Studies in the chemistry of halogenated benzyynes

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STUDIES IN THE CHEMISTRY
OF HALOGENATED BENZynes

BY

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A thesis submitted to the
University of Technology,
Loughborough,
in partial fulfilment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY

Department of
Chemistry,
University of Technology,
Loughborough,
England.
Chapter 1 deals with the principal methods for the generation of arynes and reviews briefly some of the properties of these reactive intermediates.

Chapter 2 deals with the reactions of tetrafluorobenzyne generated from pentafluorophenyl magnesium chloride or pentafluorophenyl lithium with anisole, phenetole, p-cresol methyl ether, the 3 isomeric dimethoxybenzenes, symmetrical trimethoxybenzene, 2,6-dimethoxytoluene, 1-methoxy-5,6,7,8-tetrafluoronaphthalene and N,N-dimethyl-p-toluidine. The pyrolysis and photolysis of some of the adducts are discussed. Ketonic adducts have been shown to eliminate ketenes.

Chapter 3 investigates the reactions of tetrafluorobenzyne with 2-methyl, 2,5-dimethyl and 2-methyl-5-tert.butylfurans. Attempts to prepare anthracenes by elaboration of the adducts with butadiene are discussed.

Chapter 4 studies the reactions of benzyne with various polycyclic hydrocarbons (namely fulvenes, phenanthrene, methanocyclodecapentaene, acenaphthene and acenaphthylene). The reaction of tetrafluorobenzyne with dimethyl fulvene yields interesting 2 to 1 adducts.

Chapter 5 deals with the p.m.r. spectral data of most of the adducts reported in Chapters 2, 3 and 4. Several ABX spectra have been calculated and compared with the observed spectra.
ACKNOWLEDGEMENTS

This research was carried out at the University of Technology, Loughborough from October 1967 to September 1969.
I would like to acknowledge several people and organisations for the help I have received during this time.

I record my sincerest thanks to Dr. H. Heaney for his constant inspiration, encouragement and guidance during this work.

I am indebted to the University for provision of laboratory facilities and for financial support during the first year.

I am also indebted to Hickson and Welsh Ltd., for financial support during the second year.

My thanks are also recorded to Imperial Smelting Corporation for generous supplies of fluorinated chemicals.

I should further like to express my appreciation of many helpful discussions and aid given by the staff, post-doctoral fellows and research students of the organic chemistry section of the University.

Finally I am grateful to my wife for her constant understanding and patience during difficult moments.
CONTENTS

CHAPTER 1

Introduction. Arynes - Generation and Reactions. 1

CHAPTER 2

The reaction of tetrafluorobenzyne with various methoxylated benzenes, 1-methoxy-5,6,7,8-tetrafluoronaphthalene and N,N-dimethyl-p-toluidine.

2.1. Introduction. 5
2.2. Discussion. 6
2.3. Photochemical Studies. 22
2.4. Experimental.
   2.4.1. General Methods. 23
   2.4.2. General Techniques used in generating tetrafluorobenzyne from organometallic precursors. 24
   2.4.3. Experimental Investigations. 25

CHAPTER 3

The reactions of tetrafluorobenzyne with alkyl furans, and studies on the elaboration of the adducts to triptycene derivatives.

3.1. Introduction. 42
3.2. Discussion. 43
3.3. Experimental Investigations. 50.

CHAPTER 4

The reactions of tetrafluorobenzyne with various fulvenes, phenanthrene, acenaphthene, acenaphthylene and methano-cyclodecapentaene.
4.1. Introduction. 69
4.2. Discussion. 71
4.3. Experimental. 77

CHAPTER 5

Proton magnetic resonance spectral data. 84

DIAGRAMS
TABLES
REFERENCES
CHAPTER I

Introduction Arynes Generation and Reactions

Arynes (dehydroarenes) are neutral intermediates derived from an aromatic system by the removal of two substituents leaving two p-orbitals with two electrons distributed between them. The majority of arynes are derived from compounds in which the substituents were ortho to each other, but since the methods of generation and the reactions of meta dehydro compounds are of the same general type as ortho arynes it would seem to be a false classification to place these dehydro compounds in distinct classes. I shall refer therefore to all aromatic dehydro ring systems as arynes.

The existence of the parent compound "benzyne" was first postulated in the early 1900s but it is only since the work of Wittig and Roberts that mechanisms involving aryne intermediates have been treated with credulity. Benzyne is now generally agreed to be a short lived species ($t_\lambda \approx 10^{-4}$ sec), existing in a singlet ground state with its two extra electrons (extra to the aromatic II cloud) in a lower symmetric orbital. The aromatic character is undisturbed and the reactive site behaves as a strained olefine. Benzyne therefore undergo cyclo addition reactions with conjugated dienes, \(^5\) and 1,3-dipolar systems \(^6\) very readily.

1.
Arynes also react with aromatic ring systems (such as benzenes and anthracenes), not generally considered to be dienes, to give Diels-Alder adducts. These reactions are believed to proceed by a symmetry allowed concerted mechanism. Benzyne may add 1,2- to olefines by a two step mechanism. Orbital symmetry considerations indicate that a thermal concerted mechanism is not allowed.

Benzyne reacts with nucleophiles freely but shows little tendency to react with electrophiles although in principle the reaction is possible. Radical reactions are also virtually unknown. Both benzyne and tetrafluoro benzylene have been stabilised by coordination as a nickel carbonyl complex. (figure 1)

The nomenclature used within this class of reactive intermediates is open to criticism since -yne infers localisation of the extra electrons. An alternative is to use the prefix dehydro which is often more convenient with complex systems.

Benzyynes have been generated both in solution and in the gaseous phase in a variety of ways, all of which involve an elimination of a small stable molecule. The elimination may be either concerted or stepwise. In the stepwise case the initial bond cleavage may be homolytic to give a radical or heterolytic to give an arenonium ion or a carbanion (Scheme 1). It was originally believed that benzyynes generated from different precursors had different properties
(i.e. singlet and triplet benzyne). However Huisgen and Klanderma have shown conclusively that benzyne is the same when generated from different precursors, provided that elements with low energy d-orbitals (e.g. Ag⁺ or I⁻) which modify the reaction path are absent.

The first, and for a long time the only, method of aryne generation was from ortho-halogenophenyl anions (Scheme 1C A = halogen). The better methods of this general type are:

a) Decomposition of orthomono-organometallic compounds prepared from halogenobenzenes, by the action of alkyl metal reagents. (Scheme 2)

b) Treatment of an aryl halide which has an ortho hydrogen with a metal amide, either in an inert solvent or in the presence of free amine. (Scheme 3)

c) Metal-halogen interconversion, for example by reaction of an alkyl metal reagent with 1,2-dihalogeno benzenes. (Scheme 4)

This general method of preparation suffers some severe disadvantages in that reactions may only be investigated for compounds which are not attacked by strong nucleophiles.

A non organometallic method of benzyne generation involves the aprotic diazotisation of anthranilic acid (Scheme 5). The explosive intermediate (1) is not always isolated. Friedman has isolated the hydrochloride...
salt and this is widely used as a benzyne precursor. Work in this laboratory has led to the generation of tetrahalogeno-
benzenes by aprotic diazotisation and the subsequent reactions
with a variety of carbonyl compounds has become possible.

Rees has developed the oxidation of 1-aminobenzotri-
azole with lead tetraacetate or nickel peroxide as a method
of benzyne generation. (Scheme 6)

The decomposition of 1,2,3-benzothiadiazole-1,
1-dioxide in solution at ca 20°C affords benzyne. The elimination of nitrogen and sulphur dioxide is thought to occur as a concerted process.

A number of less important methods of generation exist. These include, the pyrolysis of o-iodophenyl
mercuric iodide, diphenyliodonium 2-carboxylate and
indantrione at various temperatures; the flash photolysis of
benzene diazonium 2-carboxylate (1) and the photolysis of 1,
2-di-iodobenzene.

Further discussion of aryne chemistry is available
in the many excellent reviews of this very active field
of chemistry.
CHAPTER 2

The Reactions of Tetrafluorobenzyne with Alkoxybenzenes

(2.1.) Previous work in this laboratory 27 and elsewhere 28 has shown that highly halogenated benzyynes react with benzene and alkyl substituted benzenes, and with aliphatic dienes to form Diels-Alder adducts in good yield. The reasons suggested for the high reactivity of the halogenobenzyynes in reactions with arenes were:

i) Aromatic ring systems form charge-transfer complexes with highly fluorinated aromatic compounds.29

ii) Benzyne is itself highly electrophilic in its reactions and the presence of fluorine substituents makes highly fluorinated benzyynes even more electrophilic.27,30

iii) The greater reactivity of tetrafluorobenzyne over benzyne might be influenced by the greater stability of pentafluorophenyl Grignard 31 and lithium reagents 32 as compared with o-fluorophenyl Grignard and lithium reagents 16,14f. since this fact would indicate a higher activation energy for the formation of tetrafluorobenzyne and hence a higher reactivity.

Recently the Diels-Alder reactions of tetrafluoro, and tetrachlorobenzyne with certain conjugated steroidal dienes 33 and with styrene and its derivatives 34 have been investigated. The increased Diels-Alder reactivity of tetrafluorobenzyne over benzyne was again observed.
(2.2.) It was decided to extend the reactions of tetrafluorobenzyne to reactions with aromatic ethers in anticipation of isolating ketonic products which would prove of interest in photochemical studies. It was also hoped by these studies to learn more about the electronic and stereochemical factors which influence the bridgehead adduct to non-bridge-head adduct ratios in the Diels-Alder products. Finally it was of interest to produce compounds which would be informative in n.m.r. and mass spectroscopy studies.

Heaney and coworkers have shown that alkylbenzene-tetrafluorobenzyne adducts exhibit long range $^{19}\text{F}-^{1}\text{H}$ coupling in their n.m.r. spectra. The different electronic structure and stereochemistry of ether groups were expected to alter the $^{1}\text{H}-^{19}\text{F}$ coupling constants in the n.m.r. spectra. Chapter 5 deals with the discussion of n.m.r. results in detail.

Initially the reaction of tetrafluorobenzyne with anisole was chosen. This reaction yields two adducts (3) and (4) formed by Diels-Alder addition of the benzyne to anisole. The adducts were separated by alumina column chromatography, but extreme care was necessary because of the easy decomposition of (4) when in contact with alumina. The structures of (3) and (4) are given on the basis of elemental analysis, reduction and the application of spectroscopic methods. The bridgehead adduct (3) has an elemental analysis for $\text{C}_{13}\text{H}_{8}\text{OF}_{4}$ and the infra-red spectrum showed bands at 3070 (unsat. C-H stretch), 3000, 2940, 2840 (aliphatic C-H stretch), 1630 (C=C stretch), 1490 (highly fluorinated aromatic ring), 1190 (C-O stretch), 708, 678 (C-H out of plane deformation in a cis oléfinè).
The p.m.r. spectrum showed an eight line multiplet (AB part of ABX system) at 2.81 – 3.35 \( \gamma \) (4 protons) due to the 4 olefinic protons, a multiplet at 4.66 – 4.94 \( \gamma \) (1 proton) due to the bridgehead proton and a doublet at 6.19 – 6.24 \( \gamma \) (3 protons) due to the methyl group long range coupled to \(^{19}F\) at the \( \alpha \) position (see Chapter 5 for discussion of long range \(^{19}F\)-\(^1H\) coupling). The compound absorbed two molecules of hydrogen to yield (6) which was characterised by elemental analysis and spectroscopic methods.

Pyrolysis of (3) in a sealed tube at 300\(^o\) was carried out as further characterisation. A compound was isolated with a molecular formula by elemental analysis of \( C_{11}H_6OF_4 \) which indicated a methoxy naphthalene (7). It is reported that alkyl benzene-tetrafluorobenzylene bridgehead adducts (5) on pyrolysis yield the corresponding 1-alkynaphthalenes (8) by loss of acetylene. By analogy (3) would be expected to yield 1-methoxynaphthalene on pyrolysis. There was however some doubt about the structure of (7). The p.m.r. spectrum contains a multiplet at 2.38 – 2.76 \( \gamma \) (2 aromatic protons), a multiplet at 3.10 – 3.26 \( \gamma \) (1 aromatic proton) and a sharp singlet at 6.14 \( \gamma \) (aromatic methoxyl group). These results can readily be explained for structure (7B), the 2-methoxy-naphthalene, when the methoxyl group in the 2 position is not expected to be long range coupled to the 8-position fluorine. The two low field protons could be due to deshielding of the 1 and 4 ring protons by the perfluorine atoms at positions 5 and 8. 1-methoxynaphthalene was expected to exhibit long range \(^{19}F\)-\(^1H\) coupling between the methoxyl protons and the aromatic fluorine at position 8.
To define the structure of (7) further work was completed. Variable temperature (0 - 200°C) p.m.r. of (7) showed no change in the singlet peak at 6.14 ppm indicating that the singlet nature of the peak was not due to a "freezing out" of a particular conformer (i.e. 9).

Birch reduction of 1-methoxy and 2-methoxynaphthalene is reported to give α-tetralone and β-tetralone respectively in good yield. When Birch reduction of (7) was attempted a complex mixture was isolated. I.r. spectroscopy showed the presence of a very weak band at 1685 cm⁻¹ indicating the α-tetralone. It appears that Birch reduction of (7) involves many side reactions, possibly caused by replacement of aromatic fluorine atoms by amino groups arising from amide ion.

An alternative route to (7) was available by the action of dilute acid on the furan-tetrafluorobenzene adduct (10). (See Chapter 3) to yield a naphthol (11), which was methylated with diazomethane in ether to yield (7). It is however possible to propose two structures for the acid rearranged product (11) both of which are consistent with the spectral properties.

Attempted bromination of the naphthol (11) with bromine in carbon tetrachloride gave only dark intractable products. Reaction of the naphthol (11) with p-nitrophenyl-diazonium chloride gave a brown-red compound which was unfortunately too insoluble for a p.m.r. study to be undertaken.
The problem of the structure of (7) was finally solved by reaction of (7) with tetrafluorobenzene. The 2-methoxy compound (7B) would be expected to yield the adduct (12) which would be cleaved by dilute acid to yield the ketonic adduct (13) (Scheme 12). The methoxy compound (7A) would be predicted to yield the methoxy adduct (14). (Scheme 13).

Preparative t.l.c. work up of the crude reaction mixture gave a single product in 40% yield which was shown by spectroscopic techniques to be the adduct (14). Elemental analysis and mass spectrometry confirmed the molecular formula to be $\text{C}_{17}\text{H}_6\text{OF}_8$. I.r. spectroscopy showed aromatic C=C stretch bands at 1646 and 1618 cm$^{-1}$ and the absence of a carbonyl group in the molecule, whilst u.v. spectroscopy confirmed benzenoid conjugation only with a band at 261 n.m. The methoxyl group was long range coupled to two fluorine atoms and produced a triplet signal in the p.m.r. spectrum.

Hydrogenation of the adduct gave the expected dihydro compound (15), which again showed long range $^{19}\text{F}{}_{-}^{1}\text{H}$ coupling, the methoxyl signal again appearing as a triplet in the p.m.r. spectrum.

The ketonic product from reaction of anisole with tetrafluorobenzene was given the structure (4) on the basis of its physical properties. Elemental analysis gave a molecular formula of $\text{C}_{12}\text{H}_6\text{OF}_4$ and the i.r. spectrum showed a characteristic carbonyl stretch frequency at 1740 cm$^{-1}$. 

9.
The p.m.r. spectrum is discussed in Chapter 5. Reduction of the carbonyl group with sodium borohydride and dehydration of the crude product gave the known compound (19). Pyrolysis of the ketone (4) at 300° gave tetrafluoronaphthalene.

The adduct (4) is derived from the enol-ether non-bridgehead adduct (16). We were unable to isolate this enol ether but in subsequent experiments we isolated other enol ethers. However these compounds were hydrolysed extremely rapidly as indicated by infra-red and p.m.r. spectroscopy. We suggest two possible mechanisms for this hydrolysis (Scheme 14).

The fact that these enol ethers are hydrolysed faster than is normal for enol ethers may be explained by involvement of the other double bond as in (Scheme 14,2). Unfortunately one might predict that ketone (4A) would be formed by this mechanism. None was detected.

Vorozhtsov 37 claimed that the presence of ethylene oxide in the reaction of tetrafluorobenzyne with aromatic compounds was advantageous and that the ratio of adducts formed was affected. We have examined the anisole-tetrafluorobenzyne reaction under a variety of conditions (Table 1), but have been unable to substantiate these views. The fall in yield of adducts in the presence of ethylene oxide is undoubtedly due to the reaction of the pentafluorophenyl metallic reagent with the ethylene oxide. The reactions of tetrafluorobenzyne generated from a non-organometallic source with aromatic ethers have not been reported so that a discussion is not yet possible for these reactions.
In the absence of all other effects one would statistically expected the bridgehead adduct: non-bridgehead adduct ratio to be 1:2. Heaney and his co-workers have shown that steric effects due to the close approach of the fluorine atom and the bridgehead alkyl group in the transition state are unimportant and that the statistically predicted ratio of adducts is within experimental limits the observed ratio for alkyl benzene adducts. Any steric effect operating in the tetrafluorobenzyne—anisole reaction would be expected to decrease the bridgehead:non-bridgehead ratio. A possible explanation of the unexpectedly high adduct ratio observed is given in Scheme 15.a. However, on the basis of a two-step mechanism of this type it may be anticipated that insertion products and 1,2 adducts would be formed. A not quite concerted mechanism (Scheme 15,b) would however explain why none of these products were isolated. This would again reflect the greater electron density at the p-position in anisole and help explain the predominance of the bridgehead adduct in the reaction mixture.

In an attempt to improve the yield of (4) and investigate the effect of increased size of ether grouping on the aromatic ring on the yields of adducts, tetrafluorobenzene was reacted with phenetole. The ratio of adducts isolated was 1:6 for (4) : (17), (4) being isolated in 6.3% yield. The structure of (17) followed from its physical properties, from hydrogenation to yield (18) and from pyrolysis at 350° to yield (21).
As an alternative method of synthesis of (4), the epoxidation of (19) with monoperphthalic acid in ether, and the oxymercuration-demercuration of (19) were attempted. The reactions were not successful and (19) was recovered in each case.

