I. The β- pentapluorophemylethyl anion II. reactions of perfluoro-3,4-dimethyl-3-hexene and related compounds

Bartlett, Sheena

Bartlett, Sheena (1979) *I. The β- pentapluorophemylethyl anion II. reactions of perfluoro-3,4-dimethyl-3-hexene and related compounds*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8386/

UNIVERSITY OF DURHAM

A THESIS

entitled

I. THE β-PENTAFLUOROPHENYLETHYL ANION

II. REACTIONS OF PERFLUORO-3,4-DIMETHYL-3-HEXENE AND RELATED COMPOUNDS

Submitted by

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(Graduate Society)

A candidate for the degree of Doctor of Philosophy

1979

This thesis is dedicated to my Mum and Dad, and to Chris, with thanks.

Acknowledgements.

I would like to thank Professor R.D. Chambers for his help and encouragement and Dr. G.M. Brooke for his interest and helpful advice, particularly during the work described in the first part of this thesis.

I would also like to express my gratitude to the many technical and laboratory staff for their cheerful help and to the S.R.C. for providing a maintenance grant.

Finally, thanks are due to Chris for his patience and understanding and I must mention Jack Parkins and Joy.

Memorandum.

The work described in this thesis was carried out in the University of Durham between October 1976 and September 1979. This work has not been submitted for any other degree and is the work of the author except where acknowledged by reference.

Part of this work is the subject of the following paper:

S. Bartlett, R.D. Chambers, A.A. Lindley, and H.C. Fielding, J.C.S. Perkin I, submitted for publication.

Abstract.

Part I.

A study has been carried out on the effect of a pentafluorophenyl substituent in promoting carbanion rearrangements in a simple ethyl system. Analogous non-fluorinated systems are reported to have produced rearrangement only with caesium or alkali metal alloys. The reactions of 1-bromo-2-pentafluorophenylethane with magnesium and lithium have been studied under various conditions. The major product in the case of lithium was the corresponding ethene, formed by decomposition of the lithium compound. With magnesium the expected ethane was formed on hydrolysis. Isotopic labelling studies indicated that no rearrangement occurred in this system. The evidence suggests that a single pentafluorophenyl group is insufficiently activating to cause rearrangement to occur with the less active alkali metals.

Part II.

The reactions of an "internal" fluoroalkene (perfluoro-3,4-dimethyl-3-hexene) with various carbon and nitrogen nucleophiles have been investigated. Unusually, a terminal alkene has been produced as the major product with a carbon nucleophile, rather than the more highly substituted isomer. The reactions with nitrogen nucleophiles have resulted in products being formed from each of the three isomers of perfluoro-3,4-dimethyl-3-hexene.

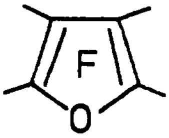
An interesting series of fluorinated furans has been prepared, with a variety of substituents at the 2-position. These are related to the internal fluoroalkene discussed above. This series has provided a useful probe for the investigation of the photochemistry of fluorinated furans. The expected products (cyclopropenylketones) were obtained in all cases except where the substituent was perfluoro-1-H-1-H-propyl, where the only observed products resulted from loss of HF from the side chain. Specificity in ring opening was only observed for one furan - perfluoro-3,4,5-trimethylfuran.

Perfluorotetramethylfuran has proved to be largely inert to nucleophilic attack and reaction with addition reagents.

Conventions.

The following conventions have been used in this thesis:

1. The prefix perfluoro is used before a name to denote that the compound or the part of the compound following the prefix is fully fluorinated.

2. F in a ring (e.g. ) denotes that the ring and its unspecified substituents are fully fluorinated.

3. ^{19}F chemical shifts are quoted as ppm relative to external $CFCl_3$ and ^{1}H chemical shifts are quoted as ppm relative to external TMS.

4. [X] indictates the reference to the work quoted.

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II. Reactions of Perfluoro-3,4-dimethyl-3-hexene and related compounds.

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I. THE β-PENTAFLUOROPHENYLETHYL ANION.

Chapter I

Introduction -

Carbanion Rearrangements and Related Topics.

I.1. Carbanion Rearrangements.

