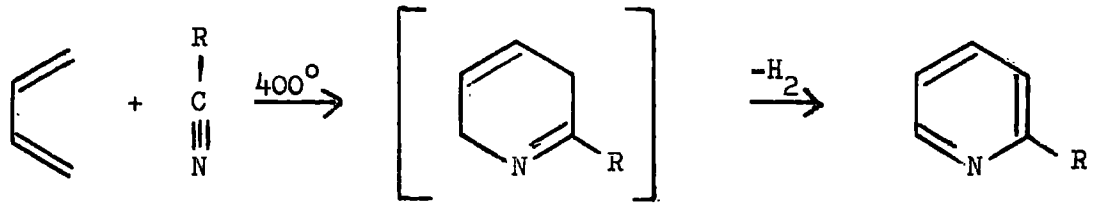
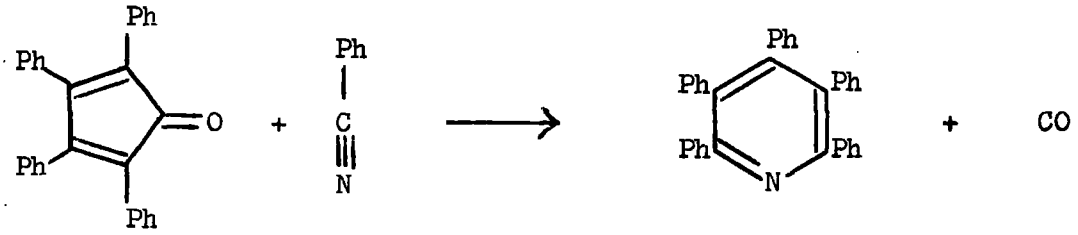


TABLE 3.1(i). Addition of nitriles to butadiene.

Nitrile R	% Yield (400°C)	ΔG° (327°C)	log K_p (327°C)
CF_3-	99·0	-11·8	4·3
C_2F_5-	97	-	-
C_3F_7-	97	-	-
CN-	34	-31·0	11·3
$ClCF_2$-	12	-	-
Ph-	1·4	- 7·7	2·8
H-	1·0	-21·2	7·7
Me-	0·1	- 9·9	3·6
Et-	0·04	-12·5	4·5
CH_2=CH-	0	-16·3	5·9

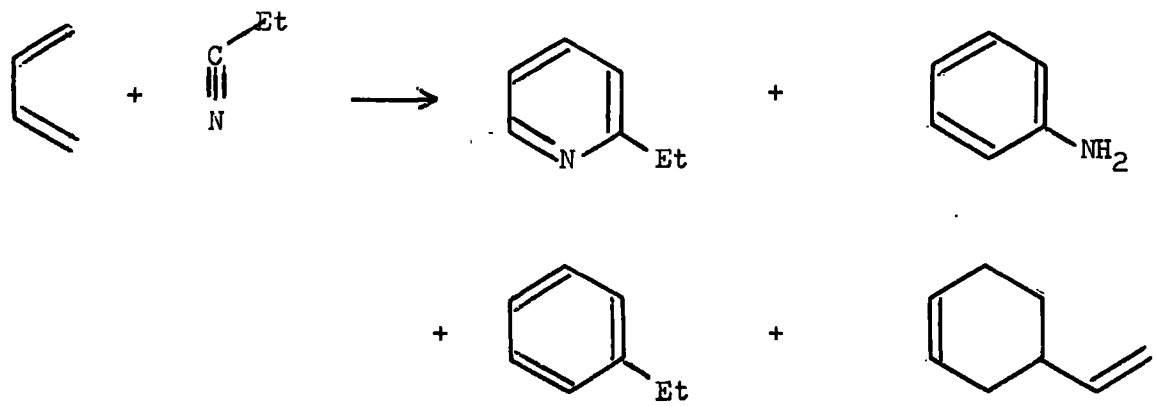
At these high temperatures the aromatic ring has a lower free energy content and the cyclohexadienic system is thermodynamically unstable.[52]

As with the addition of diphenylacetylene,[47] tetracyclone spontaneously eliminates carbon monoxide when added to benzonitrile,[53] the initial adduct being unstable with respect to an aromatic compound and a low free energy gas.

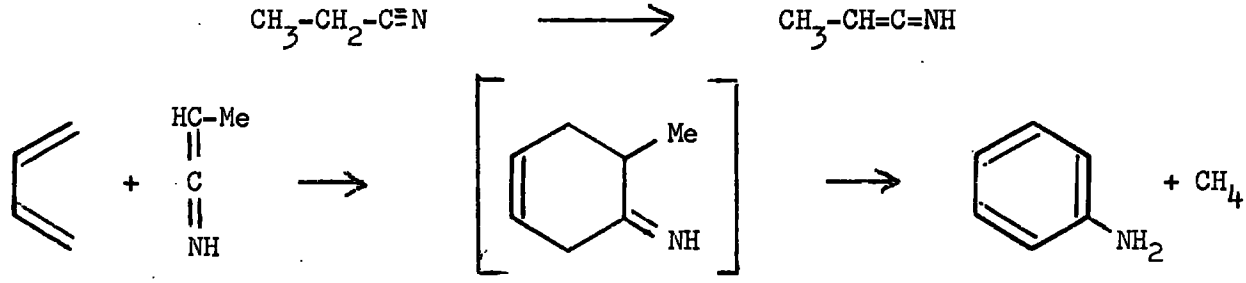


(iii) Only nitriles containing highly electronegative groups react successfully with dienes, as apparent from the yields given in Table 3.1(i). This is in agreement with the Alder Rule (Chapter 1.2) and it seems that Ph, Me, Et and H have no favourable electronic factors which can activate the cyano- group's dienophilic properties. Therefore, in reactions with other dienes, polyfluoroalkyl cyanides and cyanogens are expected to be the only efficient dienophiles. This is the case in pyridine syntheses with various butadienes such as isoprene and chloroprene.[54]

Yet another consequence of the high temperature of reaction is the possibility of competing side reactions which not only reduce yields but also produce unexpected by-products. Several examples occur in the butadiene-propionitrile reaction.



The thermal dimerization of butadiene to vinyl cyclohexene, followed by rearrangement and elimination of H_2, is an explanation for the formation of ethyl benzene.[55] Likewise, the nitrile is postulated to rearrange before cyclization, aromatization being achieved after another rearrangement.[56]

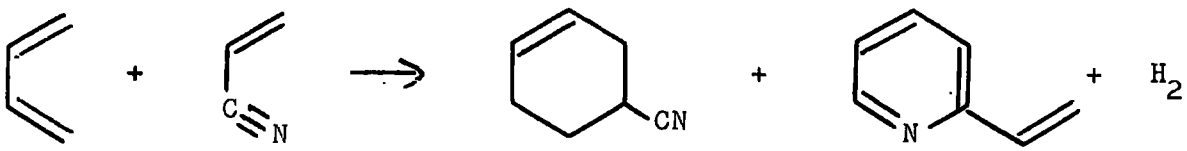


Thermodynamic calculations are in accord with these results since the ΔG° values at 400° for the formation of these compounds is ethyl-pyridine ca. -10, aniline ca. -7, ethyl benzene ca. -35, and vinyl cyclohexene ca. -9 kcal.mole^{-1}.[57]

3.2] Catalysis of nitrile additions.

The Diels-Alder addition of nitriles to dienes is susceptible to heterogeneous catalysis on alumina and chromium oxide surfaces. Yields of the pyridine product are increased, particularly with polarizable nitriles[58] [see Table 3.2(i)[59]].

Both the olefinic double bond, and the nitrile triple bond are theoretically able to act as the dienophilic function in the addition of acrylonitrile to butadiene.



Uncatalysed	77%	0
Catalysed	10%	1%

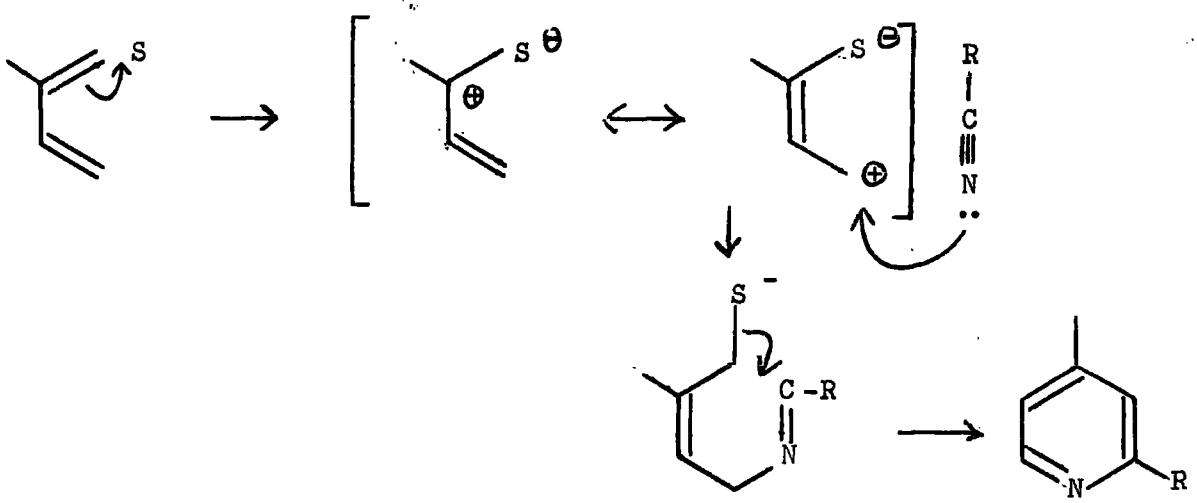
TABLE 3.2(i). Heterogeneous catalysts with butadiene at 400°C.

Nitrile R	% yield catalysed	% yield uncatalysed
Ph-	60	1·4
Et-	16·4	0·04
Me-	3·6	0·1
CH_2=CH-	1·2	0
H-	1·01	1·0

In non-catalysed conditions the C=C group has been calculated to react 5800 times more rapidly than the C≡N group, and no vinyl pyridine has been observed experimentally. However, in the presence of catalyst it reacts only 9-15 times faster (judged by product yields), and both vinyl pyridine and cyanocyclohexene are formed.[60]

The most efficient catalyst surfaces are acidic,[61] and the rate of reaction is more sensitive to substitution in the diene. The introduction of a methyl group into butadiene enhances the rate six- to tenfold.[62]

A proposed mechanism for heterogeneous catalysis thus involves the initial



adsorption of the diene at an acid site (S) followed by the attack of the dienophile on the positive centre produced.[62] Thus, the availability of the lone pair on the nitrogen of acrylonitrile could explain the observed preferential catalysis effects. However, since ammonium carbonate has sometimes been found as a side product, it is probable that there is also chemisorption of the nitrile at some stage.[62]

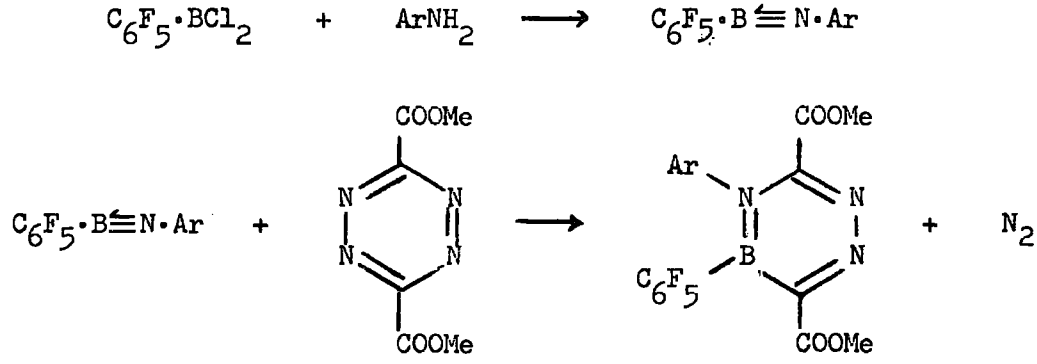
Homogeneous catalysis studies have not been carried out for nitriles in spite of numerous examples of general acid catalysis by phenols, Friedel-Crafts catalysts etc. in low temperature Diels-Alder reactions.[63]

CHAPTER 4. OTHER TRIPLE BONDS AS DIENOPHILES.

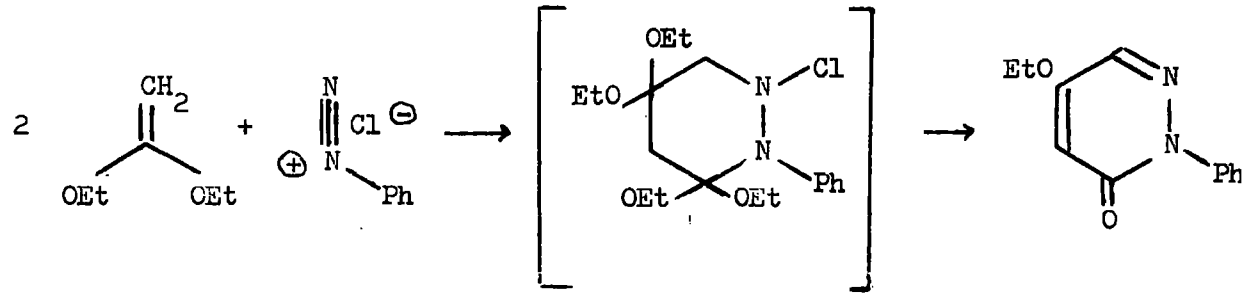
4.1] Possible triple bond systems.

The number of compounds containing triple bonds is small and limited to the elements B, C, N, O and S. Acetylenes and nitriles were discussed in Chapters 2 and 3, leaving the following compounds as possible dienophiles:- Ar-B≡N-Ar, C≡O, N≡N, Ar-$\overset{\oplus}{N}$≡N, N≡O, N≡S-X and N≡SF_3.

The only reported case of Diels-Alder addition has been with the monomeric borazynes. They add to the very reactive diene, dimethyl 1,2,4,5-tetrazine dicarboxylate.[64]



The reaction of benzene diazonium chloride gives Diels-Alder-type products, but it probably involves a multistage ionic mechanism not involving a 1,4-addition.[65]



Apart from thiazyl chloride (reported in this thesis) none of the other compounds, all gases, have a record of dienophilic properties. It is an interesting observation that only the borazynes and thiazyl halides form stable rings by dimerization, trimerization etc. Cyanuric compounds (i.e. 1,3,5-triazines) and benzenes are, of course, the cyclic trimers of cyanogens (or nitriles) and acetylenes.

4.2] Sulphur-nitrogen halides.

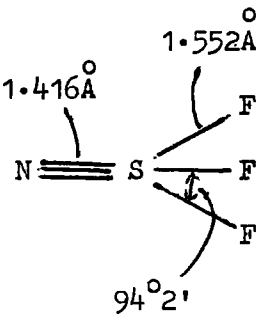
There are many compounds containing just sulphur, nitrogen and halogen. They are all shown in Table 4.2(i).[66]

Table 4.2(i). Sulphur-nitrogen halides.

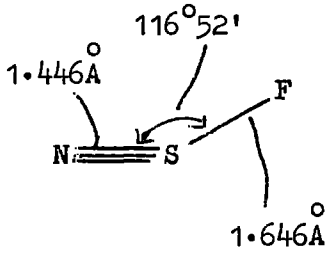
No. of S+N atoms	Fluorides	Chlorides	Bromides
2	NSF	NSCl	-
	NSF_3	-	-
5	-	S_3N_2Cl	S_3N_2Br
	$S_3N_2F_2$	$S_3N_2Cl_2$	-
6	-	S_3N_3Cl	-
	$(NSF)_3$	$(NSCl)_3$	-
7	S_4N_3F	S_4N_3Cl	S_4N_3Br
8+	$(NSF)_4$	-	$(NSBr)_x$

They can all be prepared, directly or indirectly from tetrasulphur tetranitride (S_4N_4). Of the compounds containing triple bonds thiazyl trifluoride (NSF_3) is the least reactive. Unlike thiazyl fluoride (NSF) and thiazyl chloride (NSCl) it does not polymerize and it resists hydrolysis.[67] NSF is an unstable gas, producing green-yellow crystals of $S_3N_2F_2$ by storing in glass vessels at room temperature below atmospheric pressure. It is readily hydrolysed by water.[67]

Although the sulphur-nitrogen links are being considered as triple bonds, bond length measurements indicate that bond orders are less than 3.[68-70] After NSF_3, NSF has the highest bond order of any sulphur-nitrogen compound.

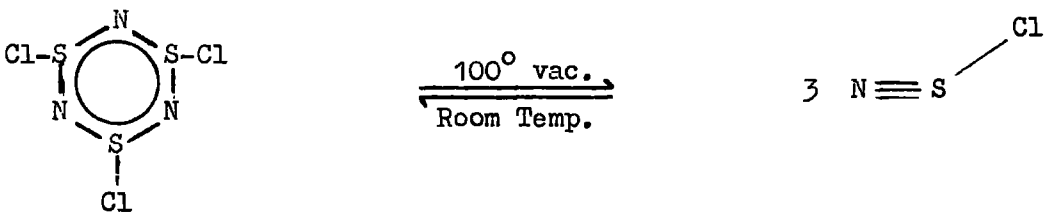


Bond order 2·7

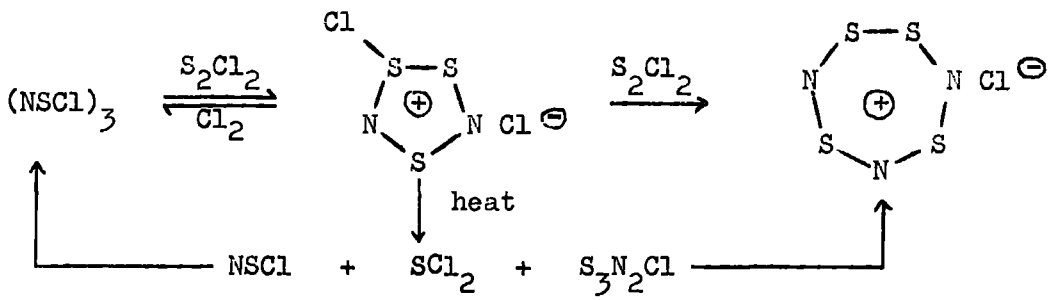


Bond order 2·5

Monomeric thiazyl chloride has a similar structure to thiazyl fluoride. It can be conveniently prepared as a green gas by heating its trimer, trithiazyl trichloride, in vacuo at 100°C. The reaction is reversible.



However, under the conditions of the Diels-Alder reaction, compounds in addition to NSCl are liable to be produced. Mechanisms and rearrangements in this field of inorganic chemistry are by no means well-defined and different types of sulphur-nitrogen ring systems tend to readily interconvert, either under the influence of heat or in the presence of sulphur halides. For instance, if $(NSCl)_3$ cracked and formed sulphur chloride all the following reactions are possible.[66,72]



$(NSCl)_3$ readily acts as a chlorinating agent, e.g. with aromatic amines, with the formation of S_4N_3Cl and a variety of unspecified side products. It is common to form unidentifiable, air-sensitive, polymeric red oils in any reactions involving this compound.[73]

Although sulphur-nitrogen multiple bonds have been utilized in the Diels-Alder reactions of S_4N_4 with olefins[74] and acetylenes[75] they have always been associated with the diene component.

The numerous unpublished reactions of $(NSCl)_3$ with chlorinated olefins, dienes, nitriles and acetylenes also do not yet appear to include the 1,4-addition of NSCl as a dienophile.[76]

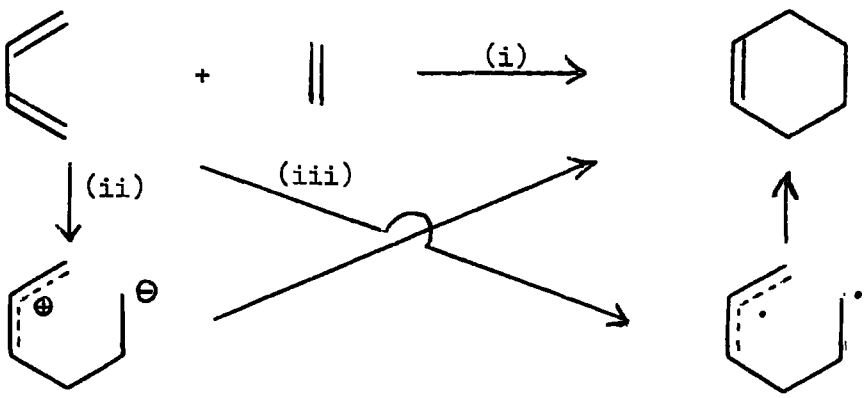
CHAPTER 5. MECHANISM OF THE DIELS-ALDER REACTION.

5.1] Possible mechanisms.

The Diels-Alder reaction can be defined as the formation of a six membered ring compound from a diene which contributes four atoms to the ring and a dienophile which contributes two. The diene must be conjugated with the double bonds cis-orientated at the time of reaction, but the dienophile can be practically any unsaturated compound.

Two new σ-bonds are formed at the expense of two π-bonds.

It is possible to envisage three distinct reaction paths:-



(i) One-step, via a concerted mechanism.

(ii) Two-step, with a zwitterionic intermediate.

(iii) Two-step, with a biradical intermediate.

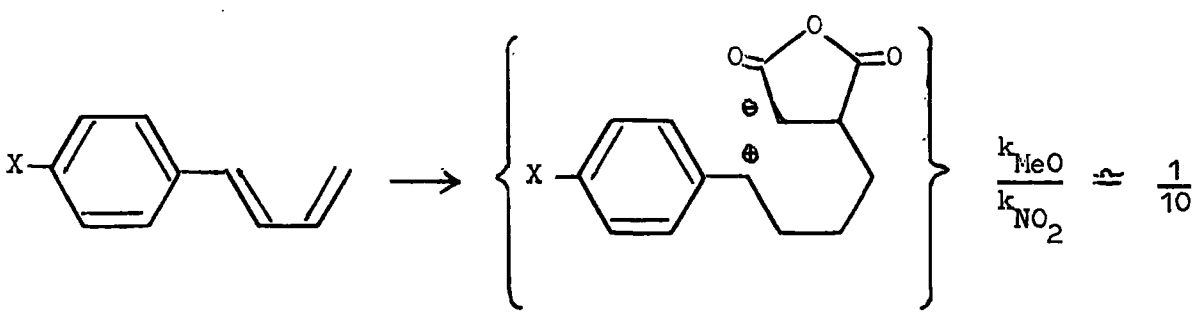
There are several reviews e.g.[4,12] on this topic, so that all the pathways will not be treated fully and examples kept to a minimum. The majority of the results support a synchronous, rather than a two-step mechanism, although evidence is also accumulating that a whole range of mechanisms may occur under appropriate conditions.

5.2] Kinetics and description of the transition state.

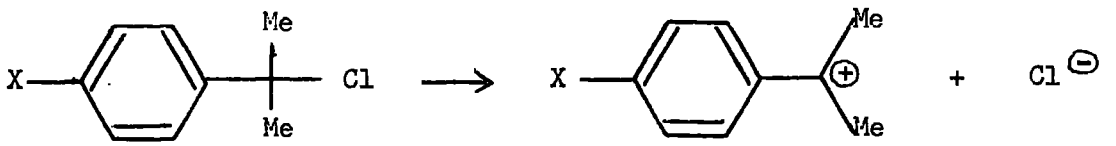
As expected the Diels-Alder reaction obeys second order kinetics:-

$$\text{Rate} = k_2 \text{ [diene] [dienophile]}$$

Chapters 1-3 gave many examples of the relevant electronic effects of substitution in the diene and dienophile and, although the effects on rate are large in absolute terms, application of the Hammett equation show that they are far too small to agree with a zwitterionic intermediate.[4] The change of rate caused by replacement of MeO with NO_2 in a typical Diels-Alder (1:10)[77] is far less than in a solvolysis reaction (1:10^8).[78]



X = MeO, NO_2 hypothetical



$$\frac{k_{MeO}}{k_{NO_2}} \simeq \frac{1}{10^8}$$

The Hammett ρ values are always low,[79] ca. 0·3 in the case of the phenyl propiolates[36] (Chapter 2), thus signifying a non-ionic mechanism, but the slightly polar nature of the transition state is shown by the correlation of rates with σ^- values [Fig. 5.2(i)].

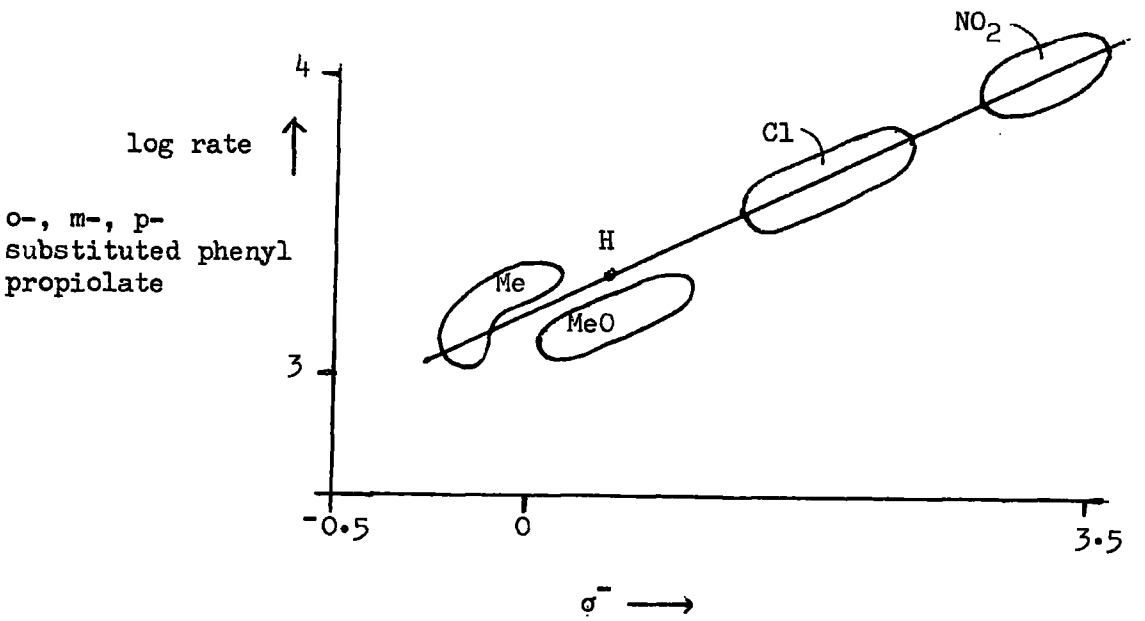


FIG. 5.2(i). Application of Hammett equation to Diels-Alder reaction.

The low polarity of the transition state is also demonstrated by comparable rates in the gas phase, and by the small solvent effect, which rarely increases by a factor of more than 10 by changing to a solvent of higher solvating power.[80]

Diels-Alder associations are equilibrium reactions which are exothermic in the forward direction, activation parameters being useful guides to mechanisms. Activation energies (E) are generally relatively small (8 - 27 kcal.mole^{-1})[81] and log A factors (4.0 to 7.5) are also small compared to the bimolecular collision theory value (ca. 11, A in l.mole^{-1}sec.$^{-1}$).[12] Activation entropies ($\Delta S^{\neq}$) are large, negative and reasonably constant (-31 to -36 e.u.). The latter in particular indicates a highly-ordered transition state with a high degree of formation of both bonds, strong evidence in favour of the concerted mechanism.

On the other hand, although still supporting the synchronous mechanism, the magnitude of the secondary kinetic isotope effect is small and indicates only a slight change in hybridization at the reaction centres i.e. the transition state is more like the reactants than the product e.g.[82-84].

Most, but not all,[85] catalytic activity has been restricted to Lewis acids ($AlCl_3$, $TiCl_4$ etc.) which can form a complex with activating substituents in the dienophile (e.g. the carbonyl group in maleic anhydride, methyl acrylate etc.).[86] Since the "cis" principle is still

obeyed, together with a greater tendency to form the endo- adduct,[87] there is probably no change in mechanism. However, in the case of heterogeneous catalysis in the nitrile-pyridine synthesis (Chapter 3.2) and catalysis with acids and phenols,[88] there has been some discussion of ionic intermediates.

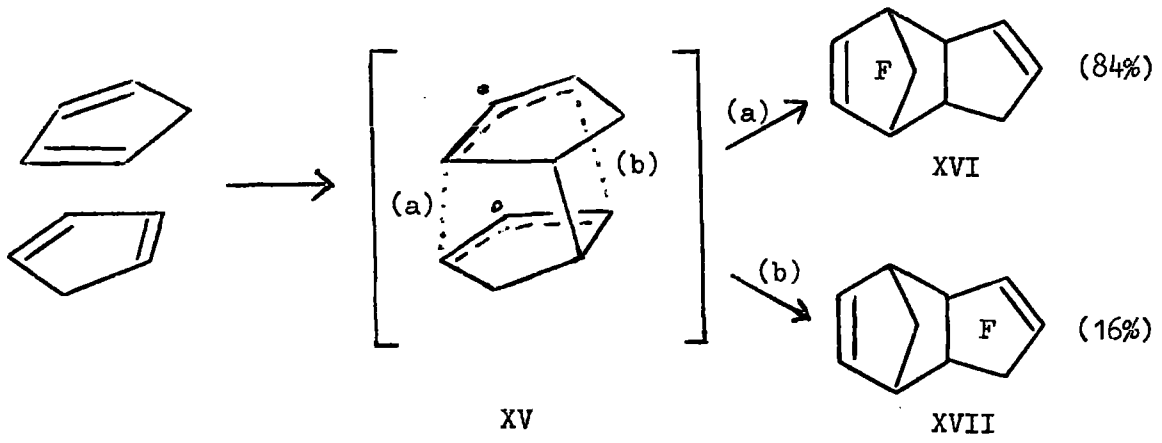
As qualitatively expected from the stoichiometry of the reaction, the rate and yield is increased by increasing the pressure.[89] A 55% yield of 2-cyanopyridine is obtained at 100° if cyanogen and butadiene are heated together in a sealed tube, whereas the atmospheric pressure, gas-phase reaction yields only 34% at 400°.[90]

Kinetic studies have not led to any unequivocable mechanism for the common preferential formation of the endo- adduct, for in certain cases the exo- isomer is kinetically favoured.[91] Methods which involve secondary non-bonding interactions such as dipole induction forces,[92] charge transfer,[93] "maximum accumulation of unsaturation", and orbital symmetry[94] cannot explain, for example, the exclusive formation of the endo- adduct in the reaction of cyclopentadiene with cyclopentene[95] or cyclopropene.[96]

In overall energy terms, however, the difference between the isomers is small (ca. 3 kcal.mole^{-1}), so that, under the influence of so many external factors, it is not surprising that it has proved impossible to predict exo- : endo- ratios with any certainty. Nevertheless, this ratio has been used to derive an empirical scale of

solvating power, Ω, which, increasing as solvent polarity increases, parallels other solvent functions.[91,97]

The above evidence would give an incorrect, biased picture. There are instances which are better explained by a radical mechanism.[98,99] For example, perfluorocyclopentadiene and cyclopentadiene yield a mixture of XVI and XVII in constant ratio (16:84) which is solvent and



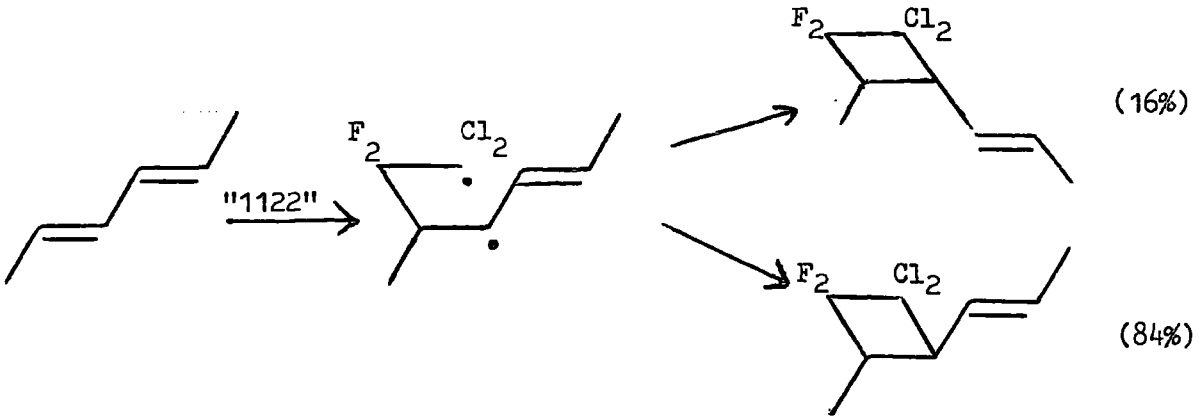
temperature independent. Since the compounds have not been made to rearrange to each other, the best interpretation is the formation of both via a common, biradical intermediate XV.[99]

Thus a complete description of the mechanism of the Diels-Alder reaction is not possible. "A graded continuum for systems of different structure, from a completely symmetrical four-centre mechanism to a fully developed two-step mechanism"[100] should be envisaged. However, for the majority of cases there is probably a collision of the four reacting centres in a favourable orientation, rapidly followed by passage through an asymmetric transition state which has a high degree of bond formation and some slight polar character.