The reaction of the three isomeric dimethoxybenzenes with tetrafluorobenzyne have been investigated in order to obtain more information on the effect of alkoxy-substituents on the course of cycloaddition reactions of tetrafluorobenzyne. 1,2-Dimethoxybenzene gave one major product (22) in 44% yield and a minor product (<2%) believed to be the non-bridgehead adduct (24). This could not be isolated in a pure form. No evidence was found for the presence of a monoketone (25) which could be derived from the non-bridgehead adduct (24). The adduct (22) was given the structure on the basis of physical data and from hydrogenation to (23). I.r. spectroscopy showed the presence of a carbonyl band at 1750 cm\(^{-1}\) whilst u.v. spectroscopy gave bands at 268 n.m. (2.81) and 300 n.m. (2.42). Mass spectroscopy showed the loss of ketene as the major fragmentation and elemental analysis confirmed the molecular formula as \(C_{13}H_8O_2F_4\). The p.m.r. spectrum is in agreement with structure (22) and is discussed in Chapter 5. Pyrolysis of (22) at 300\(^{\circ}\) resulted in loss of ketene and isolation of (7) previously obtained in other reactions. Attempted Huang-Minlon reduction of (22) gave only dark intractable products.
1,3-Dimethoxybenzene similarly gave one major adduct (26) in good yield (62%). No evidence was found for a non-bridgehead adduct or derivative (27). I.r. spectroscopy showed the presence of a carbonyl band at 1748 cm\(^{-1}\) u.v. spectroscopy bands at 269 n.m. (2.77), 291 n.m. (2.37), 305 n.m. (2.24) and 317 n.m. (2.18), and elemental analysis gave a molecular formula of \(C_{13}H_8O_2F_4\). Hydrogenation over palladium on carbon yielded the dihydro compound (28).

Previous reports \(^{27}\) have shown that no dibridgehead adduct was isolated from the reaction of 1,4-dialkylbenzenes with tetrafluorobenzene and so the reaction of 1,4-dimethoxybenzene with tetrafluorobenzene was investigated to determine whether the tendency of alkoxy compounds to form bridgehead adducts in preference to non-bridgehead adducts would result in the formation of a dibridgehead adduct. The initial reaction mixture was treated with dilute acid to ensure hydrolysis of any readily hydrolysable enol ethers. Repeated thick-layer chromatography yielded three major products (29, 31 and 32).

The dibridgehead adduct (29) (18% yield) showed olefinic C=C stretching at 1625 cm\(^{-1}\) and u.v. absorption at 266 n.m. (2.74). The p.m.r. spectrum was consistent with the structure and is discussed in Chapter 5.

The diketone (31) undoubtedly arises from hydrolysis of the dienol ether (30). The structure is based on the physical properties. The carbonyl group stretching frequency appears at 1745 cm\(^{-1}\) whilst by u.v. spectroscopy bands occur at 266 n.m. (2.73), 296 n.m. (2.47), 305 n.m. (2.37) and 316 n.m. (2.19).
The third product in the reaction mixture (isolated in 8% yield) was shown by analysis and mass spectroscopy, to have the molecular formula $C_{19}H_{8}F_{8}O_{2}$ and therefore was derived originally from p-dimethoxybenzene and two molecules of tetrafluorobenzylene. The infra-red spectrum showed the presence of a carbonyl group ($\gamma_{\text{max}}$ 1745 cm$^{-1}$) and we therefore considered structures (32A), (32B) and (32C).

The addition of tetrafluorobenzylene to the bis-enol ether (30) could occur by an orbital symmetry controlled (2+2+2) $\Pi$ cycloaddition to yield after hydrolysis (32A). Vorozhtsov has reported an adduct formed from reaction of two molecules of tetrafluorobenzylene with one molecule of benzene. The structure (33) which arises from a (2+2+2) $\Pi$ cycloaddition reaction was given to the adduct.

The compounds (32B) and (32C) could arise by (2+2) $\Pi$ cycloaddition of tetrafluorobenzylene to one double bond in (30). Hydrolysis of the initial product would again yield a ketone.

Comparison of the infra-red and p.m.r. data for the adduct with the data of a number of other compounds at hand (Table 2) suggests the exclusion of (32A). Similarly the loss of ketene from the molecular ion of the adduct would require rearrangement of (32A) $M^+ - 42 = 50\%$ of $M^+$ and suggests that the initial cleavage occurs to form the ion (34). The spectral data presently available suggests that the structure (32B) is more likely for this chiral molecule. Structure (32C) is however not entirely ruled out.
When it was known that the dibridgehead adduct (29) could be isolated from the reaction of tetrafluorobenzylene with 1,4-dimethoxybenzene it became of interest to know the effect of replacing one of the methoxyl groups with an alkyl group. The effects of the alkyl group on the stereochemistry of the molecule and the long range $^{19}$F-H coupling constants from n.m.r. spectroscopy were also of interest. The reaction of p-cresol methyl ether with tetrafluorobenzylene yielded a much simpler reaction mixture than that obtained from the 1,4-dimethoxybenzene - tetrafluorobenzylene reaction. Separation by T.L.C. or by alumina column chromatography yielded two major compounds (35) and (36) and a minor compound (37).

Compound (35) (isolated in 21%) was found from mass spectrometry and elemental analysis to have a molecular formula $C_{14}H_{10}F_{4}O$. I.r. spectroscopy showed the absence of a carbonyl group and u.v. spectroscopy the presence of benzenoid conjugation only. P.m.r. spectroscopy showed resonances centred at 3.32 (AB quartet), 6.33 (methoxyl doublet J= 3.0c/s), and 7.94 (methyl doublet J= 5.5 c/s). On the basis of these observations the compound was given the dibridgehead adduct structure (35). This conclusion was confirmed by hydrogenation over palladium charcoal and by pyrolysis. The hydrogenation product had the structure (38) on the basis of its physical properties. Pyrolysis at 300$^\circ$ yielded the naphthalene (39), which was later isolated from reactions involving the 2-methylfuran tetrafluorobenzylene adduct (Scheme 23) (See Chapter 3).
The adduct (35), the reduced adduct (38) and the naphthalene (39) are of interest in p.m.r. long-range $^{19}$F-H coupling studies (Chapter 5) since they allow a comparison to be made of methyl and methoxyl protons in similar environments.

The compound (36) (isolated in 40% yield) was shown to have a molecular formula $\text{C}_{13}\text{H}_8\text{F}_4\text{O}$. I.r. spectroscopy showed the presence of a carbonyl group ($\text{C}=\text{O}$ str. at 1736 cm$^{-1}$) whilst u.v. spectroscopy showed absorptions similar to the ketone (4). The adduct had structure (36). Reduction of (36) with hydrogen in the presence of palladium on charcoal yielded (40) quantitatively whilst pyrolysis and photolysis of (36) resulted in loss of ketene to give compound (41) which was identical to the product obtained by pyrolysis of the $p$-xylene-tetrafluorobenzene adduct (42) (Scheme 24).

The loss of ketene from ketonic adducts was readily observed in mass spectrometry studies (Chapter 5) where the resultant naphthalene was usually observed as the base peak and the molecular ion was often absent from the spectrum.

The third product (37) was isolated in very small quantities and unfortunately mass spectrometry was not available to us at that time. The p.m.r. spectrum shows obvious analogies with the spectrum of the compound (32B) and the third compound may therefore have the structure (37).

Although the non-bridgehead adduct (27) was not detected in the reaction of m-dimethoxybenzene with tetrafluorobenzene the diketonic derivative of (27) would have been expected to undergo interesting reactions. We therefore
carried out a reaction of tetrafluorobenzene with 1,3,5-trimethoxybenzene. A 1,4-cycloaddition reaction would be predicted to yield only one product, the diketone (43). However neither the dienol ether (44) or the diketone (43) was isolated and after removal of unreacted 1,3,5-trimethoxybenzene by steam distillation an acidic compound was isolated by sodium bicarbonate extraction.

Purification of the acid was difficult due to its relative insolubility in common solvents. Infra-red spectroscopy of the crude product confirmed the presence of a carboxylic acid (ν_{max} 3500 - 2500 (carboxylic acid dimers OH group); 1700 (C=O str. carboxylic acid)). P.m.r. spectroscopy showed 2 aromatic protons singlets at 2.45  \( \tau \) and 2.72  \( \tau \) and a methylene doublet at 5.65  \( \tau \) (J = 6.0 Hz) in dilute solution in trifluoroacetic acid.

The acid was reacted with diazomethane to yield a methyl ester. Elemental analysis and mass spectrometry proved the molecular formula to be C_{14}H_{10}F_{4}O_3. U.v. spectroscopy indicated a naphthalene chromaphore (λ_{max}. 266 (log 10 3.69); 275 (3.79); 286 (3.72); 318 (3.19); and 331 (3.27) n.m.), whilst i.r. spectroscopy showed the presence of an ester carbonyl group (C=O 1750 cm\(^{-1}\)) and a methoxyl group (ν_{max} 2860 cm\(^{-1}\)). The p.m.r. spectrum showed resonances at 2.8  \( \tau \) (1H); 2.96  \( \tau \) (1H); 5.95  \( \tau \) (2H doublet J\(_{H-F} = 5.9\) Hz); 6.17 (3H); and 6.28  \( \tau \) (3H).

On the basis of these results the structure (46) was given to the ester and hence the structure (45) to the acid.
We suggest that the phenolic acid (45) arises from the di-enol ether (44) and that the mechanism involves hydrolysis followed by a retro-Claisen condensation followed by aromatisation as shown in Scheme 26.

In addition to the phenolic acid we isolated a dark oil which was shown by T.L.C. to be a complex mixture. Attempted separation yielded only partially pure products containing several methoxyl groups (from p.m.r. spectroscopy). The diketonic compound (43) was not isolated.

To endeavour to isolate a 1,3-diketonic adduct we have examined the reaction of 2,6-dimethoxytoluene with tetrafluorobenzyne. A solid crystallised from the crude product and was found to be a single compound. Elemental analysis indicated the molecular formula to be $C_{14}H_{10}F_{4}O_{2}$. Infra-red spectroscopy showed the presence of a ketonic carbonyl group ($\gamma_{\text{max}} C=O \text{ str.} 1744 \text{ cm}^{-1}$), whilst the u.v. spectrum was very similar to that of previously isolated ketonic adducts. Resonances were present in the p.m.r. spectrums at 2.86 - 3.45 (AB multiplet of ABX) (2 olefinic protons); 5.13 - 5.38 (1 bridgehead proton multiplet); 6.30 (1 methoxyl group doublet $J = 2.5 \text{ Hz}$); 7.53 (1 methine proton quartet); 9.08 (1 methyl group doublet $J = 7 \text{ Hz}$). On the basis of this evidence the structure (47) was given to the compound.

The residue from the crude reaction mixture was separated to yield a further quantity of the ketone (47) and a second product. Infra-red spectroscopy showed the absence of a carbonyl group and confirmed the presence of a methoxyl group. U.v. spectroscopy showed only a benzenoid chromophore.
Elemental analysis and mass spectroscopy showed the molecular formula to be C_{16}H_{16}F_{4}O_{3}. The p.m.r.
spectrum showed resonances at 3.18-3.74\,\text{\textmu} (AB of ABX multiplet) (2 olefinic protons); 5.58\,\text{\textmu} (1 bridgehead proton multiplet); 6.42\,\text{\textmu} (1 bridgehead methoxyl doublet \text{\textit{J}}= 2\,\text{Hz}); 6.82\,\text{\textmu} (1 methoxyl singlet); 6.92\,\text{\textmu} (1 methoxyl singlet); 7.87\,\text{\textmu} (1 methylene quartet); 9.29\,\text{\textmu} (1 methyl doublet \text{\textit{J}}= 7\,\text{Hz}). This data is in accord with the structure (49).

We believe that compound (49) arose from a reaction involving the methanolic hydrochloric acid used in the hydrolysis of the crude reaction mixture. To ensure that (49) was not formed directly during the reaction of tetrafluorobenzoyne with 2,6-dimethoxytoluene the reaction was repeated. After hydrolysis with methanol a single unstable product was isolated in 52% yield. I.r. and p.m.r. spectroscopy indicate the structure to be the enol ether (48). Attempted characterisation proved unsuccessful because of the rapid hydrolysis of the enol-ether grouping. Hydrolysis was readily observed by infra-red spectroscopy by observing the growth of the carbonyl absorption band at 1744 cm\(^{-1}\).

Treatment of (48) with dilute hydrochloric acid yielded (47) in theoretical yield but no ketal (49) was detected. However after standing for several weeks the unhydrolysed methanolic solution of (48) was found to contain the ketal (49) and ketone (47).

The ketal (49) was hydrolysed with dilute acid to yield (47) quantitatively.
An attempt to prepare the ketal (49) from the ketone (47) by stirring in methanol containing a trace of hydrogen chloride proved unsuccessful. It is therefore likely that methanolysis of the enol-ether (48) leads to the ketal (49) (Scheme 27).

The reactions of tetrafluorobenzyne with para-disubstituted benzenes has been shown to give widely differing yields of dibridgehead adducts. p-Xylene afforded only the non-bridgehead adduct (42), whilst p-cresol methyl ether gave the dibridgehead adduct (35) in 21% yield and p-dimethoxybenzene yielded the dibridgehead adduct (29) in 18% yield. This variability of the yield of dibridgehead adducts led us to investigate the reaction of N,N-dimethyl-p-toluidine with tetrafluorobenzyne. We anticipated that this should provide a further route to the ketone (36), since the enamine (50) would be expected to undergo hydrolysis readily.

The reaction was carried out using the lithio compound route in ether. Four products were isolated by acid extraction.

The ketonic product (36) (9%) was found to be identical to the ketone isolated from the reaction of tetrafluorobenzyne with p-cresol-methyl ether, thus confirming the structure given.

The dibridgehead compound (51B) (7%) was characterised from its spectroscopic data which were similar to the N,N-dimethylaniline bridgehead adduct (51A). Thus p.m.r. spectral data gave lines at \( \tau \) 3.31 (AB quartet) \( (J = 9.0 \text{ Hz.}) \)

(4 olefinic protons); 7.36 (doublet) \( (J = 4.5 \text{ Hz}) \); 7.95 (doublet) \( (J = 6 \text{ Hz}) \).

20.
The benzylamine (52B) (12%) was similarly characterised by spectroscopic methods. \( \gamma \) at 2.89 - 3.46 (AB multiplet \( J = 9.0 \text{Hz} \)) (5 aromatic protons); 5.54 (broad singlet) (2 methylene protons); 7.04 (singlet) (amine methyl protons); 7.79 (singlet) (aromatic methyl group). It evidently arose by stabilisation of the betaine (53B) (Scheme 29).

The tertiary amine (54B) (29%) was characterised from its spectral properties, and was apparently derived by immediate charge neutralisation of the betaine (53B) which competes with the formation of the ylide. (55B)

A fifth compound was isolated but was not obtained pure. Subsequently the compound has been shown to be the 1,2-adduct which is susceptible to polymerisation in oxygen.

The isolation of these compounds is analogous to the reactions of tetrafluorobenzene with N,N-dimethylaniline when similar products were isolated. In the case of the N,N-dimethylaniline reaction however it was necessary to change the polarity of the reaction before the diphenylamine (54) could be isolated.

The fact that the ratio of cyclo addition products isolated was close to unity indicates some electronic effect operates to increase the amount of dibridgehead adduct. We therefore suggest that a mechanism involving the lone pair of electrons on the substituent may be involved as in Scheme (30). This is analogous to the mechanism proposed for the reaction of tetrafluorobenzene with methoxybenzenes (Scheme 15b).
2.3. Photochemical Studies

In recent years there has been much interest in the photochemistry of divinylmethanes and enones. Several groups have examined the photochemistry of barrelene and its derivatives. Previous work in this laboratory has studied the photochemistry of (19) and (56) both in the presence and absence of photosensitisers (Scheme 31). Ciabattoni and his coworkers have examined the photolysis of benzohomobarrelenone (57) which leads to (58) (Scheme 32).

Several of the adducts appeared of interest for photochemical studies. Mass spectrometry showed the major cleavage of the molecular ions of the ketonic products occurs by loss of ketene. We therefore studied the photolysis and pyrolysis of several of the adducts which we had isolated. All the ketonic adducts were found to undergo the same general photochemical reaction (Scheme 33). Similar photochemical and pyrolytic reactions have subsequently been reported.

Murray and Hart have studied the pyrolytic and photochemical reactions of (59) (Scheme 34). They report the ready photochemical elimination of dimethyl ketene to yield the naphthalene (60) but contrast this with the pyrolytic elimination which was difficult requiring temperatures of 450-550°. We did not observe difficulty in pyrolysis of our ketonic adducts, which eliminated ketene at temperature of 250° and below. Pyrolytic studies are recorded in Table 3.
2.4) **Experimental**

2.4.1. **General Methods**

Analytical gas chromatography was carried out using the Pye 104 series gas chromatographs fitted with flame ionisation detectors.

Preparative scale gas chromatography was carried out using Wilkens Aerograph model 700 and model 704 series chromatographs.

Infra-red spectra were determined as potassium bromide discs, or as thin films in the case of liquids, on a Perkin-Elmer 257 spectrophotometer.

Ultra-violet spectra were determined as ethanolic solutions, except where otherwise stated, on a Unicam S.P.800 spectrophotometer.

Proton-magnetic spectra were determined at 60 MHz and $^{19}$F n.m.r. spectra at 56.458 MHz on a Perkin-Elmer R10 spectrometer for 20% solutions in carbon tetrachloride (unless otherwise stated) using tetramethylsilane and trichlorofluoro methane as internal standards respectively.

Melting points were determined on a heated block and are uncorrected. Where no melting point is quoted the compound was a liquid. All compounds were colourless unless stated.

Mass spectra were determined on an A.E.I. M.S.12 mass spectrometer.
2.4.2. General techniques used in generating tetrafluorobenzene from organometallic precursors

A) Via the lithio compound

A solution of n-butyl lithium in pentane (2.5 molar, 1 equiv.) was added dropwise to a stirred solution of bromopentafluorobenzene (1 equiv.) in dry ether at -70°. The reaction was maintained throughout under nitrogen and protected from moisture in apparatus previously dried at 120° overnight. The resultant solution was stirred a further 30 minutes at -70° and then the co-reactant slowly added. The mixture was allowed to warm to room temperature and then stirred overnight. The reaction mixture was finally hydrolysed with excess hydrochloric acid (2N). The organic layer was separated and the aqueous layer extracted three times with ether. The combined ether extracts and organic layer were washed with water and dried over sodium sulphate. Evaporation of the ether gave the crude reaction product.

B) Via the Grignard reagent

A suspension of magnesium (3 equivalents) in dry ether was activated by the addition of 1,2-dibromoethane (a trace) at room temperature and a solution of chloropentafluorobenzene (2 equivalents) in ether was added to the stirred mixture. Further portions of 1,2-dibromoethane (total added 1 equivalent) were added over 1 hour and the reaction mixture was stirred for a further 1 hour. To this solution of the Grignard reagent was added the co-reactant (In large excess in the case of liquids and in three times excess as a solution in cyclohexane in the case of solids). The temperature was raised by distilling out ether and the reaction mixture was heated for
5 hours at 80°. The stirred mixture was allowed to cool overnight and was then hydrolysed with excess hydrochloric acid (2N). The crude product was extracted as in the case of the method involving the lithio compound.