Since the original preparation of the majority of this section[1] the field has been comprehensively reviewed by an authority, E. Grovenstein Jr.[2], in a gratifyingly similar manner to the author.

I.1.A. Introduction.

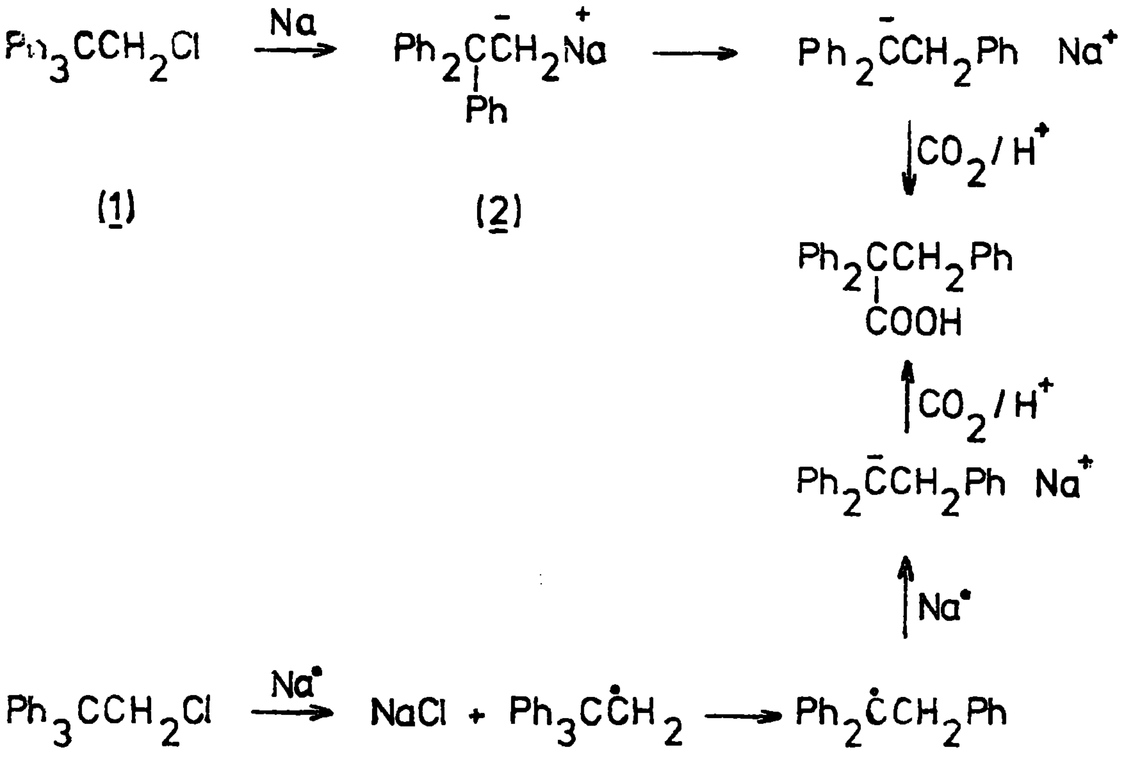
Relatively few rearrangements are known which are initiated by carbanion formation, compared with similar rearrangements of carbonium ions and free radicals and of these many involve molecules containing heteroatoms[3]. Molecular orbital calculations on various systems[4] have shown that in 1,2-aryl migrations the situation is favourable to rearrangement but that this is not the case for migration of an alkyl group. The following survey gives a general review of 1,2- and related rearrangements of aryl groups and indicates the possible mechanisms proposed for these migrations.

I.1.B. 1,2-Aryl Migrations.