5.3] 1,2-Cycloadditions.

1,2-Cycloaddition is the commonest cyclization process for fluorinated olefins,[101] and it often competes with 1,4-cycloaddition if the diene[16,17] or dienophile[5,33,98] contains fluorine atoms. Table 1.1(ii) shows the large range of values for the competing 1,2-addition of 1,1-dichloro-2,2-difluoroethylene ("1122") with various cis- constrained dienes (16-99%), where the governing factor seems to be the distance between the termini of the conjugated system. In that case it is impossible to distinguish between the concerted or two-step modes of ring closure.[5]

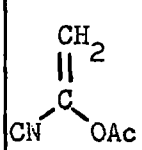
Most of the stereochemical evidence favours a biradical process for thermal 1,2-cycloadditions.[101] This is strongly supported by the free rotation about the 2,3 double bond in additions to hexa-2,4-dienes.[102]



Often, this is assumed to be the correct mechanism in other cases e.g.[103].

On the other hand Table 5.3(i) illustrates the opinion that the mechanism of competing 1,4-cycloaddition changes according to the type of dienophile. If there is a possibility of stabilizing a diradical

TABLE 5.3(i). 1,4-Addition competing with 1,2-addition.

Dienophile	Diene	% 1,4-Addition	1,4-Mechanism	Ref.
"1122"		0.86 (60°) to 2.32 (176°)	radical	104
		1.6 (R,Me) to 45 (R,C(Me)$_3$)	radical	98
		not reported	-	102
		99.98	concerted	105
		100	-	105
		77 to 91	concerted	106
		99.6	concerted	106

intermediate, as with "1122", yields of 1,4-addition products are relatively low, and the radical reaction is favoured.[98,104] However, a concerted mechanism is considered to operate with olefins having a greater electron density in the π-system, and yields of 1,4-adducts are much greater (77-100%).[105,106]

In spite of the above, it cannot always be assumed that every thermal 2+2 cycloaddition involves the diradical mechanism since the cyclic dimerization of tetrafluoroethylene to perfluorocyclobutane appears to be concerted.[107] However, the absence of cyclobutane products does not necessarily imply the absence of 2+2 addition, since it is considered

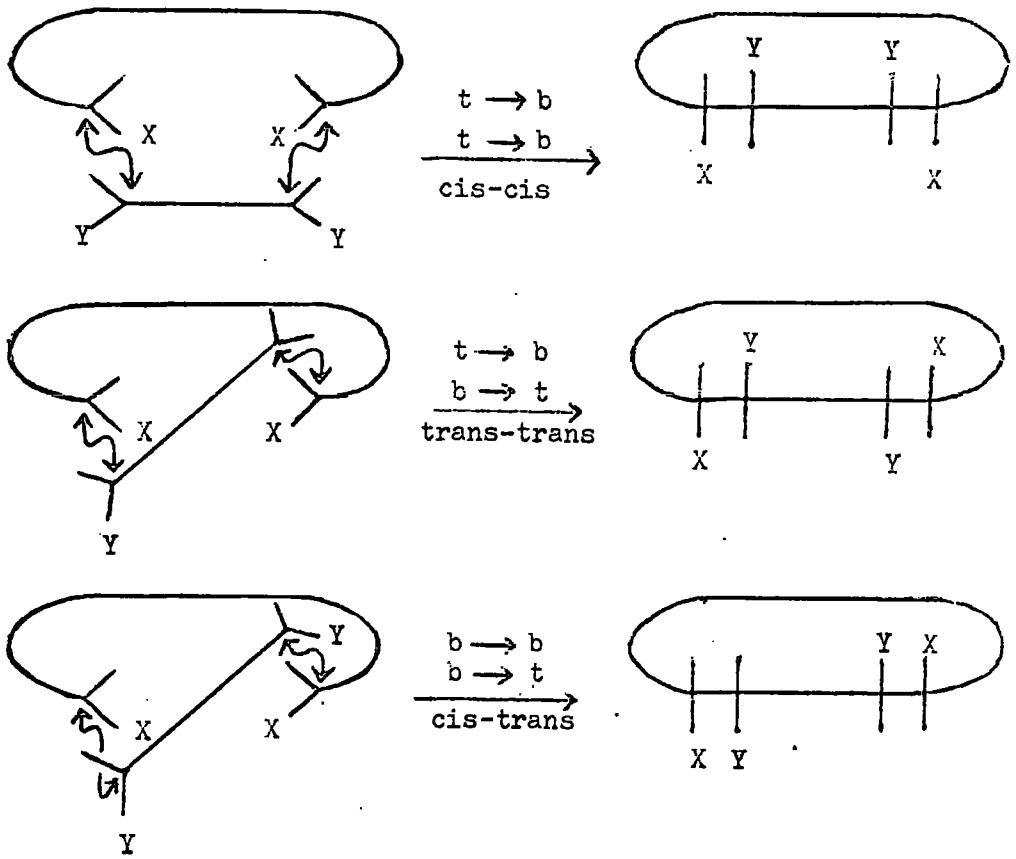
that a six membered cyclohexene is thermodynamically more stable than a four membered cyclobutane.[108,109]

5.4] Molecular orbital approaches.

Consideration of the symmetry and energy of the highest occupied molecular orbital of one reactant and the lowest unoccupied molecular orbital of the other reactant, (i.e. the frontier electron method), the properties of the remaining orbitals, and energy level correlation diagrams lead to a set of selection rules for concerted cycloaddition reactions.[110] There is quantitative support for these theories.[111] The different stereochemical ways available for the simple terminal cycloaddition of an m π-electron system to an n π-electron system are shown in Fig. 5.4(i), and the selection rules for thermal (Δ) and photochemical (hν) cycloadditions are given in Table 5.4(i).

TABLE 5.4(i). Hoffmann-Woodward selection rules for cycloaddition.

m+n	Δ	hν
4q	cis-trans trans-cis	cis-cis trans-trans
4q+2	cis-cis trans-trans	cis-trans trans-cis

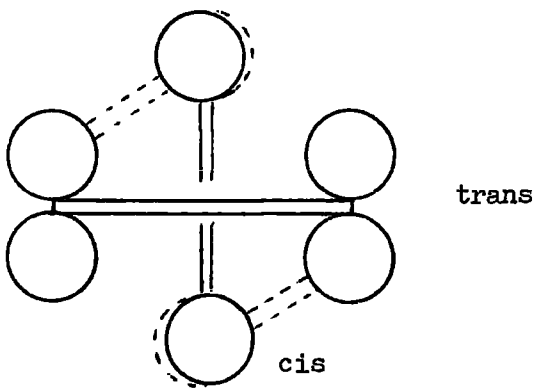


t → b indicates that the top face (t) of the lower component is adding to the bottom face (b) of the upper (Y-substituted polyene first). A trans-cis mode also exists which is distinct from the cis-trans mode.

FIG.5.4(i). Stereochemical modes of cycloaddition.

The Diels-Alder reaction is an example of a 4+2 → 6 electron system where the components add in a cis-cis fashion. In other words, the rules predict that the reaction is "thermally allowed", assuming that it is concerted.

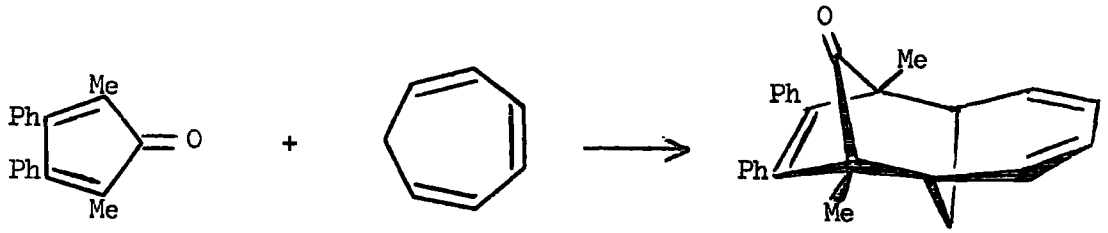
It is apparent that the trans-trans or cis-trans approach of any components is sterically unfavourable, but not impossible. The assumption that 2+2 cycloaddition must proceed via a diradical process is incorrect. Concerted thermal dimerization of tetrafluoroethylene is symmetry allowed provided that the molecules are at right angles in the transition state, to give rise to a puckered cyclobutane ring.



In the diagram above, the cis-lobes of the π-molecular orbital of the vertical olefin are overlapping with trans-lobes on the horizontal one, i.e. a cis-trans 2+2 addition [see Table 5.4(i)].

Zimmermann's method arrives at the same conclusion by using the concept of Möbius-type orbitals in twisted π-electron systems i.e. concerted 2+2 cycloadditions are thermally allowed, but require a greater activation energy than in the photochemical case.[112]

In certain fortuitous cases e.g. in the dimerization of butadiene to produce vinyl cyclohexene,[94] it is possible to invoke secondary orbital interactions which are favourable to the formation of the endo- isomer in 4+2 cycloadditions. The same methods also successfully predicted, before the reaction was performed, that 6+4 cycloadditions should lead preferentially to the exo- adduct.[113]



Extended Hückel calculations arrive at the same results, but for different reasons.[114,115] For the dimerization of cyclopentadiene calculations give an energy difference of 4.7 kcal.mole^{-1} in favour of the endo- transition state,[115] in agreement with observed values.[116,117] 90% of this value is accounted for by overlap at the primary centres alone, i.e. those eventually forming the σ-bonds.

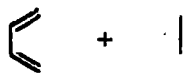
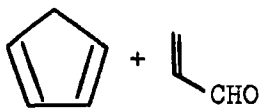
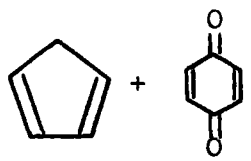
Thus, there is little need to invoke any "secondary attractive forces"[118] to explain the preponderance of endo- adducts, and such quantitative methods should work with dienophiles not having any of these "forces" available e.g. cyclopentene etc. (page 37).

5.5] Reverse Diels-Alder reaction.

Diels-Alder addition is an equilibrium reaction which is unimolecular in the reverse direction. Activation energies (E) (26-57 kcal.mole^{-1}) are higher than the corresponding values for the forward reaction (8-27 kcal.mole^{-1}). This is the natural consequence of the forward reaction being exothermic overall, and both reactions employing the same transition state.

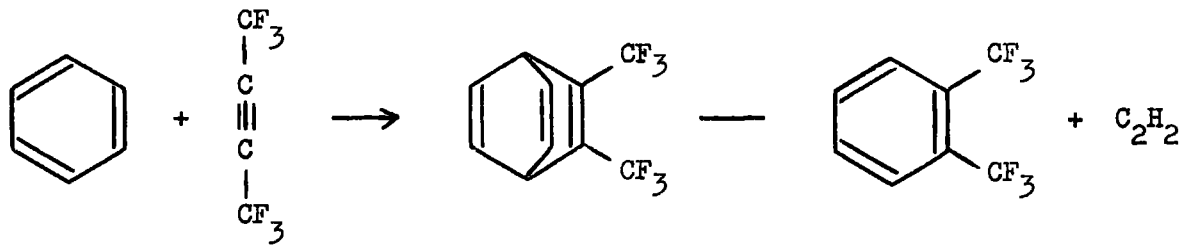
Whereas high negative entropies of activation have been noted for the forward reaction (Chapter 5.2), the reverse reaction is characterized by very low values, some comparative activation parameters are given in Tables 2.1(ii)[36] and 5.5(i).[81]

TABLE 5.5(i). Kinetic parameters of forward and reverse additions.

Addends	Forward			Reverse		
	log A	E	$\Delta S^{\ddagger}$	log A	E	$\Delta S^{\ddagger}$
	7·5	27·5	-30·6	12·9	57·5	-5·4
2 x 	6·1	16·7	-35·2	13·0	33·7	+1·4
	6·2	15·2	-35·0	12·3	33·6	-7·2
	6·5	11·6	-35·6	12·6	29·0	-3·0

The entropy figures particularly indicate that transition states are closer to adducts than addends.[119]

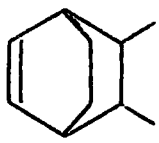
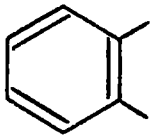
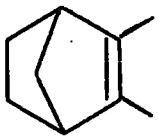
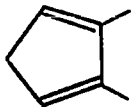
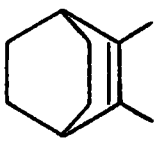
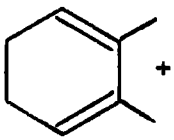
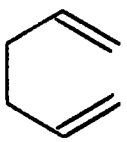
From a synthetic viewpoint the most useful adducts are those which are able to undergo a different reverse Diels-Alder reaction, e.g. in the preparation of 1,2-bis(trifluoromethyl)benzene the alternative elimination of acetylene takes place:[40,41]



Where there is such a choice of products the mode of retrogression is governed by their free energy. A reaction becomes more favourable if, for instance, there is resonance stabilization in an aromatic product, as in scheme No.1 below [Table 5.5(ii)].[119]

Of the various reactions in the table, No.1 is the only one which takes place readily; ΔG° becoming negative at about 400°C. 2a and 3a eventually take place at 700 - 800° with the elimination of ethylene, not acetylene. However, tars are also formed, so that, because the starting materials are not stable at such high temperatures, the decomposition may take place via a multistep mechanism, not a concerted reverse Diels-Alder reaction.[119]

TABLE 5.5(ii). Calculated free energies of some retrodiene reactions.

No.	Reaction	Temperature 300	500	700	1000	1200
1	 →  + C_2H_4	5·6	-4·0			
2	 a →  + C_2H_4			-0·8	-13·9	-22·5
	b →  + -C≡C-			21·9	2·4	-10·5
3	 a →  + C_2H_4			-0·3	-15·1	
	b →  + -C≡C-			26·7	5·2	

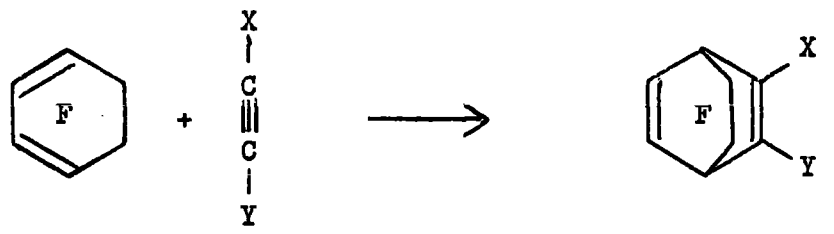
PART II

DISCUSSION

CHAPTER 6. ADDITION OF ALKYNES TO PERFLUOROCYCLOHEXA-1,3-DIENE.

6.1] Preparation of the adducts.

The expected 1,4-addition of alkynes across the conjugated diene system took place. No 1,2-addition was observed.



I II

TABLE 6.1(i). Addition of alkyne to perfluorocyclohexa-1,3-diene.

No.	Alkyne (I) X	Alkyne (I) Y	Yield (II) %	Temp. (°C)	Time (hr.)
Ia	H	Me	94	180	40
Ib	H	CF_3	92	200	100
Ic	H	CH_2Cl	88	180	17
Id	H	Ph	54	175	20
Ie	Me	Me	71	200	19
If	CH_2Cl	CH_2Cl	62	200	40
Ig	Me	CF_3	49	220	63
Ih	COOEt	COOEt	47	215	18
Ii	CF_3	CF_3	36	225	18

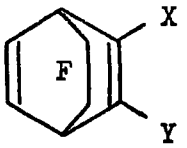
As shown in Table 6.1(i), nine alkynes (Ia - Ii) were heated with perfluorocyclohexa-1,3-diene in sealed Pyrex tubes also containing a free radical inhibitor (dipentene) and in each case a 2,3-disubstituted 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIa - IIi) was formed.

Although only qualitative comparisons can be made, because no attempt was made to standardize conditions or optimize yields, it seems that the Diels-Alder reactions of perfluorocyclohexa-1,3-diene do require "inverse electron demand" in the dienophile.[25-27] Propyne, containing the electron donating methyl group gives the best yield (94%) and, of the symmetrical butynes, dimethyl acetylene gives the greatest yield (71%). The $\equiv$C-H grouping appears to have the greatest activating influence, except in the case of phenyl acetylene, where there was a large amount of tarry product formed. The five butynes (Ie - Ii) definitely follow the trend of "inverse electron demand", perfluorobut-2-yne (Ii) giving the lowest yield (36%), and the others intermediate values up to 71%, for but-2-yne (Ie). However, a greater yield of IIi can be achieved (ca. 90%) by increasing the temperature to 264° and the time to 22 hrs.[120] Competition reactions would have given more precise values of the relative activating influences of substituent groups.

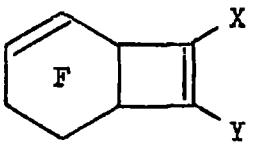
Because the yields are reduced by the competitive dimerization of perfluorocyclopentadiene, it may be unwise to infer too much from the figures, but, a higher reactivity is indicated for this five-membered ring

diene since lower reaction temperatures seem to be required; 115° for the addition of acetylene (42%, 65 hr.), and 133° for dimethyl acetylene dicarboxylate (22%, 72 hr.).[18]

The properties of the adducts confirm the basic ring structure as being a bicyclo[2,2,2]octa-2,5-diene (Structure A), formed by the 1,4-addition of the alkynes, and exclude the alternative bicyclo[4,2,0]octa-2,7-diene (Structure B), which would have been the result of 1,2-addition.



or



A B

All adducts showed an absorption in the range 1763-1777 $cm.^{-1}$ assigned to the CF=CF stretching frequency of the C5 to C6 double-bond, and all except IIc and IIf showed a second C=C stretching absorption in the region 1630-1680 $cm.^{-1}$ assigned to the 2,3 double-bond. The latter frequency is consistent with a double-bond in a six-membered ring, rather than a four-membered ring, which is required for Structure B (ca. 1566 $cm.^{-1}$).[121] The absence of a second absorption in the double-bond region when the substituent is $-CH_2Cl$ is anomalous; allyl chloride shows the expected C=C stretching absorption (1645 $cm.^{-1}$).[122]

Further strong evidence for Structure A is provided by the ^{19}F n.m.r. spectral data given in Table 6.1(ii):

TABLE 6.1(ii). ^{19}F N.m.r. spectral data for alkyne adducts (II).

No.	Adduct (II) X	Y	CF_2-CF_2	Chemical Shift [a] CF=CF	>C-F	CF_3
IIa	H	Me	-40·4	-8·4, -7·5	47·2, 49·7	
IIb	H	CF_3	-40·0	-10·6, -9·6	46·8, 52·0	-99·8
IIc	H	CH_2Cl	-41·8	-10·3, -8·6	46·6, 51·9	
IId	H	Ph	-41·0	-9·4, -8·4	45·2, 47·4	
IIe	Me	Me	-39·2	-7·8	50·1	
IIf	CH_2Cl	CH_2Cl	-40·8	-8·9	52·7	
IIg	Me	CF_3	-40·2	-10·6	47·8, 51·6	-103·8
IIh [b]	COOEt	COOEt	-41·6	-10·3	50·5	
IIi	CF_3	CF_3	-41·4	-12·4	50·3	-108·8

Notes: [a] P.p.m. from internal hexafluorobenzene in neat liquid (- downfield, + upfield).

[b] Saturated solution in ether.

(i) The adducts of the symmetrical alkynes (IIe, f, h, and i) have simple n.m.r. patterns which are only compatible with a symmetrical structure.

(ii) The similarity of the chemical shifts throughout the series indicates a common structural unit.

(iii) The tertiary fluorine resonances occur at high field (+45·2 to +52·0 p.p.m. upfield from C_6F_6) which correlates well, not only with the

equivalent resonances in Pyke's 1,4-adducts of perfluorocyclohexa-1,3-diene with olefins (+31·7 to +44·9),[16] but also with the analogous 1,4,5,6,7,7-hexafluorobicyclo[2,2,1]hepta-2,5-diene system (+48·7 and +49·9).[18] 1,2-Addition of olefins produces fused four- and six-membered rings and the tertiary fluorine resonances are shifted downfield (+35·5 to -6·9).[16]

(iv) The shifts of the vinylic, and fluorine atoms bonded to C7 and C8 are qualitatively as expected.[123]

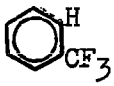
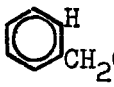
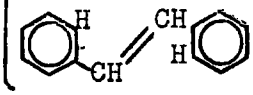
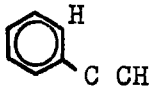
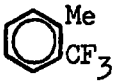
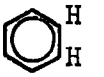
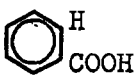
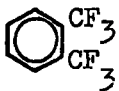
Unfortunately the fine structure of these spectra was complex and spin-spin coupling constants could not be determined. For instance, the geminal fluorine atoms on C7 and C8 are basically of type AA' BB', but the resonances are much broadened by multiple long-range coupling,[124] and, in Table 6.1(ii), only the approximate centre of gravity of many resonances is quoted.

The pyrolysis of the adducts discussed below provides evidence which is incompatible with any structure other than the bicyclo[2,2,2]octadiene skeleton (A).

6.2] Pyrolysis of the Diels-Alder adducts.

In addition to structural evidence, one of the important reasons for carrying out the pyrolyses of the adducts was the hope that an ortho-disubstituted tetrafluorobenzene would be the major product after the elimination of the $-CF_2-CF_2-$ bridge in a reverse Diels-Alder type of

TABLE 6.2(i). Pyrolysis products (III) of alkyne adducts (II).

Adduct (II)	Mass spec. base peak	Temp.	Product [a] (III)	No.	Yield %
IIa	$[C_7H_4F_4]^+$	610°		(IIIa)	95
IIb	$[C_7HF_7]^+$	630°		(IIIb)	94
IIc	$[C_7H_3F_4]^+$	600°		(IIIc)	50
				(IIId)	20
IId	$[C_{12}H_6F_4]^+$	550°		(IIIe)	71
IIe	$[C_8H_6F_4]^+$	600°		(IIIf)	99
IIf	$[C_8H_4{}^{35}ClF_4]^+$	600°		(IIIg)	ca. 82
IIg	$[C_8H_3F_7]^+$	600°		(IIIh)	95
IIh	$[C_9H_5F_4O_2]^+$	550°		(IIIi)	60
				(IIIj)	24
IIi	$[C_2F_4]^+$	500°		(IIIk)	95

Note. [a] All unmarked bonds to fluorine.

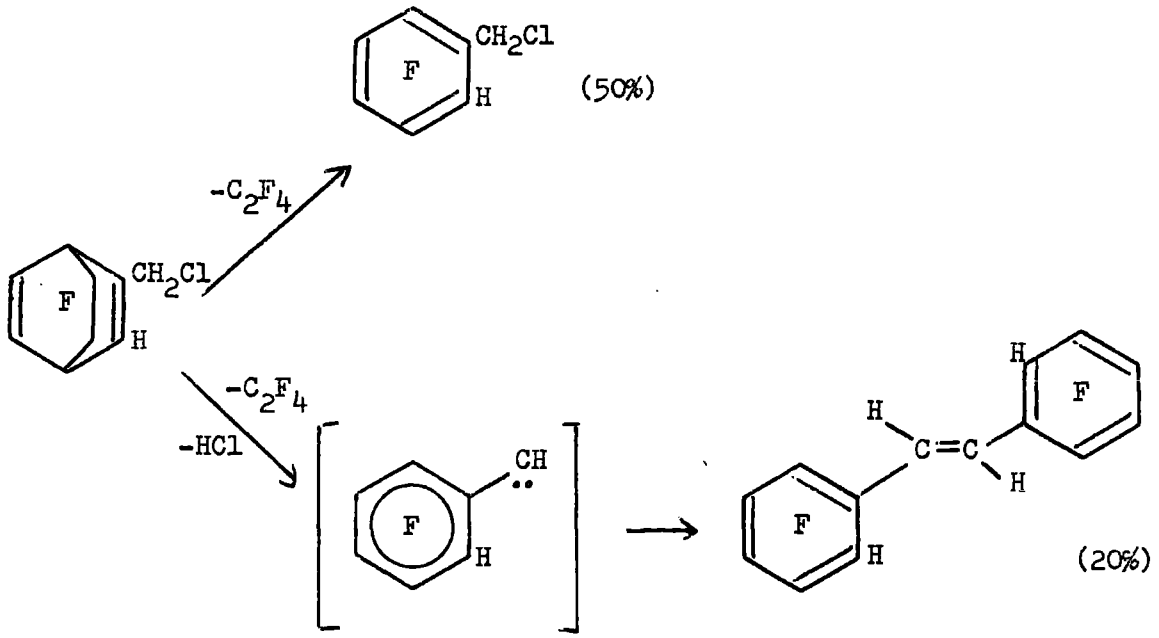
reaction (Chapter 5.5). This was thought to be particularly valuable synthetically for two reasons:-

(i) Nucleophilic substitution in pentafluorobenzene derivatives generally forms para- disubstituted products, ortho- and meta- derivatives usually only being present in an isomeric mixture which is often difficult to separate.[125]

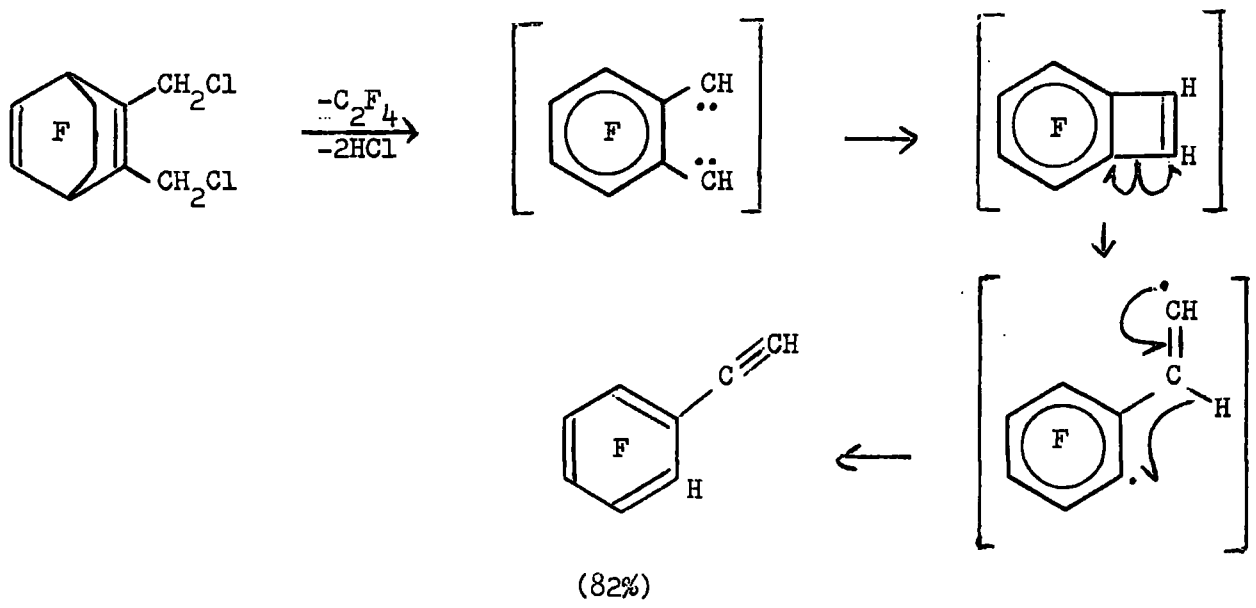
(ii) Alternative routes to ortho- derivatives suffer from a combination of low yields, experimentally difficult techniques or exotic starting materials e.g.[39,126-129]

As can be seen from Table 6.2(i), the hoped for reaction occurred, i.e. tetrafluoroethylene (TFE) was released from the strained bicyclic-[2,2,2]octa-2,5-dienes (II) in every case, simply by pyrolysis (500-630°) at reduced pressure.

In most cases, where the substituents are only H, Me, CF_3 or Ph, i.e. in adducts IIa, b, d, e, g, and i, there is an almost quantitative yield (71-99%) of the expected ortho- disubstituted tetrafluorobenzene. The $-CH_2Cl$ group eliminates HCl under these conditions and leaves a reactive carbene to undergo further reaction. There is no evidence showing the stage at which the elimination of HCl takes place; the trans-2,2',3,3',4,4',5,5'-octafluorostilbene (IIId) must be the result of an intermolecular dimerization, e.g.



and the 2,3,4,5-tetrafluorophenylacetylene (IIIg) most likely arises from the intramolecular rearrangement of an intermediate carbene and possibly via a benzocyclobutene as in the diagram below.



A similar cyclic rearrangement has been postulated in the pyrolysis of xylenes at reduced pressure.[130]

Ethylene and carbon dioxide were formed in addition to TFE in the pyrolysis of diethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate (IIh), the exact ratio of the products probably depending on the temperature and pressure conditions. The pyrolysis of the analogous perfluorocyclopentadiene adduct, at a lower temperature (480° in a sealed tube), produces carbon dioxide and an unidentified gas. However, only the yield of the phthalate diester is quoted (34%), even though the degraded products are also presumably present (page 22).[18]

Table 6.2(i) also adds weight to the theory that the mass spectrum of the adduct can often parallel the behaviour of the adduct on vigorous pyrolysis.[131] Thus, for adducts IIa, b, d, e and g the base peak of the mass spectrum corresponds (apart from charge) to the product of pyrolysis. Further, the base peak arises from the molecular ion by expulsion of a molecule of TFE; a process which was substantiated in each case by the observation of the appropriate metastable peak. Although not the base peak, m/e 286 $[C_8F_{10}]^+$, corresponding to the pyrolysis product, perfluoro-o-xylene (IIIk), it is present as 74% of the base peak at m/e 100 $[C_2F_4]^+$.

However, such correlations between mass spectra and pyrolyses must be used with some caution, since the fragment ions of IIc, IIf and IIh corresponding with the main pyrolysis products were often of low intensity. Thus, although the monochloromethyl (IIc) and bismonochloromethyl (IIf)

adducts both have a base peak corresponding to the loss of C_2F_4 and Cl from the molecular ion, the relative proportions of the peaks corresponding to the major aromatic pyrolysis product showed a large variation i.e.

IIc $\xrightarrow{-C_2F_4}$ $[C_7H_3{}^{35}ClF_4]^+$ m/e 198 (74%)

IIf $\xrightarrow[-2HCl]{-C_2F_4}$ $[C_8H_2F_4]^+$ m/e 174 (4·7%)

Likewise, little can be deduced from the mass spectrum of the diester adduct (IIh). The base peak, m/e 221 $[C_9H_5F_4O_2]^+$ corresponds to the loss of COOEt and C_2F_4, and the peaks corresponding to the identified aromatic products were of only relatively low intensity.

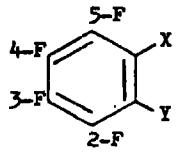
IIh → $[C_7H_2F_4O_2]^+$ m/e 194 (16·1%)

IIh → $[C_6H_2F_4]^+$ m/e 150 (1·6%)

No difficulty was experiencedin characterizing the products of pyrolysis. The gases could all be identified by means of i.r. and mass spectrometry; the aromatic products by analysis, i.r., u.v., mass and n.m.r. spectrometry.

The n.m.r. resonances in Table 6.2(ii) were assigned to particular

TABLE 6.2(ii). ^{19}F n.m.r. spectral parameters for ortho disubstituted tetrafluorobenzenes.