2.4.3. Experimental Investigations

Reaction of tetrafluorobenzyn with anisole

i) Via the Grignard reagent

The crude product was distilled under reduced pressure to give: recovered anisole and a mixture of two adducts which separated on alumina column chromatography to give:

1-methoxy-5,6,7,8-tetrafluoro-1,4-etheno-1,4-dihydronaphthalene (3) (49%) m.p. 80-82° as cubes from light petroleum b.p. 60-80°

\[
\text{Found} \quad C\ 60.9 \quad H\ 3.25 \quad F\ 29.65\%
\]

\[
\text{calc. for} \quad C_{13}H_{10}OF_4 \quad C\ 60.9 \quad H\ 3.15 \quad F\ 29.65\%
\]

\[
\text{H}^+ \text{(by Mass Spectrometry)} \quad 256 \quad \text{calc} \quad 256
\]

i.r. (cm\(^{-1}\)) 3070 (CH str. unsat.); 3000, 2940, 2840 (CH str. aliphatic); 1630 (C=C str. non cory.); 1490 (highly fluorinated aromatic ring); 1190 (C=O str. ether); 708, 678 (HC=CH cis, CH out of plane def.).

u.v. 269 n.m. (log\(_{10}\) 2.71)

and 5,6,7,8-tetrafluoro-1,4-ethenotetral-2-one (4), (10%) m.p. 81-83° as rods from hexane.

\[
\text{Found} \quad C\ 59.4 \quad H\ 2.35 \quad F\ 31.1\%
\]

\[
\text{calc. for} \quad C_{12}H_{10}OF_4 \quad C\ 59.5 \quad H\ 2.5 \quad F\ 31.35\%
\]

i.r. 3080, (CH str. unsat.); 2970, 2932, 2860, (CH str. aliphatic); 1740, (C=O str.); 1495 (highly fluorinated ring); 750
(HC=CH cis, def.).

u.v. 260 ($\log_{10} \leq 3.04$); 279 (sh.) ($\log_{10} \leq 2.86$); 303 (sh.)
($\log_{10} \leq 2.43$); 316 (sh.) ($\log_{10} \leq 2.12$).

When the above reaction was repeated in the presence of 20% ethylene oxide the yields were: (3) 23.8%, (4) 5.6%; whilst via the lithio compound the yields were (3) 41.3%, (4) 5.4%.

**Reaction of tetrafluorobenzyne with 1-methoxy-5,6,7,8-tetrafluoronaphthalene (7)**

via the G.r. route 5 x 10⁻³ molar scale 1:1 reaction

The crude product after silica gel column chromatography in hexane/benzene (9:1) gave recovered starting material (7) and 9-methoxy-1,2,3,4,5,6,7,8-octafluoro-9,10-dihydro-9,10-ethenoanthracene (14) (40%) m.p. 128-130°.

Found C 53.7 H 1.45%

C₁₁H₆OF₈ requires C 54.0 H 1.6%

i.r. 2980, 2960, 2910, 2865 (CH str. aliphatic); 1646, 1618 (C=C str. aromatic); 1504, 1490 (highly fluorinated aromatic ring); 1337, 1232, 1074, 1043, 852, 773, 731.

u.v. 261 ($\log_{10} \leq 2.95$).

**Reaction of tetrafluorobenzyne with phenetole (via the G.r. route)**

Distillation of the crude product gave:

recovered phenetole and a mixture of two adducts which were separated by alumina column chromatography to give;

1-ethoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (17)
(38.6%) m.p. 41-46° as rods after sublimation.

Found C 62.25 H 3.65 F 28.0%

C₁₄H₁₀F₄O requires C 62.25 H 3.75 F 28.1%
i.r. 3090 (CH str. unsat.); 2995, 2950, 2910 (CH str. aliphatic);
1639 (C=C str); 1505 (highly fluorinated aromatic ring); 1210
(C=O str. ether); 715, 678 (C=C cis, out of plane CH def.)
u.v. 265 ($\log_{10} \varepsilon = 2.68$).

and 5,6,7,8-tetrafluoro-1,4-ethenotetral-2-\(\alpha\ne\)ne \(\text{(4)}\) (6.3%) identical with previously isolated material.

Attempted Oxymercuration-demercuration \(\text{(38)}\) of 5,6,7,8-tetrafluoro
-1,4-dihydro-1,4-ethenonaphthalene \(\text{(19)}\)

\begin{enumerate}
\item A mixture of mercuric acetate (319 mg), water (1 ml)
\item and tetrahydrofuran (1 ml) was stirred \(\frac{1}{2}\) hour. \(\text{(19)}\) (226 mg) was added and stirred. After 24 hours only \(\text{(19)}\) was recovered,
\item Attempted epoxidation of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-
ethenonaphthalene \(\text{(19)}\).
\end{enumerate}

\(\text{(19)}\) was stirred with monoperphthalic acid in ether
(3 times excess) for 72 hours yielded only recovered \(\text{(19)}\).

Reaction of tetrafluorobenzyne with 1,2-dimethoxybenzene
via the Gr. route.

Excess 1,2-dimethoxybenzene was distilled from the crude product, which was then recrystallised from hexane and finally purified by sublimation to yield:

1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-2-\(\alpha\ne\)ne \(\text{(22)}\)
(44%) m.p. 96-97° as rods.

\begin{center}
\begin{tabular}{ccc}
\text{Found} & C & 57.5 \\
& H & 3.05 \\
\end{tabular}
\end{center}

\begin{center}
\text{C}_{13}H_{8}O_{2}F_{4} \text{ requires}
\end{center}
\begin{center}
\begin{tabular}{ccc}
& C & 57.35 \\
& H & 2.95 \\
& F & 27.9\%
\end{tabular}
\end{center}

i.r. 3085 (CH str. unsat.); 2955, 2860 (CH str. aliphatic); 1750
(C=O str. ketonic); 1616 (C=C str.); 1500 (highly fluorinated aromatic ring); 1040 (C-O str. ether).
u.v. 268 ($\log_{10} \varepsilon = 2.81$); 300 $\log_{10} \varepsilon = 2.42$.

27.
Preparative t.l.c. of the mother liquors gave a product (<2%) containing OCH₃ groups but no C=O group. Attempted purification failed due to the apparent instability of the product.

The same product (22) was isolated in very small yield when the lithio route was employed for this reaction. A colourless solid, apparently polymeric was the major product.

**Reaction of tetrafluorobenzyne with 1,3-dimethoxybenzene**

via the G.r. route.

Excess 1,3-dimethoxybenzene was distilled from the crude product which was recrystallised from hexane and sublimed to yield:  

1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (26)  

(61.5%) m.p. 79-81° as rhomboids.

Found

- C 57.7
- H 2.95
- F 27.7%

C₁₃H₈O₂F₄ requires

- C 57.35
- H 2.95
- F 27.9%

i.r. 3050, 3020 (CH str. unsat.); 2990, 2965, 2865 (CH str. aliphatic); 1748 (C=O str. ketonic); 1650, 1610 (C=C str.); 1500 (highly fluorinated aromatic ring); 718 (CH=CH cis, out of plane def.).

u.v. 317 (sh) (log₁₀ ε 2.18); 305(log₁₀ ε 2.24); 291 (log₁₀ ε 2.37); 269 (log₁₀ ε 2.77).

**Reaction of tetrafluorobenzyne with 1,4-dimethoxybenzene**

(via G.r. route)

Excess 1,4-dimethoxybenzene was distilled from the crude product which was shown by t.l.c. to be a complex mixture.

Repeated preparative t.l.c. on silica gave:
1,4-dimethoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene

(29) m.p. 79-81°

Found

\[ \text{C } 58.95 \text{ H } 3.5\% \]

\[ \text{C}_{14}\text{H}_{10}\text{O}_{2}\text{F}_{4} \text{ requires } \text{C } 58.75 \text{ H } 3.5\% \]

i.r. 3070 (CH str. unsat.); 2990, 2945, 2840 (CH str. aliphatic);
1625 (C=C str.); 1485 (highly fluorinated aromatic ring); 1335,
1172, 1035 (CF str.); 800.

u.v. 266 (log10 ε 2.74).

5,6,7,8-tetrafluoro-10-oxo-1,4-ethenotetral -2-one (31) (31%)

m.p. 161-4°.

Found

\[ \text{C } 55.55 \text{ H } 2.4\% \]

\[ \text{C}_{12}\text{H}_{6}\text{O}_{2}\text{F}_{4} \text{ requires } \text{C } 55.85 \text{ H } 2.35\% \]

i.r. 2970, 2930 (CH str. aliphatic); 1745 (C=O str. ketonic);
1495 (highly fluorinated aromatic ring); 1028 (C-F str.),

u.v. 266 (log10 ε 2.73); 296(log10 ε 2.47); 305(log10 ε 2.37);
316(log10 ε 2.19) and 3 methoxy-exo-2,3-tetrafluorobenzo-
1,2,3,4-tetrahydro -5,6,7,8-tetrafluoro-9-oxo-1,4-ethanonaphthalene

(32) (8%)

m.p. 176-8°.

Found

\[ \text{C } 54.6 \text{ H } 2.0\% \]

\[ \text{C}_{19}\text{H}_{8}\text{O}_{2}\text{F}_{8} \text{ requires } \text{C } 54.3 \text{ H } 1.9\% \]

i.r. 3000, 2940, 2840 (CH str. aliphatic); 1745 (C=O str.
ketonic); 1495, 1472 (highly fluorinated aromatic ring); 1389,
1022 (C-F str.).

u.v. 265 (log10 ε 2.94); 298(log10 ε 2.39); 308(log10 ε 2.30);
319(log10 ε 2.00)
Reaction of tetrafluorobenzene with p-cresol methyl ether via the G.r. route.

Excess p-cresol methyl ether was distilled from the crude product which was separated by silica gel column chromatography to yield:

1-methyl-4-methoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-etheno-naphthalene (35) (21%)

<table>
<thead>
<tr>
<th>Found</th>
<th>C 62.3</th>
<th>H 3.9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{14}H_{10}F_{4}O requires</td>
<td>C 62.25</td>
<td>H 3.75%</td>
</tr>
</tbody>
</table>

i.r. 3070 (CH str. unsat.); 2980, 2955, 2910, 2855 (CH str. aliphatic), 1635, 1628 (C=C str. olefinic); 1480 (highly fluorinated aromatic ring); 1343, 1070, 998, 867, 800, 710, 678. u.v. 317 (sh) (log_{10} ε 2.18); 305(log_{10} ε 2.34); 291(log_{10} ε 2.37); 269(log_{10} ε 2.77).

5,6,7,8-tetrafluoro-9-methyl-1,4-ethenotetral-2-one (36)

(40-5%)m.p. 76-80°.

<table>
<thead>
<tr>
<th>Found</th>
<th>C 60.8</th>
<th>H 3.0%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{13}H_{8}F_{4}O requires</td>
<td>C 60.9</td>
<td>H 3.15%</td>
</tr>
</tbody>
</table>

i.r. 3070 (CH str. unsat.); 3000, 2970, 2930, 2870 (CH str. aliphatic); 1736 (C=O str. ketonic); 1500 (highly fluorinated aromatic ring); 1088, 1018, 920, 883, 830, 790. u.v. 260 (log_{10} ε 2.70); 294(log_{10} ε 2.50); 304(log_{10} ε 2.46); 314(log_{10} ε 2.18).

and a minor component possibly 3-methoxy-9-methyl-exo-2,3-tetrafluorobenzo-1,2,3,4-tetrahydro-5,6,7,8-tetrafluoro-1,4-ethanonaphthalene (37) (1.9%). Further purification of the product was unsuccessful due to decomposition on chromatography using silica gel or alumina. P.m.r. of the crude adduct: (ν)
4.18 (olefinic multiplet); 5.38 (broad singlet); 5.49 (broad singlet); 5.68 (multiplet); 6.68 (methoxyl singlet); 8.35 (methyl doublet J = 2.5 Hz). Similarities in this spectrum are apparent in the p.m.r. spectrum of (32).

**Reaction of tetrafluorobenzene with 1,3,5-trimethoxybenzene**

The crude reaction mixture after acidic hydrolysis was found to be a mixture of several components (by t.l.c.). Attempted separation by preparative t.l.c. on silica gel proved unsuccessful (probably because of decomposition of the products). Excess 1,3,5-trimethoxybenzene was steam distilled from the mixture which was then extracted with excess saturated sodium bicarbonate solution. Acidification of the extract with conc. hydrochloric acid gave a colourless precipitate which was washed with chloroform to yield: (3-hydroxy-5,6,7,8-tetrafluoro-1-naphthyl) acetic acid (45) (38%).

i.r. 3500-2600 (carboxylic acid dimers); 1500 (highly fluorinated aromatic ring); 1700 (C=O str. acid); 1630 (C=C str. aromatic).

p.m.r. (in trifluoroacetic acid); 2.45 \(\delta\) (singlet) (1 aromatic proton); 2.72 \(\delta\) (singlet) (1 aromatic proton); 5.65 \(\delta\) (doublet) \((J_{\text{H-F}} = 6.0 \text{ Hz})\) (CH\(_2\) long range coupled to an aromatic fluorine).

**Methylation of (3-hydroxy-5,6,7,8-tetrafluoro-1-naphthyl) acetic acid (45)**

(45) was methylated by stirring for 12 hour with excess diazomethene in ether to yield methyl (3-methoxy-5,6,7,8-tetrafluoro-1-naphthyl) acetate (46) m.p. 123-4\(^{\circ}\)

<table>
<thead>
<tr>
<th>Found</th>
<th>C 55.6</th>
<th>H 3.3%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}<em>{14}\text{H}</em>{10}\text{F}<em>{4}\text{O}</em>{3}) requires</td>
<td>C 55.6</td>
<td>H 3.55%</td>
</tr>
</tbody>
</table>

i.r. 3010 (CH str. aromatic); 2995, 2970, 2865 (CH str. aliphatic); 1750 (C=O str. aliphatic ester); 1678, 1632 (C=C str. aromatic); 1270, 1173, 1003, 898, 788, 769, 690.
Reaction of tetrafluorobenzene with 2,6-dimethoxytoluene
(via G.r. route)

Excess 2,6-dimethoxytoluene was distilled from the crude product which slowly crystallised on standing in methanol. The crystals were separated and recrystallised from hexane to yield:

1-methoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (47)
(62%) m.p. 186 - 188°.

Found: C 58.4 H 3.45%

C_{14}H_{10}F_{4}O_{2} requires: C 58.75 H 3.5%

I.r. 2995, 2980, 2955, 2940, 2895, 2870 (CH str. aliphatic); 1744 (C=O str. ketonic); 1650, 1620 (C=C str.); 1508, 1490 (highly fluorinated aromatic ring); 718, 655.

U.v. 268, 288, 297, 309, 322 in cyclohexane.

T.i.c. separation of the mother liquors yielded a further quantity of (47) (overall yield 62%) and a second product

5,6,7,8-tetrafluoro-1,3,3-trimethoxy-2-methyl-1,4-ethenotetralin (49) (12%) m.p. 138 - 138.5°.

Found: C 57.85 H 4.8%

C_{16}H_{16}F_{4}O_{3} requires: C 57.85 H 4.85%

I.r. 2998, 2960, 2860 (CH str. aliphatic); 1635 (C=C str.); 1504, 1490 (highly fluorinated aromatic ring); 1112, 1057, 808.

U.v. 263 (log_{10} ε 2.82).

Repeat reaction:

The reaction was repeated and hydrolysis carried out with methanol, to ensure that (49) was not formed directly in
the reaction. The crude product was separated by T.L.C. on silica gel in 50% benzene in hexane to yield a single unstable product probably:

1,3-dimethoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (48) (52%)

i.r. 2855 (OH str. methoxyl); 1688 (C=C str. methoxyl substituted); 1603 (C=C str.); 1490 (highly fluorinated aromatic ring);
p.m.r. 2.70-3.55 (olefinic multiplet); 5.06 (bridgehead multiplet); 6.24 (triplet methoxyl); 6.42 (singlet methoxyl); 8.30 (methyl singlet).

However after standing for several weeks the crude methanolic solution of (48) was found to contain (47) and (49).

Decomposition of 1,3-dimethoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (48)

A. Atmospheric hydrolysis

(48) was allowed to stand in contact with air for 8 hours. Decomposition of (48) was observed by growth of the 1744 (C=O str.) frequency band in the infra-red spectrum. After 8 hours decomposition was complete and only (47) was present (by i.r. spectroscopy).

B. By acidic hydrolysis

(48) (20 mg) was stirred 10 min with dil. HCl (10 ml). The product was extracted with ether to yield (47) identical with previously isolated material.
Investigation of the reaction of tetrafluorobenzyne with 2,6-dimethoxytoluene

The general Grignard reagent route was employed. After 5 hours under reflux an aliquot was extracted using a dry syringe. I.r. and p.m.r. showed the mixture to contain (48) and 2,6-dimethoxytoluene only.

Hydrolysis of 5,6,7,8-tetrafluoro-1,3,3-trimethoxy-2-methyl-1,4-ethenotetralin (49)

(49) (10 mg) in dil. HCl (10 ml) was boiled under reflux 1 hour. The product was ether extracted to yield 1-methoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (47) (100%) identical with authentic material.

Attempted Ketal formation of 1-methoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (47)

(47) (50 mg) stirred 14 days in methanol (20 ml) containing a trace of hydrogen chloride gas gave only recovered (47). No ketal formation was detected.

Hydrogenations

General Method

The compound (100 mg) was dissolved in methanol (25 ml) and pre-reduced (5%) palladium on charcoal (20 mg) added. The mixture was hydrogenated at atmospheric pressure until uptake of hydrogen ceased. The solution was filtered free of catalyst and methanol distilled out to yield the crude product which was then purified by recrystallisation or by thin layer chromatography.
Hydrogenation of 1-ethoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (17) gave:

1-ethoxy-5,6,7,8-tetrafluoro-1,4-ethanotetralin (18) (100%)
m.p 70-72°

| Found          | C 61.4 | H 4.9 | F 27.8%
|----------------|--------|-------|-----------
| C_{14}H_{14}F_{4}O requires | C 61.3 | H 5.15 | F 27.7%

i.r. 2985, 2950, 2930, 2910, 2890 (CH str. aliphatic); 1509, 1490 (highly fluorinated aromatic ring); 1350, 1315, 1055, 980, 852.

u.v. 260 (log_{10} E 2.67).