The first reactions of this type to be observed were the reactions of 2-chloro-1,1,1-triphenylethane (1) with sodium in dioxane[5]. A red-coloured carbanion was formed which gave 2,2,3-triphenylpropanoic acid on carbonation. The reaction was thought to occur via the 2,2,2-triphenylethyl anion (2) but a free radical pathway was also considered feasible (Scheme I.1.). The driving force for the rearrangement may well be the resonance delocalisation of the charge in the intermediate. The reaction was carried out with different cations[6] - for example potassium reacted to give rearrangement products immediately at low temperatures (-50° to -60°C), while lithium only produced rearrangement products at higher temperatures. The order of reactivity towards rearrangement was found to be

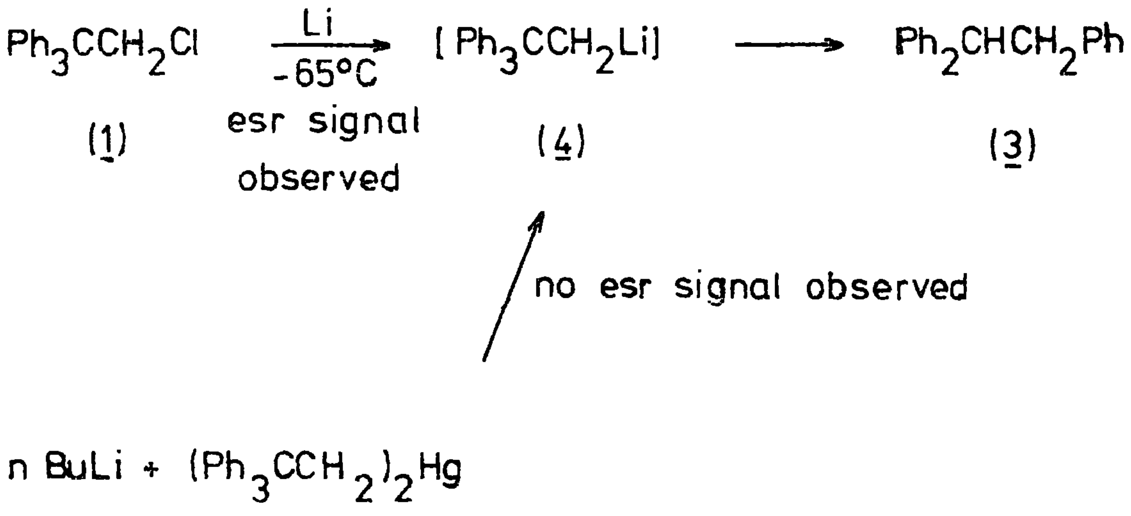
RMg (no rearrangement) < RLi < RNa < RK,

which would indicate some carbanionic character in the mechanism, since this order is that of the ionic character of the carbon-metal bond.



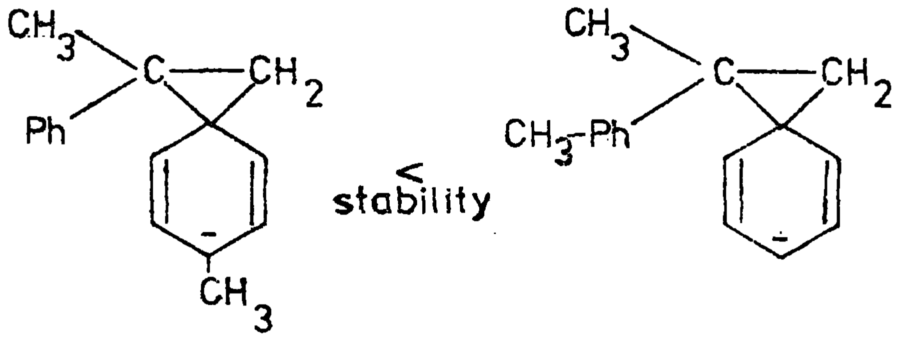
Scheme I. 1.

Later work[7] showed a possible competition between anionic and radical mechanisms in this rearrangement. When (1) was reacted with lithium metal in THF at temperatures below -65°C and the red solution formed was allowed to warm up, a signal was observed in the esr spectrum of the mixture. Subsequent work-up produced the rearranged product 1,1,2-triphenylethane (3). If, however, n-butyllithium and *bis*-(2,2,2-triphenylethyl)-mercury were used to produce the 2,2,2-triphenylethyllithium (4) and no free metal was present, no esr signals could be obtained. No paramagnetic species were observed in a CIDNP study of the mixture. Work-up produced the same products as in the reaction with free metal (Scheme I.2.).



Scheme I.2.