	Compound		Chemical Shifts [a]					F-F coupling constants [b]					
	X	Y	2-F	3-F	4-F	5-F	CF_3	$J_{2,3}$	$J_{2,4}$	$J_{2,5}$	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$
IIIa	H	Me	-17·4 (-19·0)	-5·3 (-6·9)	-2·2 (-3·4)	-21·7 (-22·2)	-	19·8	8·2	13·0	19·8	2·0	19·8
IIIb	H	CF_3	-23·4 (-22·9)	-9·6 (-10·8)	-13·3 (-15·3)	-25·8 (-26·1)	-100·0	18·5	7·7	13·3	19·2	3·8	18·6 [c]
IIIc	H	CH_2Cl	-10·4/-8·4	-3·3	-3·3	-8·4/-10·4	-	Not 1st order					
IIId	H	$C_8H_3F_4$	-24·0/-20·0	-7·6	-7·6	-20·0/-24·0	-	Not 1st order					
IIIe	H	Ph	-23·7 (-19·0)	-6·9 (-8·3	-4·9 (-6·4)	-27·6 (-23·6)	-	19·8	2·8	12·4	19·8	2·4	20·4 [d]
IIIf	Me	Me	-19·0 (-17·3)	-1·0 (-1·7)	-1·0 (-1·7)	-19·0 (-17·3)	-	Not 1st order					
IIIg	H	C≡CH	-28·9 (-28·9)	-8·8 (-11·7)	-10·8 (-13·2)	-25·0 (-27·0)	-	19·3	4·5	11·9	19·5	2·9	20·0
IIIh	Me	CF_3	-21·6 (-21·2)	-3·2 (-5·6)	-10·4 (-13·6)	-21·6 (-21·2)	-106·0	Not 1st order					
IIIj	H	COOH	-29·8 (-23·8)	-9·1 (-9·4)	-16·8 (-11·5)	-24·5 (-24·7)	-	19·8	10·5	13·9	19·5	2·4	21·0 [d]
IIIk	CF_3	CF_3	-30·6 (-25·1)	-17·4 (-17·5)	-17·4 (-17·5)	-30·6 (-25·1)	-108·8	Not 1st order					

Notes. [a] Neat liquids, with respect to C_6F_6 as external reference, predicted values (see text) in parentheses. [b] Average values, better than ± 0·5 Hz. [c] J_{FF} (CF_3-aromatic fluorines) 13·4(2), 0·8(3), 1·7(4), 0·6(5). [d] Saturated solution in CCl_4.

fluorine atoms by a combination of chemical shift and spin-spin coupling data. Chemical shifts can be predicted by assuming that shielding parameters are obtainable from the appropriately substituted pentafluorobenzene and that they are additive for tetrafluorobenzenes.[132,133] The values of Bruce[133] were used for the predictions in the table. Most of the predicted shift values, as expected, agree to within ±3 p.p.m. but the presence of larger variations is not disturbing, considering that the solvent effect on the reference used (C_6F_6), by diluting it to a 5% solution in CCl_4, shifts the resonance downfield by 5·25 p.p.m.[134] The only exception appears to be 2,3,4,5-tetrafluorobenzoic acid (IIIj), where there is a reversal of the 2-F and 5-F shifts. However, if the alternative assignment were made it would require an abnormally high meta-HF coupling constant (10·0 Hz) and an abnormally low ortho-HF coupling constant (6·5 Hz).[133] Other spin-spin coupling constants, where they could be obtained from first-order splitting patterns, are generally within the ranges of published values e.g.[133,134]

Conclusive evidence that many of the structures are as drawn is provided by the fact that five of the products produced by this pyrolysis method are known compounds: 1,2,3,4-tetrafluorobenzene (IIIi),[126] ααα,2,3,4,5-heptafluorotoluene (IIIb),[135] perfluoro-o-xylene (IIIk),[136] 2,3,4,5-tetrafluorobenzoic acid (IIIj),[127,129,137] and 2,3,4,5-tetrafluorobiphenyl (IIIe).[39] The data agrees well, except that Vorozhtov's group[137] has incorrectly assigned the structure of the latter compound (IIIe)

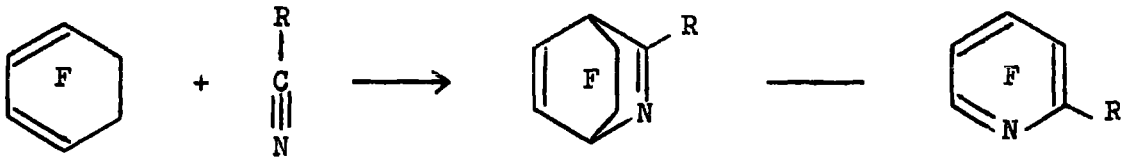
to the Diels-Alder adduct of tetrafluorobenzyne and benzene.[39] The oxidation of this product[137] to give IIIj is possibly correct, but the sample was probably impure since the melting point (79-80°) was considerably less than those reported earlier (92-92·5,[127] and 86-86·5[129]).

The 2,2',3,3',4,4',5,5'-octafluorostilbene (IIId) was assigned the trans-geometry on the basis of the similarity of the wavelength and shape of the absorption in the u.v. spectrum[138] to that of trans-stilbene. The fluorinated compound showed a multiplet absorption ($\nu_{max.}$, 293 nm.) similar to trans-stilbene ($\nu_{max.}$, 294 nm., multiplet), unlike that of cis-stilbene ($\nu_{max.}$, 280 nm., smooth absorption curve).[139]

CHAPTER 7. ADDITION OF NITRILES TO PERFLUOROCYCLOHEXA-1,3-DIENE.

7.1] Comparison with addition to butadiene.

The results of Diels-Alder addition of nitriles to perfluorocyclohexa-1,3-diene are summarised in Table 7.1(i).



IV V VI

TABLE 7.1(i). Successful reaction of nitriles with perfluorocyclohexa-1,3-diene.

Nitrile (IV) R		Temp. (°C)	Time (hr.)	Yield % V	Yield % VI
IVa	CF_3	400	16	-	40
IVb	Br	500	15	-	40
IVb	Br	380	12	9	18
IVc	$(CF_2)_3CN$	350	64	-	10 [a]
IVc	$(CF_2)_3CN$	350	16	4	1
IVd	C_6F_5	390	64	-	4

Note. [a] Together with perfluoro-1,3-bis-2,2'-pyridylpropane (VIe) 10%

Many aspects of this reaction reflect the pattern established by Janz and his co-workers (see Chapter 3). The only significant difference is that in this work it was possible to isolate, for the first time, the primary Diels-Alder adduct of a nitrile and a diene i.e. compounds Vb and Vc in Table 7.1(i). In previous work the primary adduct was inferred as an intermediate in the reaction by the nature of the isolated pyridinic products. More points of similarity and difference between this work and that reported previously are discussed below:

(i) Although a reaction temperature of 350-400° was also required, this was under static conditions, whereas Janz almost always used a flow system. The stability of the reactants and products at high temperatures is, therefore, possibly more important in obtaining a successful reaction.

(ii) The addition was attempted with seven nitriles, but it was successful in only four cases; no pyridinic products were detected when Me, Ph or CH_2Cl were the substituents in the nitrile, i.e. contrasting with the finite, though small, amounts of 2-substituted pyridines formed in homogeneous gas phase reactions with butadiene, MeCN (0·1%) and PhCN (1·4%).[51] Although the yields are less than those with butadiene, the best yields are nevertheless obtained from nitriles containing a highly electronegative substituent, 40% with CF_3CN or BrCN.

(iii) There was always an elimination of tetrafluoroethylene (TFE) from the intermediate strained heterobicyclic system (V) which resulted in the formation of the corresponding 2-substituted pyridine (VI). This is analogous to the loss of hydrogen from the postulated intermediate, dihydropyridine, in the butadiene additions.

(iv) Competing side reaction consumed starting materials and reduced yields; for example, in every case there was 1,2-addition of TFE to perfluorocyclohexa-1,3-diene to give perfluorobicyclo[4,2,0]oct-2-ene, 26% of this adduct was recovered from the reaction involving the addition of perfluoroacetonitrile and 1,3-diene, but this yield was not always recorded since this 1,2-adduct was usually collected in a liquid fraction containing the unreacted starting materials and was not separated. The most forcing conditions used in previous attempts to produce an adduct between TFE and perfluorocyclohexa-1,3-diene were to heat the compounds at 250° for 36 hr. At 400° this is a facile reaction. Another unexpected product was the dimer of the diene, formed in small proportions (4 to 5%) during the reactions lasting 64 hr.

Starting materials were lost in many other ways; etching of the glass reaction tube produced silicon tetrafluoride, perfluorocyclohexa-1,3-diene isomerized to its 1,4-isomer, and there was the inevitable "coke and tar". The addition involving cyanogen bromide produced a complex mixture of reaction products, particularly at the higher

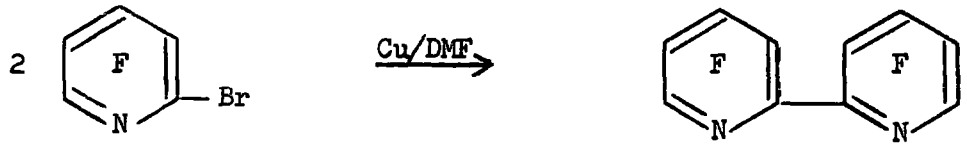
temperature. The TFE eliminated from the primary 2-bromobicyclic adduct (Vb) reacted with cyanogen bromide and free bromine to produce 1-bromo-2-cyanotetrafluoroethane and 1,2-dibromotetrafluoroethane respectively. Also isolated were monocyclic addition products of CNBr to the 1,3-diene and there was mass spectroscopic evidence for compounds with molecular formulae C_6BrF_7, C_7BrF_8N, $C_7BrF_{10}N$, $C_7Br_2F_7N$ and $C_7Br_2F_9N$, which can only be accounted for in terms of a complicated sequence of addition and elimination reactions. In view of the complexity of the mixture of minor products they were not extensively investigated. The temperatures recorded in Table 7.1(i) are probably close to the optimum values for the reactions, since at lower temperatures no adducts were formed and higher temperatures led to greater amounts of side-products and degradation.

7.2] Comparison with additions to alkynes.

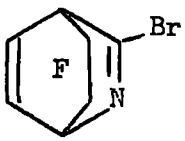
The yields presented in Table 6.1(i) indicated that alkynes showed a reactivity consistent with an "inverse electron demand" in the dienophile, Me being an activating substituent. This is clearly not the case in the addition of nitriles, and the trends of the Alder rule appear to be obeyed. It is, however, worth pointing out that all the products are thermally stable, fully fluorinated compounds. Judging by the large amounts of SiF_4 produced, it is possible that the reagents containing hydrogen form reactive radicals which abstract fluorine from

fluorinated molecules and produce species, such as HF, which can etch the glass ampoule. Janz has pointed out that yields of pyridinic products are much reduced by using such thermally unstable nitriles.[140] Thus, in the presence of such fast decompositions, it is not really justifiable to express even a qualitative idea of the reactivity of the nitrile group in the cases of benzonitrile, acetonitrile or monochloroacetonitrile. The utility of these nitriles will also be reduced by their tendency to form 1,3,5-triazines at 400° under pressure and one, 2,4,6-triphenyl-1,3,5-triazine was isolated. Carrying out these reactions at lower pressures in the gas phase by a flow process may, perhaps, be more successful.

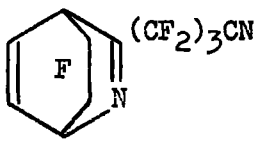
As with the addition of alkynes an important reason for carrying out these reactions was the possible synthetic value of the products. Because nucleophilic substitution of pentafluoropyridine takes places primarily in the 4-position and 2-substituted tetrafluoropyridines are not easily obtained.[141-143] Their preparation is generally restricted to indirect fluorination techniques followed by aromatization.[144,145] Unfortunately direct routes to a large range of these compounds via nitrile additions also seems unpromising, since no nitrile containing hydrogen has yet proved successful. However, this drawback may be alleviated by preparing derivatives of perfluoro-2-bromopyridine e.g. the Grignard reagent. Only one such reaction was attempted; the copper coupling of two molecules gave perfluoro-2,2'-bipyridyl.



The loss of the $-CF_2-CF_2-$ bridge from the 2-azabicyclo[2,2,2]octa-2,5-dienes (V) is exactly analogous to its loss from the alkyne adducts on pyrolysis (Chapter 6), but, owing to the high temperatures involved, the elimination step appears to take place in situ and shortly after the formation of the nitrile adduct. Thus, it was possible to isolate only two adducts, perfluoro-3-bromo- (Vb) and 3-(3-cyanopropyl)-2-azabicyclo-[2,2,2]octa-2,5-diene (Vc).

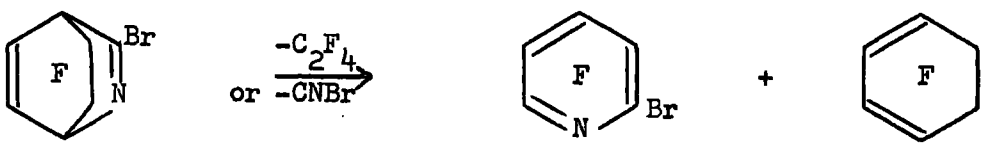


Vb



Vc

There is, however, one major difference in the respective adducts. Only the 3-bromo adduct (Vb) was available in sufficient quantity for pyrolysis, but this had an almost equal propensity for the reverse Diels-Alder reaction, not observed at all with any alkyne adduct. An interesting comparison between the mass spectrum of this adduct and the



Vb 42% 58%

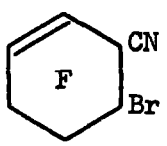
alkyne adducts predicted that this retrodiene reaction was liable to occur. M/e 224 $[C_6F_8]^+$ was the base peak for Vb and the peaks corresponding to the pyridine product $[C_5BrF_4N]$ had a total intensity of only 57%. This contrasts with the majority of the alkyne adducts, in which the base peak corresponded to the eventual aromatic product; m/e 224 was always insignificantly small. Vc had a base peak at m/e 100 $[C_2F_4]^+$, owing to the abundance of CF_2 groups in the molecule, but here also, m/e 224 (43%) was far larger than m/e 326 $[C_9F_{10}N_2]^+$ (3·5%). This indication that the cyanopropyl adduct (Vc) is even more likely to undergo reverse Diels-Alder addition is borne out by the lower overall yields of products, the elimination of TFE having to compete with the faster retrodiene reaction.

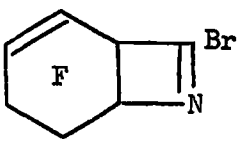
A possible reason for these results is that the C-N single bond energy (66 kcal.mole^{-1}) is lower than the C-C bond energy (80 kcal.mole^{-1}) and is thus more easily broken.[146] As shown in Table 5.5(i), the activation energy for a forward Diels-Alder reaction involving cyclic dienes is only about 18 kcal.mole^{-1} less than the activation energy for its reverse. An adduct formed with a nitrile will have these values even closer, since the major difference is the cleavage of a C-N bond rather than a C-C bond. The effect, therefore, should be to enable both the forward and reverse reactions to occur almost equally easily.

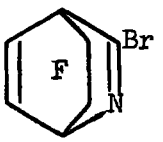
7.3] Characterization of the nitrile adducts and 2-substituted pyridines.

Only one 2-azabicyclo[2,2,2]octa-2,5-diene has been reported previously and this was without any i.r. data.[147,148] However, the i.r. absorptions at 1765, 3-bromo derivative (Vb), and 1775 $cm.^{-1}$ 3-(3-cyanopropyl) derivative (Vc) can be readily assigned to the CF=CF stretching frequency by analogy to the alkyne adducts (1763 to 1777 $cm.^{-1}$). The C=N stretching absorption of Vc occurs at 1660 $cm.^{-1}$, within the range expected (1680 to 1630 $cm.^{-1}$), but the value for Vb is slightly lower, 1615 $cm.^{-1}$, owing to the similar known reduction of C=C stretching frequencies by bromine bonded to an olefinic carbon atom.[149a]

The cyanogen bromide adduct has three possible structures:

(i) 

(ii) 

(iii) 

Structure (i) can be eliminated not only by the i.r. evidence, which does not include a C≡N stretching vibration, but this, or its monocyclic isomers, also occured as identified by-products. Both (ii) and (iii) could be expected to have similar n.m.r. spectra, but the ring strain in a 4-membered ring should reduce the C=N stretching frequency to ca. 1570 $cm.^{-1}$,[149b] and only (iii) has a structure compatible with an equally facile reverse Diels-Alder addition of CNBr and elimination of TFE. The same basic structure must be envisaged for the 1 : 1

1,3-dicyanopropane adduct (Vc) to account for the observed formation of the pyridinic products.

The ^{19}F n.m.r. spectra can be analysed purely on the basis of chemical shifts, as with the alkyne adducts, into tertiary, vinylic and methylene fluorine resonances, as shown in Table 7.3(i). Insufficient

TABLE 7.3(i). ^{19}F n.m.r. spectra of nitrile adducts.

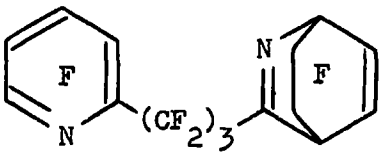
Compound	Chemical Shift (rel. intensity in brackets)		
	>C-F	CF=CF	CF_2
Vb [a]	+29·4(1), +9·4(1)	-10·5(1), -17·7(1)	-42·5(4)
Vc [b]	+48·2(1), +14·1(1)	-8·4(1), -16·2(1)	-41·4(6), -50·2(2), -58·6(2)

Notes. [a] neat liquid, external C_6F_6; [b] 20% solution in CCl_4, internal C_6F_6.

work has been done on model compounds to assign precisely all the resonances, but those at +9·4 (Vb) and +14·1 (Vc) are presumably of the tertiary fluorines adjacent to the nitrogen atoms, since ring nitrogen always causes a large shift to lower field when it replaces a carbon atom.

In spite of their high lability, it may be possible to isolate all the adducts, under suitable conditions. The most likely precursor of

the bispyridyl compound is the adduct of perfluoro-2-(3-cyanopropyl)-pyridine and perfluorocyclohexa-1,3-diene, although there is no chemical evidence.



The 2-substituted tetrafluoropyridines were characterized, as usual, by analysis, i.r., u.v., mass and n.m.r. spectroscopy. The data for perfluoro-2-methylpyridine agrees well with that published previously.[144,150] Although not strictly applicable, owing to the nitrogen atom perturbing the π-electron system,[151,152] the values of ^{19}F n.m.r. substituent shielding parameters obtained from pentafluoropyridine[150] and substituted pentafluorobenzenes[133] were used to assign chemical shifts [see Table 7.3(ii)]. Apart from the fluorine atom adjacent to the nitrogen (6-F), the predicted values agree reasonably with the measured values. First-order spin-spin coupling patterns enabled coupling constants to be evaluated. They agreed qualitatively with published values[150] and are internally consistent e.g. $J_{5,6}$ (22·7 to 24·9 Hz) is always less than $J_{3,6}$ (25·4 to 28·1 Hz). The shifts of the aliphatic fluorine atoms in the pyridyl propanes were assigned by comparison with the values of the shifts in 1,3-dicyanohexafluoropropane.

TABLE 7.3(ii). ^{19}F n.m.r. spectral parameters of 2-substituted tetrafluoropyridines (VI).

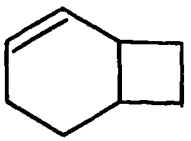
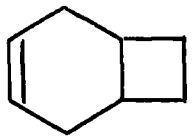
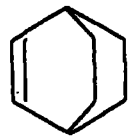
Substituent	Chemical Shift [a]				F-F Coupling Constants [b]						Notes
	3-F	4-F	5-F	6-F	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	
CF_3	-21·4(-20·6)	-28·0(-28·5)	-13·5(-12·7)	-82·0(-76·3)	17·7	10·1	28·1	17·0	19·8	24·1	c,d
Br	-33·2(-27·9)	-29·3(-28·2)	-7·5(-5·7)	-82·6(-72·0)	18·2	4·6	25·6	17·2	17·0	22·7	c
C_6F_5	-22·7(-22·6)	-24·7(-28·5)	-8·2(-9·5)	-81·7(-76·3)	17·4	4·7	25·4	17·2	17·8	24·9	e,f
$(CF_2)_3CN$	-23·4	-28·0	-14·0	-83·2	17·8	—	26·5	17·8	18·8	24·3	g,h
$(CF_2)_3C_5F_4N$	-23·4	-26·8	-12·4	-82·3	18·2	—	27·4	18·2	18·6	24·2	i,j

Notes. [a] Predicted values in parentheses. [b] Average values, generally better than ±0·5 Hz. [c] Neat liquid, external C_6F_6. [d] CF_3 chemical shift at -97·5. [e] 30 vol. % in CCl_4, internal C_6F_6. [f] C_6F_5 chemical shifts at -1·2 (meta- to pyridyl), -12·0 (para-) and -22·1 (ortho-). [g] 50 vol. % in CCl_4, internal C_6F_6. [h] CF_2 chemical shifts at -51·2 (α, adjacent to pyridyl), -39·8 (β), and -58·0 (γ). [i] 20 vol. % in CCl_4, internal C_6F_6. [j] CF_2 chemical shifts at -50·0 (α) and -39·0 (β).

7.4] Other cycloadditions of perfluorocyclohexa-1,3-diene.

As briefly mentioned above, perfluorocyclohexa-1,3-diene formed a 1,4- Diels-Alder adduct with itself and a 1,2- addition product with TFE under the conditions of the nitrile addition reactions. The numbers of possible structures for these compounds is increased by the presence of perfluorocyclohexa-1,4-diene, which, as shown in a separate experiment, is the result of the isomerization of the 1,3-diene.

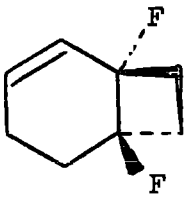
Since the TFE adduct has only one CF=CF stretching frequency (1740 $cm.^{-1}$) only the bicyclic structures (i) to (iii) need be considered. Of these, the perfluorobicyclo[4,2,0]oct-3-ene (ii), and [2,2,2]oct-2-ene

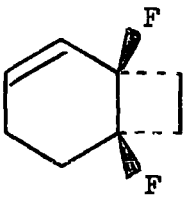
(i)  (ii)  (iii) 

(all unmarked bonds to F)

(iii) can be eliminated simply on symmetry grounds, the ^{19}F n.m.r. spectrum shows eight distinct resonances [Table 7.4(i)]. It was, of course, possible to prepare this compound by heating the 1,3-diene and TFE at 400°. Unfortunately, it was not always possible to purify it by this route since it has almost the same retention time as 1,4-diene on the g.l.c. columns used. The quantity of 1,4-diene produced was variable, ranging from zero to 40% even though conditions were similar. No TFE was recovered, it always dimerized to perfluorocyclobutane.

The stereochemistry of the ring-junction of the adduct has not been elucidated. There are two possible arrangements of the tertiary fluorine atoms, either trans-disposed (I), on opposite sides of the ring system, or cis-disposed (II). The most likely means of





(All unmarked bonds to F)

I Trans-Perfluorobicyclo[4,2,0]oct-2-ene

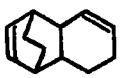
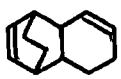
II Cis-

ascertaining this would be by studying the n.m.r. of this adduct and other cyclobutane derivatives, (feasible only if spin-decoupling equipment were available). With these symmetrical addends, however, it is not possible to prove whether the addition takes place by a thermally concerted or a radical mechanism. The Woodward-Hoffmann rules for 2+2 cycloaddition (see Chapter 5.5) predict that the trans-isomer (I) can arise from a thermal trans-cis addition (trans-lobes of a diene double-bond overlapping with the cis-lobes of TFE) or a radical trans-trans addition. II could arise from either a thermal cis-trans addition or a radical cis-cis addition.

Chapter 5.3 pointed out that 2+2 cycloaddition is normal for TFE[101] so that the [4,2,0] octene was the expected product. It came as a surprise that, in one isolated attempt to prepare this material, the product was largely bicyclo[2,2,2]oct-2-ene (iii), even though the conditions

appeared practically identical. This has the same molecular weight, but a different i.r., cracking pattern in the mass spectrum (base peak at m/e 155, not m/e 255), and n.m.r., which shows a completely symmetrical structure. The latter also provided the only evidence supporting the [2,2,2]-bicyclic skeleton, since the high upfield position (+59·4 p.p.m.) of the tertiary fluorine atoms indicates that they are not attached to adjacent carbon atoms[15-18] [Table 7.4(i)].

TABLE 7.4(i). ^{19}F n.m.r. of isomeric perfluorocyclohexa-1,3-diene adducts.

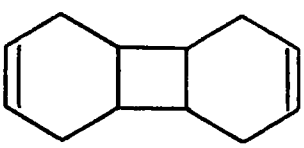
Compound (all perfluoro-)	Chemical Shift (rel. intensity in brackets)		
	CF_2	CF=CF	$\geqslant$CF
	-46·5 to -38·5(8)	-21·8, -19·0	+25·3, +34·7
	-40·0(8)	-14·2(2)	+59·4(2)
 endo?	-59·2 to -34·2(8)	-24·2, -21·4 -20·2, -14·2	-3·4, +16·6 +48·8(2)
 exo?	-64·6 to -32·6(8)	-27·4, -23·4 -20·6, -17·6	-12·2, +4·6 +44·4, +47·2

Unfortunately, this impure product was isolated in only one experiment and attempts to repeat its preparation have, so far, been unsuccessful.

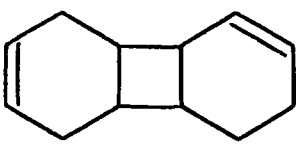
Presumably this anomalous result was due to the presence of isomeric impurities in the recovered starting materials or some unidentified impurities.

Further verification of these structures should have been possible by permanganate oxidation of the double-bonds, but, for some reason, also found by Pyke,[16] some fluorinated bicyclic systems do not appear to produce stable polybasic acid products which can be identified via any of the usual derivatives.

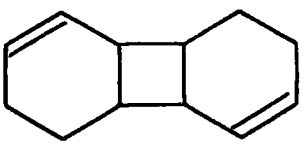
Prolonged heating of perfluorocyclohexa-1,3-diene at 390° for 144 hr. produced a fair yield (ca. 40%) of a dimeric product (m/e 448), shown by a combination of g.l.c. and n.m.r. to consist of a mixture of two very similar isomers in a ratio of about 1 : 8. Also the i.r. absorptions occur at practically identical frequencies, so that they are clearly exo-endo isomers. Possible structures should include 1,4- and 1,2-addition products of perfluorocyclohexa-1,4-diene since this was also produced in the reaction i.e.



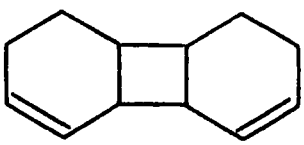
(i)



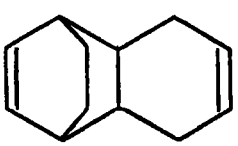
(ii)



(iii)



(iv)



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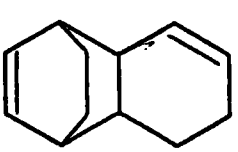
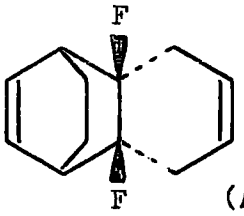


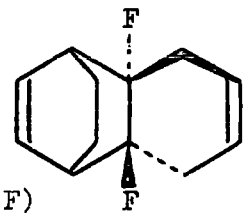
(vi)

(All unmarked bonds to F)

Structure (vi) is the only one compatible with the ^{19}F n.m.r. spectra [Table 7.4(i)]. (i) to (iv) can be eliminated on grounds that adjacent tertiary fluorine atoms could not account for the upfield resonances at about +45 p.p.m., (see also Chapter 6.1, page 52), and (v) is untenable since it posseses a plane of symmetry. Perfluorotricyclo[6.2.2.$0^{2,7}$]dodeca-4,9-diene (v) actually has an unsymmetrical stereoisomer in which the adjacent tertiary fluorine atoms on C2 and



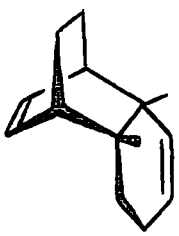
(All unmarked bonds to F)



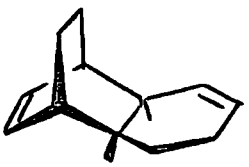
cis- trans-

C7 are trans-disposed, but such a structure should not be formed in a Diels-Alder reaction, since this would be contrary to the "cis-" principle (Chapter 1.1). Again unidentifiable products rendered permanganate oxidations useless for structure confirmation. However, pyrolysis of the major isomer produced practically only 1,3-diene (there were traces of TFE in the gases), thus supporting structure (vi).

The remaining problem is the stereochemistry of the Diels-Alder addition of the dimerization. The reasons for naming the longer



endo- (ca. 89%)



exo- (ca. 11%)

retained, major isomer as the endo-adduct are tenuous; (i) the empirical Alder "endo" rule predicts that the isomer produced in the greatest yield will have endo- orientation of the double bonds (Chapter 2.2); (ii) consideration of 3-dimensional models seems to indicate that the tertiary fluorine atom on C-2 and C-7 will be less shielded in the endo- form (-3·4, +16·6 p.p.m.) by the C-9 to C-10 double bond than in the exo- form (-12·2, +4·6 p.p.m.). Only measurements of long-range ^{19}F n.m.r. coupling constants is likely to produce confirmation of this postulate.

7.5] Catalysis with boron trifluoride.

Nitrile additions to butadiene are facilitated by alumina/chromium oxide catalysts (Chapter 3.2), but since BF_3 has been used as a catalyst in 1,3-dipolar additions involving nitriles[153] it was hoped that this easily-handled gas would also be effective in the Diels-Alder reaction. Either a reduction in reaction temperature or an acceleration of addition would have reduced the possibility of unproductive side-reactions. Although a full study was not undertaken, BF_3 appeared to have no favourable catalytic activity. No reaction took place by heating CF_3CN and 1,3-diene in the presence of BF_3 at 200° for 16 hr. and there was not full conversion of starting materials at 300° for 24 hr. The green and orange colours observed before heating were probably owing to some complex formed between the nitrile and BF_3. However, it is likely

$$CF_3—C\equiv N \rightarrow BF_3$$

that this complex dissociated at the temperature of reaction, and the possible favourable reduction in electron density of the nitrile triple bond was not present.

The other attempts at catalysis were made with MeCN, which does not add under normal conditions. Again, there was no positive effect; at low temperature (195° for 28 hr.) only starting materials were recovered, and at 400° for 17 hr. the only result was deep etching of the glass reaction tube and a residual hard, black, carbonaceous material.

CHAPTER 8. ATTEMPTED DIELS-ALDER REACTION OF THIAZYL CHLORIDE.

8.1] The reaction of thiazyl chloride with perfluorocyclohexa-1,3-diene.

The trimer of thiazyl chloride, $(NSCl)_3$, was heated with perfluorocyclohexa-1,3-diene at 100°. The literature[71,154] shows that this should dissociate into thiazyl chloride, NSCl, enabling the triple bond of the molecule to act as the dienophile in a Diels-Alder reaction. This is probably the best explanation for the observed products, since a 1:1 adduct, $C_6F_8.NSCl$, was separated from the reaction mixture when there was excess 1,3-diene, equation A. Another product, $C_6F_8.NS_2$, was also formed; to the exclusion of $C_6F_8.NSCl$ when the reactants were in approximately equimolar proportions, equation B.

A: C_6F_8 + $(NSCl)_3$ $\xrightarrow[62\ hr.]{100^\circ}$ $C_6F_8.NSCl$ + $C_6F_8.NS_2$

20·4 mmoles 12·3 mmoles (NSCl) 45% 27%

B: C_6F_8 + $(NSCl)_3$ $\xrightarrow[17\ hr.]{100^\circ}$ $C_6F_8.NS_2$ + red oil

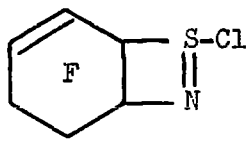
11·5 mmoles 9·5 mmoles (NSCl) 75% (w.r.t. NSCl)

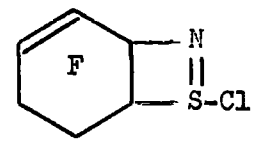
Unfortunately subsequent experiments could not definitely assign their structures, partly owing to the difficulties involved in handling these air-sensitive substances and also due to the absence of any similar compounds in the literature. It cannot be definitely claimed that $C_6F_8.NSCl$ is the result of 1,4-addition of NSCl, since this

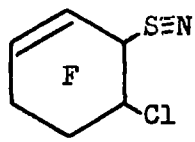
proposed dienophile was not actually observed at any stage.

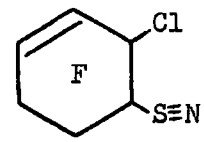
8.2] The products of the reaction.

$C_6F_8.NSCl$, a colourless volatile liquid, has several possible structures from the i.r. and mass spectra:

(i)a 

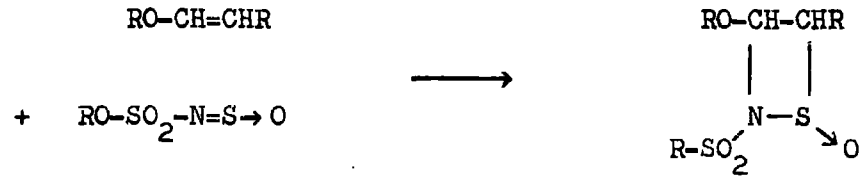
(i)b 

(ii)a 

(ii)b 

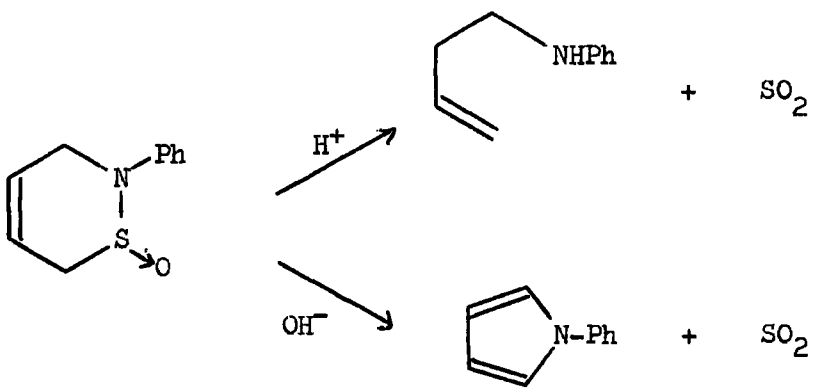
(iii) 

The parent molecular ion occurs at m/e 305 (P+2 indicating one chlorine atom) and prominent i.r. absorptions are observed at 1740 (CF=CF) and 1490 $cm.^{-1}$ (S-N multiple bond).[155] This latter frequency corresponds to bond order appreciably in excess of two. This may be considered to be due to either a formal triple bond, or a formal double bond with further bonding contributions arising from (a) an ionic component $N^{\delta+}=S^{\delta-}$ and/or (b) π-donation i.e. the interaction between the lone-pair of electrons in a nitrogen p-orbital and the vacant d-orbitals of sulphur. Highly electronegative atoms attached to sulphur enhance both (a) and (b). For example, $MeN=SOF_2$ has a formal



of N-sulphinylsulphonamides and vinyl ethers being similarly unstable.[157a]

A clear crystalline solid is formed on exposure to air or on contact with water, with the exothermic evolution of a gas. The ^{19}F n.m.r. spectrum shows a multiple of six fluorine atoms; two CF_2 groups (-45·5 and -33·6 p.p.m.), and two CF groups (-26·3 and +2·4 p.p.m.). The CF resonance at -26·3 p.p.m. is a broadened triplet, i.e. it appears to be adjacent to a nitrogen atom. The proton n.m.r. spectrum indicates at least seven hydrogen atoms and the i.r. spectrum shows that a carbonyl group (1735 $cm.^{-1}$) may be present in the molecule. The mass spectrum has highest m/e at 236, which normally indicates an even number of nitrogen atoms. No structure could be devised which is consistent with all this data. By analogy with the hydrolysis of the 1,4-adducts of N-sulphinyl compounds and butadiene,[158] the gas produced is probably a mixture of SO_2 and HCl. However, a similar ring-opening or

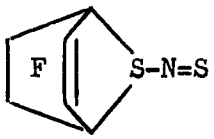


cyclization is prevented from occuring by the C_2F_4 bridge in $C_6F_8.NSCl$.