Hydrogenation of 1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-2-one (22) gave:

1-methoxy-5,6,7,8-tetrafluoro-1,4-ethanotetral-2-one (23)

(96%) m.p. 115-115.5°

| Found          | C 57.15 | H 3.75%
|----------------|---------|----------
| C_{13}H_{10}F_{4}O requires | C 56.95 | H 3.95%

i.r. 2965, 2940, 2905, 2860 (CH str. aliphatic); 1757 (C=O str. ketonic); 1512, 1495 (highly fluorinated aromatic ring); 924, 910, 840, 819.

u.v. 266 (log_{10} E 2.79); 298 (log_{10} E 2.42).

Hydrogenation of 1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one- (26) gave:

1-methoxy-5,6,7,8-tetrafluoro-1,4-ethanotetral-3-one (28)

(97%) m.p. 73-4°

| Found          | C 56.95 | H 3.8%
|----------------|---------|----------
| C_{13}H_{10}F_{4}O requires | C 56.95 | H 3.95%

i.r. 2980, 2965, 2940, 2900, 2855 (CH str. aliphatic); 1740 (C=O str. ketonic); 1490 (highly fluorinated aromatic ring); 1050, 860.
Hydrogenation of 5,6,7,8-tetrafluoro-1,3,3-trimethoxy-2-
methyl-1,4-ethenotetralin (49) gave: 5,6,7,8-tetrafluoro-
1,3,3-trimethoxy-2-methyl-1,4-ethanotetralin (100%)
m.p. 92.5 - 95°C.

Found     C 57.7     H 5.6%

C_{16}H_{18}F_{16}O_{3} requires  C 57.5     H 5.45%

Pyrolytic Studies

General Method

The compound (150 mg) was placed in a pyrex tube
(500 ml capacity), evacuated (0.2 mm Hg), and flushed with dry
oxygen free nitrogen. The tube was re-evacuated, sealed and
heated for 12-15 hours at the pyrolysis temperature. The cold
tube was opened and the product extracted with ether.

Recrystallisation or thin layer chromatography on silica gel
yielded the pure product.

Pyrolysis of 1-methoxy-5,6,7,8-tetrafluoro-1,4-etheno-1,4-
dihydronaphthalene (3) at 300°C gave:
1-methoxy-5,6,7,8-tetrafluoronaphthalene (7A) (92%)
m.p. 76°C purified by sublimation

Found     C 56.9     H 2.7     F 33.3%

Calc. for C_{9}H_{6}F_{4}O     C 57.3     H 2.6     F 33.0%

i.r. 3030 (CH str. aromatic); 2995, 2960, 2875, 2850
(CH str. aliphatic); 1672, 1620 (C=C str. aromatic); 1416, 1375, 1048, 980, 880, 796, 748.

u.v. 292 (log $\varepsilon_{10} 3.77$); 311(log $\varepsilon_{10} 3.66$); 321(sh.) (log $\varepsilon_{10} 3.52$); 325(log $\varepsilon_{10} 3.59$).

Pyrolysis of 1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-2-one (22) also gave 1-methoxy-5,6,7,8-tetrafluoronaphthalene (7) (79%) at 300°.

Pyrolysis of 1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (26) also gave 1-methoxy-5,6,7,8-tetrafluoronaphthalene (7) (94%) at 300°.

Pyrolysis of 1-methoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (47) similarly gave 1-methoxy-5,6,7,8-tetrafluoronaphthalene (7) (98%) at 300°.

Pyrolysis of 1,3,3-trimethoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-ethenotetralin (49) also gave 1-methoxy-5,6,7,8-tetrafluoronaphthalene (87%) at 300°.

Pyrolysis of 5,6,7,8-tetrafluoro-1,4-ethenotetral-2-one (4) at 300° gave 1,2,3,4-tetrafluoronaphthalene (87%) which was purified by t.l.c. on silica gel in hexane.
m.p. 106° (lit 31 110-111°) identical with authentic material. 27

Pyrolysis of 5,6,7,8-tetrafluoro-9-methyl-1,4-ethenotetral-2-one (36) at 350° gave 2-methyl-5,6,7,8-tetrafluoronaphthalene (41) (86%) m.p. 62 - 62.5° (lit 27 62°) identical with authentic material.

Pyrolysis of 1-methyl-4-methoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (35) at 300° for 15 hours gave:
1-methyl-4-methoxy-5,6,7,8-tetrafluoronaphthalene (39) (71%)
m.p. 118 - 120°.

Found C 59.0 H 3.35%
C_{12}H_{8}F_{4}O requires C 59.0 H 3.3%
i.r. 3050 (CH str. aromatic); 2995, 2965, 2895, 2870 (CH str. aliphatic); 1667, 1601 (C=C str. aromatic); 1497 (highly fluorinated aromatic ring); 1400, 1077, 1036, 996, 862, 819.

Attempted Huang-Minlon Reduction of 1-methoxy-5,6,7,8-
tetrafluoro-1,4-ethenotetral-2-one (22)

A mixture of (22), (415 mg), hydrazine hydrate (60 mg), potassium hydroxide (270 mg) and diethylene glycol (10 ml) was boiled under reflux for 3 hours. Liquid was distilled from the mixture until the temperature of the distillate reached 180° when the remaining mixture was boiled under reflux a further 5 hours. Extraction of this resultant mixture gave only intractable polymeric material.

Photolytic Studies

Unless otherwise stated all photolytic reactions were carried out under oxygen free nitrogen in a quartz flask at the boiling point of the solvent employed (normally ether). The ultra violet radiation was provided by a medium pressure mercury vapour lamp (Hanovia Ltd.) and unless stated no filter was used.

Photolysis of 5,6,7,8-tetrafluoro-1,4-ethenotetral-2-one (4)

(4) (50 mg) in ether (50 ml) after 3 hours gave 38.
1,2,3,4-tetrafluoronaphthalene (98%) m.p. 107° identical with authentic material. The same product was isolated when 5% acetone in ether was used as a photosensitiser.

Photolysis of 1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-2-one (22)

(22) (100 mg) in ether (40 ml) after 4 hours gave:
1-methoxy-5,6,7,8-tetrafluoronaphthalene (7A) (97%) identical with material isolated on pyrolysis of (22).

Photolysis of 1-methoxy-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (26)

(26) similarly gave (7A) in 88% yield after 3 hours.

Photolysis of 1-methoxy-2-methyl-5,6,7,8-tetrafluoro-1,4-ethenotetral-3-one (47)

(47) also gave (7A) in 81% yield after 3 hours.

Photolysis of 5,6,7,8-tetrafluoro-9-methyl-1,4-ethenotetral-2-one (36)

(36) (50 mg) in ether (100 ml) after 3 hours gave 2-methyl-5,6,7,8-tetrafluoronaphthalene (92%) identical with authentic material.27

Variable temperature p.m.r. studies with 1-methoxy-5,6,7,8-tetrafluoronaphthalene (7A)

A solution of 7A (10% in dimethyl sulphoxide d⁶) was studied by p.m.r. spectroscopy at temperatures of 60-200°.

The singlet at 6,05 ppm showed no change in multiplicity between these temperature limits.

Pyrolysis of 1-ethoxy-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-ethenonaphthalene (17) at 350° gave 1-ethoxy-5,6,7,8-tetrafluoronaphthalene (21) (62%) colourless gum from t.l.c.
Found  C 59.2  H 3.45%

$C_{12}H_{8}F_{4}O$ requires  C 59.0  H 3.3%

i.r. ($\text{cm}^{-1}$) 3010 (CH str. aromatic); 2960, 2910, 2870 (CH str. aliphatic); 1674, 1620, 1608 (C=C str. aromatic); 1500 (highly fluorinated aromatic ring); 1420, 1378, 1283, 1250, 1050, 1006, 928, 798, 749.

u.v. 284 (sh.) (3.56); 294 (3.60); 308 (3.45); 313 (3.46); 323 (sh.) (3.35); 327 (3.43).

**Reaction of tetrafluorobenzyne with N, N-dimethyl-p-toluidine**

(via the lithio compound route)

Excess N, N-dimethyl-p-toluidine was distilled under reduced pressure from the crude product which was extracted with gradually increasing concentrations of hydrochloric acid to yield:

A) 5,6,7,8-tetrafluoro-1-dimethylamino-4-methyl-1,4-dihydro-1,4-ethenonaphthalene (51) (7%) p.m.r. ($\delta$) 3.31 (AB quartet) ($J_{AB} = 8.4\text{Hz}$) (4 olefinic protons); 7.36 (doublet) ($J_{HF} = 4.5\text{Hz}$) (6 methyl protons); 7.95 (doublet) ($J_{HF} = 6.0\text{Hz}$) (3 methyl protons).

i.r. 3020 (CH str. olefinic); 2970, 2930, 2900, 2870, 2840, (CH str. aliphatic); 1640 (C=C str. aromatic); 1500 (highly fluorinated aromatic ring); 1342 (C-N vib. tert. amine); 710, 690 (CH=CH cis olefine).

B) N-2,3,4,5-tetrafluoro benzyl-N-methyl-p-toluidine (52) (12%) pale yellow liquid.

p.m.r. ($\delta$) 3.18 (AB quartet) ($J_{AB} = 9.0\text{Hz}$) (4 aromatic protons); 5.53 (broad singlet) (2 methylene protons); 7.05 (singlet) (3 methyl protons); 7.79 (singlet) (3 methyl protons).
i.r. 3020 (CH str. aromatic); 2935, 2880, 2840 (CH str. aliphatic); 1625 (C=C str. aromatic); 1520, 1495 (highly fluorinated aromatic ring); 1350 (C-N vib. tert. amine); 808 (p-disubst. benzene ring). u.v. 249 (log₁₀ ε 2.99); 303(log₁₀ ε 2.18) and an acid insoluble mixture which was separated by t.l.c. to yield:

3) N-methyl-N-p-tolyl-tetrafluoro-ortho-toluidine (54) (29%) pale yellow liquid.

p.m.r. (γ) 3.30 (AB quartet (Jₐₐ = 8.4Hz) (4 olefinic protons); 6.82 (singlet) (3 methyl protons); 7.78 (singlet) (3 methyl protons); 7.93 (doublet) (Jₕₚ = 3Hz) (3 methyl protons).

i.r. 3045 (CH str. aromatic); 2940, 2880, 2840 (CH str. aliphatic); 1620 (C=C str. aromatic); 1510, 1495 (highly fluorinated aromatic ring); 806 (1,4-disubst. benzene ring).

u.v. 245 (log₁₀ ε 2.76) 292 (log₁₀ ε 2.34) and 4) 5,6,7,8-tetrafluoro-9-methyl-1,4-ethenotetral-2-one (36) (9%) m.p. 78-80° identical with previously isolated material (p. 30).
(3.1.) **Introduction**

The reaction of tetrafluorobenzyne with furan has been reported. However it was of interest to repeat this work and extend the reactions of tetrafluorobenzyne to substituted furans for several reasons:

i) It was of interest to cleave the furan adduct (10) with acid to synthesise 5,6,7,8-tetrafluoro-1-naphthol (11) because of work on the pyrolysis of the anisole-tetrafluorobenzyne bridgehead adduct (3) (Chapter 2) (Scheme 35, \( R^1 = R^2 = H \)).

ii) Long range \(^{19}F - ^1H\) spin-spin coupling has been observed in a variety of adducts prepared by reaction of tetrafluorobenzyne with arenes. The furan adduct has also been reported to show pronounced long-range coupling between the fluorine atoms at positions 5 and 8, and the proton atoms at positions 1 and 4 respectively. It was of interest to investigate the effect of small changes in bond angle that exist between compounds (5) and (65) (Scheme 36).

iii) Previous work has reported restricted rotation in the bridgehead adduct from the reaction of tetrafluorobenzyne with tert-butylbenzene (5, \( R = tBu \)). It was therefore of interest to determine if any restriction of rotation...
existed in the 2 methyl-5-tert, butylfuran-tetrafluorobenzyne adduct (66). A synthetic route to 1-methyl-4-tert, butyl-5,6,7,8-tetrafluoronaphthalene (67) was believed possible by the action of acid on (68). The naphthalene (67) was also a compound which might show restricted rotation (Scheme 35).

iv) It was hoped by application of a previously reported route \(^{53}\) to synthesise 9,10-substituted anthracenes (64) (Scheme 37) and to investigate the long range \(^{19}F - ^1H\) long range coupling in these molecules.

v) Finally it was hoped to achieve a good synthetic route to 9,10-substituted highly fluorinated \(-9,10-\circ-\) benzenoanthracenes (i.e. substituted triptycenes) by reaction of tetrafluorobenzyne with 9,10-substituted anthracenes (Scheme 37).

(3.2.) **Discussion**

Initially the reaction of tetrafluorobenzyne with furan was repeated to yield the 1,4-adduct (10) in good yield (82\%). This was cleaved with dilute hydrochloric acid to yield 5,6,7,8-tetrafluoro-1-naphthol (11) which was methylated with ethereal diazomethane to yield the methoxynaphthalene (7A). (11) was also isolated by pyrolysis of the furan adduct (10) in a sealed tube at 200\°. Some other reactions of (10) have been discussed in Chapter 2.
When 2-methyl and 2,5-dimethylfuran were reacted with tetrafluorobenzine the sole products were (69) and (70) respectively. The structures were confirmed by spectroscopic methods and elemental analysis. Treatment of the 2-methylfuran adduct (69) with dilute hydrochloric acid under reflux for 12 hr. caused cleavage of the epoxy group to yield 4-methyl-5,6,7,8-tetrafluoro-1-naphthol (71), the structure of which was confirmed by methylation with diazomethane to yield the methoxy compound (39) identical with product isolated from the pyrolysis of the p-cresol methyl ether-tetrafluorobenzine adduct (35).

Both (69) and (70) have been reduced to yield the corresponding dihydro adducts (72) and (73) respectively. Treatment of these compounds with acetic anhydride readily gave the corresponding naphthalenes (74) and (75). The naphthalene (74) has been previously reported, from the pyrolysis of the bridgehead toluene-tetrafluorobenzine adduct (76) (Scheme 9) and was confirmed as an identical sample.

The reaction of tetrafluorobenzine with 2-methyl-5-tert-butylnuran (77) has been investigated. A single product in 58% yield was isolated and shown to be (66), the 1,4-adduct. The reduction of (66) with hydrogen over palladium on charcoal in methanol resulted in uptake of 1 mole of hydrogen to yield (68) which was dehydrated with acetic anhydride to
yield 1-methyl-4-tert.butynaphthalene (67). The p.m.r. spectra of these compounds have been examined and are discussed in Chapter 5. Briefly however no restricted rotation was observed unlike the bridgehead tetrafluorobenzene-tert.butylbenzene adduct. 35

2-Methyl-5-tert.butylfuran (77) has not been previously reported and its synthesis provided some interesting problems. Reaction of bromopinacolone with ethyl acetoacetate in sodium ethoxide solution yielded (78). If the reaction mixture became slightly acidic, cyclisation occurred and the furan (79) was the product. The compound (78) was converted to (79) by stirring with dilute hydrobromic acid.

Hydrolysis of (78) with sodium hydroxide and spontaneous decarboxylation of the resulting acid yielded (80) readily. However attempted cyclisation of the diketone (80) with zinc chloride in acetic anhydride yielded a Friedel-Crafts product (81) of two possible structures. Cyclisation of (80) was achieved using acetic anhydride alone to yield (77), 2-methyl-5-tert.butylfuran. The overall yield from bromopinacolone was 39%. Attempted polyphosphoric acid cyclisation of the dione (80) gave only intractable tars.
It was also shown to be possible to synthesise (77) in improved yield from the furan derivative (79). Hydrolysis of the ester (79) yielded the acid (82) which was decarboxylated with cupric oxide in quinoline to yield 2-methyl-5-tert-butylfuran (77). The overall yield from bromopinacolone was 58%. These reactions are summarised in Scheme (38).

To determine the structure of the Friedel-Crafts product (81) which was formed from the furan (77) we considered two possible structure (81A) and (81B). The p.m.r. spectral data for (81) is recorded in Table 4 along with other spectral data for similar compounds. Comparison of the line positions of (81) with similar compounds shows that the Friedel-Crafts product has the structure (81A).

The ring proton in (81) appears at 3.85 which is comparable to the positions of the ring protons of (79), (82) and (83). The ring methyl group signal appears at 7.49 and is slightly broadened by allylic coupling to the ring proton. There was however no change in attempted spin decoupling experiments with (81).

Comparison of the methyl positions of (77) and (81) shows a shift from 7.82 to 7.49. This is comparable to the position of the methyl group to the acetyl group at 7.51 in (83). The methyl group in (83) is situated at 7.75, shifted
from 7.82 \( \tau \) in the parent furan (85). The position of the ring methyl groups in (79) and (82) appear as expected at a slightly lower field than the methyl group in (81). The position of the tert-butyl group signal shows little difference in any of the compounds studied.

When the carbonyl group in (81) was reduced with sodium borohydride both the methyl and ring proton signals shifted markedly indicating the closeness of these atoms to the carbonyl group. The shift in methyl group signal would not be expected to be as large in (81B). Similarly it is difficult to explain the p.m.r. positions of (81) if the structure is (81B). We therefore conclude that the Friedel-Crafts product has the structure (81A).

Elaboration of substituted furan-tetrafluorobenzyne adducts to anthracene derivatives has been attempted. The 2-methylfuran adduct (69) reacts with butadiene in a sealed tube at 70\(^\circ\) to yield the adduct (86). The structure was confirmed by spectroscopic studies. Reduction of (86) with hydrogen over palladium on charcoal resulted in the uptake of one mole of hydrogen and formation of (87) quantitatively. Treatment of the hydrogenated adduct (87) with acetic anhydride resulted in the formation of the naphthalene (88). Similar reactions of the 2,5-dimethylfuran adduct were
completely analogous. Thus (70) reacted with butadiene to yield (89) which was reduced to (90) and dehydrated to yield the naphthalene (91).

The attempted reaction of the 2-methyl-5-tert. butylfuran adduct (66) with butadiene in a sealed tube at 70° failed and starting materials only were recovered. This may be explained by considering the steric size of the tert-butyl group which we believe prevents the close approach of the butadiene molecule in the transition state.

The reactions of the naphthalenes (88) and (91) with tetrafluorobenzyne have been investigated; (88) formed (92) in 47% yield, whilst (91) yielded (93) in 52% yield as the single products of the reactions.

As stated we wished to investigate the reaction of tetrafluorobenzyne with anthracenes of type (64) in anticipation of producing substituted triptycenes (94). There appeared to be three suitable routes to the synthesis of (64) from the epoxyanthracenes (86) and (89) (Scheme 41).