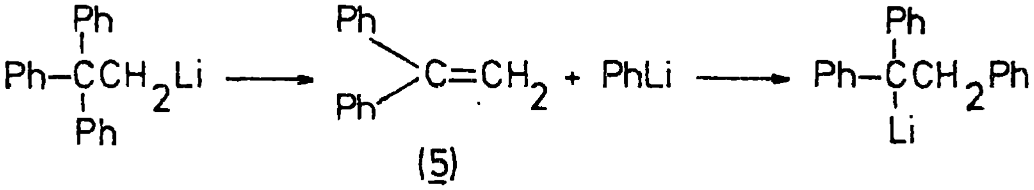
Further support for carbanionic mechanisms in aryl migration reactions was found in the rearrangement of 2,2-diphenylpropyllithium and 2-phenyl-2-(p-tolyl)-propyllithium[4]. Rearrangement of the p-tolyl group occurred much less readily than rearrangement of phenyl. This was thought to support an anionic mechanism, since an anionic intermediate would be less stable for p-tolyl migration than for phenyl migration, but free-radical migratory aptitudes for the two groups would not be expected to be widely different[8].



No further studies were carried out at this stage (e.g. replacement of p-methyl by trifluoromethyl or nitro groups to enhance the rate of migration) in order to test the theory. In later work[9] p-phenyl groups were used.

Radioactive tracer studies on two rearrangements led to the postulation of two separate mechanisms for these systems[9,10,11]. Compound (4) rearranged at 5°C to give 1,1,2-triphenylethyllithium by a phenyl migration and when the reaction was carried out in the presence of labelled phenyllithium no incorporation of labelled material was observed. The intramolecular nature of this reaction was further confirmed by carrying out the rearrangement in the presence of benzyllithium[10]. This is known to react more rapidly than phenyllithium with 1,1-diphenylethene (5)[10] and therefore if phenyllithium were eliminated as a solvent separated ion pair, which could then recombine with (5) (equation I.1.), some products from incorporation of benzyllithium would be expected. No such products were observed.

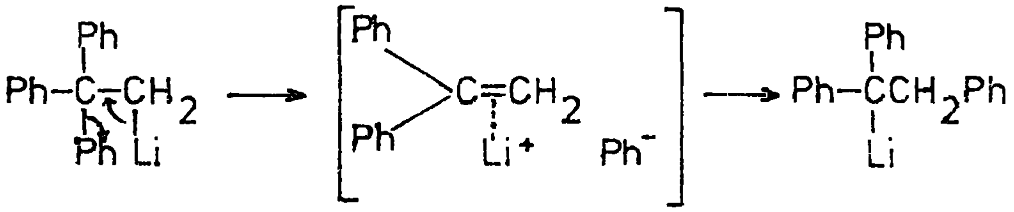
I.1.



$$Ph_3CCH_2Li \longrightarrow Ph_2C{=}CH_2 + PhLi \longrightarrow Ph_2C(Li)CH_2Ph$$

Two possible intramolecular pathways were therefore proposed: (i) by elimination of phenyllithium as an ion pair to which (5) is bound as a ligand of the lithium atom (equation I.2.)

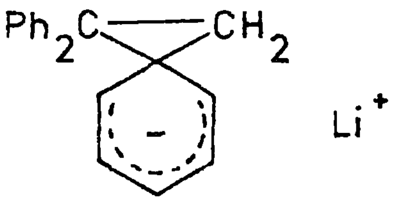
I.2.



$$Ph_3CCH_2Li \longrightarrow \left[Ph_2C{=}CH_2 \cdots Li^{+} \quad Ph^{-} \right] \longrightarrow Ph_2C(Li)CH_2Ph$$

A variation on this involving rapid elimination of phenyl anion to give (5) and phenyllithium in a solvent cage, followed by recombination before diffusion of labelled material into the cage, was dismissed[14] since ordinary phenyllithium is known to react slowly with (5)[10].