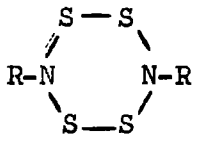
$C_6F_8.NSCl$ is not formed when $(NSCl)_3$ and C_6F_8 are reacted in stoichiometric proportions. It was only formed when there was a 66% excess of 1,3-diene, and even then, the second product $C_6F_8.NS_2$ was observed. The latter compound, a viscous pale-yellow liquid, was a most unexpected product. It appears to be an odd-electron molecule or free radical, for which it is impossible to satisfy the common valencies of sulphur and nitrogen by normal two-centre bonds, i.e.

This structure seems to be the one most consistent with the spectroscopic evidence. The i.r. spectrum showed a CF=CF stretching vibration at 1750 $cm.^{-1}$, and the highest peak in the mass spectrum was correct at m/e 302. Since the compound is not very volatile a dimeric form was considered, but an approximate cryoscopic molecular weight determination (M, 330) at least showed that it was not a dimer in benzene solution. The molecule is symmetrical since there are only three resonances in the n.m.r. spectrum [at -36·2 (CF_2), -15·3 (vinylic fluorine) and at +26·2 p.p.m. (tertiary fluorine) with total relative intensities 2 : 1 : 1]. One fact that does not correlate well is that

the tertiary fluorine resonance appears further upfield than expected, by comparison with $C_6F_8.NSCl$ (+8·4 or +12·0 p.p.m.). The n.m.r. spectrum also does not rule out symmetrical structures which involve a five-membered ring in the bicyclic system. Lack of data on similar



compounds makes the definite assignment of structure difficult. Although only circumstantial, certain evidence favours the [3,2,2] bicyclic system since cyclic S-N-S sequences have been identified in other systems, e.g.[159,160]



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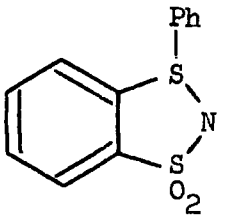

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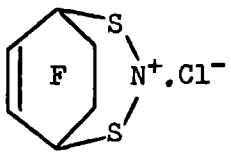
An alternative to the odd-electron molecule, which would not show chlorine in the mass spectrum, is an ionic form:



However, its volatility and separation by g.l.c. exclude such a structure.

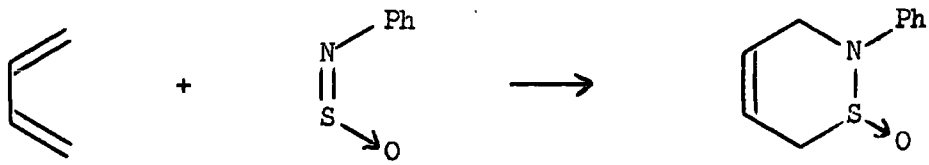
In addition, although elemental analyses seem unreliable with sulphur-nitrogen halogen compounds in general,[73] the carbon analysis was correct for $C_6F_8.NS_2$. Halogen analyses were invariably high, one explanation being that $CNS^{\ominus}$, formed during the potassium fusion, interferes with the estimation procedures used.

8.3] Possible mechanisms.

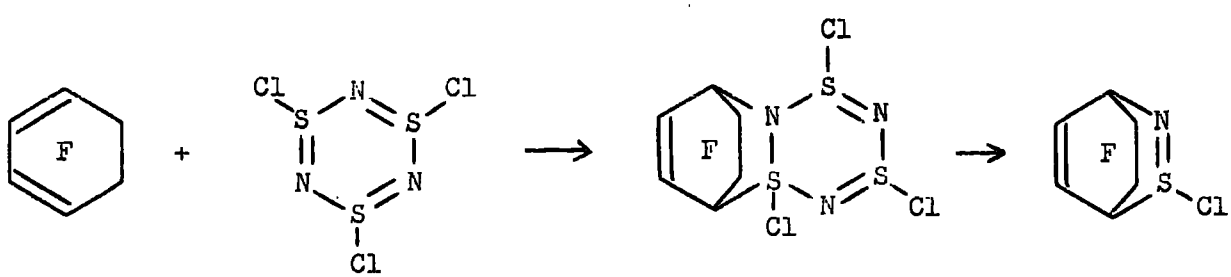
Preliminary experiments were carried out at about 200°C, i.e. in comparable conditions to the alkyne addition. This resulted in etching of the glass tube, unidentified gaseous products, dichloro-octafluorocyclohexene, and unidentified polymeric oils and solids. One reaction tube exploded. These temperatures were obviously too high, causing decomposition of starting materials and/or products, and only illustrated the chlorinating ability of thiazyl chloride. Reproducible results were possible by lowering the temperature of reaction to 100°C. Thus, it could be concluded that the triple bond in NSCl is far more reactive than in either alkynes or nitriles, which require reaction temperatures of ca. 200 and ca. 400° respectively. A method for proving this theory would be to carry out the experiment by using genuine NSCl monomer, e.g. in a gaseous flow reaction, and compare the yield obtained with other dienophiles in similar conditions.

From present evidence it cannot be categorically stated that the reaction involves the 1,4-cycloaddition of the triple bond in thiazyl

chloride. The compound heated in the reaction tube is its trimer, $(NSCl)_3$, and although it depolymerizes above 50°,[154] there can be no guaranteee that this occurs before other reactions take place. As illustrated in Chapter 4, there are many possible fragmentation paths available for the trimer, and other compounds containing multiple N-S bonds are potentially capable of reacting as dienophiles cf. N-sulphinyl compounds:[158]



Thus, it is possible to devise alternative mechanisms involving, for instance, the trimer itself.



+ 2NSCl

Similarly the hetero-atoms in $C_6F_8.NS_2$ may arise directly from the trimer, but mass spectral evidence suggests that $C_6F_8.NSCl$ may be the precursor of $C_6F_8.NS_2$, at least in the mass spectrometer and possibly

PART III

EXPERIMENTAL

INTRODUCTION.

This is a summary of the apparatus and instruments used for obtaining the results throughout the Experimental section.

Vacuum system. - An efficient vacuum system, employing a two-stage rotary oil pump and mercury diffusion pump, capable of attaining a "sticking" vacuum (ca. 10^{-5} mm.) was used for transferring volatile compounds in vacuo, storage and measurement of gas. Small amounts of gases (< 10 mmoles) were measured by noting the pressure in a small bulb (485 ± 5 ml.) fitted with a wide bore manometer, and, by increasing the volume to 4020 ± 30 ml., larger amounts could be measured. This section utilized mercury float valves.

Infrared spectra. - Spectra were recorded on Perkin Elmer 137 and 157 sodium chloride spectrophotometers.

Ultraviolet spectra. - Unicam SP800 u.v. spectrophotometer.

Mass spectra. - A.E.I. MS9 spectrometer.

N.M.R. spectra. - Perkin Elmer R10 spectrometer, operating at 56.46 MHz for ^{19}F and 60 MHz for ^{1}H spectra, operating temperature 33.5°. Unless otherwise stated, the chemical shifts are in p.p.m. from an internal reference in the neat liquid, hexafluorobenzene or tetramethylsilane (-ve downfield). Coupling constants are in Hz.

Analytical g.l.c. - A Perkin Elmer 452 with a variety of stationary phases using hydrogen carrier gas and a hot wire detector were used. Peak areas were measured by a Honeywell Integrator Model 5530000.

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

Column A: 4·9 m. x 75 mm. diam., dinonyl phthalate-Celite, 1 : 2; ca. 60 l./hr.

Column B: 6·1 m. x 13 mm. diam., dinonyl phthalate-Celite, 1 : 2; ca. 10 l./hr.

Column C: As column B, but silicone elastomer-Celite, 1 : 2.

Column D: Perkin Elmer F21 Präparativer Gaschromatograph, 4·5 m. x 9·5 mm. diam., di-n-decyl phthalate-Chromosorb P, 1 : 4; ca. 12 l./hr.

Column E: As Column D, but silicone oil-Chromosorb P, 1 : 4.

Column F: Perkin Elmer F21, 11 m. x 10 mm. diam., glass column; dinonyl phthalate-Celite, 1 : 2; ca. 6 l./hr.

CHAPTER 9. EXPERIMENTAL FOR CHAPTER 6 - ALKYNE ADDITION.

9.1] Reagents.

Perfluorocyclohexa-1,3-diene[161,162] and 3,3,3-trifluoropropyne[163] were prepared by the published routes. 1,1,1-Trifluorobut-2-yne was prepared by a modification of an existing route.[164] The other alkynes were commercially available and all were redistilled, dried (P_2O_5) and degassed before use.

9.2] Preparation of 1,1,1-trifluorobut-2-yne.

Direct dehydroiodination of cis- and trans-1,1,1-trifluoro-3-iodobut-2-ene by molten potassium hydroxide produced 1,1,1-trifluorobut-2-yne. Earlier preparations of the olefin[164,165] were prior to the general introduction of g.l.c. and failed to separate the mixed isomers, cis- (83%) and trans- (17%). The structural assignment is based on consideration of Courtauld models which indicate an unfavourable steric interaction between the cis- disposed trifluoromethyl and iodine in trans-1,1,1-trifluoro-3-iodobut-2-ene, the minor product. This assignment is consistent[166] with the marginally easier dehydroiodination of the trans-isomer (loss of trans- disposed H and I) as compared with the cis-isomer (loss of cis- disposed H and I) but it cannot be regarded as definitive owing to the lack of knowledge about reaction mechanisms under the dehydroiodination conditions used.

(a) Addition of trifluoromethyl iodide to propyne. - Propyne (4·12 g., 103 mmoles) and trifluoromethyl iodide (17·7 g., 90·3 mmoles) were irradiated (500 watt U.V. lamp) in a 100-ml. Pyrex ampoule for 36 hr. at ca. 50° to give: (i) propyne (5·63 mmoles); (ii) a mixture of cis- and trans-1,1,1-trifluoro-3-iodobut-2-ene (19·81 g., 84·0 mmoles, 93%), 83% cis-isomer by ^{19}F n.m.r.; (iii) tar (0·88 g.). The mixture of cis- and trans-1,1,1-trifluoro-3-iodobut-2-ene was separated by preparative g.l.c. (Column A, 100°) and in a typical run (25·50 g.) gave: (i) cis-1,1,1-trifluoro-3-iodobut-2-ene (19·71 g.), [Found: M (mass spectrometry), 235·931011. $C_4H_4F_3I$ requires M, 235·931165], b.p. 94·0°/749 mm., I.R. No.1 ν_{max} 3060 (vinyl C-H), 2920 (Me), 1645 $cm.^{-1}$ (C=C). The ^{19}F n.m.r. spectrum showed a resonance at -104·0. The ^{1}H n.m.r. spectrum showed resonances at -6·25 (vinylic proton) and -2·62 (Me) with respect to benzene (-7·27) as internal reference. J_{HF} 2·0 (Me protons), 7·7 (vinyl proton), J_{HH} 1·5; (ii) trans-1,1,1-trifluoro-3-iodobut-2-ene (4·12 g.), [Found: M (mass spectrometry), 235·929867. $C_4H_4F_3I$ requires M, 235·931165], b.p. 114°/746 mm., I.R. No.2 ν_{max} 3030 (vinylic C-H), 2960 (Me), 1658 $cm.^{-1}$ (C=C). The ^{19}F n.m.r. spectrum showed a resonance at -103·0. The ^{1}H n.m.r. spectrum showed resonances at -6·13 (vinylic proton) and -2·58 (Me) with respect to benzene (-7·27) as internal reference. J_{HF} 2·1 (Me protons), 7·1 (vinyl proton), J_{HH} 1·5.

(b) Dehydroiodination of 1,1,1-trifluoro-3-iodobut-2-ene. - (1) cis-1,1,1-Trifluoro-3-iodobut-2-ene (1·103 g., 4·68 mmoles) was passed (nitrogen carrier) through molten potassium hydroxide at 180°, the products were collected in a trap cooled in liquid air and separated by vacuum transfer to give: (i) cis-1,1,1-trifluoro-3-iodobut-2-ene (0·075 g., 0·32 mmoles); and (ii) 1,1,1-trifluorobut-2-yne (Ig) (2·50 mmoles, 57% yield, 93% conversion), [Found: M (mass spectrometry), 108. Calculated for $C_4H_3F_5$: M, 108], ν_{max} 2310(m) and 2275(s) $cm.^{-1}$ (C≡C) (lit.[165] 2304(m) and 2273(s) $cm.^{-1}$). (2) By using the same procedure as in (1), trans-1,1,1-trifluoro-3-iodobut-2-ene (1·176 g., 4·98 mmoles) was dehydroiodinated to give: (i) unreacted iodide (0·082 g., 0·35 mmoles); (ii) 1,1,1-trifluorobut-2-yne (3·58 mmoles, 77% yield, 91% conversion). (3) By using the same procedure as in (1), dehydroiodination of cis-/trans-1,1,1-trifluoro-3-iodobut-2-ene gave cis-1,1,1-trifluoro-3-iodobut-2-ene and 1,1,1-trifluorobut-2-yne, both with correct i.r. spectrum.

9.3] Diels-Alder reactions of perfluorocyclohexa-1,3-diene.

(a) With propyne. - Perfluorocyclohexa-1,3-diene (10·86 g., 48·5 mmoles), propyne (2·13 g., 55·3 mmoles) and dipentene (ca. 0·07 g.) were heated at 180° for 40 hr. in a 100-ml. Pyrex ampoule, which had been sealed under vacuum. The products were separated by conventional vacuum line techniques to give: (i) a gaseous fraction (1·49 mmoles) which was

shown by i.r. and mass spectroscopy to contain hydrocarbons (mainly propane) and perfluorocyclohexa-1,3-diene; (ii) 2-methyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIa) (12·07 g., 45·8 mmoles, 94%), [Found: C, 40·6; H, 1·5; F, 57·2%; M (mass spectrometry), 264. $C_9H_4F_8$ requires C, 40·9; H, 1·5; F, 57·6%; M, 264], b.p. 138°/763 mm., I.R. No.3 ν_{max} 3060 (vinylic C-H), 2910 (Me), 1763 (CF=CF) and 1655 $cm.^{-1}$ (CH=C(Me)). The ^1H n.m.r. spectrum showed resonances at -6·14 (vinylic proton) and -2·10 (Me); (iii) an involatile viscous brown oil (trace).

(b) With 3,3,3-trifluoropropyne. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (11·52 g., 51·5 mmoles), 3,3,3-trifluoropropyne (5·05 g., 53·7 mmoles) and dipentene (ca. 0·07 g.) were heated in a 100-ml. Pyrex ampoule at 200° to give: (i) a gaseous fraction (7·51 mmoles), the i.r. spectrum was consistent with a mixture of trifluoropropyne and tetrafluoromethane; (ii) perfluorocyclohexa-1,3-diene (0·25 g., 1·12 mmoles); (iii) 2-trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIb) (14·83 g., 47·6 mmoles, 92%), [M (mass spectrometry), 317·9872. C_9HF_{11} requires M, 317·9903], b.p. 101·5°/759 mm., I.R. No.4 ν_{max} 3080 (vinylic C-H), 1760 (CF=CF) and 1667 $cm.^{-1}$ ($CH=C(CF_3)$). The ^1H n.m.r. spectrum showed a broad resonance at -7·0.

(c) With 3-chloropropyne. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (10·76 g., 48·0 mmoles), 3-chloropropyne

(3·84 g., 51·5 mmoles) and dipentene (ca. 0·07 g.) were heated in a 100-ml. Pyrex ampoule at 180° for 17 hr. to give: (i) a mixture of 3-chloropropyne and perfluorocyclohexa-1,3-diene (1·16 g.); (ii) 2-monochloromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIc) (12·58 g., 42·1 mmoles, 88%), [Found: C, 36·3; H, 1·1; Cl, 12·0; F, 50·7%; M (mass spectrometry), parent ion (P) m/e 298, P+2 indicating one chlorine atom. $C_9H_3ClF_8$ requires C, 36·2; H, 1·0; Cl, 11·9; F, 50·9%; M, 298·46], b.p. 164°/759 mm., I.R. No.5 ν_{max} 1763 $cm.^{-1}$ (CF=CF). The ^1H n.m.r. spectrum showed resonances at -6·87 (vinylic proton) and -4·51 (CH_2Cl protons) with respect to tetramethylsilane as external reference.

(d) With phenylacetylene. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (8·79 g., 39·2 mmoles), phenylacetylene (4·15 g., 40·7 mmoles) and dipentene (ca. 0·07 g.) were heated in a 150-ml. Pyrex ampoule at 175° for 20 hr. to give: (i) perfluorocyclohexa-1,3-diene (0·62 g., 2·8 mmoles); (ii) a black solid which was extracted with ether [insoluble material (0·68 g.)], evaporation of the ether solution followed by distillation at reduced pressure gave: (a) 2-phenyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IId) (6·87 g., 21·3 mmoles, 54%), [Found: C, 51·9; H, 1·8; F, 46·7%; M (mass spectrometry, 326. $C_{14}H_6F_8$ requires C, 51·6; H, 1·8; F, 46·6%; M, 326], m.p. 32·5°, b.p. 119°/25 mm., I.R. No.6 ν_{max} 3070

(vinylic/aromatic C-H), 1763 (CF=CF) and 1630 $cm.^{-1}$ (CH=C(Ph)). The ^1H n.m.r. spectrum showed resoances at -6·15 (vinylic proton, and -7·23 (aromatic protons); (b) a black tar (4·39 g.).

(e) With but-2-yne. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (5·71 g., 25·4 mmoles), but-2-yne (1·48 g., 29·3 mmoles) and dipentene (ca. 0·07 g.) were heated in a 100-ml. Pyrex ampoule at 200° for 19 hr. to give: (i) a mixture of perfluorocyclohexa-1,3-diene and but-2-yne (1·97 g.); (ii) 2,3-dimethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIe) (4·98 g., 17·9 mmoles, 71%), [Found: C, 43·0; H, 2·4; F, 54·7%; M (mass spectrometry), 278. $C_{10}H_6F_8$ requires C, 43·2; H, 2·2; F, 54·7%; M, 278], m.p. ca. 20°, b.p. 158°/752 mm., I.R. No.7 ν_{max} 2910 (Me), 1770 (CF=CF) and 1680 $cm.^{-1}$ (CMe=(Me)). The ^1H n.m.r. spectrum showed a broad resonance at -2·0; (iii) a brown tar (0·26 g.).

(f) With 1,4-dichlorobut-2-yne. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (6·93 g., 31·0 mmoles), 1,4-dichlorobut-2-yne (4·13 g., 33·6 mmoles) and dipentene (ca. 0·07 g.) were heated in a 100-ml. Pyrex ampoule at 200° for 40 hr. to give: (i) perfluorocyclohexa-1,3-diene (1·70 g., 7·6 mmoles); (ii) a dark viscous residue, which on distillation gave 2,3-bis(monochloromethyl)-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIf) (6·65 g., 19·2 mmoles, 62%), [Found: C, 34·3; H, 1·2; Cl, 20·3; F, 43·5%; M (mass spectrometry),

parent ion m/e 346, P+2 and P+4 m/e indicating two chlorine atoms. $C_{16}H_4Cl_2F_8$ requires C, 34·6; H, 1·2; Cl, 20·5; F, 43·8%; M, 346·92], b.p. 40°/2 mm., I.R. No.8 ν_{max} 2960 (C-H) and 1766 $cm.^{-1}$ (CF=CF). The ^1H n.m.r. spectrum showed a resonance at -4·76. There was no distillation residue (0·59 g.); (iii) a black solid (2·22 g.).

(g) With 1,1,1-trifluorobut-2-yne. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (3·91 g., 17·45 mmoles), 1,1,1-trifluorobut-2-yne (1·78 g., 16·50 mmoles) and dipentene (ca. 0·07 g.) were heated in a 75-ml. Pyrex ampoule at 220° for 63 hr. to give: (i) 1,1,1-trifluorobut-2-yne (2·88 mmoles); (ii) a mixture (2·30 g.) shown by g.l.c. to consist of perfluorocyclohexa-1,3-diene with trace amounts of 1,1,1-trifluorobut-2-yne, cis-1,1,1-trifluoro-3-iodobut-2-ene and 2-methyl-3-trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene; (iii) a mixture (2·96 g.), shown by ^{19}F n.m.r. spectroscopy to consist of 2-methyl-3-trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIg) (2·65 g., 8·00 mmoles, 49%) and perfluorocyclohexa-1,3-diene (0·31 g., 1·41 mmoles). Preparative g.l.c. (Column B, 105°) on the combined fractions from several experiments gave 2-methyl-3-trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene, [Found: C, 35·9; H, 1·0; F, 62·5%; M (mass spectrometry), 332. $C_{10}H_3F_{11}$ requires C, 36·1; H, 0·9; F, 62·9%; M, 332], b.p. 110°/742 mm., I.R. No.9 ν_{max} 1770 (CF=CF) and 1670 $cm.^{-1}$ (C(Me)=C(CF_3)). The ^1H n.m.r. spectrum showed a resonance at -2·45.

(h) With diethyl acetylenedicarboxylate. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (6·22 g., 27·8 mmoles), diethyl acetylenedicarboxylate (4·21 g., 24·8 mmoles) and dipentene (ca. 0·07 g.) were heated in a 100-ml. Pyrex ampoule at 215° for 18 hr. to give: (i) perfluorocyclohexa-1,3-diene (2·37 g., 10·6 mmoles); (ii) a brown semi-solid product, recrystallised from diethyl ether to give diethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate (IIh) (4·61 g., 11·7 mmoles, 47%), [Found: C, 42·5; H, 2·6; F, 38·4%; M (mass spectrometry), 394. $C_{14}H_{16}F_8O_4$ requires C, 42·5; H, 2·5; F, 38·6%; M, 394], m.p. 65°, I.R. No.10 ν_{max} 1772 (CF=CF), 1745 and 1725 (COOEt) and 1658 $cm.^{-1}$ (C(COOEt)=C(COOEt)).

(i) With perfluorobut-2-yne. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (6·80 g., 30·4 mmoles), perfluorobut-2-yne (4·59 g., 28·3 mmoles) and dipentene (ca. 0·07 g.) were heated in a 100-ml. Pyrex ampoule at 225° for 18 hr. to give: (i) perfluorobut-2-yne (2·46 g., 15·0 mmoles); (ii) a mixture (8·51 g.) which was separated by g.l.c. (Column A, 85°) to give perfluorocyclohexa-1,3-diene, and perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5-diene (IIi) (3·46 g., 8·96 mmoles, 67% yield, 54% conversion), [Found: C, 30·9; F, 68·5%; M (mass spectrometry), 386. $C_{10}F_{14}$ requires C, 31·1; F, 68·9%; M, 386], b.p. 40°/50 mm., I.R. No.11 ν_{max} 1770 (CF=CF) and 1663 $cm.^{-1}$ ($C(CF_3)=C(CF_3)$).

9.4] Pyrolysis of Diels-Alder adducts.

The apparatus consisted of a silica tube (59 cm. x 1·4 cm. int. diam.) lightly packed with silica wool, a Pyrex reservoir containing the compound to be pyrolysed was attached at one end and a Pyrex trap at the other end of the tube; both reservoir and trap could be cooled in liquid air, all connections were through ground glass joints, the exit from the trap was connected to a vacuum system. The middle 44 cm. of the silica tube were heated in an electric furnace, the temperature at the outer surface of the tube was measured using a Chromel-alumel thermocouple. The sample to be pyrolysed was placed in the reservoir, which was then cooled in liquid air. The apparatus was evacuated (ca. 10^{-3} mm.) and the trap was cooled in liquid air whilst the reservoir warmed up to room temperature. When all the material had evaporated from the reservoir (the less volatile materials required heating), the contents of the trap were allowed to warm up. Gaseous products were expanded into the calibrated gas measuring system, a volatile liquid fraction was obtained by bulb to bulb transfer, and other products were worked up by vacuum distillation or recrystallisation.

(a) 2-Methyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIa) (0·383 g., 1·45 mmoles) was pyrolysed at 610° to give: (i) a gas, shown to be tetrafluoroethylene (TFE), with an impurity (Probably $CF_3CF=CF_2$), by i.r. spectroscopy; (ii) 2,3,4,5-tetrafluorotoluene (IIIa) (0·224 g., 1·37 mmoles, 95%), [Found: C, 50·9; H, 2·3;

F, 46·5%; M (mass spectrometry), 164. $C_7H_4F_4$ requires C, 51·2; H, 2·5; F, 46·3%; M, 164], b.p. 122°/753 mm., I.R. No.12 ν_{max} 2920 (C-H), 1525 and 1490 $cm.^{-1}$ (aromatic nucleus), λ_{max} 262·5 nm. (ϵ 686) in cyclohexane (0·203 g./l.). The ^1H n.m.r. spectrum showed resonances at -6·8 (aromatic proton J_{HF}^{ortho} 10·7, J_{HF}^{meta} 1·5, J_{HF}^{para} 2·4), and -2·3 (Me), shifts calculated with respect to benzene as internal reference (-7·27).

(b) 2-Trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIb) (2·024 g., 6·36 mmoles) was pyrolysed at 630° to give: (i) a gas (6·10 mmoles), shown to be mainly TFE by i.r. spectroscopy; (ii) ααα,2,3,4,5-heptafluorotoluene (1·30 g., 5·96 mmoles, 94%) with a trace of higher boiling impurity. Purification by preparative g.l.c. (Column C, 100°) gave ααα,2,3,4,5-heptafluorotoluene (IIIb), [Found: M (mass spectrometry), 217·9967. Calculated for C_7HF_7: M, 217·9966], b.p. 101·5°/759 mm. (lit.[135] 102-105·5°), I.R. No.13 ν_{max} 1530 and 1500 $cm.^{-1}$ (aromatic nucleus), λ_{max} 264 nm. (ϵ 965) in cyclohexane (0·244 g./l.). The ^1H n.m.r. spectrum showed a resonance at -7·3 (J_{HF}^{ortho} 9·2, J_{HF}^{meta} 5·5 and 7·4, J_{HF}^{para} 2·6).

(c) 2-Monochloromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIc) (1·99 g., 6·66 mmoles) was pyrolysed at 600° to give: (i) gas (10·27 mmoles, 154%), shown to be TFE and hydrogen chloride by i.r. and mass spectrometry; (ii) α-chloro-2,3,4,5-tetrafluorotoluene (0·681 g.) containing a lower boiling impurity. Purification by

preparative g.l.c. (Column C, 150°) gave α-chloro-2,3,4,5-tetrafluorotoluene (IIIc), [Found: M (mass spectrometry), parent ion m/e 198, P+2 m/e indicating one chlorine atom. $C_7H_3ClF_4$ requires M, 198·46], b.p. 166-169°/763 mm., I.R. No.14 ν_{max} 1530 and 1490 $cm.^{-1}$ (aromatic nucleus), λ_{max} 265 nm. (ε 840) in cyclohexane (0·300 g./l.). The ^1H n.m.r. spectrum showed resonances at -7·30 (aromatic proton), and -4·80 (CH_2Cl) with respect to external tetramethylsilane; (iii) trans-2,2',3,3',4,4',5,5'-octafluorostilbene (IIId) (0·214 g., 0·661 mmoles, 19·8%), which after purification by preparative g.l.c. (Column C, 180°) and sublimation gave pure IIId, [Found: C, 51·9; H, 1·3; F, 46·3%; M (mass spectrometry), 324. $C_{14}H_4F_8$ requires C, 51·8; H, 1·2; F, 46·9%; M, 324], m.p. 94°, I.R. No.15 ν_{max} 3010 (C-H), 1620 (C=C), 1520 and 1480 $cm.^{-1}$ (aromatic nucleus), λ_{max} 193 nm. (multiplet) (ε 18,800) in cyclohexane (0·0286 g./l.). The ^1H n.m.r. spectrum (CCl_4 solution) showed two overlapping resonances at ca. -7·5 with respect to external tetramethylsilane.

(d) 2-Phenyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IId) (1·988 g., 6·10 mmoles) was pyrolysed at 550° to give: (i) TFE (6·15 mmoles), with correct i.r. spectrum; (ii) 2,3,4,5-tetrafluorobiphenyl (IIIe) (0·984 g., 4·35 mmoles, 71%), [Found: C, 63·2; H, 2·5; F, 33·2%; M (mass spectrometry), 226. Calculated for $C_{12}H_6F_4$: C, 63·7; H, 2·8; F, 33·6%; M, 226], m.p. 66-67° (from CCl_4, and sublimed) (lit.[137*] 75-76°), I.R. No.16 ν_{max} 1525 and 1480 (aromatic

nucleus), λ_{max} 241 nm. (ϵ 13,800) in cyclohexane (0·0256 g./l.). The ^{1}H n.m.r. spectrum (saturated solution in CCl_4) showed resonances at -7·3 (Ph) and -6·9 (C-6 proton, J_{HF}^{ortho} 11·0, J_{HF}^{meta} 7·9, J_{HF}^{para} 2·4) (lit.[137]* -6·8 and -5·2 respectively). *Lit.[137] values suspect, see p.60.

(e) 2,3-Dimethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIe) (0·965 g., 3·47 mmoles) was pyrolysed at 600° to give: (i) TFE (3·41 mmoles), with correct i.r. spectrum; (ii) 3,4,5,6-tetrafluoro-ortho-xylene (IIIf) (0·614 g., 3·45 mmoles, 99%), [Found: C, 54·0; H, 3·4; F, 42·6%; M (mass spectrometry), 178. $C_8H_6F_4$ requires C, 53·9; H, 3·4; F, 42·7%; M, 178], b.p. 118°/755 mm., I.R. No.17 ν_{max} 2920 (C-H), 1510 and 1495 cm.$^{-1}$ (aromatic nucleus), λ_{max} (doublet) 260 and 263·5 nm. (ϵ 453) in cyclohexane (0·22 g./l.). The ^{1}H n.m.r. spectrum showed a resonance at -2·14.

(f) 2,3-Bis(monochloromethyl)-1,4,5,6,7,7,8,8-octafluorobicyclo-[2,2.2]octa-2,5-diene (IIf) (1·571 g., 4·53 mmoles) was pyrolysed at 600° to give 3 fractions. Fraction (i) was a gas (10·33 mmoles, 228%) shown to be TFE and hydrogen chloride by i.r. and mass spectrometry. Fraction (ii) was a pale yellow liquid (0·647 g.) shown by analytical g.l.c. to be predominantly one component, preparative g.l.c. (Column C, 175°) gave 2,3,4,5-tetrafluorophenylacetylene (IIIg), [Found: M (mass spectrometry), 174·0098. $C_8H_2F_4$ requires M, 174·0093], b.p. 135-136°/760 mm., I.R. No.18 ν_{max} 3280 (acetylenic C-H), 3040 (aromatic C-H), 1520 and 1480 cm.$^{-1}$ (aromatic nucleus), λ_{max} 274·5 nm. (ϵ 1,430), 279 nm. (ϵ 1,460) and 283·5 nm. (ϵ 1,360) in

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cyclohexane (0·193 g./l.). The ^{1}H n.m.r. spectrum showed resonances at -7·33 (aromatic proton J_{HF}^{ortho} 9·7, J_{HF}^{meta} 5·6 and 7·4, J_{HF}^{para} 2·24) and -3·48 (acetylenic proton J_{HF} with fluorine atoms two and four ca. 0·9) with respect to external tetramethylsilane. After several days it polymerizes to an unidentified yellow solid. Fraction (iii) was a residue (0·223 g.) of 2,3,4,5-tetrafluorophenylacetylene and several higher boiling materials.