The reactions of (86) and (89) with chloranil in xylene were investigated. After heating under reflux for 3 hours no reaction had apparently occurred and only starting materials were recovered.
The reaction of (86) with a quinone of higher redox potential (dichlorodicyanobenzoquinone) was therefore investigated. A complex mixture was isolated and it appeared that the quinone attacked the epoxy group in (86) to yield phenolic products. No starting material or dehydrogenated anthracene was detected. Boiling the crude mixture with acetic anhydride to dehydrate any hydroxy compounds to anthracenes failed to yield any hydrocarbon products.

The use of palladium on carbon dehydrogenation of (86) was attempted at 270°. A complex mixture of products was isolated and not identified. When the reaction was examined with (89) at a lower temperature (200°) for a shorter time a complex mixture was similarly isolated.

The dehydrogenation of (88) and (91) was attempted also with a lack of success. When (88) and (91) were heated with chloranil in xylene only starting materials were recovered after 20 hours.

The dehydration of (89) was carried out by heating under reflux with acetic anhydride containing a small quantity of hydrobromic acid. Although the crystals which separated were recrystallised several times a satisfactory elemental analysis could not be obtained for (94). Mass spectrometry showed the presence of brominated products. We now believe that some addition of HBr occurred across the 2,3-double
bond and that we were unable to separate (94) from the brominated impurities. The structure of (94) was confirmed by catalytic hydrogenation with palladium on carbon. The previously identified product (91) was isolated and shown by i.r. and mixed melting point to be authentic.

An attempt to dehydrogenate (94) to (64) \((R^1 = R^2 = \text{Me})\) heating under reflux with chloranil in xylene was unsuccessful and a complex mixture, which could not be separated, was isolated. Similar results with the epoxyanthracene (86) were anticipated and so the analogous reactions were not investigated.

(3.3.) Experimental

Reaction of tetrafluorobenzene with furan (via the lithio compound route)

The crude product was distilled to yield:

5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (10) (82\%) b.p. 80°/5 mm m.p. 59-60° (lit. 28b 56-57°) i.r. 1495 (highly fluorinated aromatic ring); 1293 (epoxy group); 825 (cis epoxy group); 720 (cis olefine CH \(_2\) out of plane def.)

u.v. 264 (log \(_{10} c\) 2.57).

Reaction of tetrafluorobenzene with 2-methylfuran (via the lithio compound route)

Distillation of the crude product yielded:

5,6,7,8-tetrafluoro-1-methyl-1,4-dihydro-1,4-epoxynaphthalene (69)
(76.5%) b.p. 56-60°/0.3 mm m.p. 27-28°.

Found C57.55 H 2.85%
C₁₁H₆F₄O requires C57.4 H 2.65%

i.r. 3040 (CH str. unsat.); 3000, 2955 (CH str. aliphatic); 1650 (C=C str. olefine); 1500 (highly fluorinated aromatic ring); 727 (cis olefine).

u.v. 265 (log₁₀ε 2.78)

Reaction of tetrafluorobenzyne with 2,5-dimethylfuran
(via the lithio compound route)

Distillation of the crude product yielded:
5,6,7,8-tetrafluoro-1,4-dimethyl-1,4-dihydro-1,4-epoxynaphthalene
(70) (67.5%) b.p. 59 - 61°/0.6 mm m.p. 52 - 54°

Found C 58.85 H 3.45%

C₁₂H₈F₄O requires C 59.0 H 3.3%

i.r. 2995, 2950, 2890, (CH str. aliphatic); 1645 (C = C str. olefine); 1500 (highly fluorinated aromatic ring); 728 (cis olefine)

u.v. 264 (log₁₀ε 3.01).

Cleavage of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (10)
(10) (500 mg) was boiled under reflux in methanolic hydrochloric acid (80 ml methanol, 20 ml conc. hydrochloric acid) for 14 hr. Excess methanol was evaporated off and water was added to precipitate 5,6,7,8-tetrafluoronaphth-1-ol (11) (62%) m.p. 119 - 122° (lit 28b 124 - 125°)

51.
i.r. 3400 (OH broad); 1682, 1628, 1612 (C = C
str. aromatic); 1510 (highly fluorinated aromatic
ring); 1415, 1008, 898, 851, 802, 750.
p.m.r. 2.35 – 3.05 (complex multiplet – 3
aromatic ring protons); 3.60 (broad CH).

Pyrolysis of 5,6,7,8-tetrafluoro-1,4-dihydro-1,4-
epoxy napthalene (10) at 300° yielded 5,6,7,8-
tetrafluoronaphthalene-1-ol (11) (70%) identical with
the compound isolated above.

A coupling reaction of 5,6,7,8-tetrafluoronaphthalene-1-ol
in alkaline solution with p-nitrobenzenediazonium
chloride yielded an orange dye m.p. 264-5° which
was extremely insoluble in all common solvents.
The structure could therefore not be fully elucidated.

Attempted Birch reduction of 5,6,7,8-tetrafluoronaphthalene-1-ol (11)

Amyl alcohol (0.63g) and sodium metal (0.16g
in small pieces) was added to a mixture of (11) (0.75g)
and finely powdered sodamide (0.14g) in liquid
ammonia (20 ml). After the blue colour had
disappeared the ammonia was evaporated off and the
residue decomposed with ice cold water (10 ml).
The mixture was ether extracted and acidified.
T.l.c. of the products showed 5 major products.
I.r. showed a very weak band at 1685 cm⁻¹. The
mixture was not further investigated.
Attempted bromination of 5,6,7,8-tetrafluoronaphth-1-ol (11)

Treatment of (11) (100 mg) with bromine (40 mg) in carbon tetrachloride at ambient temperature for 4 to 50 hr. gave only intractable dark residues.

Methylation of 5,6,7,8-tetrafluoronaphth-1-ol (11)

(11) (250 mg) in ether with excess diazomethane in ether gave 1-methoxy-5,6,7,8-tetrafluoronaphthalene (7A) (95%) identical with previously isolated material.

Cleavage of 5,6,7,8-tetrafluoro-1-methyl-1,4-dihydro-1,4-epoxynaphthalene (69)

(69) (100 mg) was heated under reflux in methanol (45 ml) containing conc. hydrochloric acid (10 ml) for 12 hr. The mixture was evaporated and the residue recrystallised from hexane to yield:

5,6,7,8-tetrafluoro-4-methylnaphth-1-ol (71) (100%)

m.p. 125 - 126° needles from hexane.

Found C 57.25 H 2.55%

C_{11}H_{6}F_{4}O requires C 57.4 H 2.65%

i.r. 3380 (broad) (OH str.); 1670, 1624 (C = C str. aromatic); 1508, 1403 (highly fluorinated aromatic ring) 1378, 1080, 914, 869, 834, 825.

u.v. 303 (log_{10}ε 3.72); 322 (log_{10}ε 3.68); 336 (log_{10}ε 3.67)
Methylation of 5,6,7,8-tetrafluoro-4-methylnaphth-1-ol (71)

Reaction of (71) (100 mg) in ether (20 ml) with excess diazomethane in ether gave 1-methoxy-4-methyl-5,6,7,8-tetrafluoronaphthalene (39) identical with previously isolated material (page 39).

Hydrogenation of 1-methyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (69)

(69) gave 1-methyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (72) (100%) m.p. 36.5-37° as needles after sublimation.

Found C 56.85 H 3.45%

C_{11}H_{8}OF_{4} requires C 56.9 H 3.45%

i.r. 3000, 2965, 2930, 2890 (CH str. aliphatic); 1510, 1492 (highly fluorinated aromatic ring); 1412, 1052, 933, 838

u.v. 259 (log_{10}ε 2.41)

Action of acid on 1-methyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (72)

(72) (50 mg) in acetic anhydride (10 ml) containing concentrated hydrobromic acid (1 ml) was heated under reflux for 12 hr. to yield 1-methyl-5,6,7,8-tetrafluoronaphthalene (74) (95%) (lit 95-97°) identical with authentic material.

Hydrogenation of 1,4-dimethyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (70)

(70) gave 1,4-dimethyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (73) (100%) m.p. 80-81° phase change 68-74°.
Found  C 58.45  H 3.95%

C₁₂H₁₀OF₄ requires C 58.55  H 4.1%

i.r. 3000, 2960, 2920, 2880 (CH str. aliphatic); 1500 (highly fluorinated aromatic ring); 1414, 1318, 1239, 1100, 1040, 899, 818.

u.v. 259 (log₁₀ E 2.48)

Action of acid on 1,4-dimethyl-5,6,7,8-tetrafluoro-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (73)

(73) (50 mg) in acetic anhydride (10 ml) containing conc. hydrobromic acid (1 ml) after 12 hr. under reflux gave 1,4-dimethyl-5,6,7,8-tetrafluoronaphthalene (75) (48%) m.p. 124-7° phase change 74-85°.

Found  C 63.25  H 3.5%

C₁₂H₈F₄ requires  C 63.15  H 3.55%

i.r. 2995, 2955, 2895 (CH str. aliphatic); 1668, 1602 (aromatic C = C str.); 907, 863, 832.

u.v. 286 (log₁₀ E 3.86); 311 (log₁₀ E 3.39); 321 (log₁₀ E 3.27); 325 (log₁₀ E 3.40).

Reaction of tetrafluorobenzyne with 2-methyl-5-tert. butylfuran

(77) (via the lithio compound route)

The crude product was distilled to yield:

1-methyl-4-tert. butyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (66) (58%) as an oil b.p. 140°/2 mm.

Found  C 62.8  H 4.7%

C₁₅H₁₄OF₄ requires C 62.95  H 4.95%

i.r. 2990, 2975, 2950, 2920, 2890 (CH str. aliphatic);
1640 (C = C str. olefine); 1500 (highly fluorinated aromatic ring); 738, 723 (cis olefine)
u.v. 264 (log₁₀ E 2.73)

Hydrogenation of 1-methyl-4-tert.butyl-5,6,7,8-
tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (66)

(66) gave 1-methyl-4-tert.butyl-5,6,7,8-tetrafluoro
-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (68) (100%)
after distillation. b.p. 140°/2 mm.
Found C 62.7 H 5.55%
C₁₅H₁₆OF₄ requires C 62.5 H 5.6%
i.r. 2990, 2955, 2950, 2930, 2890 (CH str. aliphatic);
1500 (highly fluorinated aromatic ring); 1411, 1055, 1041,
908.
u.v. 258 (log₁₀ E 2.51)

Action of acid on 1-methyl-4-tert.butyl-5,6,7,8-
tetrafluoro-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (68)

(68) (100 mg) in acetic anhydride (10 ml) containing
hydrobromic acid (1 ml) after heating for 12 hr. under
reflux gave a mixture. T.l.c. on silica gel in light petroleum (b.p. 60-80°)
gave recovered (68) (20%) and
1-methyl-4-tert.butyl-5,6,7,8-tetrafluoronaphthalene (67)
(88% based on converted (68)) m.p. 99.5-100°
Found C 66.95 H 5.35%
C₁₄H₁₄F₄ requires C 66.65 H 5.2%
i.r. 3040 (CH str. unsat.); 2990, 2950, 2895 (CH
str. aliphatic); 1670, 1550 (aromatic C = C str.);
899, 857, 841.
Reaction of bromopinacolone with ethyl acetoacetate

Ethyl acetoacetate (38.8 g) was added with stirring to a solution of sodium ethoxide prepared from absolute ethanol (150 ml) and sodium metal (6.8 g) at 50°. Bromopinacolone \(54\) (53 g) was added dropwise to maintain gentle reflux and the mixture then heated under reflux for 64 hr. Ethanol was distilled from the reaction and the residue treated with water (50 ml). The ester layer was separated, dried over HgSO\(_4\) and distilled to yield:

**ethyl 2-acetyl-5,5-dimethyl-4-oxohexanone** (78)

b.p. 98-100°/0.8 mm (54.15 g) (80.5%)

Found

\[ \text{C} 62.95 \quad \text{H} 8.75\% \]

C\(_{12}\)H\(_{20}\)O\(_4\) requires

\[ \text{C} 63.15 \quad \text{H} 8.85\% \]

i.r. (cm\(^{-1}\)), 2985, 2950, 2920, 2880 (C - H str. aliphatic); 1752 (ester C = O str.); 1728, 1718 (ketonic C = O str.); 1402, 1374 (\((\text{CH}_3\))\(_3\)C deformation); 1251 (\((\text{CH}_3\))\(_3\)C skeletal).

P.m.r. \((\tau) = 5.86\) (quartet) (ester methylene \(J = 6\text{Hz}\));

6.07 (multiplet) (X part of ABX) (methine proton);

7.00 (8 line multiplet) (AB part of ABX) (2 methylene protons); 7.70 (singlet) (acetylmethyl); 8.74 (triplet) \((J = 6\text{Hz})\) (ester methyl); 8.86 (singlet) (t-butyl group).

u.v. 252 (\(\log_{10}\varepsilon 2.89\)).
The above method was repeated using slightly less sodium metal (6.5g) with the same work up to yield:

**ethyl 5-tert.butyl-2-methyl-3-furoate** (79)

b.p. 80°/0.9 mm (75.8%)

Found  C 68.65  H 8.65%

C₁₂H₁₈O₃ requires  C 68.55  H 8.65%

i.r. 2975, 2945, 2920, 2880 (CH str. aliphatic); 1725 (ester C = O str.); 1620, 1585 (C = C str.); 1122 (C - O str. ester); 1073, 780 (ring CH vibration).

u.v. 254 (log₁₀ ε 3.60).

**Attempted ring opening of ethyl 5-tert.butyl-2-methyl-3-furoate** (79)

No cleavage of the ester (79) (1g) occurred after heating under reflux for 10 hr. with dil. hydrochloric acid (20 ml 1N.)

**Hydrolysis of ethyl 2-acetyl-5,5-dimethyl-4-oxohexanoate** (78)

The ester (78) (50 g) was stirred for 4 hr. with excess 5% sodium hydroxide (containing 10.9g NaOH). The oily layer of unsaponified ester was separated and the aqueous layer slowly acidified with sulphuric acid (50%). The resultant mixture was then distilled until half the volume had been collected and then the distillate was ether extracted to yield the crude product which was purified by distillation to yield:

**2,2-dimethylhepta-3,6-dione** (80) b.p. 80-82°/8mm

22.7g (66.4%)
Found  C  69.1  H 10.6%

C₂H₁₆O₂ requires  C  69.2  H 10.3%

i.r. 2980, 2945, 2920, 2880 (CH str. aliphatic); 1728, 1715 (C = O str. ketonic); 1402, 1372 (CH₃)₂C deform).

u.v. 279 (log₁₀ E 1.71).

Dehydration of 2,2-dimethylhepta-3,6-dione (80)

A. With Zinc chloride in acetic anhydride

Acetic anhydride (40 ml) and zinc chloride (1.5g) were added slowly with stirring to the diketone (80) (20 g). When the exothermic reaction had ceased the mixture was heated under reflux for 3 hours. The cold mixture was made alkaline with sodium hydroxide (6N). The product was steam distilled from the mixture and purified by steam distillation to yield:

3-acetyl-5-tert-butyl-2-methylfuran (81A) (79.4%)
m.p. 39-40° b.p. 106-108/15 mm.

Found  C  73.05  H 9.05%

C₃H₁₆O₂ requires  C  73.3  H 8.95%

i.r. 2980, 2940, 2920, 2885 (CH str. aliphatic); 1688 (C = O str. unsat.); 1608, 1576 (C = C str. furan); 1405, 1374, (CH def. (CH₃)₂C group); 1240 (C - O vib. ketonic);

u.v. 276 (log₁₀ E 3.72)

B. With polyphosphoric acid

Heating the ketone (80) (5g) with polyphosphoric acid (prepared from P₂O₅ (20g) in H₃PO₄ (100 ml)) at
120 - 150° for 30-60 mins. gave only intractable tars.

C. With acetic anhydride

A mixture of diketone (80) (12g) and acetic anhydride (30 ml) was heated under reflux for 5 hr. After cooling and making alkaline with sodium hydroxide (6N) the mixture was steam distilled to yield the crude product which was purified by distillation to give:

2-methyl-5-tert.butylfuran (77) (73.5% b.p. 140°)

Found        C 78.25   H 10.4%
C₉H₁₄O requires  C 78.2   H 10.2%
i.r. 3120 (CH str. unsat.); 2980, 2940, 2920, 2885 (CH str. aliphatic); 1622, 1568 (C = C str. furan).
u.v. 272 (log₁₀ε 2.75)

Spin decoupling studies in the p.m.r. spectrum of 3-acetyl-5-tert.butyl-2-methylfuran (81A)

Irradiation of the olefinic proton resonance line at 3.85Γ with radiation of 5mv and inspection of the resonance lines at 7.49Γ and 7.73Γ showed no apparent change.

Hydrolysis of ethyl-5-tert.butyl-2-methyl-3-furoate (79)

The ester (79) (50g) was heated under reflux in ethanolic sodium hydroxide (NaOH (100g) in ethanol (200ml) and water (400ml) for 20 hr. The resultant mixture was acidified to yield:

2-methyl-5-tert.butyl-3-furoic acid (82) (94.8%)

60.
Found  
C 65.8  
H 7.95%  
C_{10}H_{14}O_3 requires  
C 65.9  
H 7.75%  

i.r. 3400 - 2600 (broad OH = acid dimers); 1700,  
(C = 0 str. acid); 1620, 1585 (C = C str. furan).  
u.v. 253 (log_{10} ε 3.68).  

Decarboxylation of 2-methyl-5-tert.butyl-3-furoic acid (82)  

Cupric oxide (3g) was added to the acid (82) in quinoline (160 ml). The mixture was heated to 200°  
and fractionated through a long Vigreux column to yield 2-methyl-5-tert.butylfuran (77) b.p. 140° (80.4%)  
identical with previously isolated material.  

Acetylation of 2-methyl-5-tert.butylfuran (77)  

A mixture of the furan (77) (5g) in acetic anhydride (30 ml) and zinc chloride (1g) was heated under reflux 3 hr. The mixture was made alkaline with sodium hydroxide (6N) and then steam distilled to yield 3-acetyl-2-methyl-5-tert.butylfuran (81A) (82%) identical with previously isolated material.  

Acetylation of 2,5-dimethylfuran  

The above method was used to yield 3-acetyl-2,5-dimethylfuran (83), (32.5%) b.p. 190 - 200° (Lit. 55 193 - 196°)  

Reduction of 3-acetyl-2-methyl-5-tert.butylfuran (81A)  

The ketone (81A) (1.8g) was stirred 3 hr. with sodium borohydride (0.42g) in methanolic sodium hydroxide at room temperature to yield:  

m.p. 88 - 92°.
1-(2-methyl-5-tert.butyl-3-furyl) ethanol (84) 98%

from hexane m.p. 57.5 - 59°

Found     C 72.25     H 9.9%

C_{11}H_{18}O requires C 72.5     H 9.95%

i.r. 3300 (O-H str.); 2980, 2940, 2920, 2890 (CH str. aliphatic); 1640, 1575 (C=C str. furan).