(g) 2-Methyl-3-trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo-[2,2,2]octa-2,5-diene (IIg) (2·057 g., 6·19 mmoles) was pyrolysed at 600° to give: (i) TFE (6·17 mmoles), with correct i.r. spectrum; (ii) 1-methyl-2-trifluoromethyl-3,4,5,6-tetrafluorobenzene (IIIh) (1·367 g., 5·89 mmoles, 95%) containing traces of low boiling impurities. Preparative g.l.c. (Column B, 105°) separated pure IIIh, [Found: C, 41·4; H, 1·7; F, 57·7%; M (mass spectrometry), 232·0115. $C_8H_3F_7$ requires C, 41·4; H, 1·3; F, 57·3%; M, 232·0123], b.p. 129-130°/742 mm., I.R. No.19 ν_{max} 2920 (C-H), 1520 and 1490 cm.$^{-1}$ (aromatic nucleus), λ_{max} 269·5 nm. (ϵ 1,400) in cyclohexane (0·120 g./l.). The ^{1}H n.m.r. spectrum showed a resonance at -2·53 with respect to external tetramethylsilane.

(h) Diethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate (IIh) (0·908 g., 2·33 mmoles) was pyrolysed at 550° to give: (i) gas (10·83 mmoles, 465%), shown to be a mixture of TFE, hexafluorocyclopropane, carbon dioxide and ethylene by i.r. and

mass spectrometry; (ii) a liquid mixture (0·276 g.), which was shown to be predominantly 1,2,3,4-tetrafluorobenzene (ca. 90%) and another tetrafluorobenzene derivative, by i.r., ^{19}F n.m.r. and mass spectrometry. The ^{19}F n.m.r. spectrum of the minor component showed resonances at -21·9, -17·0 and -5·7 (total relative intensities 1 : 1 : 2); the mixture showed a peak in the mass spectrum at m/e 264 (ethyl tetrafluorophthalate parent m/e, 266); (iii) 2,3,4,5-tetrafluorobenzoic acid (IIIj) (0·325 g., 1·68 mmoles, 23%), [Found: C, 43·4; H, 0·8; F, 39·3%; M (mass spectrometry), 194. Calculated for $C_7H_2F_4O_2$: C, 43·3; H, 1·0; F, 39·2%; M, 194], m.p. 88·6-88·8° (recrystallised from CCl_4) (lit. 92-92·5°,[127] 86-86·5°,[129] 79-80°[137]), I.R. No.20 ν_{max} (KBr disc) 1690 (CO_2H), 1530, 1490 $cm.^{-1}$ (aromatic nucleus), (lit.[137] ν_{max} (CCl_4) 1715, 1505, 1495 $cm.^{-1}$). The ^1H n.m.r. spectrum showed a resonance at -12·3 (carboxyl proton) and -7·7 (aromatic proton, J_{HF}^{ortho} 10·1, J_{HF}^{meta} 6·5 and 8·3, J_{HF}^{para} 2·6).

(i) Perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5-diene (IIi) (1·093 g., 2·84 mmoles) was pyrolysed at 500° to give: (i) TFE (2·38 mmoles), with correct i.r. spectrum; (ii) perfluoro-ortho-xylene (IIIk) (0·786 g., 2·75 mmoles, 97%), [Found: C, 33·4; F, 66·8%; M (mass spectrometry), 286. Calculated for C_8F_{10}: C, 33·6; F, 66·4%; M, 286], b.p. 122°/753 mm. (lit.[136] 128°), I.R. No.21 ν_{max} 1630, 1530 and 1485 $cm.^{-1}$ (aromatic nucleus), λ_{max} 272 nm. (ϵ 1,560) in cyclohexane (0·217 g./l.) [lit.[136] 272 nm. (ϵ 1,753)].

CHAPTER 10. EXPERIMENTAL FOR CHAPTER 7 - NITRILE ADDITION.

10.1] Reagents.

Perfluorocyclohexa-1,3-diene was prepared as previously.[161,162] Perfluoroacetonitrile,[167] and 1,3-dicyanohexafluoropropane[168] were prepared by published routes from perfluoroacetamide and perfluoroglutaryl chloride respectively. Commercial samples of cyanogen bromide and perfluorobenzonitrile were used. As in Chapter 9 all reagents were redistilled, dried (P_2O_5) and degassed before use.

10.2] Diels-Alder reactions of perfluorocyclohexa-1,3-diene with nitriles.

(a) With perfluoroacetonitrile. - By using the same procedure as in Chapter 9.3, perfluoroacetonitrile (3·24 g., 35·1 mmoles), perfluorocyclohexa-1,3-diene (7·81 g., 34·9 mmoles) and dipentene (ca. 0·07 g.) were heated at 400° for 16 hr. in a 90-ml. Pyrex ampoule to give: (i) a gaseous fraction (2·38 mmoles) shown by i.r. spectroscopy to consist of a mixture of unreacted perfluoroacetonitrile and tetrafluorosilane; (ii) a liquid mixture (8·06 g.) which was separated by preparative g.l.c. (Column B, 125°) into 2 fractions. The shorter retained was perfluorobicyclo[4,2,0]oct-2-ene (2·89 g., 8·9 mmoles, 26%). The longer retained component was perfluoro-(2-methylpyridine) (VIa) (2·91 g., 13·9 mmoles, 39·8%), [Found: C, 32·9; F, 60·5%; M (mass spectrometry), 218·9925. Calculated for C_6F_7N: C, 32·9; F, 60·7%; M, 218·9919],

b.p. 102-103°/758 mm., I.R. No.22 ν_{max} 1480 $cm.^{-1}$ (liquid film), λ_{max} 256 nm. (ϵ 2340) in cyclohexane (0·162 g./l.), [lit.[144] b.p. 102-103°/767 nm., ν_{max} 1480 $cm.^{-1}$ (vapour), λ_{max} 256 nm. (ϵ 2320) (hexane)].

(b) With cyanogen bromide - Experiment I. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (14·61 g., 65·3 mmoles), cyanogen bromide (9·68 g., 91·2 mmoles) and dipentene (ca. 0·07 g.) were heated in a 100-ml. Pyrex ampoule at 380° for 12 hr. to give three fractions. The first (i) a liquid mixture (15·06 g.), ^{19}F n.m.r. showed the major components to be perfluorocyclohexa-1,3-diene (50%), perfluorocyclohexa-1,4-diene (ca. 2%), perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene(Vb) (ca. 5%), 1-bromo-2-cyanotetrafluoroethane (ca. 2%), 1,2-dibromotetrafluoroethane (29%) and perfluoro-2-bromopyridine (VIb) (12%), where the figures in parenthesis are mole percent with respect to total moles of fluorinated material. Analytical g.l.c. did not resolve all these compounds but showed the presence of cyanogen bromide. Distillation accomplished a partial separation into a liquid mixture (7·46 g.) (b.r. 28-56°), solid cyanogen bromide (ca. 0·5 g.) (56-60°), and a distillation residue (5·32 g.). The liquid mixture was separated by preparative g.l.c. (Column B, 110°) to give: (a) impure [contaminated with perfluorocyclohexa-1,4-diene (ca. 15%), by i.r. and n.m.r. spectroscopy] 1-bromo-2-cyanotetrafluoroethane, ν_{max} 2280 $cm.^{-1}$ (-C≡N). Mass spectrometry showed the parent molecular ion at m/e 205, $[C_3{}^{79}BrF_4N]^+$, P+2 m/e

indicating one bromine atom, the base peak was at m/e 126, $[C_3F_4N]^+$. The ^{19}F n.m.r. spectrum showed resonances at -94·2 and -58·8 [triplets (J 10 Hz) of equal total relative intensity]; (b) perfluorocyclohexa-1,3-diene with correct i.r. spectrum; (c) 1,2-dibromotetrafluoroethane with correct i.r. spectrum,[169] b.p. 47-48°/763 mm. [lit.[170] 46·4°], M (mass spectrometry), parent ion m/e 258, P+2 and P+4 m/e indicating two bromine atoms, and the ^{19}F n.m.r. spectrum showed a sharp resonance at -102·4. The distillation residue was a complex mixture of not less than 12 components, by analytical g.l.c., but only the three major long retained peaks were separated, preparative g.l.c. (Column D, 115°). The first fraction (0·39 g.) was two compounds, ν_{max} 2250 (C≡N), 1740 $cm.^{-1}$ (CF=CF). The mass spectrum showed parent ion m/e 329 $[C_7{}^{79}BrF_8N]^+$, P+2 m/e indicating one bromine atom, the base peak was at m/e 250 $[C_7F_8N]^+$. There was insufficient material for a diagnostic ^{19}F n.m.r. spectrum. This data is consistent with an isomeric mixture of bromocyanocyclohexenes. The second fraction was pure perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene (0·95 g., 2·9 mmoles, 4·4%), [Found: C, 25·7; Br, 24·1; F, 46·5%; M (mass spectrometry) at parent ion m/e 329, P+2 indicating one bromine atom (with base peak at m/e 224 $[C_6F_8]^+$, and a peak at m/e 229 $[C_5{}^{79}BrF_4N]^+$ (57·3%)). C_7BrF_8N requires C, 25·5; Br, 24·5; F, 46·1%; M, 330], b.p. 133-135°/769 mm., I.R. No.27 ν_{max} 1765 (CF=CF), 1615 $cm.^{-1}$ (C=N). The final fraction was perfluoro-2-bromopyridine (VIb) (1·53 g., 6·7 mmoles, 10·2%), [Found: C, 25·8;

Br, 35·4; F, 33·4%; M (mass spectrometry) parent ion m/e 229, P+2 indicating one bromine atom. C_5BrF_4N requires C, 26·1; Br, 34·8; F, 33·1%; M, 230], b.p. 140–142°/769 mm., I.R. No.23 ν_{max} 1610, 1515, 1465 $cm.^{-1}$ (pyridine nucleus), λ_{max} 265 nm., (ϵ 3600) in cyclohexane (0·103 g./l.). Fraction (ii) was also a liquid mixture (5·86 g.), ^{19}F n.m.r. indicated only perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene (21%) and perfluoro-2-bromopyridine (79%), but analytical g.l.c. also detected several shorter retained components. Preparative g.l.c. (Column D, 110°) gave the same fractions as the distillation residues above: a mixture of isomeric bromocyanocyclohexenes (0·31 g.), perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene (0·946 g., 2·9 mmoles, 4·4% yield); perfluoro-2-bromopyridine (1·854 g., 4·3 mmoles, 7·5%); residual components (0·984 g.). The residue (iii) was a black solid (1·74 g.).

Experiment II. - Perfluorocyclohexa-1,3-diene (7·52 g., 33·6 mmoles), cyanogen bromide (10·58 g., 100 mmoles) and dipentene (ca. 0·07 g.) were heated in a 90-ml. Pyrex ampoule at 400° for 15 hr. to give free bromine, starting materials, 1,2-dibromotetrafluoroethane, perfluoro-2-bromopyridine and several brominated by-products; the mass spectrum showed ions at m/e 322 $[C_6{}^{79}BrF_9]^+$, 329 $[C_7{}^{79}BrF_8N]^+$, 367 $[C_7{}^{79}BrF_{10}N]^+$, 389 $[C_7{}^{79}Br_2F_7N]^+$, 427 $[C_7{}^{79}BrF_9N]^+$, and the i.r. spectrum showed a characteristic absorption at 2280 $cm.^{-1}$ (C≡N). Only perfluoro-2-bromopyridine (VIb) (2·77 g., 12·0 mmoles, 40%) was separated from this complex mixture by preparative g.l.c. (Column C, 200°).

Copper coupling of perfluoro-2-bromopyridine. - Perfluoro-2-bromopyridine (0·90 g., 3·9 mmoles) and copper bronze powder (2 g.) were refluxed for 18 hr. in dry (BaO) DMF. The solution was extracted with ether, and the extract washed with water to remove excess DMF before drying ($MgSO_4$) and evaporating. Sublimation (100°, ca. 10^{-2} mm.) of the crude ether extract yielded a liquid/solid mixture (ca. 0·2 g.) which had the same i.r. spectrum as an authentic specimen of perfluoro-2,2-bipyridyl,[145] but the mass spectrum also showed peaks at m/e 431 (tripyridyl) and 562 (tetrapyridyl).

(c) With 1,3-dicyanohexafluoropropane. - Experiment I. - By using the same procedure as in (a), 1,3-dicyanohexafluoropropane (4·90 g., 24·2 mmoles), perfluorocyclohexa-1,3-diene (11·16 g., 49·8 mmoles) and dipentene (ca. 0·07 g.) were heated in a 90-ml. Pyrex ampoule at 350° for 16 hr. to give: (i) a gas (3·48 mmoles) shown to be a mixture of starting materials and tetrafluorosilane by i.r. spectroscopy; (ii) a mixture (13·02 g.) shown by ^{19}F n.m.r. to consist of perfluorocyclohexa-1,3-diene (39·2 mmoles) and 1,3-dicyanohexafluoropropane (20·9 mmoles) [-60·7 (total relative intensity 2) and -41·7 p.p.m. (total relative intensity 1)]; (iii) a pale yellow liquid (1·82 g.) shown by i.r. and ^{19}F n.m.r. spectroscopy to consist principally of perfluorocyclohexa-1,3-diene (ca. 45%), perfluoro-2-aza-3-(3-cyanopropyl)bicyclo[2,2,2]octa-2,5-diene (Vc) (ca. 35%), perfluoro-2-(3-cyanopropyl)pyridine (VIc) (ca. 12%) and perfluoroglutaramide (ca. 8%). On preparative g.l.c.

(Column E, 90°), 1·424 g. of this mixture gave: (a) perfluorocyclohexa-1,3-diene (0·282 g.); (b) perfluoro-2-aza-3-(3-cyanopropyl)-bicyclo[2,2,2]octa-2,5-diene (0·431 g., 1·01 mmoles, 4·2%), [Found: M (mass spectrometry), 425·9837. $C_{11}F_{14}N_2$ requires M, 425·9910], I.R. No.28 ν_{max} 2280 (C≡N), 1775 (CF=CF) and 1660 $cm.^{-1}$ (C=N); (c) perfluoro-2-(3-cyanopropyl)pyridine (0·038 g., 0·21 mmoles, 0·9%), [Found: C, 32·9; F, 58·1%; M (mass spectrometry), 325·9906. $C_9F_{10}N_2$ requires C, 33·2; F, 58·2%; M, 325·9974], b.p. 161-163°/769 mm., I.R. No.24 ν_{max} 2280 (C≡N), 1625, 1530 and 1485 $cm.^{-1}$ (fluorinated pyridine nucleus), λ_{max} 257·5 nm. (ε 3320) in cyclohexane (0·1053 g./l.); (d) a mixture (0·203 g.) in the residual components trap, shown to contain the previous components and perfluoroglutaramide, by ^{19}F n.m.r. spectroscopy.

Experiment II. - Perfluorocyclohexa-1,3-diene (8·79 g., 39·2 mmoles) and 1,3-dicyanohexafluoropropane (4·23 g., 20·9 mmoles) were heated in an 80-ml. Pyrex ampoule at 350° for 64 hr. to give: (i) a gas (2·35 mmoles) consisting principally of tetrafluorosilane; (ii) a mixture (2·02 g.) of starting materials and perfluorobicyclo[4,2,0]oct-2-ene; (iii) a liquid mixture (8·37 g.) shown by ^{19}F n.m.r. to contain 1,3-dicyanohexafluoropropane (ca. 4%), perfluorobicyclo[4.2.0]oct-2-ene (ca. 33%), perfluorocyclohexa-1,3-diene (ca. 11%), the dimer of perfluorocyclohexadiene (ca. 5%), and perfluoro-2-(3-cyanopropyl)pyridine (ca. 47%). Preparative g.l.c. (Column D, 110°) of this mixture (7·41 g.) gave perfluorocyclohexadiene dimer (0·63 g., 1·40 mmoles, 3·6%) and

perfluoro-2-(3-cyanopropyl)pyridine (1·29 g., 3·96 mmoles, 10%); (iv) a brown oil (0·97 g.). Distillation (45-55°/ca. 10^{-1} mm.) yielded perfluoro-1,3-bis-(2,2'-pyridyl)propane (VIe) (0·87 g., 1·93 mmoles, ca. 10%), [Found: C, 34·8; F, 58·8; M (mass spectroscopy), 449·9904. $C_{13}F_{14}N_2$ requires C, 34·6; F, 59·1%; M, 449·9910], I.R. No.26 ν_{max} 1620, 1525 and 1480 $cm.^{-1}$ (fluorinated pyridine nucleus), λ_{max} 258·5 nm. (ϵ 6410) in cyclohexane (0·0860 g./l.).

(d) With perfluorobenzonitrile. - By using the same procedure as in (a), perfluorocyclohexa-1,3-diene (10·14 g., 45·3 mmoles), perfluorobenzonitrile (8·94 g., 46·3 mmoles) and dipentene (ca. 0·07 g.) were heated in an 80-ml. Pyrex ampoule at 390° for 64 hr. to give: (i) a gas (7·12 mmoles), shown to be tetrafluorosilane by i.r. spectroscopy; (ii) a mixture (7·16 g.) shown by i.r. spectroscopy and anlaytical g.l.c. to contain principally perfluorocyclohexa-1,3- and 1,4-diene and perfluorobicyclo[4,2,0]oct-2-ene; (iii) a mixture (9·18 g.) estimated by analytical g.l.c. to contain perfluorocyclohexadiene dimer (10%), perfluorobenzonitrile (86%) and perfluoro-2-phenylpyridine (VId) (2%). This mixture was distilled and the fraction distilling below 150° (7·63 g.) was separated by preparative g.l.c. (Column D, 100°) to give: (a) perfluorocyclohexadiene dimer (0·37 g., 0·83 mmoles, 3·6% yield); and (b) perfluorobenzonitrile (4·88 g.); (iv) a sticky residue, which was extracted with acetone, the extract was combined with the distillation residues (1·55 g.) of the previous fraction, and on vacuum distillation

(ca. 10^{-2} mm.), gave a pale yellow oil (1·14 g.). Preparative g.l.c. (Column E, 125°) yielded pure perfluoro-2-phenylpyridine (0·60 g., 1·9 mmoles, 4·2% yield), [Found: C, 41·4; F, 53·4% M (mass spectrometry), 316·9867. $C_{11}F_9N$ requires C, 41·6; F, 53·9%; M, 316·9923], b.p. 200°/759 mm., I.R. No.25 ν_{max} 1660, 1625, 1520 (pyridine nucleus), 1480, 1105, 1050, 1000 and 750 $cm.^{-1}$ λ_{max} 265 nm. (ϵ 9100) in cyclohexane (0·0456 g./l.).

10.3] Pyrolysis of perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene.

Perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene (0·230 g., 0·85 mmoles) was pyrolysed at 600° by using the same procedure as in Chapter 9.4 to give: (i) a gas (1·34 mmoles, 158%) shown by i.r. spectroscopy to consist of TFE, perfluorocyclohexa-1,3-diene and a trace of tetrafluorosilane. No cyanogen bromide was detected; (ii) perfluoro-2-bromopyridine (0·086 g., ca. 0·37 mmoles, ca. 42%) with correct i.r. spectrum, but shown by analytical g.l.c. to be contaminated with ca. 5% of perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene and other lower boiling material.

10.4] Unsuccessful additions.

Nitrile	Temp.(°C)	Time (hr.)	Recovery
MeCN	200	40	Starting materials.
MeCN	320	42	SiF_4, starting materials, acetic acid, black solid.[a]
MeCN	400	24	SiF_4, intractable black solid.
MeCN + BF_3	195	28	Starting materials.
MeCN + BF_3	400	17	SiF_4, intractable black solid.
PhCN	325	3	Starting materials.
PhCN	390	32	SiF_4, black solid.[b]
$ClCH_2CN$	340	17	SiF_4, starting materials,[c] black solid.[d]
$ClCH_2CN$	400	16	SiF_4, black solid.[d]

Notes. [a] Soxhlet extraction with acetone separated an ester consistent with methyl pentafluorobenzoate; ν_{max} 1760, 1680, 1650 $cm.^{-1}$, m/e 226, ^{19}F n.m.r. resonances at -19·7 (2), -6·0 (1), -0·6 (2).

[b] Small quantity of white solid sublimed out, m/e 309, corresponds to $(PhCN)_3$.

[c] Contaminated with several protonated and chlorinated fluorocarbons (mass spectrum) but not isolable by preparative g.l.c.

[d] Soxhlet extraction with water separated a sublimable inorganic white solid; C, absent; H, ca. 6; Cl, ca. 50; F, ca. 7; N, ca. 20%.

10.5] Addition of TFE to perfluorocyclohexa-1,3-diene.

Only two examples of this addition are described. Experiment I is fairly typical of the reaction in most cases, except that no 1,4-diene was detected, whereas Experiment II is most unusual and could not be repeated.

Experiment I. - Perfluorocyclohexa-1,3-diene (6·10 g., 27·2 mmoles) and TFE (2·64 g., 26·4 mmoles) were heated at 400° for 47 hr. in a 90-ml. Pyrex ampoule. By using the same procedure as in the previous addition reactions the reaction mixture was separated into three fractions: (i) perfluorocyclobutane (1·31 g., 6·56 mmoles, 50% yield) with correct i.r.[171] and n.m.r. spectrum;[123] (ii) a liquid mixture (6·53 g.) which was shown by n.m.r. and analytical g.l.c. to consist of perfluorocyclobutane (0·758 g., 3·79 mmoles, 29% yield, w.r.t. TFE), perfluorocyclohexa-1,3-diene (3·75 g., 17·5 mmoles, 64% recovery), and perfluorobicyclo[4,2,0]oct-2-ene (2·02 g., 6·23 mmoles, 23% yield). Preparative g.l.c. (Column D, 40°) separated pure perfluorobicyclo-[4,2,0]oct-2-ene, [Found: C, 29·5; F, 70·1%; M (mass spectrometry), parent molecular ion at m/e 324 $[C_8F_{12}]^+$ (6·3% of base peak at m/e 255 $[C_7F_9]^+$, other peaks at m/e 305 (6·3), 224 (98), 205 (82), 174 (35), 155 (93), 100 (46), 69 (79), 31 (19). C_8F_{12} requires C, 29·6; F, 70·4%; M, 324], b.p. 90-92°/769 mm., I.R. No.29 ν_{max} 1750 $cm.^{-1}$ (CF=CF) and a characteristic triplet at 870, 865, 825 $cm.^{-1}$ The ^{19}F n.m.r.

spectrum is given in Table 7.4(i) (page 72); (iii) a liquid mixture (0·62 g., 1·38 mmoles, 5% yield) shown by i.r. and analytical g.l.c. to consist of both isomers of perfluorodicyclohexadiene.

Experiment II. - By using the same procedure as in Experiment I, perfluorocyclohexa-1,3-diene (ca. 6·0 g., 26·8 mmoles) also containing perfluorocyclohexa-1,4-diene (ca. 13%) and perfluorodicyclohexadiene (ca. 9%) and TFE (5·49 g., 54·9 mmoles) were heated at 400° for 51 hr. in an 80-ml. Pyrex ampoule to give: (i) perfluorocyclobutane with correct i.r. spectrum; (ii) a liquid mixture estimated by n.m.r. spectroscopy to consist of perfluorocyclobutane (ca. 14 mole %), impure perfluorobicyclo[2,2,2]oct-2-ene (ca. 24 mole %), perfluorocyclohexa-1,4-diene (ca. 42 mole %), and perfluorocyclohexa-1,3-diene (ca. 20 mole %). Preparative g.l.c. (Column D, 30°) separated impure perfluorobicyclo[2,2,2]oct-2-ene, I.R. No.30 ν_{max} 1770, 1745 (CF=CF), 1330, 1240, 1100, 1025, 995, 970, 940 $cm.^{-1}$ [Found: M (mass spectrometry), parent molecular ion at m/e 324 (11·5% of base peak at m/e 155 $[C_5F_5]^+$), other peaks at m/e 305 $[C_8F_{11}]^+$ (9·5), 255 $[C_7F_9]^+$ (13·5), 224 $[C_6F_8]^+$ (66), 205 $[C_6F_7]^+$ (66·5), 186 (14·5), 174 (34), 155 (100), 131 (48·5), 124 (32), 100 (61·5), 93 (30), 69 (50·5), 31 (31·5). C_8F_{12} requires M, 324]. It is a glassy solid at room temperature, but b.p. or m.p. could not be taken owing to its great volatility. The ^{19}F n.m.r. spectrum is given in Table 7.4(i) (page 72); (iii) a trace of a colourless oil.

Several attempts at the oxidation of perfluorobicyclo[4,2,0]oct-2-ene both with potassium permanganate/acetone[172] and aqueous permanganate[173] produced only very low (ca. 10%) yields of a hygroscopic solid which showed two peaks on analytical g.l.c. It was not possible to isolate either the pure anilinium or S-benzylthiouronium derivative.

10.6] Dimerization of perfluorocyclohexa-1,3-diene.

Experiment I. - Perfluorocyclohexa-1,3-diene (0·73 g., 3·2 mmoles) was heated in a 20-ml. Pyrex ampoule at 390° for 15 hr. to give: (i) a liquid mixture (0·66 g., 3·0 mmoles, ca. 92% recovery) estimated by analytical g.l.c. to consist of perfluorocyclohexa-1,3- (ca. 90%) and -1,4-diene (ca. 10%); (ii) a trace of a less volatile liquid which could not be identified by i.r. spectroscopy; (iii) a black solid residue which was insoluble in acetone. No dimerization was detected.

Experiment II. - Perfluorocyclohexa-1,3-diene (11·24 g., 50·2 mmoles) was heated in an 80-ml. Pyrex ampoule at 390° for 144 hr. to give: (i) silicon tetrafluoride (0·116 g., 1·11 mmoles) with correct i.r. spectrum; (ii) a liquid mixture (6·12 g., 27·4 mmoles) estimated by ^{19}F n.m.r. to consist of 1,3-diene (ca. 87%) and 1,4-diene (ca. 13%), but analytical g.l.c. also showed the presence of the presumed exo- (ca. 2%) and endo- (ca. 6%) dicyclohexadiene; (iii) a liquid mixture (4·85 g., 10·83 mmoles, ca. 43·5% yield) estimated by ^{19}F n.m.r. to consist of

exo- dicyclohexa-1,3-diene (ca. 15%) and endo- dicyclohexa-1,3-diene (ca. 85%). Again analytical g.l.c. also showed the presence of other compounds, perfluorocyclohexa-1,3-diene (ca. 5%) and a slightly longer retained unidentified compound (ca. 4%). Preparative g.l.c. (Column F, 65°) was very difficult owing to practically identical retention times, but separated: (1) the shorter retained exo-perfluorotricyclo[6,2,2,$0^{2,7}$]-dodeca-4,9-diene (0·32 g., 0·71 mmoles, 2·8% yield), [Found: M (mass spectrometry, 448. $C_{12}F_{16}$ requires M, 448], b.p. 162°/755 mm., I.R. No.32 ν_{max} 1770, 1735 (CF=CF), 1370, 1300, 945, 770 (doublet) $cm.^{-1}$ The ^{19}F n.m.r. is given in Table 7.4(i) (page 72); (2) endo-perfluoro-bicyclo[6.2,2,$0^{2,7}$]dodeca-3,9-diene (3·05 g., 6·81 mmoles, 27·2%), [Found: M (mass spectrometry), 448. $C_{12}F_{16}$ requires M, 448], b.p. 163°/256 mm., I.R. No.31 ν_{max} 1770, 1735 (CF=CF), 1370, 1300, 945 (doublet), 770 $cm.^{-1}$ The ^{19}F n.m.r. is given in Table 7.4(i) (page 72).

Oxidation of the endo- isomer with acetone/permanganate[172] did give an anilide with a sharp melting point (194-195°), but not having the properties of the expected tetrabasic acid, [Found: C, 50·4; H, 3·87; F, 29·2%; highest m/e in mass spectrum 524. $C_{36}H_{32}F_{12}N_4O_8$ requires C, 56·0; H, 3·67; F, 30·8%; M, 776]. The i.r. spectrum showed absorptions at 2630, 1775 (CF=CF ?), 1660 (carbonyl), 1495, 1375, 1150, 990, 960, 815, 745, 685 $cm.^{-1}$ The ^{19}F n.m.r. spectrum in acetone solution indicated that decomposition of the compound had occurred, since only one resonance was detected (no reference).

10.7] Pyrolysis of perfluorodicyclohexadiene.

By using the same procedure as in Chapter 9.3, the presumed endo-perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-3,9-diene (0·268 g., 0·60 mmoles) was pyrolysed at 600° to give: (i) a gas (0·625 mmoles), shown by i.r. spectroscopy to consist mainly of perfluorocyclohexa-1,3-diene, with a trace of tetrafluoroethylene and an unidentified gas (1130, 1030 $cm.^{-1}$) There were no absorptions corresponding to the 1,4-diene; (ii) a liquid mixture (0·199 g.), the i.r. spectrum only showed 1,3-diene but analytical g.l.c. showed that it also contained the starting material (ca. 5%) and shorter retained compounds (ca. 5%).

10.8] Attempted use of BF_3 as a catalyst.

(a) With perfluoroacetonitrile. - By using the same procedure as in 10.2 (a) perfluoroacetonitrile (2·44 g., 25·8 mmoles), perfluoro-cyclohexa-1,3-diene (4·75 g., 21·2 mmoles), boron trifluoride (0·745 g., 4·94 mmoles) and dipentene (ca. 0·07 g.) were heated in an 80-ml. Pyrex ampoule at 200° for 16 hr. and work up subsequently showed no apparent reaction. The same reagents were used in the second experiment and heated in an 80-ml. Pyrex ampoule at 300° for 24 hr. to give: (i) a gas (3·4 mmoles), shown to be principally trifluoroacetonitrile by i.r. spectroscopy; (ii) a liquid mixture (3·87 g.) which was shown by i.r. and analytical g.l.c. to consist of starting materials, perfluorobicyclo[4,2,0]oct-2-ene and perfluoro-2-methylpyridine (VIa).

Preparative g.l.c. (Column B, 100°) separated pure VIa (0·50 g., 2·3 mmoles, 11%); (iii) a black residual solid (ca. 3 g.).

(b) With acetonitrile. - As shown in 10.4 no addition products were observed in reactions at either 195 or 400°.

CHAPTER 11. EXPERIMENTAL FOR CHAPTER 8 - THIAZYL CHLORIDE ADDITION.

11.1] Preparation of trithiazyl trichloride.

Tetrasulphur tetranitride (S_4N_4) was prepared by a published route from disulphur dichloride and ammonia.[174] S_4N_4 (4 g.) was placed in one limb of a Schlenk tube under an atmosphere of dry nitrogen. On the addition of sulphuryl chloride (25 ml.) SO_2 was evolved, the large orange crystals of S_4N_4 broke up and produced the smaller bright yellow crystals of $(NSCl)_3$. The suspension was stirred (3 hr.) with a magnetic stirrer and the product separated from the dark red liquor by filtration at the sinter in the Schlenk tube. The $(NSCl)_3$ was recrystallised from sulphuryl chloride and excess solvent removed in vacuo (rotary oil pump). The contents of the Schlenk tube (2·72 g., 26% yield) were weighed and transferred while inside a dry nitrogen glove-box. This is probably not an essential procedure since $(NSCl)_3$ does not seem excessively air-sensitive while in large crystalline form and it can be transferred in air between receptacles which are well flushed with dry nitrogen.

11.2] Attempted addition of thiazyl chloride to perfluorocyclohexa-1,3-diene.

Experiment I. - By using the same procedure as in Chapter 9.3 trithiazyl trichloride (1·00 g., 12·3 mmoles as NSCl) and perfluorocyclohexa-1,3-diene (4·56 g., 20·4 mmoles) were heated in a 50-ml. Pyrex

ampoule at 100° for 62 hr. (no reaction was observed at 60° for 10 minutes), to give a liquid mixture (4·91 g.) estimated by ^{19}F n.m.r. to consist of perfluorocyclohexa-1,3-diene (2·18 g., 9·7 mmoles, 48% recovery), and compounds provisionally assigned the structures perfluoro-2-chloro-2,3-thiazabicyclo[2,2,2]octa-2,5-diene (1·71 g., 5·6 mmoles, 45% yield w.r.t. SNCl), and 2,4,3-dithiaza-1,5,6,7,8,8,9,9-octafluorobicyclo[3,2,2]non-6-ene (1·02 g., 3·4 mmoles, 27%). The mixture was separated by preparative g.l.c. (Column D, 30°) to give three fractions.