Reaction of 1-methyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (69) with buta-1,3-diene

A mixture of (69) (2g), hydroquinone (a trace) and butadiene (0.75g) was heated at 70° for 14 days in a sealed tube to yield:

5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9-methyl-9,10-epoxynanthracene (86) (98%) m.p. 58 - 59° cuboids.

Found     C 63.1     H 4.3%

C_{15}H_{12}F_4 requires C 63.4     H 4.25%

i.r. 3050, 3035, 3015 (CH str. unsat.); 2965, 2910, 2855, (CH str. aliphatic); 1640 (C=C str.); 1500 (highly fluorinated aromatic ring); 712 (cis olefine).

u.v. 261 (log_{10} E 2.51); 280 (sh) (log_{10} E 2.09).

Hydrogenation of 5,6,7,8-tetrafluoro-9-methyl-1,4,4a,9,9a,10-hexahydro-9,10-epoxynphanthracene (86)

(86) gave 5,6,7,8-tetrafluoro-9-methyl-1,2,3,4,4a,9,9a,10-octahydro-9,10-epoxynanthracene (87) (100%)

m.p. 74.5 - 75°

Found     C 63.0     H 4.95%

C_{15}H_{14}F_4 requires C 62.95     H 4.95%

i.r. 2960, 2925, 2880 (CH str. aliphatic); 1508, 1495 (highly fluorinated aromatic ring); 1408, 1047, 940,
Action of acid on 5,6,7,8-tetrafluoro-9-methyl-1,2,3,4, 4a,9,9a,10-octahydro-9,10-epoxyanthracene (87)

(87) (100 mg) in acetic anhydride (25 ml) containing hydrobromic acid (5 ml) was heated under reflux for 4 hr. On cooling needles of 5,6,7,8-tetrafluoro-9-methyl-1,2,3,4-tetrahydroanthracene (88) separated m.p. 114.5 - 115°. Further product was isolated on evaporation of the mother liquors (total yield after recrystallisation 95%).

Found  C 67.3  H 4.4%

C_{15}H_{12}F_4 requires  C 67.15  H 4.5%

i.r. 2960, 2890, 2860 (CH str. aliphatic); 1674, 1620, 1591 (C = C str. aromatic); 1515, 1485, 1007.

u.v. 271 (log\textsubscript{10} ε 3.56); 281 (log\textsubscript{10} ε 3.68); 290 (log\textsubscript{10} ε 3.71); 299 (log\textsubscript{10} ε 3.58); 325 (log\textsubscript{10} ε 2.73).

Reaction of 1,4-dimethyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (70) with buta-1,3-diene

A mixture of (70) (2g) hydroquinone (a trace) and butadiene (0.75g) was sealed in a Carius tube and heated at 70° for 14 days to yield:

5,6,7,8-tetrafluoro-9,10-dimethyl-1,4,4a,9,9a,10-hexahydro-9,10-epoxyanthracene (89) (100%) m.p. 86.5 - 88°

Found  C 64.65  H 4.75%

C_{16}H_{14}F_4O requires  C 64.45  H 4.75%

i.r. 3080, 3060, 3015, 3000 (CH str. unsat.); 2980
2955, 2945, 2920, 2860 (CH str. aliphatic); 1643
(C = C str.); 1500 (highly fluorinated aromatic ring);
712 (cis olefine).
u.v. 260 (log₁₀ ε 2.44); 280 (log₁₀ ε 2.02).
Hydrogenation of 5,6,7,8-tetrafluoro-9,10-dimethyl-
1,4,4a,9,9a,10-hexahydro-9,10-epoxyanthracene (89)
(89) gave 5,6,7,8-tetrafluoro-9,10-dimethyl-
1,2,3,4,4a,9,9a,10-octahydro-9,10-epoxyanthracene (90)
(100%) m.p. 123-123.5° as rods from hexane
Found  C 64.2  H 5.3%
C₁₆H₁₆OF₄ requires  C 64.0  H 5.35%
i.r. 3000, 2955, 2925, 2890 (CH str. aliphatic); 1500
(highly fluorinated aromatic ring); 1032 (C – F str.).
u.v. 259 (log₁₀ ε 2.47).
Action of acid on 5,6,7,8-tetrafluoro-9,10-dimethyl-
1,2,3,4,4a,9,9a,10-octahydro-9,10-epoxyanthracene (90)
(90) (100 mg) in acetic anhydride (25 ml)
containing conc. hydrobromic acid (5 ml) was heated
under reflux for 4 hr. On cooling needles of 5,6,7,
8-tetrafluoro-9,10-dimethyl-1,2,3,4-tetrahydroanthracene
(91) separated. m.p. 194-5°. Further product was
isolated from the mother liquor. (92% yield).
Found  C 68.2  H 5.1%
C₁₆H₁₄F₄ requires  C 68.1  H 5.0%
i.r. 2950, 2880, 2850 (CH str. aliphatic); 1672, 1579,
(C = C str. aromatic).
u.v. 287 (log₁₀ ε 3.72); 296 (log₁₀ ε 3.74); 331
(log₁₀ ε 3.11).

64.
Attempted reaction of 1-methyl-4-tert.butyl-5,6,7,8-tetrafluoro-1,4-dihydro-1,4-epoxynaphthalene (66) with buta-1,3-diene

No reaction was observed when a mixture of (66) (2g), hydroquinone (a trace) and butadiene (1g) were heated together in a sealed Carius tube for 14 days at 70° or 85°.

Reaction of tetrafluorobenzyne with 5,6,7,8-tetrafluoro-9-methyl-1,2,3,4-tetrahydroanthracene (88) (via the G.r. route, 10⁻² molar scale).

The crude product was purified by silica gel thick layer chromatography in hexane to yield recovered (88) and 5,6,7,8,11,12,13,14-octafluoro-1,2,3,4,9,10-hexahydro-9-methyl-9,10-o-benzenoanthracene (92) (47%) m.p. 126 - 9° rods from hexane.

Found C 60.25 H 2.95%

C₂₁H₁₂F₈ requires C 60.6 H 2.9%
i.r. 2955, 2900, 2875, 2855 (CH str. aliphatic); 1628 (C = C str. aromatic); 1500, 1480 (highly fluorinated aromatic ring); 1057, 982, 667.
u.v. 258 (log₁₀ε 3.09).

Reaction of tetrafluorobenzyne with 5,6,7,8-tetrafluoro-9,10-dimethyl-1,2,3,4-tetrahydroanthracene (91) (via the G.r. route, 10⁻² molar scale)

The crude reaction mixture was purified by t.l.c. to yield recovered (91) and 5,6,7,8,11,12,13,14-octafluoro-1,2,3,4,9,10-hexahydro-9,10-dimethyl
-9,10-o-benzenoanthracene (93) (52%) m.p. 130 - 131°.

Found C 61.3 H 3.4%
C_{22}H_{14}F_8 requires C 61.4 H 3.3%
i.r. 2985, 2955, 2900, 2880, 2860 (CH str. aliphatic);
1640 (C=C str olefinic); 1490 (highly fluorinated
aromatic ring); 1294; 1119; 1057, 892
u.v. 259 (log_{10} \varepsilon 3.24).

**Attempted dehydrogenation of 5,6,7,8-tetrafluoro-
9,10-dimethyl-1,4,4a,9,9a,10-hexahydro-9,10-
epoxyanthracene (89)**

A. With chloranil (equimolar reaction)

(89) (500 mg) and chloranil (420 mg) in xylene
(20 ml) were boiled under reflux for 3 hr.
Evaporation yielded a dark residue which was separated
by t.l.c. to yield only recovered (89)

B. With 10% palladium on carbon

(89) (30 mg) was heated with palladium (10% on
carbon) (30 mg) under nitrogen at 270° for 10 mins.
The mixture was ether extracted to yield a dark solid
shown by t.l.c. to be a complex mixture.

**Attempted dehydrogenation of 5,6,7,8-tetrafluoro-
methyl-1,4,4a,9,9a,10-hexahydro-9,10-epoxyanthracene**
(86)

a) With chloranil (equimolar reaction)

(86) (500 mg) and chloranil (400 mg) in xylene
(20 ml) after boiling 3 hrs, under reflux yielded only
recovered starting material (86).
b) With 10% palladium on carbon

(86) (50 mg) was heated with 10% palladium on carbon (50 mg) under nitrogen at 200° for 5 min. Extraction with ether yielded a solid which was shown by t.l.c. to be a complex mixture.

c) With dichlorodicyanobenzoquinone (D,D,Q.) (equimolar reaction)

(83) (500 mg) and D,D,Q. (420 mg) in xylene were boiled under reflux for 10 hr. On cooling the black precipitate of hydroquinone was separated. The xylene solution was evaporated and the residue separated by t.l.c. in benzene chloroform. The resultant products were shown to be impure phenolic compounds (by FeCl₃ test and i.r.). The mixture was therefore boiled under reflux for 1 hour with acetic anhydride and found on re-examination by t.l.c. to be a complex mixture. No further investigation was carried out.

Attempted dehydrogenation of 5,6,7,8-tetrafluoro-9,10-dimethyl-1,2,3,4-tetrahydroanthracene (91)

(91) (100 mg) and chloranil (100 mg) were heated in xylene (10 ml) under reflux. After 20 hr, only (91) was recovered in good yield from the mixture.

Attempted dehydrogenation of 5,6,7,8-tetrafluoro-9-methyl-1,2,3,4-tetrahydroanthracene (88)

(88) (100 mg) and chloranil (100 mg) in xylene (20 ml) similarly gave only recovered (88) after
48 hrs. heating under reflux.

**Reaction of 5,6,7,8-tetrafluoro-1,4,4a,9,9a,10-hexahydro-9,10-dimethyl-9,10-epoxyanthracene (89)** with acetic anhydride

(89) (1g) in acetic anhydride (70 ml) and hydrobromic acid (10 ml) was boiled under reflux under nitrogen for 4 hr. On cooling the crystals which separated were collected and recrystallised from ethanol to yield:

5,6,7,8-tetrafluoro-9,10-dimethyl-1,4-dihydroanthracene (94) (72%) m.p. 154 - 156° needles from methanol

i.r. 2970, 2910, 2860 (CH str. aliphatic); 1668, 1580, 1528 (C=C str. aromatic); 1394, 1378, 1268, 1157, 1046, 935.

u.v. 267 ($\log_{10} \varepsilon$ 3.83); 288 (sh) ($\log_{10} \varepsilon$ 3.79); 298 ($\log_{10} \varepsilon$ 3.82); 309 (sh) ($\log_{10} \varepsilon$ 3.69); 331 ($\log_{10} \varepsilon$ 3.04).

p.m.r. 3.95 (broad singlet) (2 olefinic protons); 6.50 (broad singlet) (4 methylene protons); 7.33 (multiplet) (6 methyl protons).

**Hydrogenation of 5,6,7,8-tetrafluoro-9,10-dimethyl 1,4-dihydroanthracene (94)** gave 5,6,7,8-tetrafluoro-9,10-dimethyl-1,2,3,4-tetrahydroanthracene (91) (100%) identical with previously isolated material.

**Attempted dehydrogenation of 5,6,7,8-tetrafluoro-9,10-dimethyl-1,4-dihydroanthracene (94)**

(94) (100 mg) and chloranil (100 mg) were heated under reflux for 4 hours in xylene (10 ml). A complex mixture (by t.l.c.) was isolated and not further investigated.
CHAPTER 4

4.1. Introduction

Although the precise mechanism of the cycloaddition reactions of tetrafluorobenzyne is at present unknown some considerations do allow certain generalisations to be made.

No positive evidence has been adduced which supports the idea that benzyne exists as a diradical although electron paramagnetic techniques have been used in studies of the decomposition of a number of benzyne precursors. Recent calculations are in accord with a singlet structure in which the two electrons are in the lower symmetric orbital.

The Woodward-Hoffman rules indicate that the formation of 1,4-adducts by an ionic mechanism could either occur by a concerted or stepwise mechanism. But one would predict that the transition state for a concerted reaction would be of lower energy than that of a dipolar intermediate. Reactions of benzyne with trans,trans-hexa-2,4-diene show that the 1,4-cycloadduct is formed sterospecifically and hence by a concerted mechanism.

Work in the laboratory on the reactions of tetrafluorobenzyne with aromatic hydrocarbons has shown a lack of evidence for a stepwise cycloaddition mechanism. Such a mechanism would involve the same initial steps as the electrophilic substitution of
an aromatic ring, followed by collapse of the Zwitterion intermediate to yield product. It should be possible however to yield insertion products by expulsion of a proton on this mechanism (Scheme 42). In all cases examined the products isolated arose from 1,4-cycloaddition reactions and no evidence for insertion or 1,2-addition products was found. Such evidence mitigates against a stepwise mechanism. Friedman and Stiles have shown however in the reaction of benzyne with benzene that 1,2-adducts and insertion products are formed in low yields. In the presence of silver ions the ratio of 1,4-adducts to other products is reduced from 88 : 12 to 17 : 83 whilst the ratio of 1,2-adducts rose from 12 to 53. Friedman explains this in terms of a two step mechanism (Scheme 44).

It has been shown that a strong steric effect exists in the bridgehead tert-butylbenzene-tetrafluorobenzene adduct (5, R = t-Bu). A similar effect may be expected to operate in the transition state involved in a concerted mechanism resulting in reduced yields of bridgehead adducts. Such an effect was not observed and the ratio of bridgehead to non-bridgehead adducts formed were in general those statistically predicted. However, as mentioned in connection with the reaction of tetrafluorobenzene with anisole a non-symmetrical transition state

70.
would explain the observed results without changing the essentially concerted nature of the reaction.

**Discussion**

In view of these results the reactions of tetrafluorobenzyne with aromatic hydrocarbons were extended by studying the reactions with several polycyclic ring systems.

We investigated the reaction of tetrafluorobenzyne with phenanthrene. T.l.c. investigation of the crude mixture showed the presence of one major product and several extremely minor products (combined yield less than 1%). U.v. and p.m.r. spectroscopy of the major product showed the presence of a naphthalene chromophore and 2 dissimilar bridgehead protons. The structure is therefore undoubtedly (95).

The reaction of tetrafluorobenzyne with acenaphthene was also investigated. A single product was isolated in 53% yield. Elemental analysis confirmed a 1 : 1 addition reaction had occurred. P.m.r. studies showed the structure to be that of the cycloadduct (96). Hydrogenation over palladium on carbon led to the reduced adduct (97). No evidence was found for insertion or 1,2 cycloaddition products.

We then studied the reaction of acenaphthylene with tetrafluorobenzyne to see if we could obtain a 1,2-cycloadduct from reaction of tetrafluorobenzyne
with the nucleophilic olefinic double bond. Removal of excess acenaphthylene by steam distillation followed by trituration caused the crude product to crystallise. Separation and recrystallisation of the crystalline product yield a single compound which was showed by spectroscopic methods to be the 1,2-cyclo adduct (98).

Examination of the mother liquors showed that a second product was present. Attempted separation by t.l.c., however, failed to yield a pure product as decomposition was apparently occurring. In view of this we were unable to characterise fully the second product.

Vogel and his coworkers have studied the chemistry of non-benzenoid aromatic ring systems. In particular they have studied the chemistry of bridged cyclodecapentaene ring systems (100) and produced evidence for the delocalised ring structure (100A) in several derivatives. They report the addition of dimethyl acetylene dicarboxylate with (100) to form the Diels-Alder adduct (101).

We wished to investigate the reaction of tetrafluorobenzyne with this ring system. Vogel has reported the synthesis of (100) from naphthalene (Scheme 48) and so (100) was prepared and reacted with tetrafluorobenzyne to yield a single product which was separated from excess (100) by preparative
scale G.l.c. and shown by spectroscopy to be the adduct (102). We have been unable to decide whether the adduct structure is endo or exo (i.e. (102A) or (102B)) since the spectral data may be explained for either. Hydrogenation of the adduct double bonds was expected to be of use in differentiating between (102A) and (102B) by a p.m.r. study. Unfortunately however when hydrogenation was attempted the cyclopropane ring was cleaved to yield a highly hydrogenated compound (presumably (103)). Vogel reports the endo structure (101) for the dimethyl acetylene dicarboxylate - (100) adduct.

We have investigated the pyrolysis of the adduct (102) to see if the novel bridged benzocyclodecapentaene ring (104) could be isolated by loss of acetylene from the adduct (Scheme 51). The expulsion of an acetylene constitutes the major pathway to fragmentation of benzobarralenes. Loss of benzo-cyclopropene occurred however and tetrafluoronaphthalene was isolated in good yield. A similar fragmentation was observed from the molecular ion in mass spectrometric studies. These results are analogous to Vogels results with the pyrolysis of (101) (Scheme 50).
It has been reported that benzyne reacts with 6,6-dimethylfulvene (105) to yield the 1,4-cycloadduct (106) (Scheme 52). We expected that by reacting tetrafluorobenzyne with (105) to isolate the related tetrafluoro 1,4-cycloadduct (107) which we intended to use in photochemical studies. Separation of the crude product from the reaction involving the lithium compound route yielded two products which we believed were the 1,4-cycloadduct (107) and a 1,2-cyclo adduct (108). However mass spectrometric studies showed that both these products contained two C₆F₄ units to one mole of 6,6-dimethylfulvene.

Four possible structures were considered for these products. I.r. and p.m.r. studies showed the presence of olefinic protons and hence rule out structures (109) and (110).

Examination of one of the adducts showed the presence of a weak benzenoid chromophore by u.v. spectroscopy. I.r. spectroscopy showed the presence of olefinic bands. P.m.r. spectroscopy gave resonances at (\( \delta \)) 3.15 (triplet) (2 olefinic protons); 5.36 (broad multiplet) (2 bridgehead protons); 8.46 (singlet) (6 methyl protons). The molecular ion peak appeared at 402. The symmetrical nature of the p.m.r. spectrum and equivalence of the methyl group would indicate the structure to be (111). The bridgehead and olefinic protons would approximate to an AA'BB' spectrum with complications to the AA' part because of long range coupling with the aromatic fluorine atoms. The symmetrical nature of the molecule explains the equivalence of the methyl groups. We suggest the fragmentation of the molecule occurs as in Scheme 54.
Two configurations of (111) are possible depending upon whether the benzyne attack is endo or exo (Scheme 55). It is anticipated that in both cases the methyl groups would be shielded by either the olefinic double bond or the aromatic π cloud. From Dreiding models the distances apart appear to be similar in each case. Reduction of the olefinic double bond would be anticipated to cause a large shift in the methyl group resonance position for (111A) and only a small change for (111B). When reduction was carried out one molecule of hydrogen was absorbed to yield the dihydro compound (112). The methyl resonance appeared at 9.16 ppm showing a shift of 0.7 ppm on hydrogenation. On the basis of this evidence we believe the configuration to be (111A).

The second compound (113) similarly showed the presence of olefinic bonds in the i.r. spectrum, and a benzenoid chromophore in the u.v. spectrum. P.m.r. spectroscopy showed 2 olefinic protons at (τ) 3.10, 2 dissimilar bridgehead protons with peaks at 5.28 and 5.88, and 2 dissimilar methyl groups with singlets at 8.42 and 8.52. Mass spectrometry showed a stable molecular ion peak at 402 with loss of CH₃ to yield a peak at 387. On the basis of this spectral data we believe the structure to be (113).

The reaction of fulvenes with aryl lithium reagents is well known. We suggest that a similar reaction occurs with pentafluorophenyl lithium prior to generation of the benzyne and the reactions to generate (111) and (113) occur as shown in Scheme 56.
In view of this unexpected result with tetrafluorobenzine we re-examined the reaction\(^\text{62}\) of (105) with benzyne. The reported 1,4-cycloadduct (106) was isolated in 31\% yield and its structure confirmed.

We believed the difference between the two reactions to be further evidence of the effect of electronegative groups on benzyne upon the ease of undergoing cyclo addition reactions. We therefore examined the reaction of tetrachlorobenzine with dimethylfulvene (105). No evidence was found for a 2 to 1 tetrachlorobenzine adduct. The single product of reaction using both the lithium compound route and the tetrachloroanthranilic acid route was the 1,4 adduct (114).

The possibility that larger groups than methyl on the fulvene would retard the formation of 5,6-cyclo addition reactions of the fulvene was examined. The reaction of tetrafluorobenzine with 6,6-di-n-propylfulvene was carried out using the lithium compound route to determine if any 2 to 1 benzyne to fulvene adducts could be isolated. A single compound only was isolated and shown to be the 1,4-cyclo adduct (115).

It therefore appears that the 2 to 1 benzyne to fulvene reaction is peculiar to the dimethylfulvene-tetrafluorobenzine reaction, since it has not been observed in other reactions. Work is however continuing in this laboratory\(^\text{64}\) to try to explain these observations further.
Experimental

Reaction of benzyne with 6,6-dimethylfulvene

0-Bromo trifluorobenzene (3.75g) and 6,6-dimethylfulvene (5.24g) in dry tetrahydrofuran (60 ml) was added dropwise onto magnesium turnings (1.22g) with vigorous stirring under nitrogen. When the addition was complete the mixture was heated under reflux for 1½ hr. The bulk was reduced under reduced pressure and poured onto ice. The product was extracted with ether, dried over sodium sulphate and the pure product isolated by silica gel column chromatography to yield:

7-isopropylidene-2,3-benzonorbornadiene (106) (31.4%)
m.p. 90-91° (lit. 91-91.5)
p.m.r. \( A_2B_2 \) multiplet at 3.0 (4 aromatic protons), triplet at 3.22 (2 olefinic protons), triplet at 5.77 (2 bridgehead protons), singlet at 8.46 (6 methyl protons).

Reaction of tetrafluorobenzyn with 6,6-dimethylfulvene
(via the lithio compound route)

Excess dimethyl fulvene was distilled from the crude product under reduced pressure. The crude product was then separated by t.l.c. on silica gel in hexane to yield:

a) 7,7-(2\(^{1,2}\),2\(^{1,2}\)-spiro-1,1\(^{1,2}\)-dimethyl-tetrafluorobenzocyclobutenyl) tetrafluorobenzonorbornadiene (111). (24%) m.p. 76-80° from hexane
p.m.r. \( \gamma \) 3.15 (triplet) (2 olefinic protons);
5.36 (broad multiplet) (2 bridgehead protons);
\( '8.46 \) (singlet) (6 methyl protons);

i.r. 3050, 3035 (CH str. olefinic); 2990, 2950,
2930, 2000, 2870 (CH str. aliphatic); 1505, 1400
(highly fluorinated aromatic ring); 1302, 1283, 1176,
1121, 1060, 1040, 955, 825, 750 cm\(^{-1}\).

u.v. 250 n.m. (log \(10 \Sigma 3.16\))

Mass Spectrometry \(\frac{M^+}{M} = 402\) (100%); \(\frac{M^+}{-CH_3} = 297\)
(54%); \(\frac{M^+}{C_6F_4} = 254\) (58%); \(\frac{M^+}{C_6F_4-CH_3} = 239\)
(46%); \(\frac{M^+}{C_6F_4-CH_3-HF} = 219\) (33%).

and b) 7,7-(2\(^1\),2\(^1\)-spiro-1\(^1\),1\(^1\)-dimethyl-tetrafluorobenzo-
cyclobutetyl)tetrafluorobenzobicyclo (3,2,0) hept-
3,6-diene (113) (16%) m.p. 79-82° from hexane
p.m.r. (\(\delta\)); 3.10 (multiplet) (2 olefinic protons);
5.28 (multiplet) (1 methine proton); 5.58 (multiplet)
(1 methine proton); 0.42 (singlet) (3 methyl protons);
0.52 (singlet) (3 methyl protons)

i.r. 3090, 3030, 3000 (CH str. unsat.); 2940, 2800
(CH str. aliphatic); 1660, 1640, 1618 (C=C str.);
1506, 1470 (highly fluorinated aromatic ring); 1303,
1225, 1098, 1067, 995, 760, 720.

u.v. 222 (log \(10 \Sigma 3.03\))

Hydrogenation of 7,7-(2\(^1\),2\(^1\)-spiro-1\(^1\),1\(^1\)-dimethyl-tetra-
fluorobenzocyclobutetyl) tetrafluorobenzonorbornadiene (111)
gave 7,7-(spiro-1\(^1\),1\(^1\)-dimethyl-tetrafluorobenzocyclobutetyl)
tetrafluorobenzonorbornene (112) (100%)
m.p. 26-30°.

76.
p.m.r. (\(\gamma\)) 6.48 (broad multiplet) (2 bridgehead protons)
7.87 - 9.13 (multiplet) (4 methylene protons)
9.16 (singlet) (6 methyl protons)

i.r. 2970, 2940, 2900 (CH str. aliphatic); 1508, 1490 (highly fluorinated aromatic ring); 1410, 1320, 1043, 950
u.v. 260 (\(\log_{10}E\) 2.68)

**Reaction of tetrachlorobenzyn with 6,6-dimethylfulvene**

A) **Via the lithium compound route**

Excess 6,6-dimethylfulvene was removed from the crude product under reduced pressure. TLC purification of the residue in hexane on silica gel gave:

1,2,3,4-tetrachloro-7-isopropylidenebenzonorbornadiene (114) (41%) m.p. colourless gum.

p.m.r. (\(\gamma\)) 3.10 (triplet) (2 olefinic protons)
5.37 (triplet) (2 bridgehead protons)
8.56 (singlet) (6 methyl protons)

i.r. 3030, 2990, 2945, 2915, 2870, 1403, 1378, 1360, 1294, 1207, 1160, 1136, 796, 750, 711, 704, 699
u.v. 233 (\(\log_{10}E\) 3.06), 238 (\(\log_{10}E\) 3.06)

B) **Via the tetrachloroanthranilic acid route**

Tetrachloroanthranilic acid (5.5g) in ether (20 ml) and dichloromethane (60 ml) was added dropwise over 1 hr. to dimethyl fulvene (4.24g) dissolved in a mixture of dichloromethane (50 ml) and isoamyl nitrite (7 ml) at 40°. The mixture was stirred at 40° for a further 1 hr. and evaporated to dryness under reduced pressure. Isoamyl alcohol and isoamyl nitrite was removed by azeotroping...
with toluene to yield a black solid residue. Silica gel column chromatography of this residue in hexane yielded: 1,2,3,4-tetrachloro-7-isopropylidenebenzonorbornadiene (114) (56%) identical with previously isolated material

**Reaction of tetrafluorobenzene with di-n-propylfulvene**

(via the lithium compound route)

The crude product was distilled under reduced pressure to yield a pale yellow oil which was finally purified by t.l.c. in hexane on silica gel to yield: 7,7-hept-4-enyldene-2,3-benzonorbornadiene(115) (32%) as an oil

p.m.r. (7) 3.11 (triplet) (2 olefinic protons)
5.30 (multiplet) (2 bridgehead protons)
7.98 - 9.31 (multiplet) (14 aliphatic protons)
i.r. 3085, 3035, 2975, 2945, 2885, 1507, 1487, 1304, 1174, 1129, 1054, 958, 825, 760.
u.v. 256 (log₁₀E 2.74)

**Reaction of tetrafluorobenzene with acenaphthene** (via the Grignard reagent route).

Acenaphthene was steam distilled from the crude reaction mixture which was recrystallised from hexane to yield:

7,8,9,10-tetrafluoro-6,10a-dihydro-6,10a-etheno-aceanthrene (96) (53%) m.p. 106 - 143°.

Found
C₁₈H₁₀F₄ \( \text{requires} \) C 71.55 F 24.7 H 3.55%

C₁₈H₁₀F₄ \( \text{requires} \) C 71.55 F 25.1 H 3.35%
p.m.r. (7) 2.75 - 3.25 (multiplet)(5 aromatic protons)
4.39 - 4.55 (multiplet)(1 bridgehead methine proton)
6.05 - 7.44 (multiplet)(4 methylene protons)
i.r. 3080 (olefinic CH str.); 3030, 3010 (aromatic CH str.)
2955, 2930, 2880, 2850 (aliphatic CH str.) 1640 (C=C str.)
1480 (highly fluorinated aromatic ring); 1068 (CF sym. str.);
1048 (CF assym str.).
u.v. 262 (log₁₀ ε 2.96).

Hydrogenation of 7,8,9,10-tetrafluoro-6,10a-dihydro-6,10a-
ethenoanthrene (96) gave:

7,8,9,10-tetrafluoro-6,10a-dihydro-6,10a-ethanoanthrene
(97)(100%) m.p. 109-110°C

Found         C  70.8   H  4.0%
C₁₈H₁₉F₄ requires C  71.05  H  4.0%
p.m.r.(τ) 2.87 (singlet)(3 aromatic protons); 5.22
(singlet)(1 bridgehead proton); 6.27 - 7.66 (multiplet)
(4 methylene protons); 8.02 - 8.74 (multiplet)(4 methylene
protons).
i.r. 2990, 2960, 2890, 2870 (CH str. aliphatic); 1503,
1490, 1475 (highly fluorinated aromatic ring); 1321, 1110,
1084, 1043, 920, 830, 794, 778.
u.v. 263 (log₁₀ ε 2.89).

Reaction of tetrafluorobenzynie with phenanthrene (via the
Grignard reagent route)

Excess phenanthrene was sublimed from the crude product
which was purified further by t.l.c. in hexane on silica
gel to yield:

8,9,10,11-tetrafluoro-7,12-dihydro-7,12-ethenobeno (a)
anthracene (95) (41%) as an oil. Separated from methanol
as a glass m.p. 56-58°C.

Found         C  73.2   H  3.25%
C₂₀H₁₀F₄ requires C  73.5   H  3.1%

81.
Reaction of tetrofluorobenzylene with 1,6-methanocyclodecapentaene
(via the Grignard reagent)

The crude product was separated by preparative g.l.c. on a 5 ft. SE,52 column at 200° to yield a pale yellow oil which was purified by t.l.c. on silica gel in 20% benzene in hexane to yield:

5,6,7,8-tetrafluoro-4a,9a,10-tetrahydro-4a,9a-methano-9,10-ethenoonthracene102)(66%) m.p. 53 - 75° (decomp)

Found C 70.3 H 3.45%

C₁₇H₁₀F₄ requires C 70.35 H 3.45%

p.m.r. (r) 3.68 (triplet)(2 olefinic protons); 4.19 (multiplet)(4 olefinic protons); 5.59 (multiplet)(2 bridgehead protons); 7.76 (doublet J=6Hz)(1 cyclopropane proton); 10.03 (doublet J=6Hz)(1 cyclopropane proton).

i.r. 3075, 3050, 3015 (CH str. unsat.); 2980, 2940, 2870 (CH str. aliphatic); 1630 (C=C str.); 1510, 1495 (highly fluorinated aromatic ring); 1087, 1048, 1021 (ring def. of cyclopropane); 925, 899, 874, 847, 723, 678, 657.

u.v. 271 (log₁₀ E 3.20) in cyclohexane.
Hydrogenation of 5,6,7,8-tetrafluoro-4a,9,9a,10-tetrahydro-4a,9a-methano-9,10-ethenoanthracene (102) resulted in cleavage of the cyclopropane ring in (102) p.m.r. 8.40 - 9.15 (multiplet). The product was not further studied.

Pyrolysis of 5,6,7,8-tetrafluoro-4a,9,9a,10-tetrahydro-4a,9a-methano-9,10-ethenoanthracene (102) at 375° gave 1,2,3,4-tetrafluoronaphthalene (72%) identical with authentic material.

Reaction of tetrafluorobenzylene with acenaphthylene

Excess acenaphthylene was steam distilled from the crude product which was triturated with hexane to cause crystallisation. Separation of the crystals and purification by recrystallisation from hexane yielded:

7,8-tetrafluorobenzocyclobutaacenaphthylene (98) (42%)
m.p. 233 - 234° as needles from hexane

Found  C 72.0  H 2.65%

C₁₈H₆F₄ requires  C 72.0  H 2.65%
p.m.r. (γ) 2.18 - 2.53 (multiplet)(6 aromatic protons);
4.67 (broadened singlet)(2 methine protons)
i.r. 3050 (CH str. unsat.); 2950 (CH str. aliphatic);
1618, 1604 (C=C str. aromatic); 1495, 1470 (highly fluorinated aromatic ring); 1278, 1133, 1056, 972, 934, 817, 778, 775.
u.v. 269, 279, 291, 301, 317 in cyclohexane.

Separation of the mother liquors by t.l.c. in hexane on either silica gel or alumina yielded a further quantity of (98) (overall 42%) and a second compound (99) which could not be isolated pure

p.m.r. showed 2.57 - 2.75 (multiplet)(3 protons);
3.45 - 3.80 (multiplet)(3 protons); 5.58 - 5.90 (multiplet)
(2 protons).
CHAPTER 5

P.m.r. Spectral Data Long range $^{19}F$ - $^1H$ coupling and hindered rotation studies

Long range coupling has been reviewed and discussed in terms of specific arrangements of the nuclei involved. The requirement of a near planar zig-zag configuration has been emphasised. Although long range coupling between nuclear and side chain protons is not normally observed in the p.m.r. spectra of aromatic compounds, $^{19}F$ - $^1H$ coupling has been reported between ring fluorine atoms and side chain protons separated by 5 bonds. It was suggested the effect could be "through space" or through the 5 bonds. Later work carried out in this laboratory with 1,4-cycloadducts derived from tetrafluorobenzene and alkylbenzenes has shown long range coupling between ring fluorine atoms and side chain protons separated by up to 6 bonds. These results were best explained using the "through space" concept involving angular dependence and a proximity factor.

Many of the compounds reported in this thesis exhibited long range coupling between bridgehead substituents and aromatic fluorine atoms. The results with these compounds are best explained using the "through space" concept of coupling. The spectral data collected during this research are summarised in Tables 4. The main points of interest are described for the major types of compound studied.
Series 4.1. and 4.2. compounds

Bridgehead protons showed long range coupling with fluorine atoms at positions 5 and 8 but because further spin-spin coupling to adjacent protons occurred the resonances appeared as complex multiplets and were not analysed in detail.

The bridgehead methoxyl protons in these compounds exhibited long range coupling constants of \( J = 2.0 - 2.6 \) Hz and appeared as doublets. Distances and angles between methoxyl protons and fluorine atoms appear from models to be very similar in both series and probably explains the similarity in size of coupling constant and \( ABX \) coupling of the olefinic protons (see later) observed in both series.

Coupling constants for methyl substituents in series (4.1) were larger than the corresponding methoxyl coupling constants. Thus in (35) \( J \) methyl = 5.4Hz compared with \( J \) methoxyl = 2.1Hz. We believe this difference is a further example of the proximity effect, in that the distance between the methyl protons and the fluorine atoms is less than the distance between the methoxyl protons and the fluorine atoms.

The olefinic region of the spectrum of monosubstituted bridgehead adducts from both series 4.1 and 4.2 give rise to the anticipated 8 line multiplets for the AB protons of an \( ABX \) system. Full analyses by the method of Banwell have been completed and the calculated spectra showed good correlation with the observed spectra. Thus calculated spectra (olefinic regions only shown) for (17) (series 4.1) and (26) (series 4.2)
are shown in Scheme 57. It is notable that (22) is an exception and did not exhibit an ABX multiplet for the olefinic protons. This characteristic ABX multiplet for the olefinic protons was also observed in the spectra of (14) and (49) (Table 4.8).

The ring methylene protons next to unsubstituted bridgehead positions in the ketone series (4.2) exhibited characteristic 8 line multiplets due to the AB protons of an ABX system. This pattern was similarly observed in the spectrum of (31). Full analysis of the methylene protons of (22) was completed and the calculated spectrum showed good agreement with the spectrum observed (Scheme 58). This ABX pattern was indicated in the spectrum of (36) but because the olefinic methyl group resonance appeared at the same position in the 60 m Hz spectrum we were unable to analyse the spectrum fully. At 220 M Hz the spectrum was readily analysed as an ABX system. The two spectra are shown in Scheme 59.

Series 4.3 Compounds

In general long range coupling constants for this series of hydrogenated adducts were larger than for the corresponding adducts (series 4.1 and 4.2). This observation is in agreement with previous work on alkylbenzene-tetrafluorobenzene adducts. 35,27
Series 4.4, 4.5 and 4.6 Compounds

Long range coupling constants in this series were very small compared with coupling constants for the analogous substituted benzene-tetrafluorobenzene adducts (5). We believe this is due to the distortion of the bridgehead substituent from planarity with the ring fluorine atoms which occurs in this ring system.

Studies on compound (66) showed a distorted AB quartet for the olefinic protons. We believed that this distortion may be due to coupling of the 2-position proton with the methyl protons at position 1. However, spin-spin decoupling studies showed on irradiation of the methyl signal no apparent change in the olefinic resonance.

Long range coupling constants for coupling between the methyl protons and between the tert.butyl protons and the perifluorine atoms at positions 5 and 8 were again small (1.2 Hz and 0.8 Hz respectively).