Fraction (1), a clear volatile liquid, perfluoro-2-chloro-2,3-thiaza-bicyclo[2,2,2]octa-2,5-diene (0·60 g., 2·0 mmoles, 16·1%), [Found: Parent molecular ion at m/e 305, P+2 indicating one chlorine atom (10·7 and 3·8% respectively of base peak at m/e 139 $[C_3F_3NS]^+$), other peaks at m/e 302 $[C_6F_8NS_2]^+$ (16·7), 240 $[C_6F_7Cl]^+$ (11·3), 224 $[C_6F_8]^+$ (29·4), 193 (16·0), 169 (12·0), 155 (21·4), 143 (18·0), 139 (100), 124 (15·3), 112 (16·7), 100 (12·0), 94 (17·3), 93 (46·7), 69 (38·0), 64 $[S_2]^+$ (18·7), 46 $[SN]^+$ (64·7). C_6F_8NSCl requires M, 305·5], I.R. No.33 ν_{max} 1740 (CF=CF), 1490 (S=N?), 1380, 1340, 1270, 1175, 1145, 1120, 1035, 980 (doublet) $cm.^{-1}$ The ^{19}F n.m.r. spectrum (20% in CCl_4) consisted of two AB quadruplets (total relative intensity 2), one at -56·0, -51·0, -39·0 and -34·0 and the other at -46·2, -41·2, -27·6 and -22·6 assigned to the two CF_2 groups; two peaks assigned to the vinylic fluorine atoms on C5 and C6 (intensity 1) at -19·0 and -9·8; and two peaks assigned to the tertiary fluorine atoms on C1 and C4

(total relative intensity 1) at +8·4 and +12·0 p.p.m.; Fraction (2), perfluorocyclohexa-1,3-diene (0·97 g., 4·3 mmoles) with correct i.r. spectrum; Fraction (3), a pale yellow viscous liquid, 2,4,3-dithiaza-1,5,6,7,8,8,9,9-octafluorobicyclo[3,2,2]non-6-ene (0·82 g., 2·7 mmoles, 22%), [Found: C, 24·1%; halogen analyses were high and unreliable; highest peak in mass spectrum at m/e 302 $[C_6F_8NS_2]^+$ (10·3% of base peak at m/e 139 $[C_3F_3NS]^+$, other peaks at m/e 221 (6·9), 193 (15·9), 143 (15·0), 139 (100), 112 (15·0), 94 (17·8), 93 (34·1), 69 (20·3), 64 (11·9), 46 (19·4); M (cryoscopic in benzene solution), 330. $C_6F_8NS_2$ requires C, 23·8; F, 50·4%; M, 302], b.p. 125°/759 mm., I.R. No.34 ν_{max} 1750 (CF=CF), 1370, 1310, 1140, 1030, 980, 925 $cm.^{-1}$ The ^{19}F n.m.r. spectrum consisted of resonances centred at: (i) -36·2 (total relative intensity 2), doublet (J 15) assigned to CF_2 groups; (ii) -15·3 (intensity 1), vinylic fluorine atoms; (iii) +25·2 (intensity 1), tertiary fluorine atoms.

A tube containing a 20% solution of perfluoro-2-chloro-2,3-thiazabicyclo[2,2,2]octa-2,5-diene in CCl_4 accidentally had some water added. There was an exothermic reaction and evolution of gas. Evaporation of the liquid left a clear unidentified crystalline solid with parent ion m/e 236·0157 (base peak), other peaks at m/e 233 (87% of base peak), 221 (12), 205 (96), 186 (40), 171 (44), 143 (88), 112 (40), 93 (80), 59 (42), 15 (93). The only ion containing nitrogen with a similar

mass is $C_6F_6NO_2H_4$, m/e 236·0146. The i.r. spectrum showed absorptions at 3320 (amide ?), 1735 (CF=CF ?), 1455 and 995 $cm.^{-1}$ The ^{19}F n.m.r. spectrum (10% solution in acetone, Varian A-56/60) indicated a multiple of six fluorine atoms and consisted of resonances at: (i) -45·2, a double (J 20) of doublets (J 12) of triplets (J 6·5) assigned to a CF_2 group; (ii) -33·6, a quartet (J 6·5) assigned to a CF_2 group; (iii) -26·3, a triplet (J 12·5) broadened presumably by being adjacent to a nitrogen atom assigned to a CF group (either tertiary or vinylic); (iv) +2·3, a triple (J 20) of quartets (J 6·5) assigned to a CF group. The ^1H n.m.r. spectrum (10% solution in acetone, external TMS, Varian A-56/60) indicated more protons than compatible with the mass spectrum and consisted of resonances at: (i) -5·03 (total relative intensity 2), broad peaks, possibly an amide proton; (ii) -3·04 (intensity 3), doublet (J 2); (iii) -0·65 (intensity 2), doublet (J 6·5).

Experiment II. - By using the same procedure as in Experiment I, trithiazyl trichloride (0·77 g., 9·46 mmoles as NSCl) and perfluorocyclohexa-1,3-diene (2·57 g., 11·5 mmoles) were heated in a 20-ml. Pyrex ampoule at 100° for 17 hr. to give: (i) a liquid mixture (2·39 g.) shown by analytical g.l.c. to consist principally of 2,4,3-dithiaza-1,5,6,7,8,8,9,9-octafluorobicyclo[3,2,2]non-6-ene (ca. 90%). This is equivalent to ca. 7·1 mmoles and a yield of ca. 75% w.r.t. SNCl; (ii) an unidentified viscous liquid (0·36 g.); (iii) a residual dark red oil (ca. 0·5 g.).

A P P E N D I X

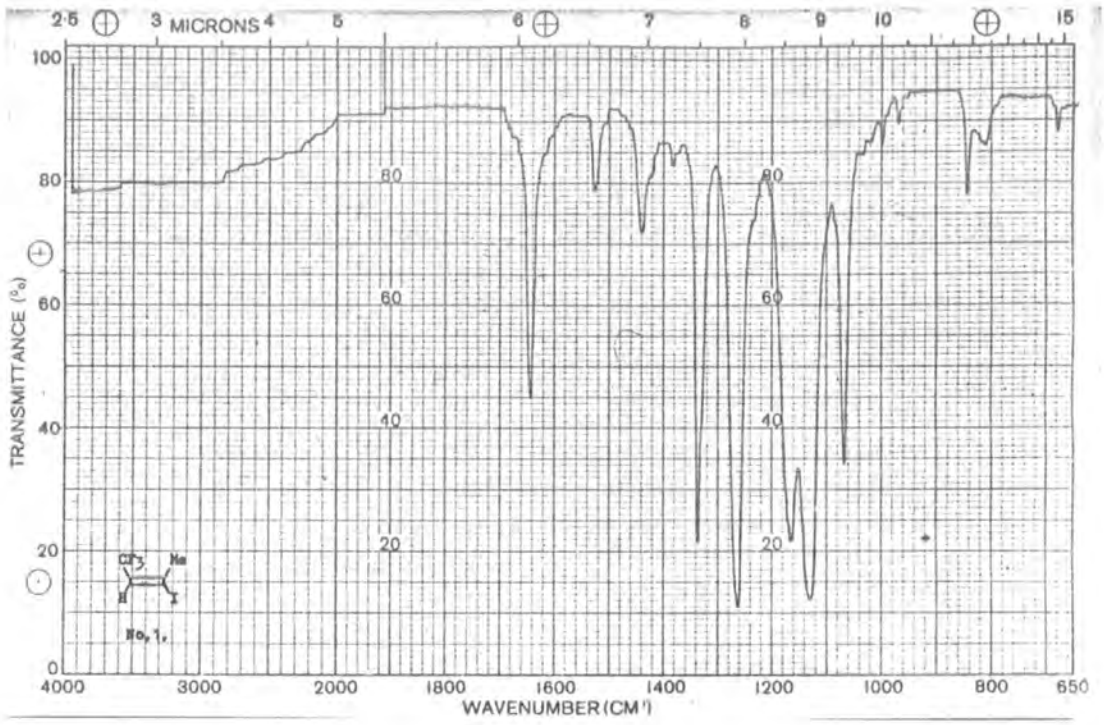
INFRARED SPECTRA.

I.R. No.	Name of Compound
1.	Cis- 1,1,1-trifluoro-3-iodobut-2-ene.
2.	Trans- 1,1,1-trifluoro-3-iodobut-2-ene.
3.	2-Methyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IIa).
4.	2-Trifluoromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo-[2,2,2]octa-2,5-diene (IIb).
5.	2-Monochloromethyl-1,4,5,6,7,7,8,8-octafluorobicyclo-[2,2,2]octa-2,5-diene (IIc).
6.	2-Phenyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene (IId).
7.	2,3-Dimethyl-1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]-octa-2,5-diene (IIe).
8.	2,3-Bis(monochloromethyl)-1,4,5,6,7,7,8,8-octafluoro-bicyclo[2,2,2]octa-2,5-diene (IIf).
9.	2-Methyl-3-trifluoromethyl-1,4,5,6,7,7,8,8-octafluoro-bicyclo[2,2,2]octa-2,5-diene (IIg).
10.	Diethyl 1,4,5,6,7,7,8,8-octafluorobicyclo[2,2,2]octa-2,5-diene-2,3-dicarboxylate (IIh).
11.	Perfluoro-2,3-dimethylbicyclo[2,2,2]octa-2,5-diene (IIi).

I.R. No.	Name of Compound
12.	2,3,4,5-Tetrafluorotoluene (IIIa).
13.*	ααα,2,3,4,5-Heptafluorotoluene (IIIb).
14.	α-Chloro-2,3,4,5-tetrafluorotoluene (IIIc).
15.	Trans- 2,2',3,3',4,4',5,5'-octafluorostilbene (IIId).
16.*	2,3,4,5-Tetrafluorobiphenyl (IIIe).
17.	3,4,5,6-Tetrafluoro-ortho-xylene (IIIf).
18.	2,3,4,5-Tetrafluorophenylacetylene (IIIg).
19.	1-Methyl-2-trifluoromethyl-3,4,5,6-tetrafluorobenzene (IIIh).
20.*	2,3,4,5-Tetrafluorobenzoic acid (IIIj).
21.*	Perfluoro-ortho-xylene (IIIk).
22.*	Perfluoro-2-methylpyridine (VIa).
23.	Perfluoro-2-bromopyridine (VIb).
24.	Perfluoro-2-(3-cyanopropyl)pyridine (VIc).
25.	Perfluoro-2-phenylpyridine (VId).
26.	Perfluoro-1,3-bis-2,2'-pyridylpropane (VIe).
27.	Perfluoro-2-aza-3-bromobicyclo[2,2,2]octa-2,5-diene (Vb).
28.	Perfluoro-2-aza-3-(3-cyanopropyl)bicyclo[2,2,2]octa-2,5-diene (Vc).
29.	Perfluorobicyclo[4,2,0]oct-2-ene.
30.	Perfluorobicyclo[2,2,2]oct-2-ene.
31.	Endo-? perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-3,9-diene.

I.R. No.	Name of Compound
32.	Exo-? perfluorotricyclo[6,2,2,$0^{2,7}$]dodeca-3,9-diene.
33.	Perfluoro-2-chloro-2,3-thiazabicyclo[2,2,2]octa-2,5-diene?
34.	2,4,3-Dithiaza-1,5,6,7,8,8,9,9-octafluorobicyclo-[3,2,2]non-6-ene?

Note. * Previously published compounds.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WAVENUMBER (CM⁻¹)
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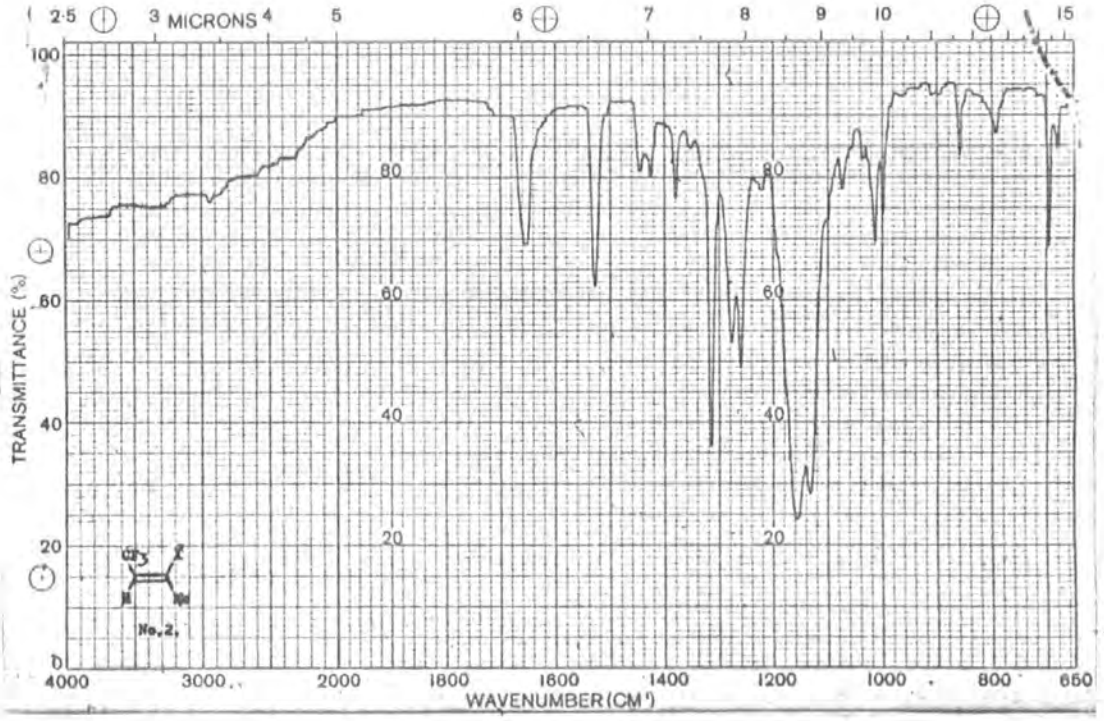
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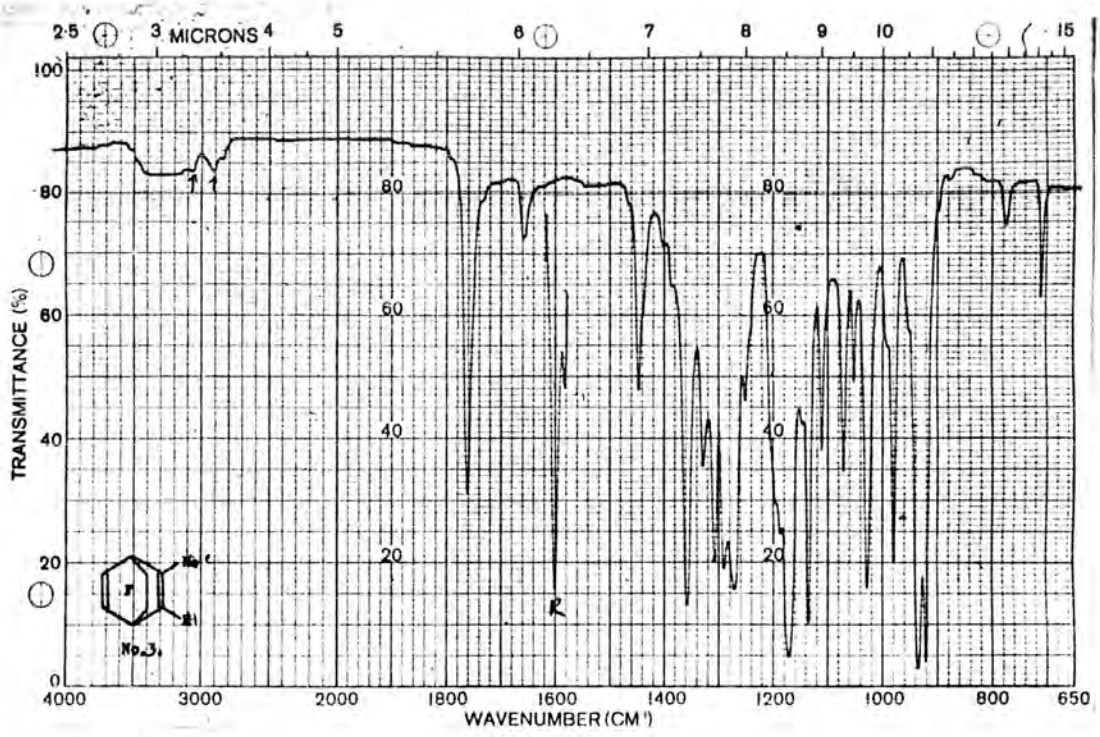
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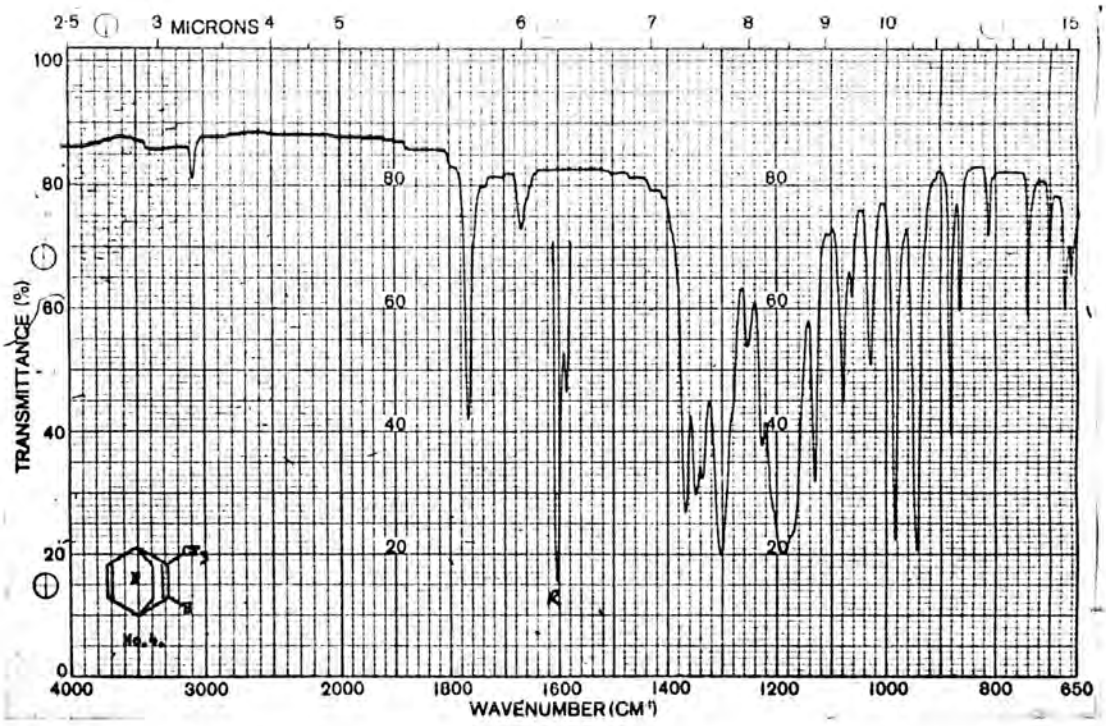
WAVENUMBER (CM⁻¹)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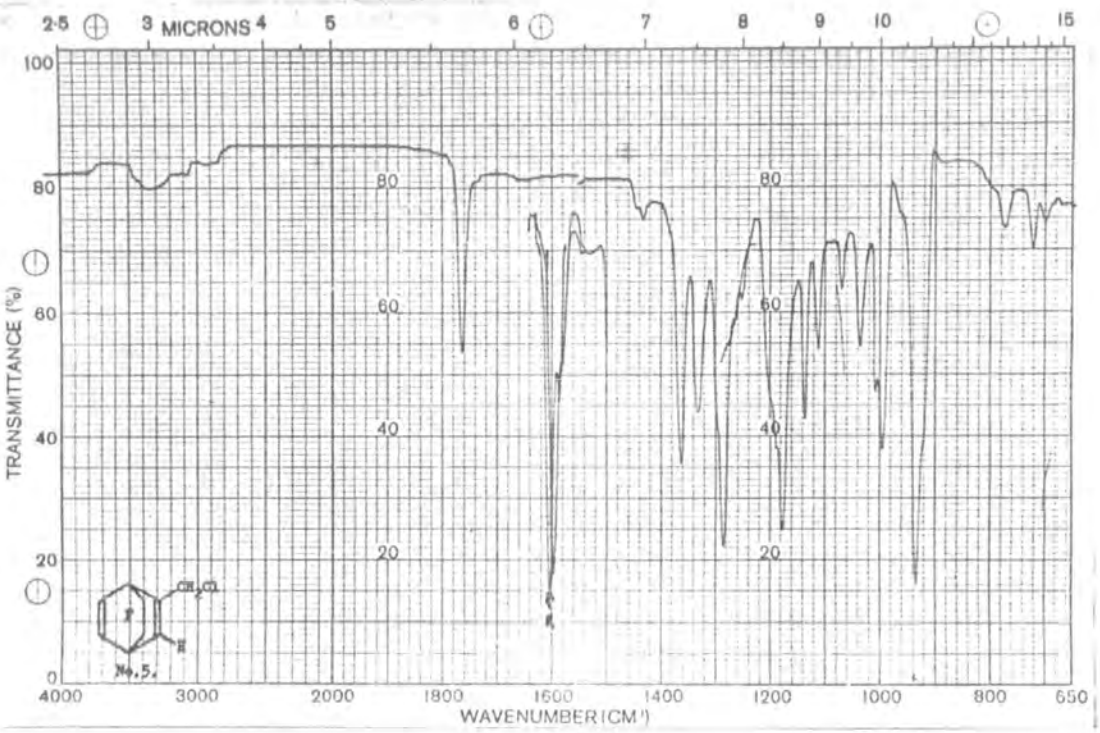
WAVENUMBER (CM⁻¹)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WAVENUMBER (CM⁻¹)
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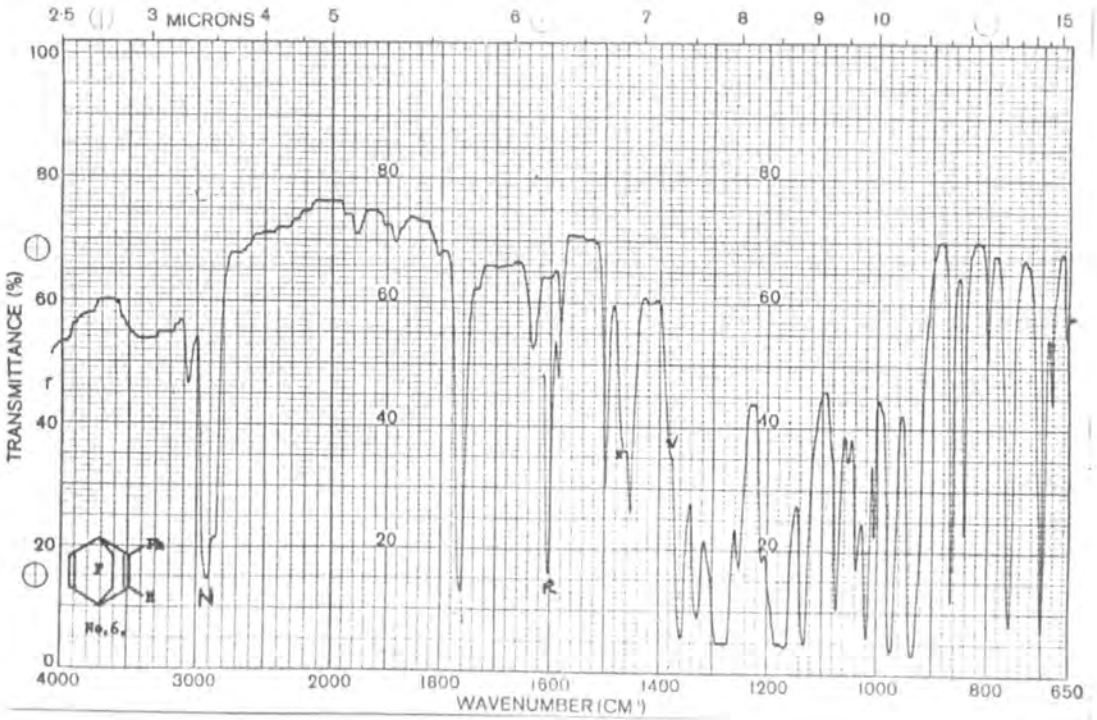
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3 MICRONS
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WAVENUMBER (CM⁻¹)
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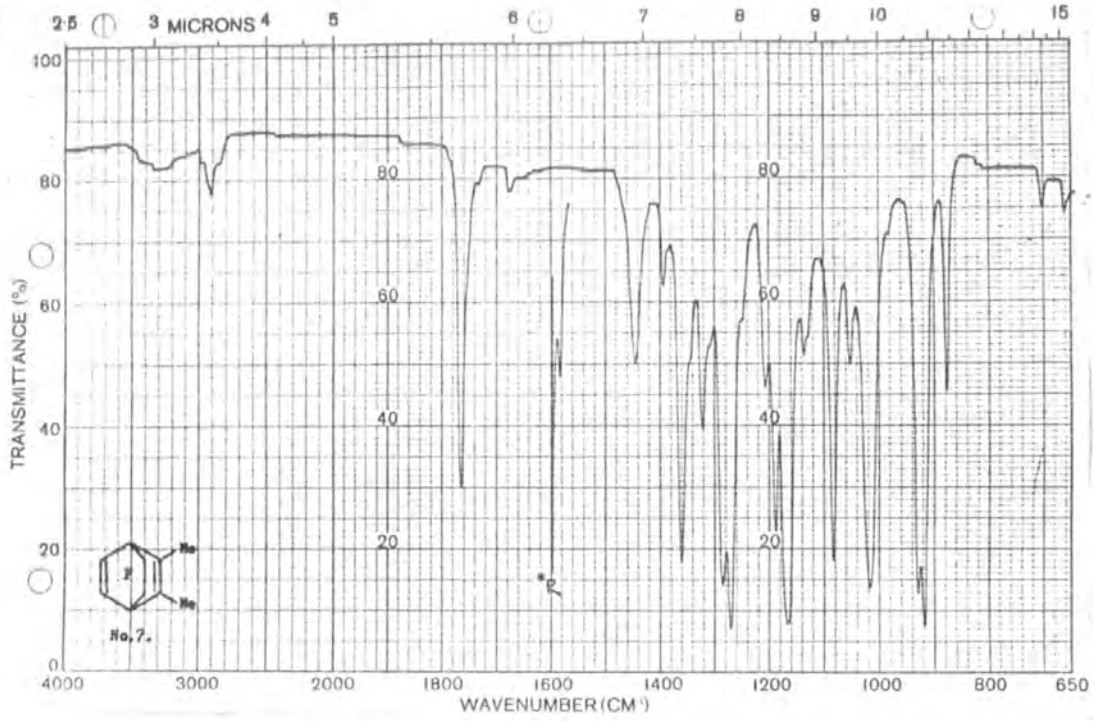
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3 MICRONS
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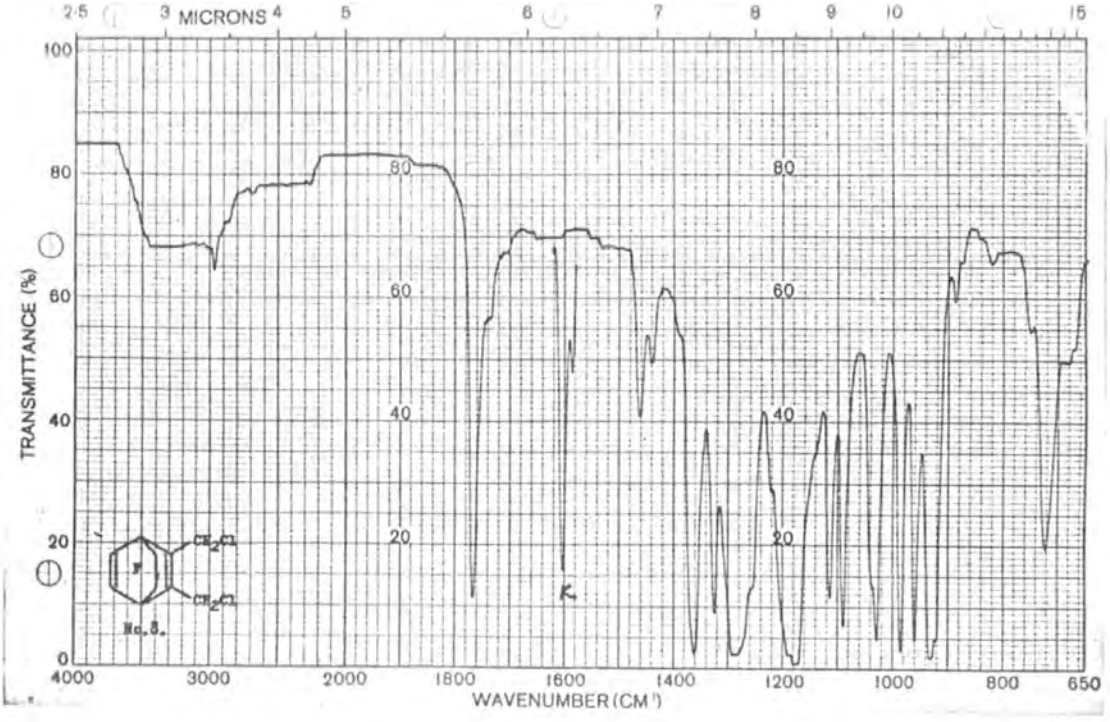
WAVENUMBER (CM⁻¹)
No. 7.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WAVENUMBER (CM⁻¹)
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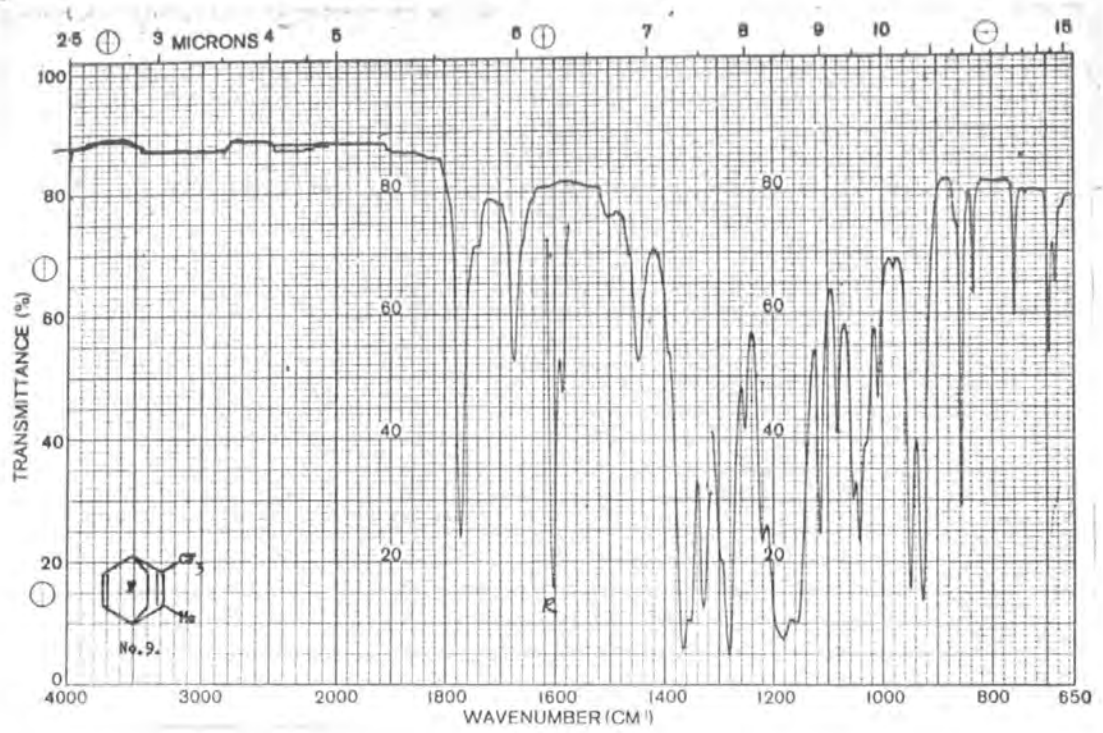
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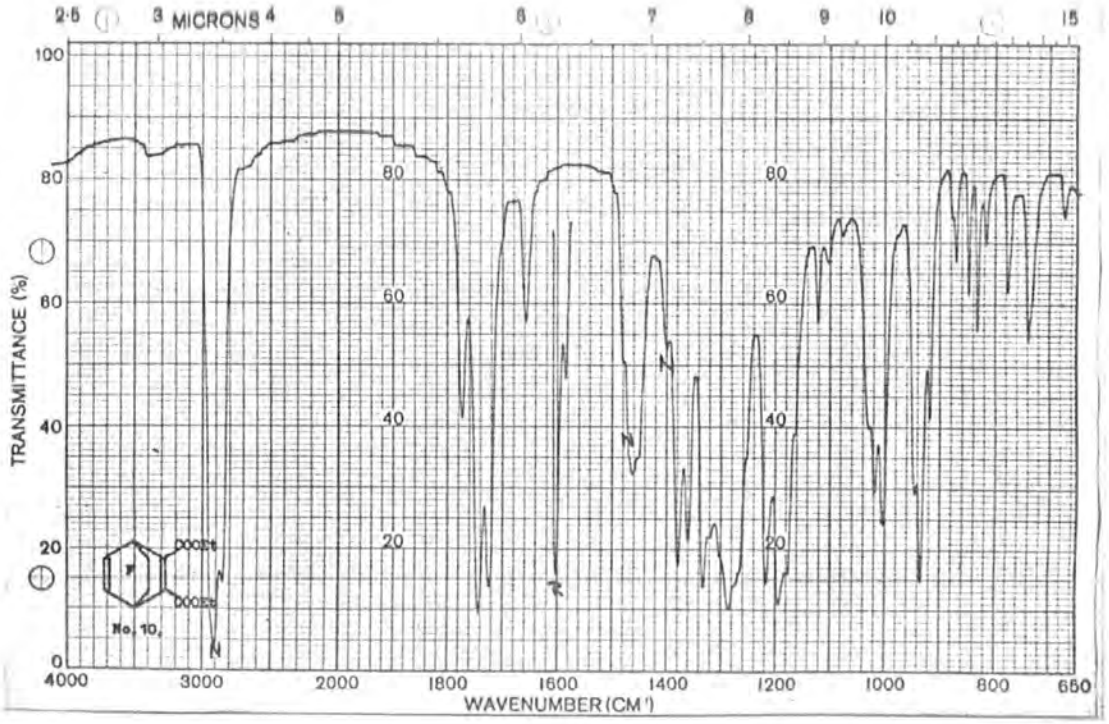
WAVENUMBER (CM⁻¹)
No. 9.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3 MICRONS
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TRANSMITTANCE (%)
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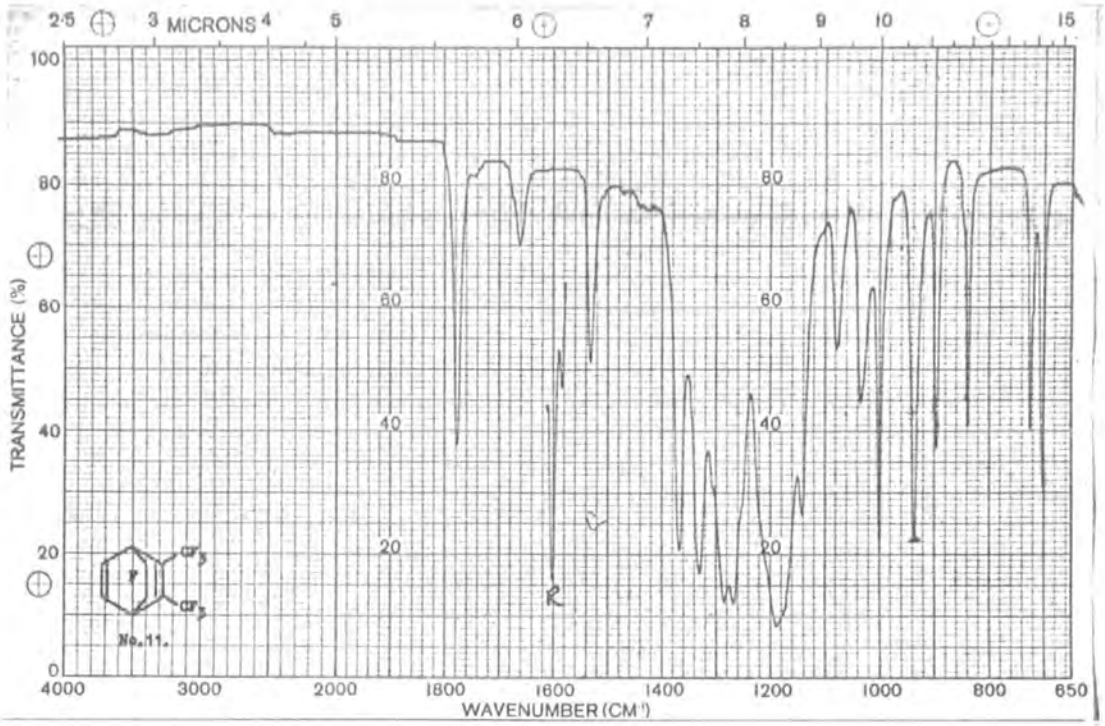
WAVENUMBER (CM⁻¹)
No. 10.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TRANSMITTANCE (%)
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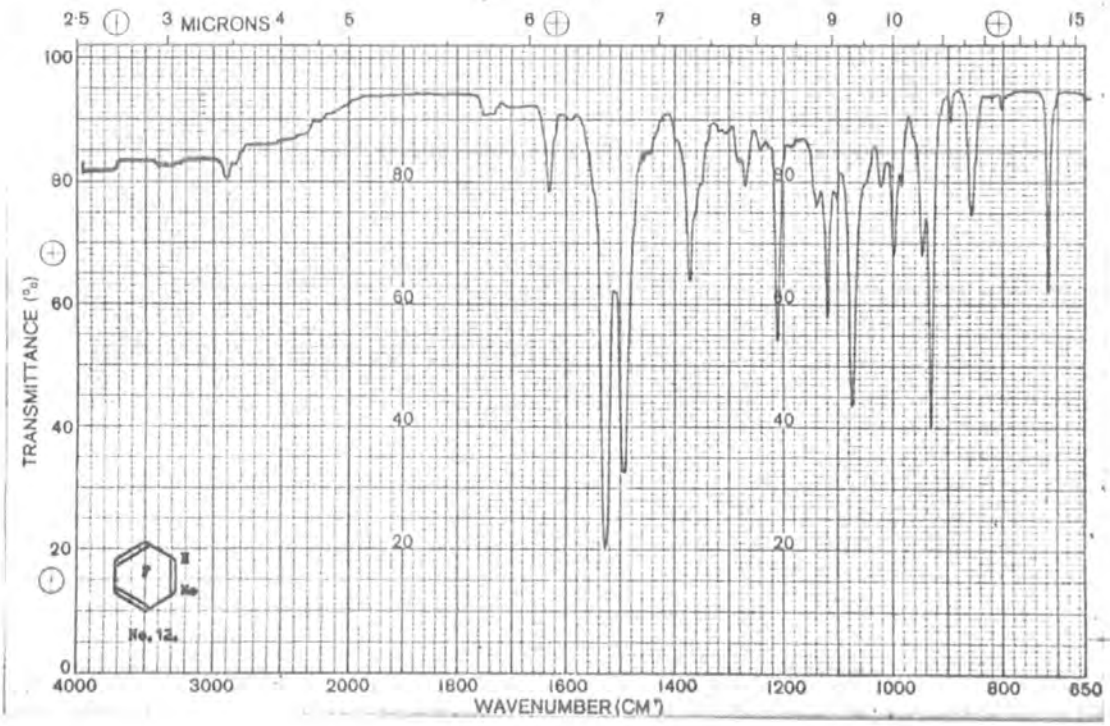
WAVENUMBER (CM⁻¹)
No.11.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TRANSMITTANCE (%)
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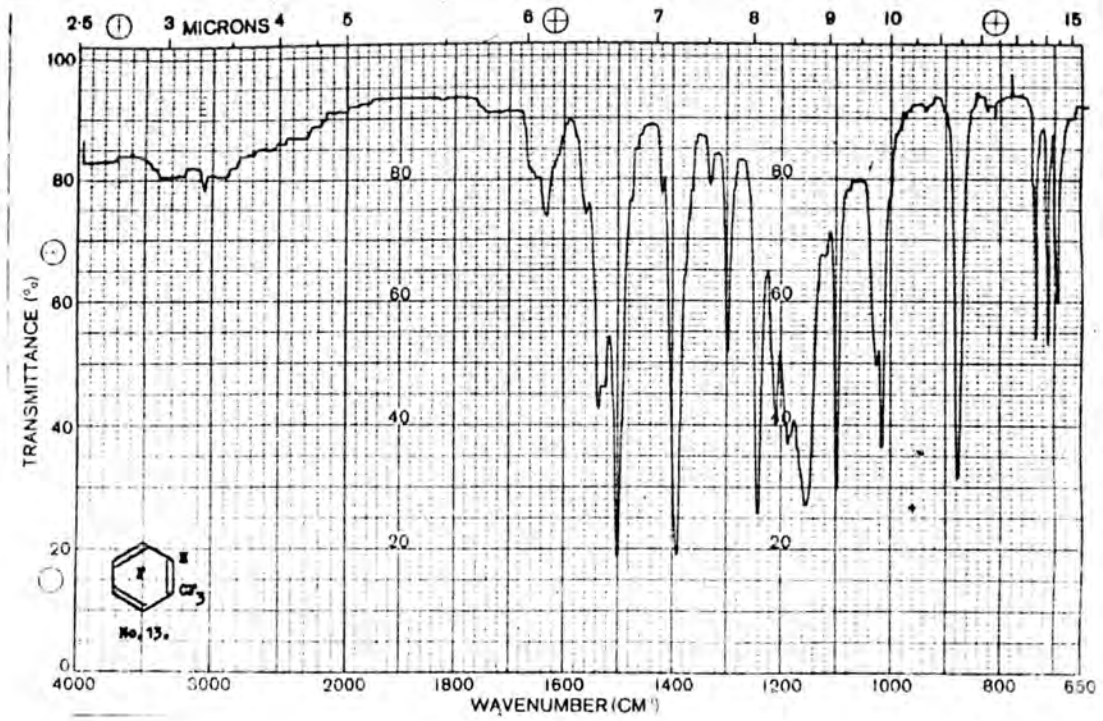
WAVENUMBER (CM⁻¹)
No.12.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3 MICRONS
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TRANSMITTANCE (%)
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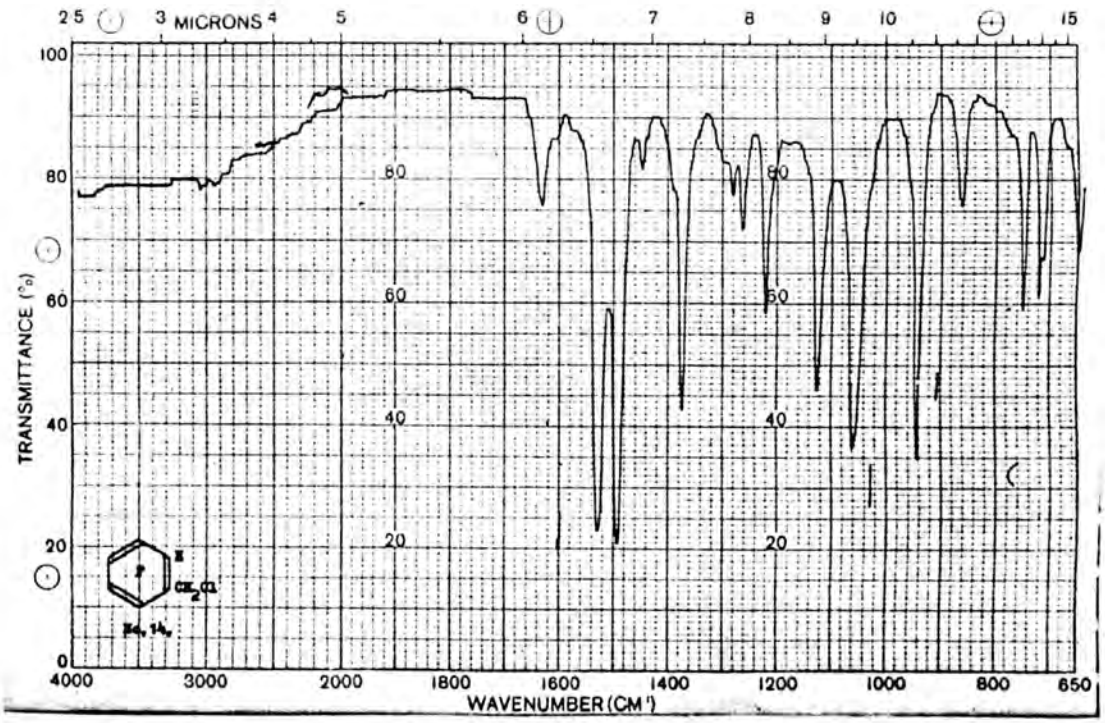
WAVENUMBER (CM⁻¹)
No. 13.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3 MICRONS
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TRANSMITTANCE (%)
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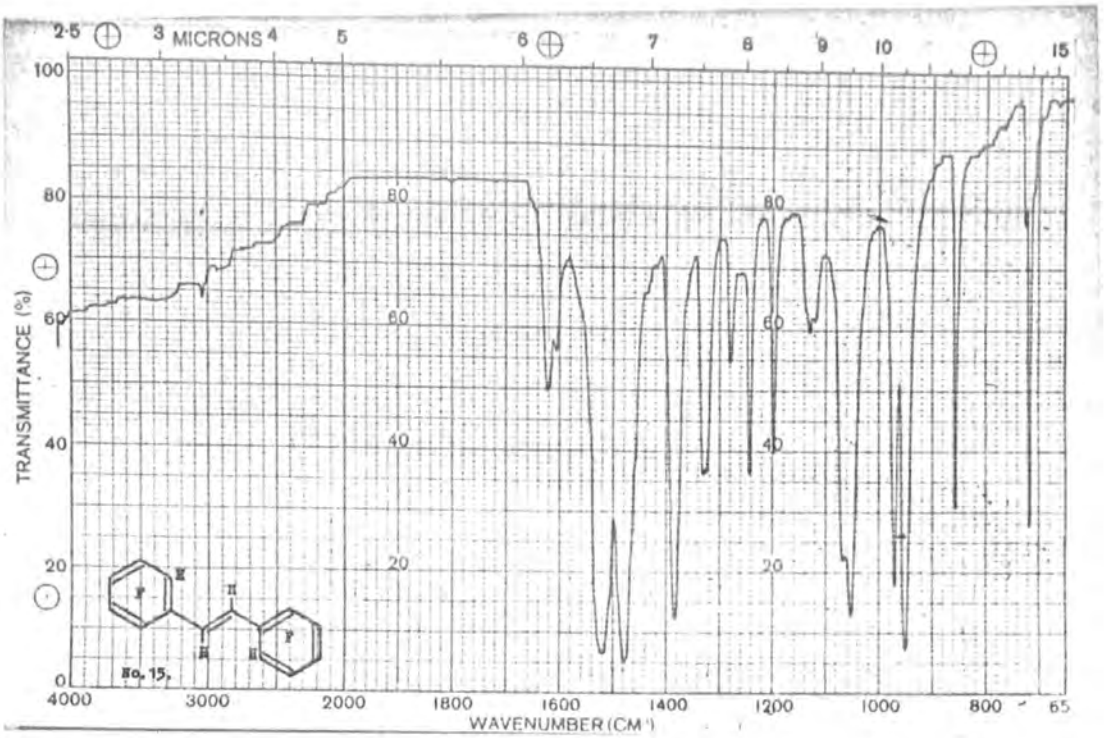
WAVENUMBER (CM⁻¹)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3 MICRONS
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TRANSMITTANCE (%)
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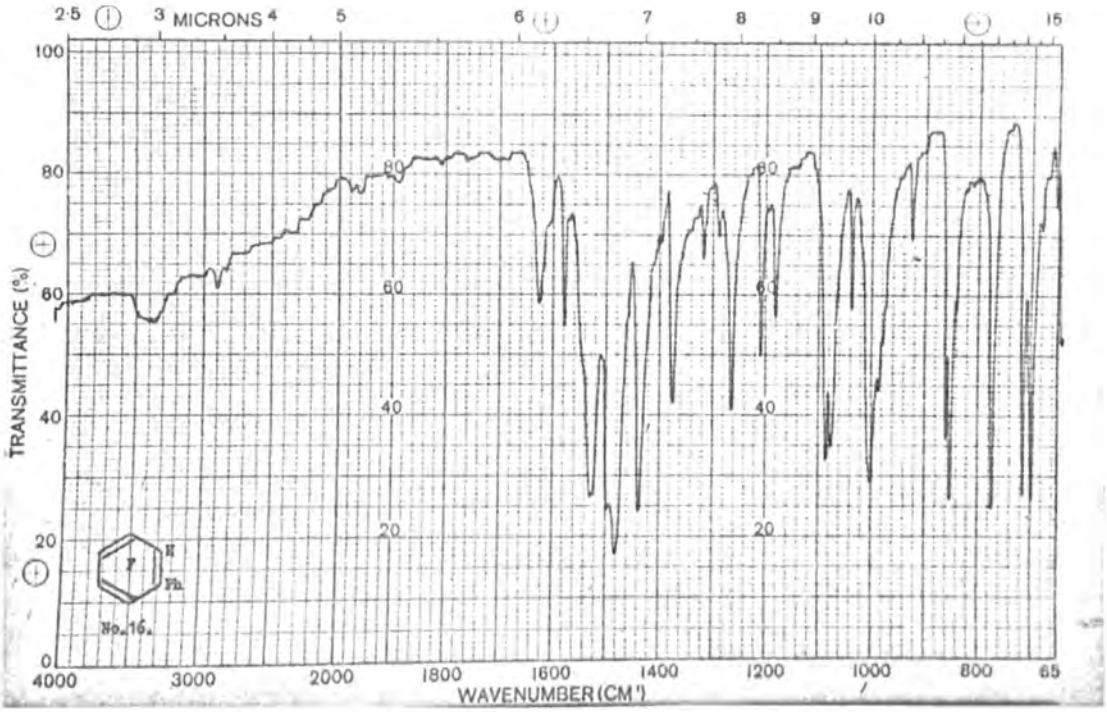
650
WAVENUMBER (CM⁻¹)
No. 15.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3 MICRONS
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100
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0
TRANSMITTANCE (%)
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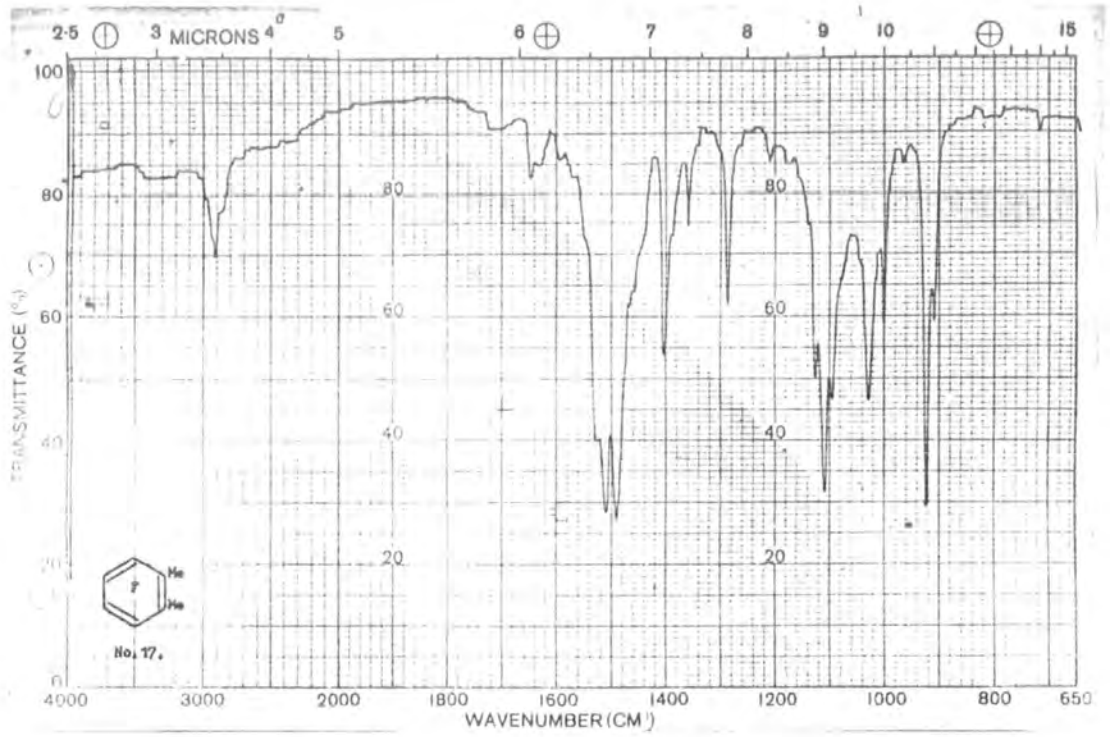
650
WAVENUMBER (CM⁻¹)
No. 16.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3 MICRONS
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15
100
80
60
40
20
0
TRANSMITTANCE (%)
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1600
1400
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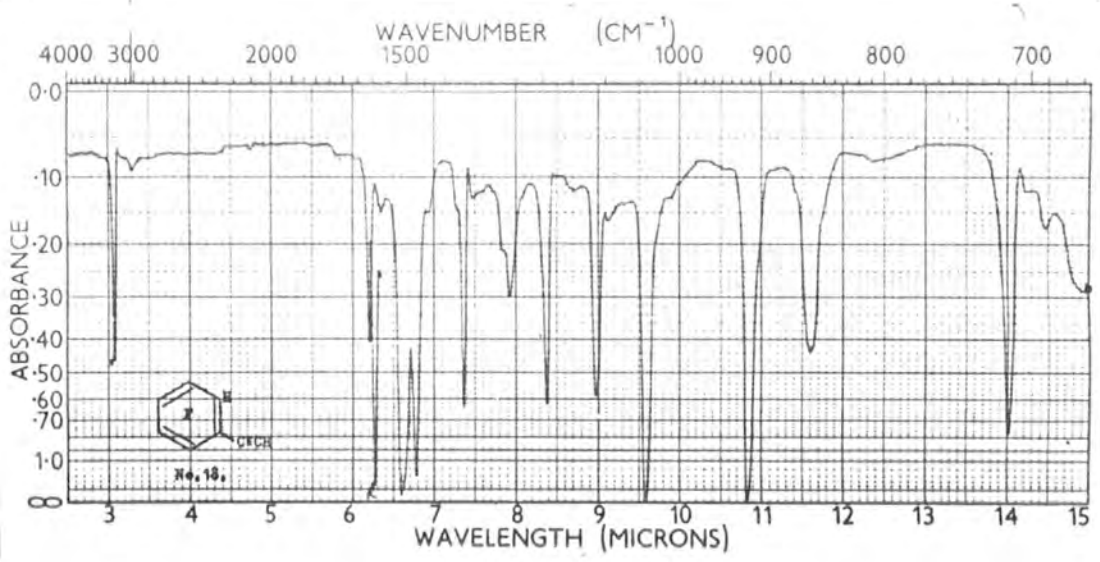
1000
800
650
WAVENUMBER (CM⁻¹)
Me
Me
No. 17.