Previous studies \(^{35}\) have shown a strong steric effect existed in compound (5, \(R = t.Bu.\)). The p.m.r. spectrum at room temperature showed magnetic non-equivalence between the methyl groups. This was believed to be due to the conformation (5A). At elevated temperatures (200\(^{\circ}\)) the methyl groups were all magnetically equivalent and the resonance appeared as a simple doublet (due to \(^{19}F - ^1H\) coupling). We therefore anticipated some steric effect would operate in (66). The tert.butyl and methyl groups in (66) appeared as simple doublets.
showing no restriction to rotation at room temperature. A variable temperature p.m.r. study was therefore completed (temperature range $^{+}40^\circ - ^{-}110^\circ$) to determine if any restriction to rotation was present at lower temperatures. At about $^{\sim}40^\circ$ broadening of both the methyl and t.butyl peaks occurred. The resonance due to the t.butyl group at $^{\sim}90^\circ$ to $^{\sim}110^\circ$ although considerably broadened was resolved into 2 peaks indicating some hindrance of rotation and a preferred conformation (presumably 66A) (Scheme 61).

Series 4.7 and 4.8 Compounds

Alkyl substituents in 1 and 4 positions in the naphthalene series (4.7) and in 9 and 10 positions in the anthracene series (4.8) exhibited large long range coupling constants whilst methoxy protons in these positions exhibited only broadening of the singlet resonance. Thus in (39) the methoxyl signal showed only a broadened singlet whilst the methyl signal showed as a doublet $J_H - F = 9.0$ Hz. This difference may be explained by a proximity effect in that the bond lengths are different and the methoxyl protons do not approach as closely to the fluorine atoms as the methyl protons, or by considering a contribution of "through bonds" coupling which would involve coupling through an oxygen atom for the methoxyl protons.

Dimethyl 1,4-substituted compounds were found to exhibit a multiplet signal for the methyl protons which we named the 'Batman' multiplet, because of its shape. (see (75) in Scheme 62)
The multiplet shape was unchanged in variable temperature p.m.r. studies (\(+40^\circ\) to \(+100^\circ\)) and appears typical of 1,4-dimethyl substitution.

The spectrum of (67) was investigated at various temperatures for hindrance of rotation of the t.butyl group as with (5 R = t.Bu) and (66). No change in the signal was observed between \(+40^\circ\) and \(-100^\circ\).
Scheme 1

Fig. 1

$X = \text{H or F}$
Scheme 2.

\[
\begin{align*}
\text{A} & \quad \text{F, Cl, Br.} \\
\text{M} & \quad \text{Li, Na.} \\
\text{R} & \quad \text{Me, Ph, tBu, nBu.}
\end{align*}
\]

Scheme 3.

\[
\begin{align*}
\text{A} & \quad \text{halogen.} \\
\text{M} & \quad \text{Li, Na, K.} \\
\text{Y} & \quad \text{NH}_2, \text{NMe}_2, \text{HN}\]
\]
Scheme 4.

A = halogen.
R = Me, Ph, nBu.

Scheme 5.
Scheme 6

Scheme 7
Scheme 8

\[
\begin{align*}
&\text{Scheme 9} \\
R = \text{Me, Et, iPr, tBu.}
\end{align*}
\]
Scheme 10

Fig. 2
Scheme 11

10 \[ \xrightarrow{\text{H}^+} \] 11a or 11b

7a \[ \xrightarrow{} \] 7b

Scheme 12

7b \[ \xrightarrow{\text{OCH}_3} \] 12

12 \[ \xrightarrow{\text{H}^+} \] 13
Scheme 13
Scheme 14.1
Scheme 14.2
Scheme 20
Scheme 22

Scheme 24

Scheme 25
Scheme 23
Scheme 26
Scheme 27.
Scheme 28

$R=H=\text{Series A}$

$R=\text{Me}=\text{Series B}$
Scheme 29

Scheme 30
\[
\begin{array}{c}
\text{Scheme 31A} \\
\text{sensitised} = 61(66\%) + 62(\text{trace}) \\
\text{unsensitised} = 61(17\%) + 62(56\%)
\end{array}
\]
Scheme 33

\[ R^1 = R^2 = R^3 = R^4 = H = 4 \]
\[ R^1 = \text{OMe}, R^2 = R^3 = R^4 = H = 26 \]
\[ R^1 = R^3 = R^4 = H, R^2 = \text{OMe} = 22 \]
\[ R^1 = \text{OMe}, R^2 = R^4 = H, R^3 = \text{Me} = 47 \]
\[ R^1 = R^2 = R^3 = H, R^4 = \text{Me} = 36 \]

Scheme 34

\[ R^1 = R^2 = R^4 = H \]
\[ R^1 = \text{OMe}, R^2 = R^4 = H = 7 \]
\[ R^1 = R^2 = H, R^4 = \text{Me} = 41 \]
Scheme 36

\[
\begin{align*}
\text{R}^1 & \text{R}^2 \\
\text{F} & \text{F} \\
5 & 65
\end{align*}
\]

Scheme 37

\[
\begin{align*}
\text{R}^1 & \text{R}^2 \\
\text{F} & \text{F} \\
64 & 94
\end{align*}
\]
Scheme 38

$\text{Br} \quad \text{tBu} \quad \xrightarrow{80\%} \quad \text{CO}_2\text{Et} \quad \text{tBu} \quad \xrightarrow{66\%} \quad \text{CHOHMe} \quad \text{tBu} \quad \xrightarrow{100\%} \quad \text{COMe}$

$\text{CO}_2\text{Et} \quad \text{tBu} \quad \xrightarrow{95\%} \quad \text{CO}_2\text{H} \quad \text{tBu} \quad \xrightarrow{80\%} \quad \text{CH}_2\text{OMe} \quad \text{tBu} \quad \xrightarrow{82\%} \quad \text{COMe}$

$\text{tBu} \quad \xrightarrow{76\%} \quad \text{Me} \quad \text{tBu} \quad \text{tBu} \quad \text{tBu} \quad \text{tBu} \quad \text{tBu} \quad \text{tBu} \quad \text{tBu} \quad \text{tBu}$

$\text{tBu} \quad \xrightarrow{79\%} \quad \text{Me} \quad \text{tBu} \quad \text{CO}_2\text{Et} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu}$

$\text{tBu} \quad \xrightarrow{77\%} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me}$

$\text{tBu} \quad \xrightarrow{78\%} \quad \text{Me} \quad \text{tBu} \quad \text{CO}_2\text{Et} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me}$

$\text{tBu} \quad \xrightarrow{80\%} \quad \text{Me} \quad \text{tBu} \quad \text{CO}_2\text{H} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me}$

$\text{tBu} \quad \xrightarrow{84\%} \quad \text{Me} \quad \text{tBu} \quad \text{CHOHMe} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me} \quad \text{tBu} \quad \text{Me}$
Scheme 39

Scheme 40
Scheme 41
Scheme 42

Scheme 43
Scheme 46

Scheme 47

+ Unknown
Scheme 48

\[ \text{Scheme 48} \]
Scheme 52

\[
\begin{align*}
\text{X} & = \text{H}, \ R = \text{Me} = 106 \\
\text{X} & = \text{Cl}, \ R = \text{Me} = 114 \\
\text{X} & = \text{F}, \ R = \text{nPr} = 115 \\
\text{X} & = \text{F}, \ R = \text{Me} = 107
\end{align*}
\]

Scheme 53
Scheme 54

Reaction pathway:

\[
\text{Product} \xrightarrow{\text{loss of } \text{Me}} \text{Intermediate} \xrightarrow{\text{loss of } \text{C}_6\text{F}_4} \text{Product}
\]

- Initial molecule with \( m/e = 402 \)
  - Loss of Me results in \( m/e = 387 \)
- Intermediate with \( m/e = 239 \)
  - Loss of \( \text{C}_6\text{F}_4 \) results in \( m/e = 187 \)
- Final product with \( m/e = 200 \)
**Possible Configurations of 111**

**Corresponding dihydro compound (112A),** \( b = 2.6 - 2.9 \text{Å} \)

\[ a = 2.2 - 2.5 \text{Å} \]
\[ b = 2.8 - 3.2 \text{Å} \]

**Corresponding dihydro compound (112B),**

\[ a = 2.5 - 2.8 \text{Å} \]
\[ b = 2.6 - 2.9 \text{Å} \]

*Scheme 55*
Scheme 56
Scheme 57.2

calculated

observed

\( \gamma \) values

3 4

Scheme 58

calculated

observed

\( \gamma \) values

7 8
Scheme 59
The 'Batman' effect
# TABLE I

The reaction of anisole with various tetra-halogeno-benzenes

![Reaction Diagram](attachment:image.png)

<table>
<thead>
<tr>
<th>X</th>
<th>Precursor</th>
<th>Reference</th>
<th>% yield of (3A)</th>
<th>% yield of (4A)</th>
</tr>
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<tbody>
<tr>
<td>F</td>
<td>Grignard reagent</td>
<td>page 25</td>
<td>49%</td>
<td>10%</td>
</tr>
<tr>
<td>F</td>
<td>Grignard reagent + 20% ethylene oxide</td>
<td>page 26</td>
<td>23.8%</td>
<td>5.6%</td>
</tr>
<tr>
<td>F</td>
<td>ditto</td>
<td>N.N.Vorozhtsov</td>
<td>% yields were not reported, (ratio 4:1 quoted)</td>
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</tr>
<tr>
<td>F</td>
<td>Lithio reagent</td>
<td>page 26</td>
<td>41.3%</td>
<td>5.4%</td>
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<tr>
<td>Cl</td>
<td>Lithio reagent</td>
<td>J.M.Jablonski</td>
<td>62</td>
<td>0.8%</td>
</tr>
<tr>
<td>Br.</td>
<td>tetrabromo anthranilic acid</td>
<td>J.M.Sketchley</td>
<td>40</td>
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<td>Compound</td>
<td>H</td>
<td>H H</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-CH&lt;sub&gt;2&lt;/sub&gt;CO-</td>
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<td>----------------</td>
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<tr>
<td>(22)</td>
<td>5.4</td>
<td>3.26</td>
<td>6.3</td>
<td>7.9</td>
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<td>(26)</td>
<td>5.36</td>
<td>3.04-3.52</td>
<td>6.38</td>
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<td>(29)</td>
<td>-</td>
<td>3.0</td>
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<td>-</td>
</tr>
<tr>
<td>(31)</td>
<td>5.7</td>
<td>-</td>
<td>-</td>
<td>7.34</td>
</tr>
<tr>
<td>(32)</td>
<td>5.59 and 6.31</td>
<td>-</td>
<td>6.6</td>
<td>8.0</td>
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<tr>
<td>Adduct</td>
<td>Temp.</td>
<td>Product</td>
<td>Yield</td>
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<td><img src="image3" alt="Adduct 3" /></td>
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<td><img src="image7" alt="Product 7" /></td>
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</tr>
<tr>
<td><img src="image4" alt="Adduct 4" /></td>
<td>270°</td>
<td><img src="image7" alt="Product 7" /></td>
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<td></td>
</tr>
<tr>
<td><img src="image26" alt="Adduct 26" /></td>
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<td>7</td>
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<tr>
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<td><img src="image36" alt="Adduct 36" /></td>
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<td><img src="image41" alt="Product 41" /></td>
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<tr>
<td>Adduct</td>
<td>Temp.</td>
<td>Product</td>
<td>Yield</td>
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<td><img src="image1" alt="Adduct 35" /></td>
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<td><img src="image8" alt="Product 21" /></td>
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<td><img src="image9" alt="Adduct 31" /></td>
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<td>not pyrolysed</td>
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<td><img src="image10" alt="Adduct 102" /></td>
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<td><img src="image11" alt="Product" /></td>
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<td>$R_2$</td>
<td>$R_3$</td>
<td>H</td>
<td>CH$_3$</td>
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</tr>
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<td>85</td>
<td>Me</td>
<td>H</td>
<td>4.24(S)</td>
<td>7.82(S)</td>
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<tr>
<td>77</td>
<td>t.Bu</td>
<td>H</td>
<td>4.29(S)</td>
<td>7.82(S)</td>
</tr>
<tr>
<td>83</td>
<td>CH$_3$</td>
<td>COCH$_3$</td>
<td>3.79(S)</td>
<td>7.51(S)</td>
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<tr>
<td>79</td>
<td>t.Bu</td>
<td>COOCH$_2$</td>
<td>3.80(S)</td>
<td>7.43(S)</td>
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<tr>
<td>81</td>
<td>t.Bu</td>
<td>COCH$_3$</td>
<td>3.85(S)</td>
<td>7.49(S)</td>
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<td>84</td>
<td>t.Bu</td>
<td>CHOCH$_3$</td>
<td>3.99(S)</td>
<td>7.76(S)</td>
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<tr>
<td>82</td>
<td>t.Bu</td>
<td>COOH</td>
<td>3.80(S)</td>
<td>7.45(S)</td>
</tr>
<tr>
<td>Compound No.</td>
<td>R&lt;sup&gt;1&lt;/sup&gt;</td>
<td>R&lt;sup&gt;2&lt;/sup&gt;</td>
<td>H&lt;sup&gt;R1&lt;/sup&gt;</td>
<td>H&lt;sup&gt;R2&lt;/sup&gt;</td>
</tr>
<tr>
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<td>-----------</td>
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<td>-------------</td>
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<tr>
<td>3</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>Doublet</td>
<td>Multiplet</td>
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<tr>
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<td></td>
<td>6.25</td>
<td>4.68-5.05</td>
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<td>17</td>
<td>OCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>H</td>
<td>J = 6.2</td>
<td>Multiplet</td>
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<td>Octet 6.03</td>
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<td>(CH&lt;sub&gt;2&lt;/sub&gt;)</td>
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<td>Triplet 8.57</td>
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<td>(CH&lt;sub&gt;3&lt;/sub&gt;)</td>
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<td>29</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>OCH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Broadened singlet 6.24</td>
<td>Broadened singlet 6.24</td>
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<td>35</td>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Doublet</td>
<td>Doublet</td>
</tr>
<tr>
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<td></td>
<td>6.33</td>
<td>7.94</td>
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<td>51</td>
<td>N(CH&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Doublet</td>
<td>Doublet</td>
</tr>
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<td></td>
<td></td>
<td>7.36</td>
<td>7.95</td>
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**TABLE 4.1.**
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<th>Compound No.</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>R&lt;sup&gt;3&lt;/sup&gt;</th>
<th>R&lt;sup&gt;4&lt;/sup&gt;</th>
<th>&lt;sup&gt;2&lt;/sup&gt;H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>&lt;sup&gt;2&lt;/sup&gt;H&lt;sub&gt;1&lt;/sub&gt;</th>
<th>&lt;sup&gt;3&lt;/sup&gt;H&lt;sub&gt;1&lt;/sub&gt;</th>
<th>&lt;sup&gt;3&lt;/sup&gt;H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>&lt;sup&gt;3&lt;/sup&gt;H&lt;sub&gt;3&lt;/sub&gt;</th>
<th>&lt;sup&gt;4&lt;/sup&gt;H&lt;sub&gt;1&lt;/sub&gt;</th>
<th>&lt;sup&gt;4&lt;/sup&gt;H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>&lt;sup&gt;4&lt;/sup&gt;H&lt;sub&gt;3&lt;/sub&gt;</th>
<th>Integration low-high field</th>
<th>J&lt;sub&gt;H-19F&lt;/sub&gt;</th>
<th>J&lt;sub&gt;H-1&lt;/sub&gt;</th>
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<td>4</td>
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<td>H</td>
<td>H</td>
<td>H</td>
<td>ABX octet 7.94</td>
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<td>Multiplet</td>
<td>Multiplet</td>
<td>5.18-5.55</td>
<td>3.02-3.48</td>
<td>5.18-5.55</td>
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<td>H</td>
<td>H</td>
<td>ABX octet 7.90</td>
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<td>Multiplet</td>
<td>Doublet</td>
<td>5.4</td>
<td>3.26</td>
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<td>Doublet</td>
<td>ABX octet</td>
<td>Multiplet</td>
<td>6.38</td>
<td>2.97-3.45</td>
<td>5.24-5.42</td>
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<tr>
<td>36</td>
<td>H</td>
<td>H</td>
<td>H</td>
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<td>Singlet</td>
<td>Multiplet</td>
<td>5.73</td>
<td>7.98</td>
<td>3.81</td>
<td>Double of doublet 5.45 J&lt;sub&gt;HF&lt;/sub&gt; = 2.0 J&lt;sub&gt;AX&lt;/sub&gt; = 5.15</td>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>Quartet 7.52</td>
<td>Doublet</td>
<td>Doublet</td>
<td>ABX octet</td>
<td>9.19</td>
<td>6.31</td>
<td>2.88-3.44</td>
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<td>5.15-5.37</td>
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<td>R²</td>
<td>R³</td>
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<td>J_H⁻¹⁹F</td>
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<tr>
<td>18</td>
<td>OCH₂CH₃</td>
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<td>H₂</td>
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<td>H</td>
<td>H</td>
<td>O</td>
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<td>Multiplet 6.07</td>
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<td>OCH₃</td>
<td>H</td>
<td>CH₃</td>
<td>(OCH₃)₂</td>
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<td>Doublet 6.45</td>
<td>Doublet 9.33</td>
<td>Multiplet 7.68-8.52</td>
<td>2 singlets</td>
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<td>-</td>
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<tr>
<td>Compound No.</td>
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<td>R²</td>
<td>H¹</td>
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<td>J₁H⁻¹⁹F</td>
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<td>10</td>
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<td>H</td>
<td>Multiplet 3.96</td>
<td>Multiplet 2.82</td>
<td>2 : 2</td>
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<td>H</td>
<td>Singlet 8.00</td>
<td>Broadened triplet 4.16</td>
<td>AB of ABX</td>
<td>Vₐ = 3.12</td>
<td>V. slight peak broadening only</td>
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<td>Vₐ = 3.12</td>
<td>V. slight peak broadening only</td>
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<td>CH₃</td>
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<td>V. slight peak broadening only</td>
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* Spectrum in trifluoroacetic acid
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REFERENCES


c. F. Minisci and A. Quilico., Chemica e Industria, 1964, 46, 428.


e. H. Gilman and H.W. Melvin jnr., ibid., 1950, 72, 995.


    idem., 1962, 27, 4152;
    idem., 1963, 28, 1.

    idem., 1956, 78, 6265.

e. J.D. Roberts; D.A. Semenow, H.E. Simmons jnr., and
    L.A. Carlsmit, ibid., 1956, 78, 601.

f. R.A. Benkeser and G. Scho1l, ibid 1953, 75, 3196.


    idem., 1957, 79, 2625.


d. J. Gach, Chemie, 1958, 10, 143-5.

q. R. Huisgen, Theoretical Organic Chemistry (Kekule Symposium), 158, Butterworth.

r. V. Franzen, Chemiker Ztg., 1960, 84, 3.


1966, 143.


b. idem., ibid., 1969, 379.
55. Magnanini and Bentivoglio, Gazz., 24, 1, 435.
56. See reference 26b page 266.
64. H. Heaney and A. P. Price, Personal Communication