WAVENUMBER (CM⁻¹)
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1500
1000
900
800
700
0·0
·10
·20
·30
·40
·50
·60
·70
1·0
ABSORBANCE
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13
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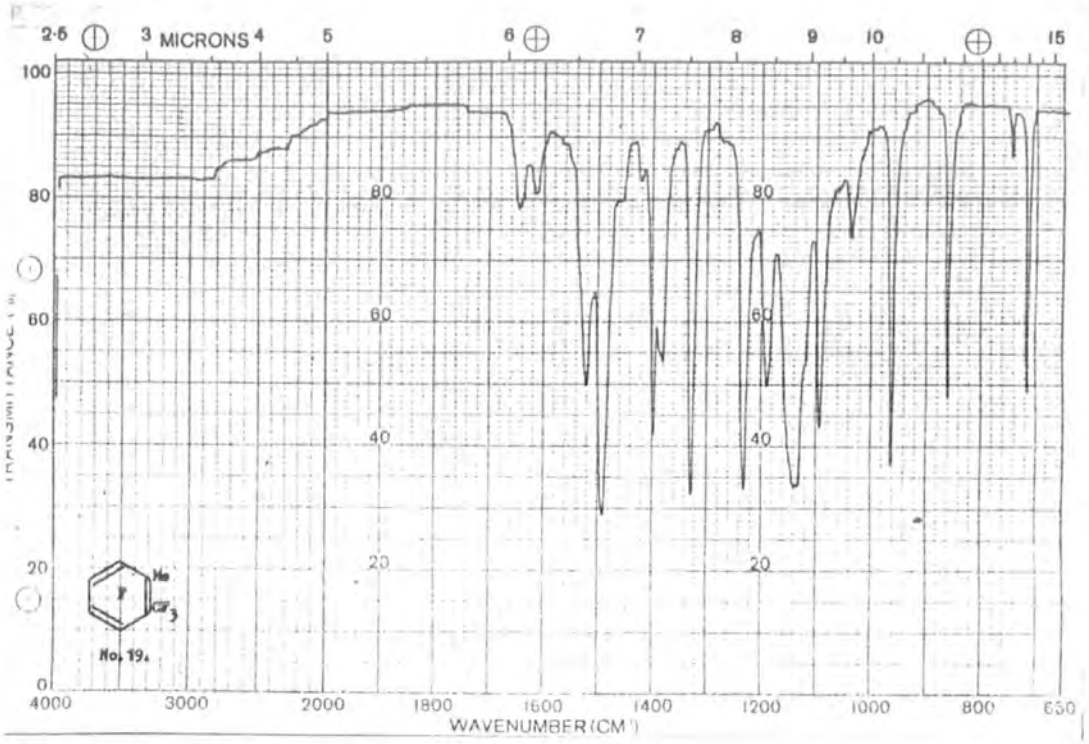
15
WAVELENGTH (MICRONS)
CH=CH
No. 18.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3 MICRONS
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100
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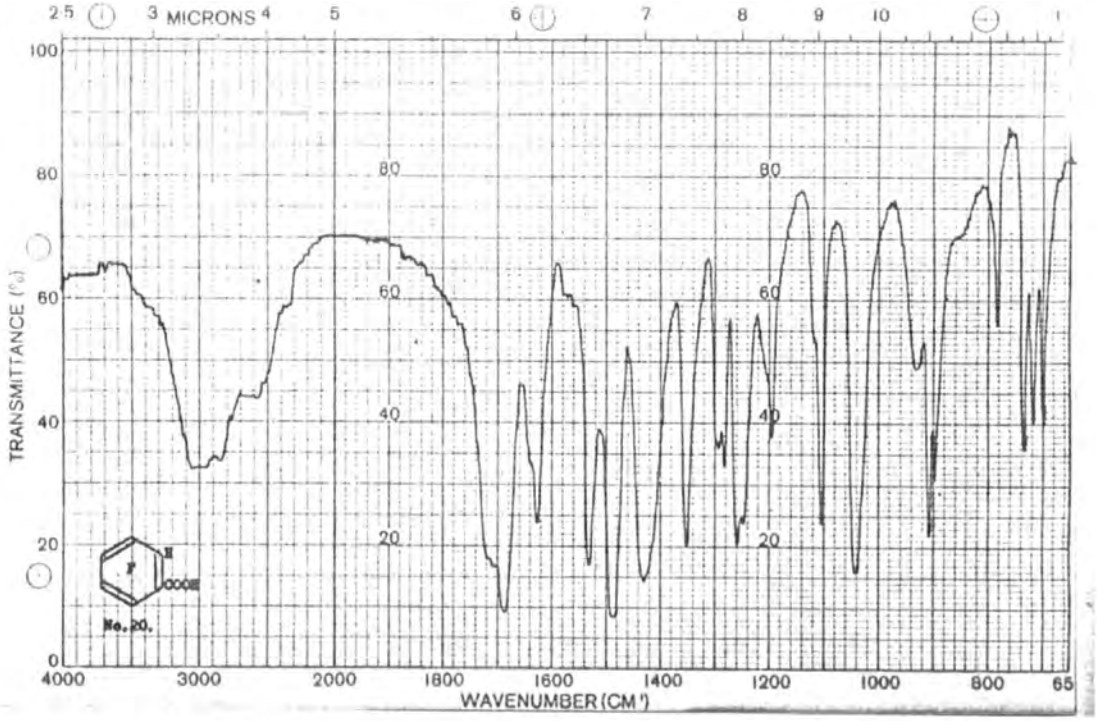
650
WAVENUMBER (CM⁻¹)
No. 19.


2·5
3 MICRONS
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10
100
80
60
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20
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4000
3000
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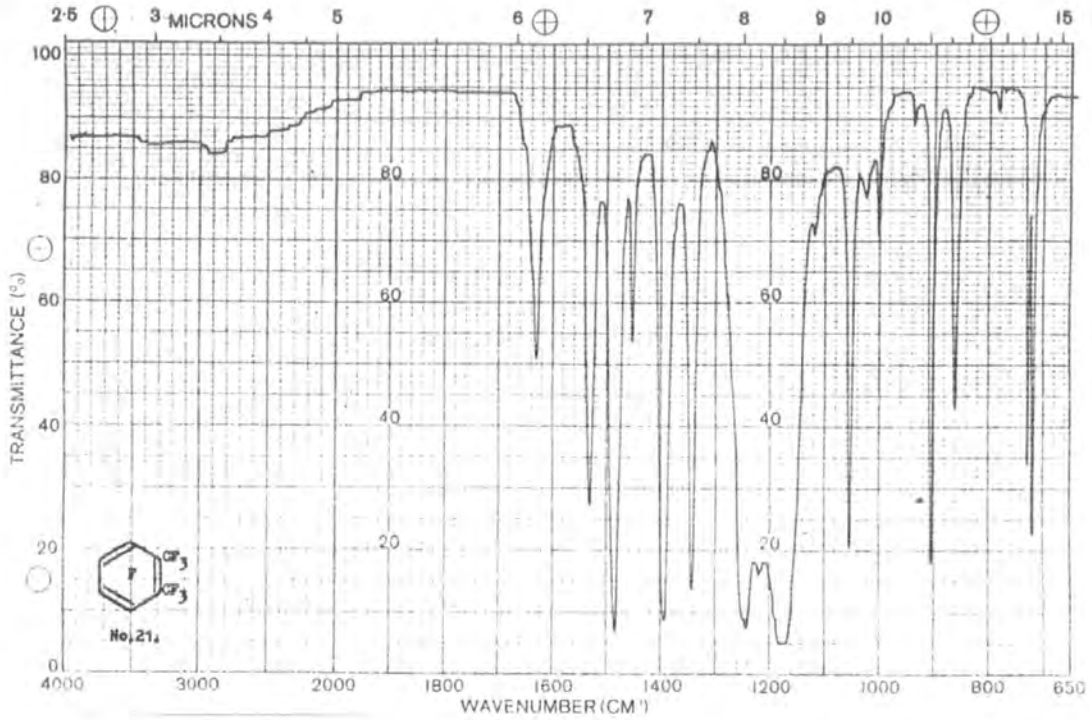
WAVENUMBER (CM⁻¹)
No. 20.


2·5
3 MICRONS 4
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100
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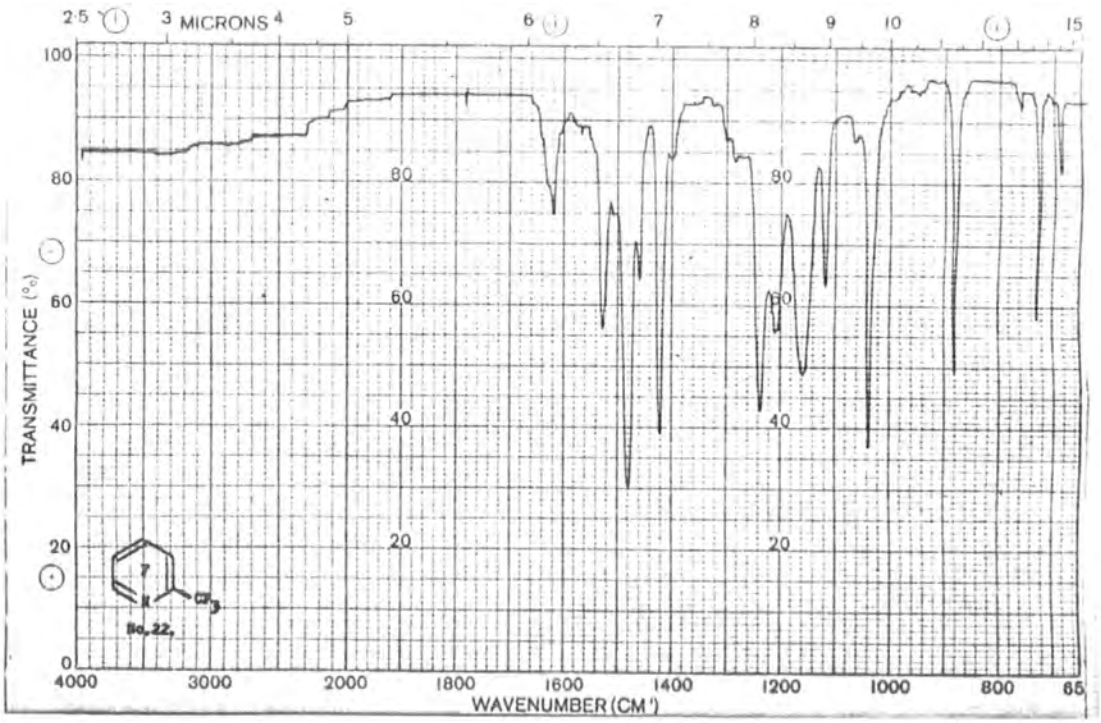
WAVENUMBER (CM⁻¹)
No. 21.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3 MICRONS 4
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WAVENUMBER (CM⁻¹)
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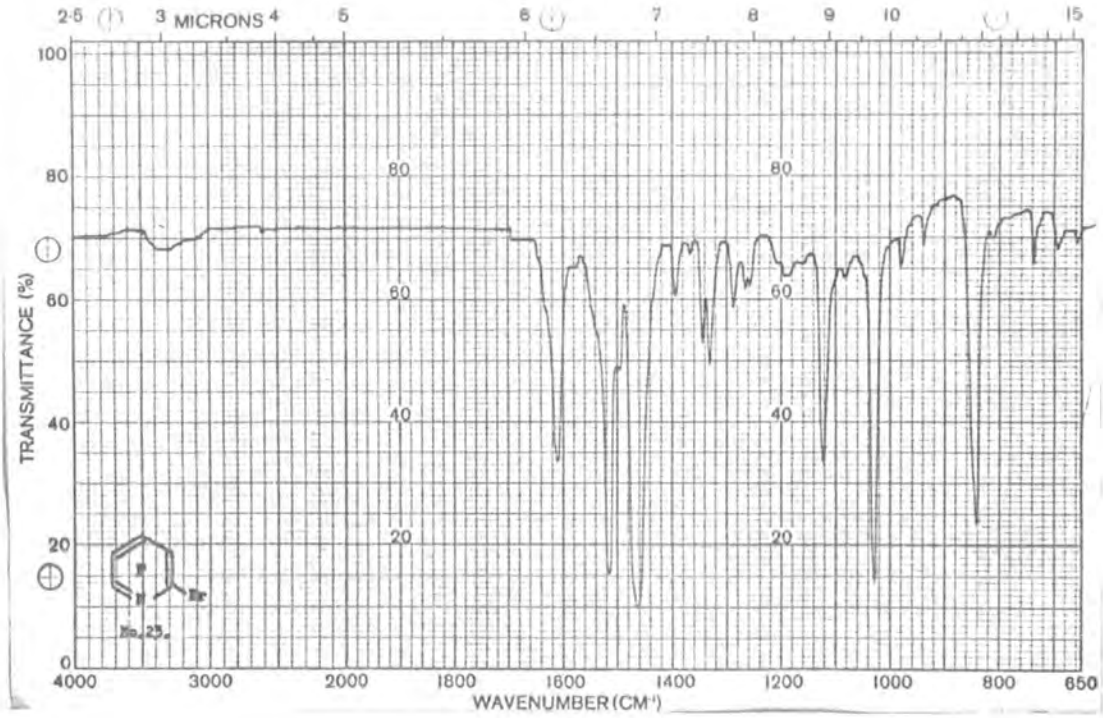
2·5
3 MICRONS
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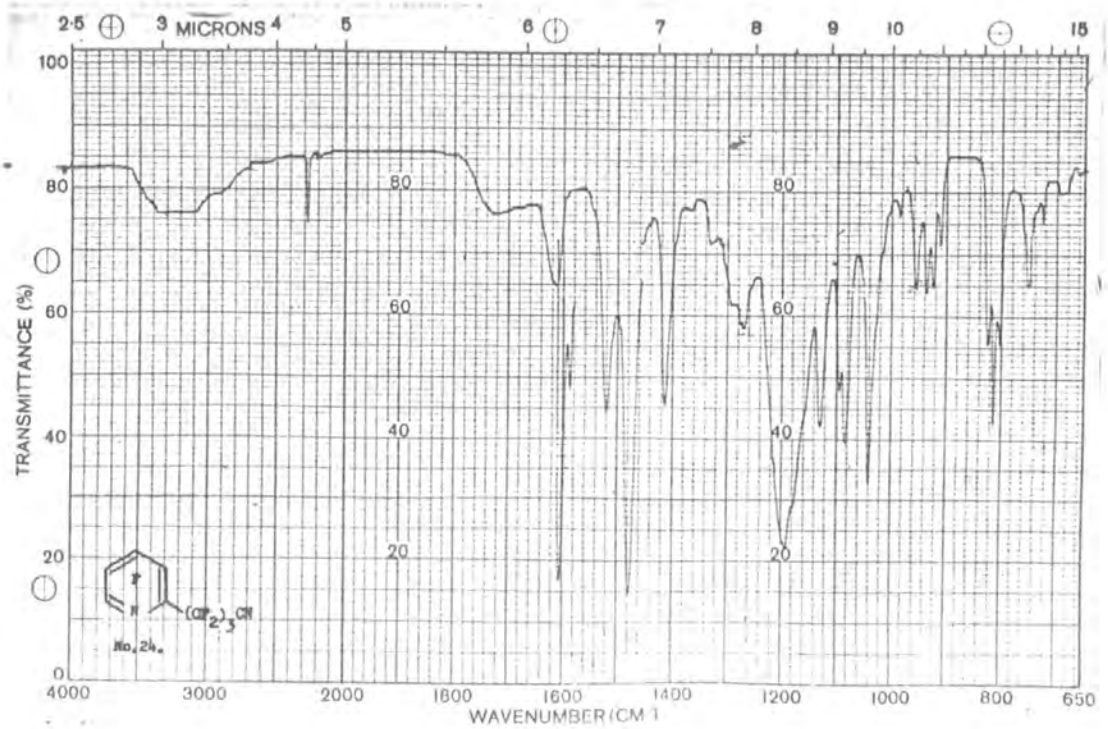
WAVENUMBER (CM⁻¹)
No. 23.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3 MICRONS
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100
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0
TRANSMITTANCE (%)
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WAVENUMBER (CM⁻¹)
No. 24.


2·5
3 MICRONS 4
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100
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60
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0
TRANSMITTANCE (%)
3000
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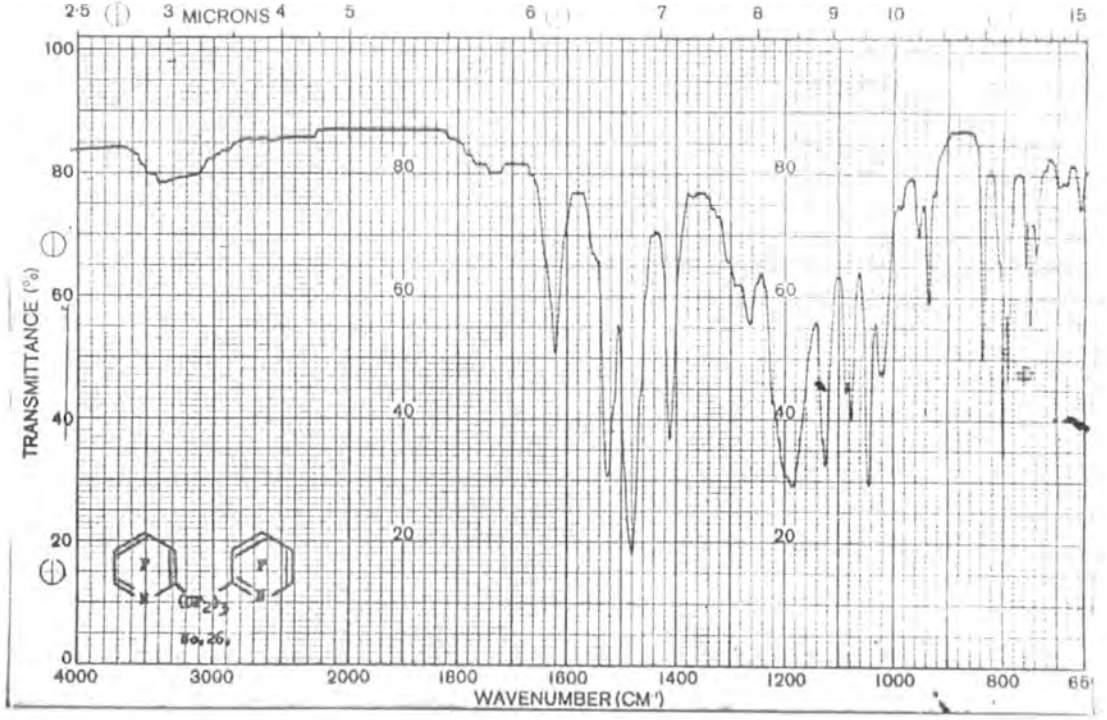
650
WAVENUMBER (CM⁻¹)

No. 25.


2·5
3 MICRONS 4
5
6
7
8
9
10
15
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
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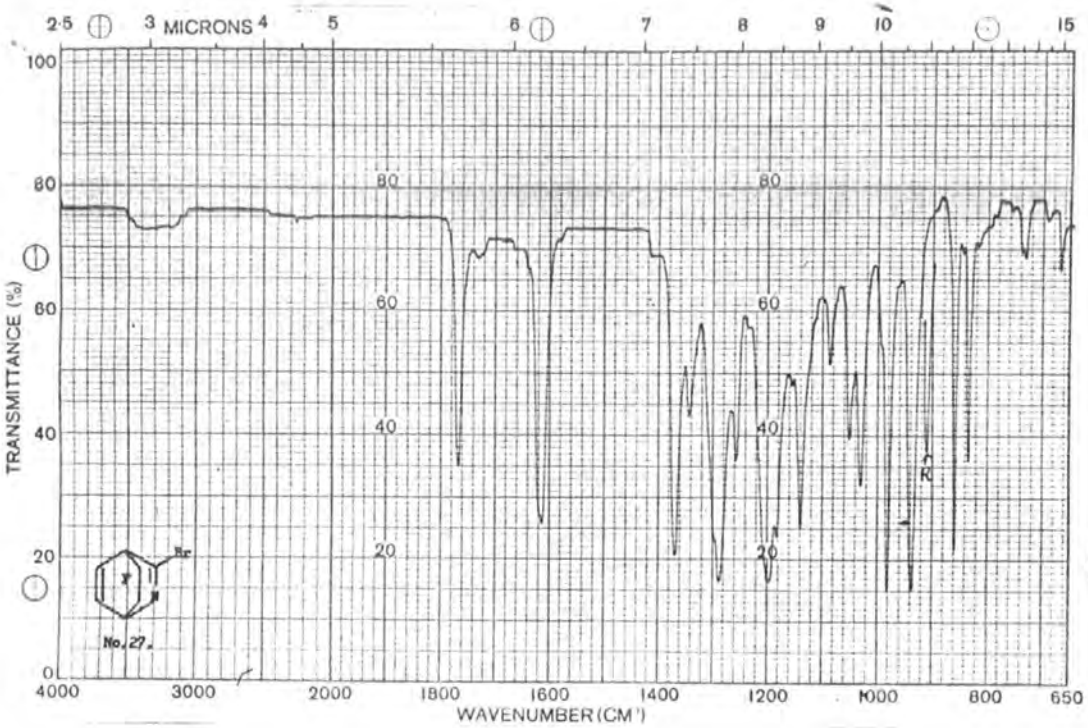
800
WAVENUMBER (CM⁻¹)

No. 26.


2·5
3 MICRONS
4
5
6
7
8
9
10
15
100
80
60
40
20
0
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1600
1400
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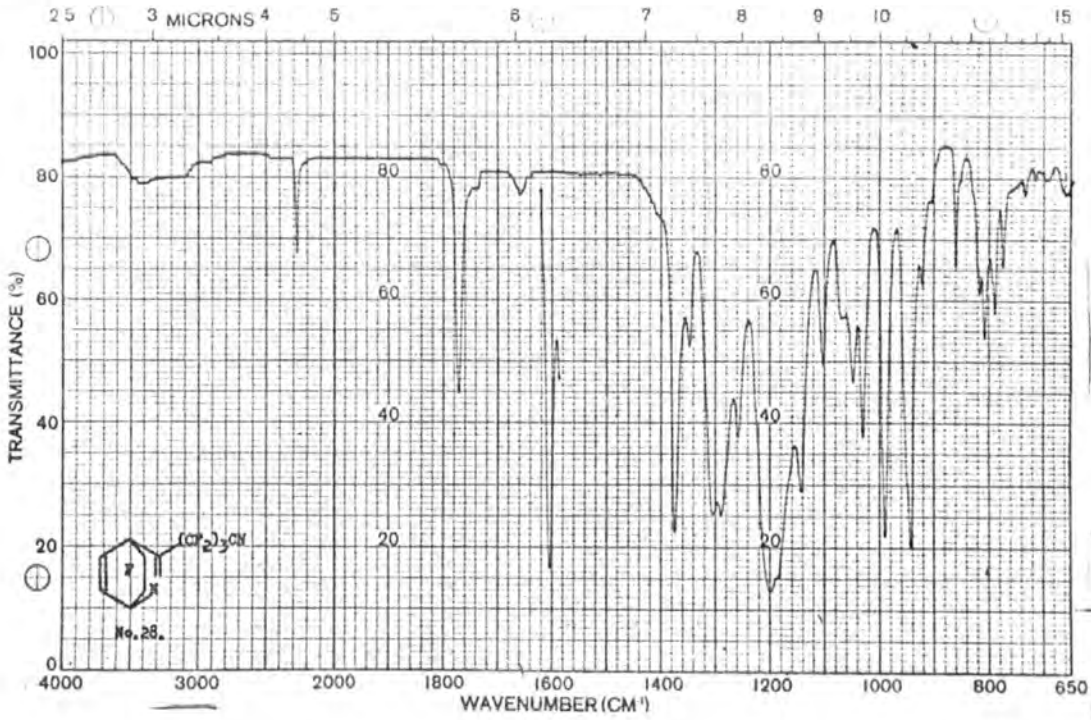
650
WAVENUMBER (CM⁻¹)
Br
No. 27.


2·5
3 MICRONS
4
5
6
7
8
9
10
15
100
80
60
40
20
0
TRANSMITTANCE (%)
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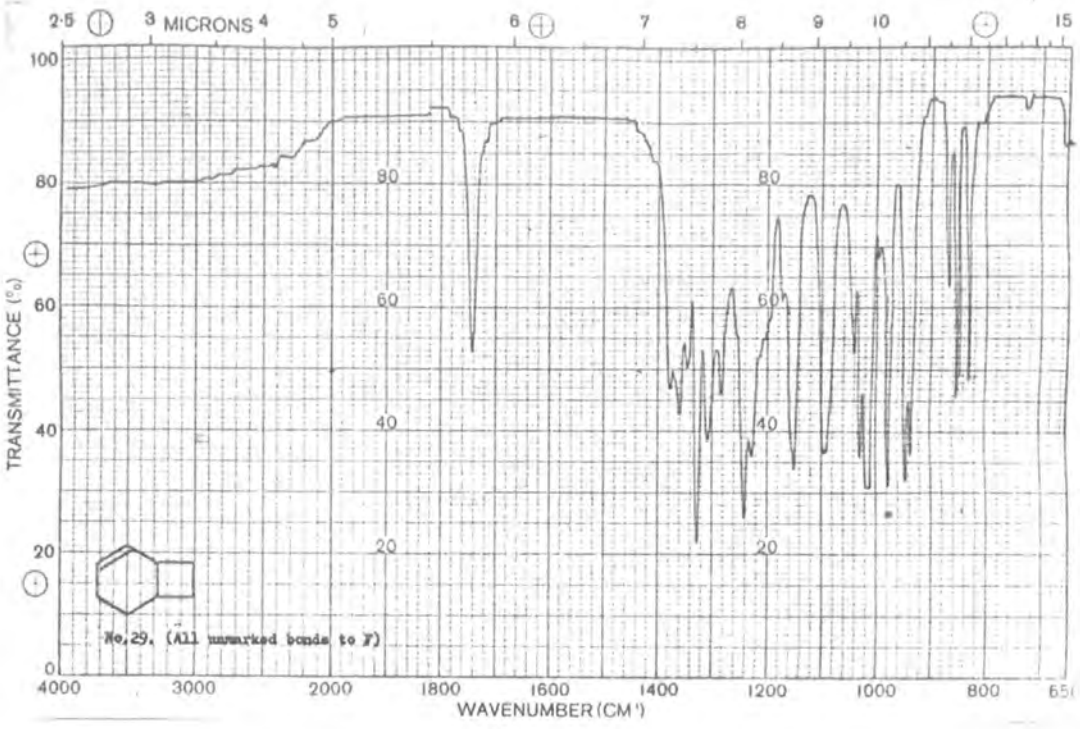
WAVENUMBER (CM⁻¹)
(CF2)3CN
No. 28.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3 MICRONS
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5
6
7
8
9
10
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100
80
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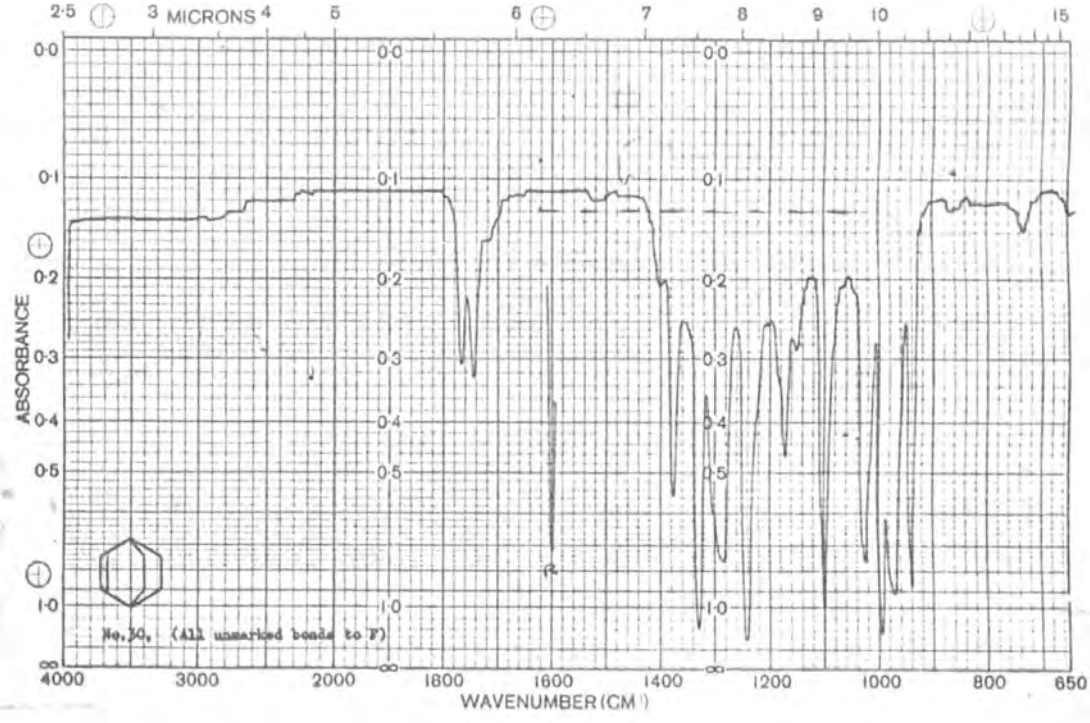
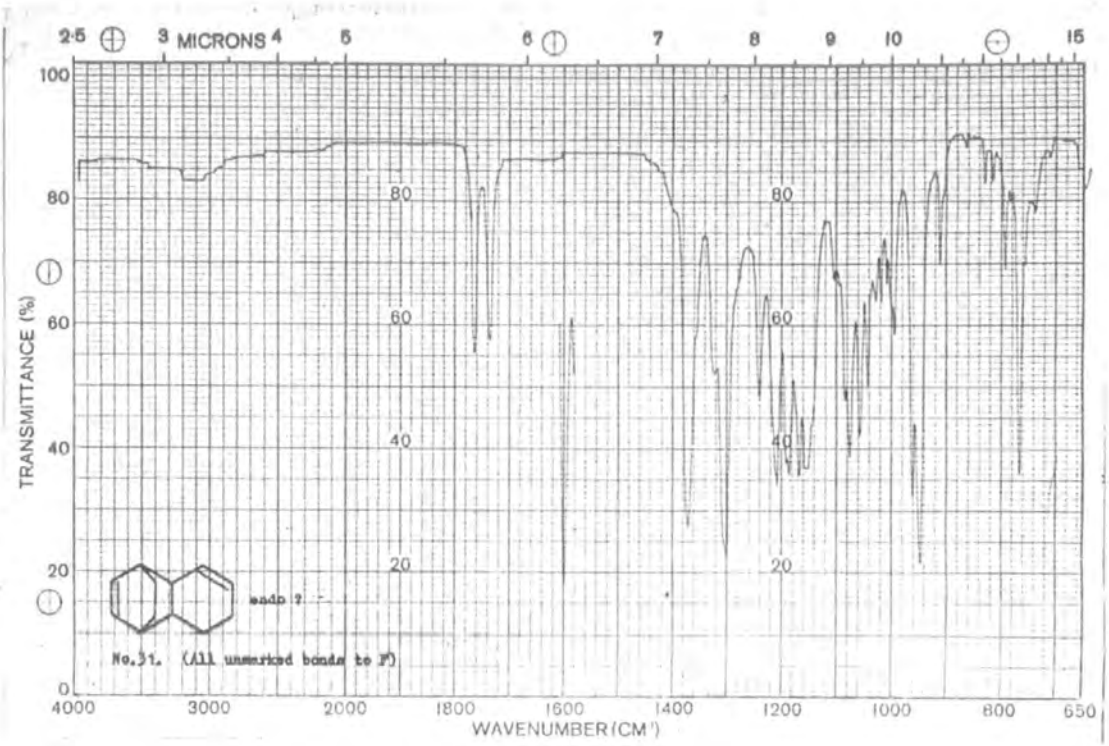
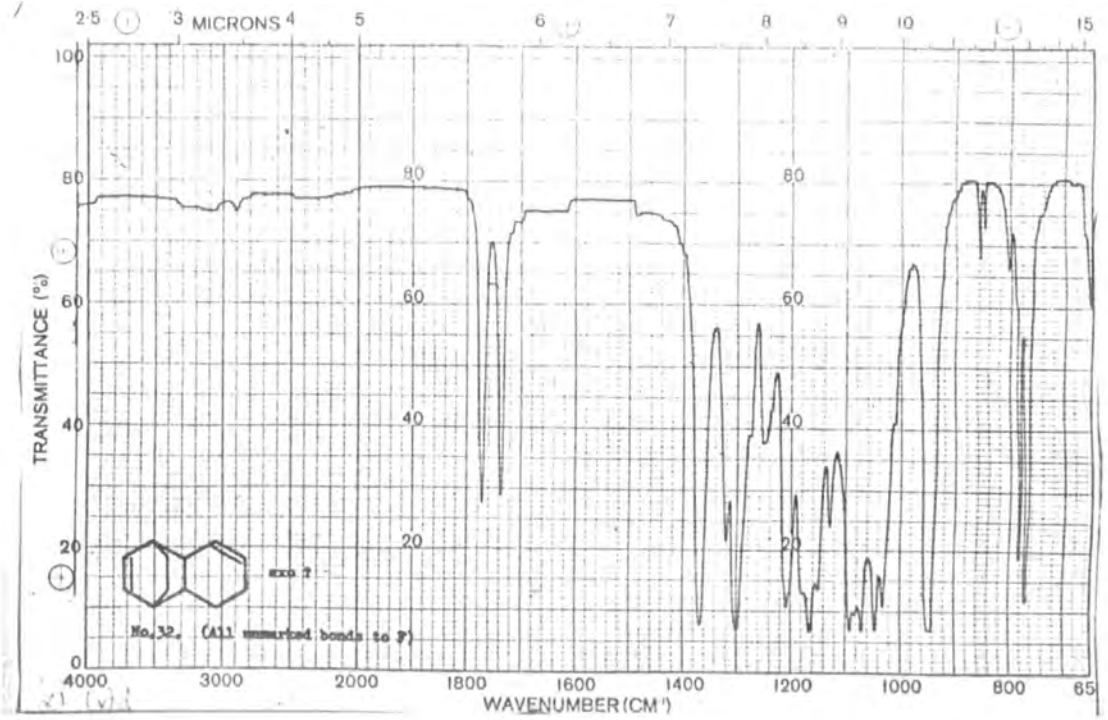
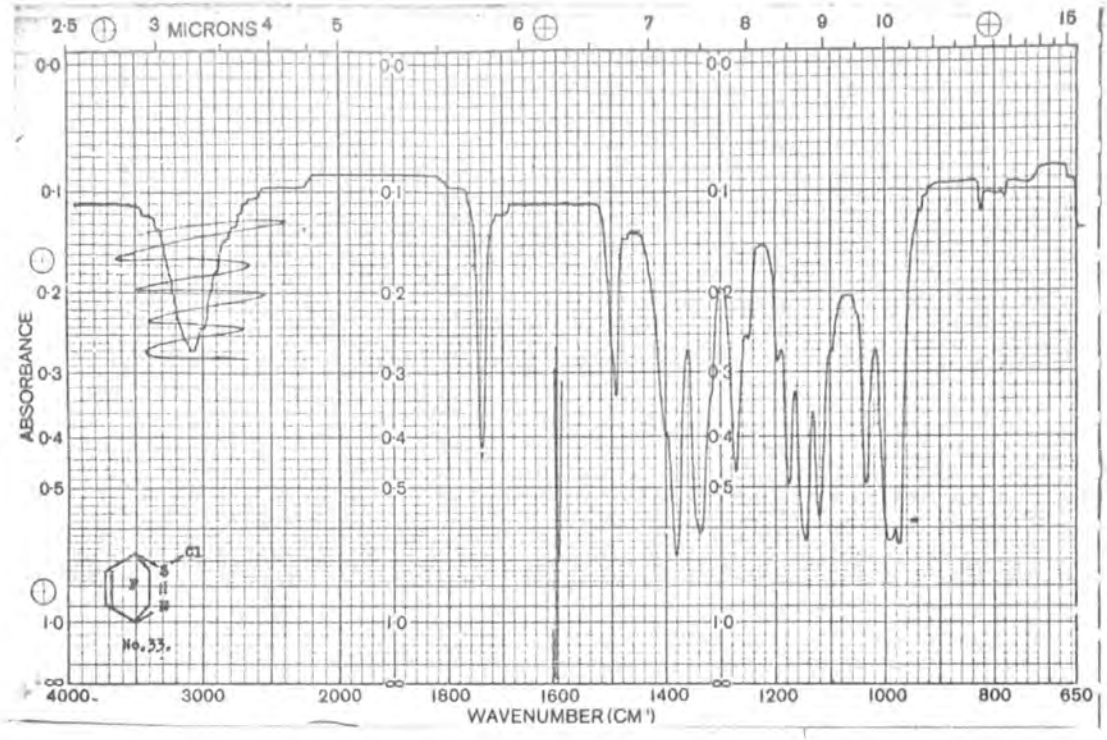
40
20
0
TRANSMITTANCE (%)
4000
3000
2000
1800
1600
1400
1200
1000
800
650
WAVENUMBER (CM⁻¹)
No.29. (All unmarked bonds to F)


2·5
3 MICRONS
4
5
6
7
8
9
10
15
0·0
0·1
0·2
0·3
0·4
0·5
1·0
∞
ABSORBANCE
4000
3000
2000
1800
1600
1400
1200
1000
800
650
WAVENUMBER (CM⁻¹)
No.30. (All unmarked bonds to F)


2·5
3 MICRONS
4
5
6
7
8
9
10
15
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3000
2000
1800
1600
1400
1200
1000
800
650
WAVENUMBER (CM⁻¹)
endo ?
No.31. (All unmarked bonds to F)


2·5
3 MICRONS
4
5
6
7
8
9
10
15
100
80
60
40
20
0
TRANSMITTANCE (%)
4000
3000
2000
1800
1600
1400
1200
1000
800
65
WAVENUMBER (CM⁻¹)
exo ?
No.32. (All unmarked bonds to F)


2·5
3 MICRONS
4
5
6
7
8
9
10
15
ABSORBANCE
0·0
0·1
0·2
0·3
0·4
0·5
1·0
∞
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1600
1400
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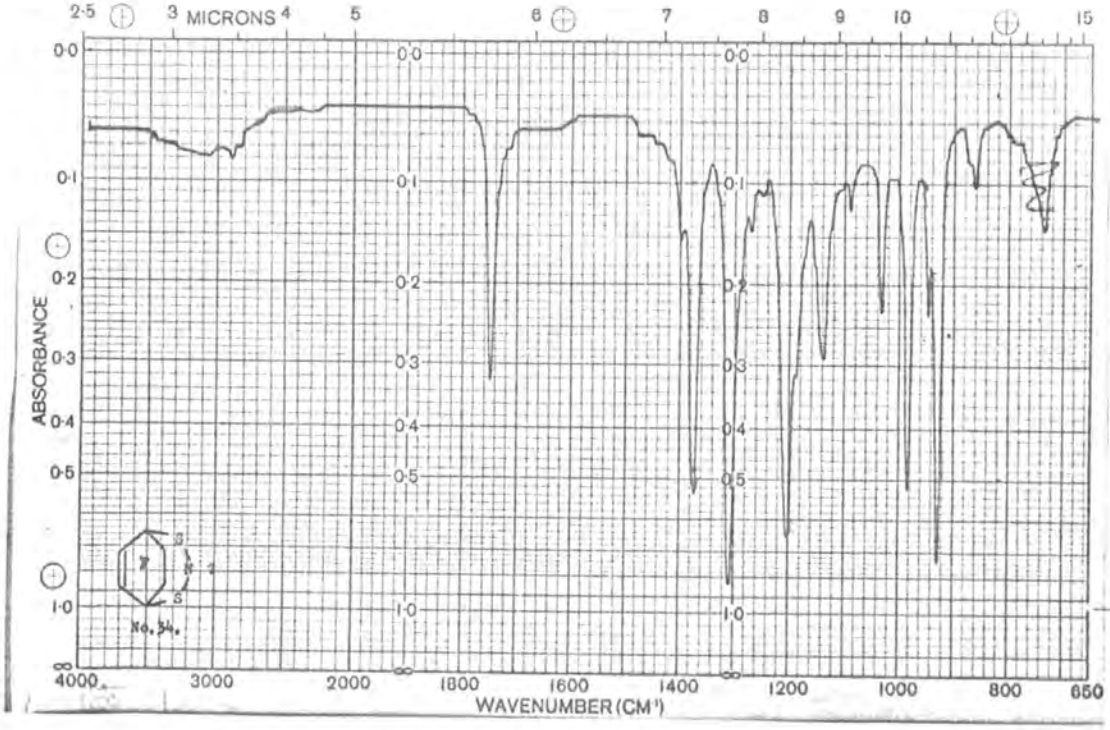
1000
800
650
WAVENUMBER (CM⁻¹)
No.33.


2·5
3 MICRONS
4
5
6
7
8
9
10
15
ABSORBANCE
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0·1
0·2
0·3
0·4
0·5
1·0
∞
4000
3000
2000
1800
1600
1400
1200
1000
800
650
WAVENUMBER (CM⁻¹)
No.34.

A.2] Index of ^{19}F n.m.r. tables.

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$k_2 = A \exp(-E/RT)$

$A = X (kT/h) \exp(x) \exp(-\Delta S/R)$. $x = 1$ (condensed), 2 (gas).

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in the synthetic reactions. In the mass spectrum of pure $C_6F_8.NSCl$ the peak at m/e 302 $[C_6F_8.NS_2]^+$ is more intense than that at m/e 305 $[C_6F_8.NSCl]^+$, and all the fragment ions observed in the spectrum of pure $C_6F_8.NS_2$ are also observed in the spectrum of pure C_6F_8,NSCl. No explanation of this phenomenon is fully satisfactory. For instance, a complicated fast reaction at the ion source involving the cleavage of a C-N bond and the insertion of a sulphur atom seems highly unlikely.

Further discussion of the possible mechanisms is not particularly fruitful since even the structure of the adducts is still in doubt. More research into this system must be carried out before reasonable conclusions can be drawn. Nevertheless, the evidence presented above is consistent with the occurence of a Diels-Alder reaction between perfluorocyclohexa-1,3-diene and the hetero-dienophile thiazyl chloride.

In particular, the weight of the n.m.r. evidence strongly supports the provisional assignment of the structure perfluoro-2-chloro-2,3-thiaza-bicyclo[2,2,2]octa-2,5-diene to the 1:1 adduct.

double bond, but the i.r. absorption at 1493 $cm.^{-1}$ indicates a bond order of 2·6, whereas the formal triple bond of N≡S-F, absorbing at 1372 $cm.^{-1}$, would appear to have a bond order of only 2·5.[155]

The ^{19}F n.m.r. spectrum strongly favours structure (iii). The absence o a resonance at ca. -30 p.p.m.,[156] expected for a fluorine atom geminal to a chlorine atom, eliminates structures (ii). The observed shifts of the tertiary fluorines (+8·4 and +12·0 p.p.m.) are much higher than those expecte from structures (i). The tertiary fluorines in the carbocyclic [4,2,0] system, occur at least 25 p.p.m. downfield from those in the carbocyclic [2,2,2] system,[16] and an additional downfield shift of ca. 40 p.p.m. is expected for the adjacent nitrogen atoms [by analogy, see Table 7.3(i)] and a similar effect is expected for sulphur; thus a shift in the region -20 to -1 p.p.m. is expected for tertiary fluorines in (i). Finally the shifts of the CF_2 groups (AB quadruplets at ca. -40 p.p.m.) and vinylic fluorines (-19·0 and -19·8 p.p.m.) and the overall appearance of the spectrum closely resembles that of the unambiguous 1,4 adducts described earlier.

By comparison with the additions of the other triple bonds, the [4,2,0] ring system (i) seems the less likely alternative. Evidence from other compounds containing sulphur and nitrogen in four membered rings does not exclude either possibility. Disulphur dinitride (S_2N_2) and its derivatives are thermally unstable and explode above 30°,[154,157] which does not correlate with $C_6F_8.NSCl$ being stable at 200° in preparative g.l.c. However, there is no report of the 1,2-cycloadducts