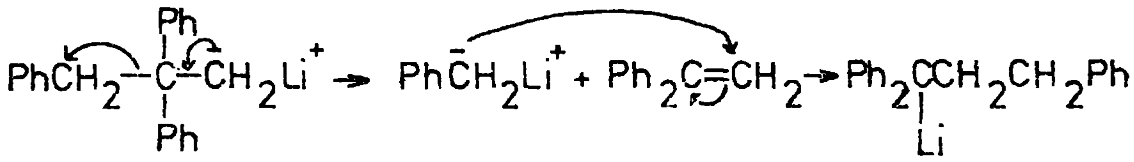
(ii) via a spiroanion (6)



(6)

The second study involved the rearrangement of 2,2,3-triphenylpropyllithium (7)[10,11]. In this case benzyl migration was observed giving 1,1,3-triphenylpropyllithium. In the presence of ^{14}C labelled benzyllithium some incorporation of ^{14}C was observed in the product. This led to the postulation of the following intermolecular elimination-readdition mechanism (equation I.3.).

I.3.



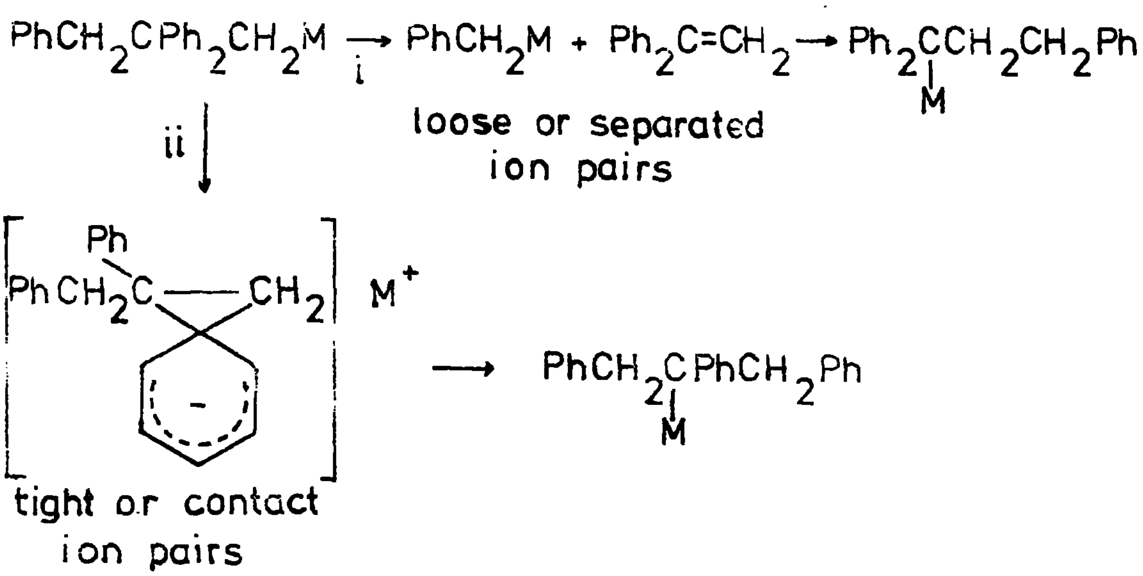
$$\mathrm{PhCH_2{-}C(Ph)_2{-}CH_2Li^+} \rightarrow \mathrm{Ph\bar{C}H_2Li^+} + \mathrm{Ph_2C{=}CH_2} \rightarrow \mathrm{Ph_2C(Li)CH_2CH_2Ph}$$

(7) (5)

Lack of competition by the organolithium compound (7) for alkene (5) is explained by the observed higher reactivity of benzyllithium for (5) than n-alkyllithium compounds, to which compound (7) is likened. The higher reactivity can be accounted for by the lower degree of association of benzyllithium in solution (it is monomeric whilst n-alkyllithiums tend to be oligomeric), its higher polarisability and the greater ionic character of the carbon-metal bond than in n-alkyllithiums[10].

In both of these studies radical mechanisms were not excluded from consideration although anionic routes were more favoured.

The rearrangements of organometallic compounds such as (7) were observed under a variety of conditions[12] and it was found that both benzyl and phenyl migrations could be achieved, the choice of route being critically dependent upon such conditions as solvent, temperature and the nature of the cation. The two routes are outlined in Scheme I.3.

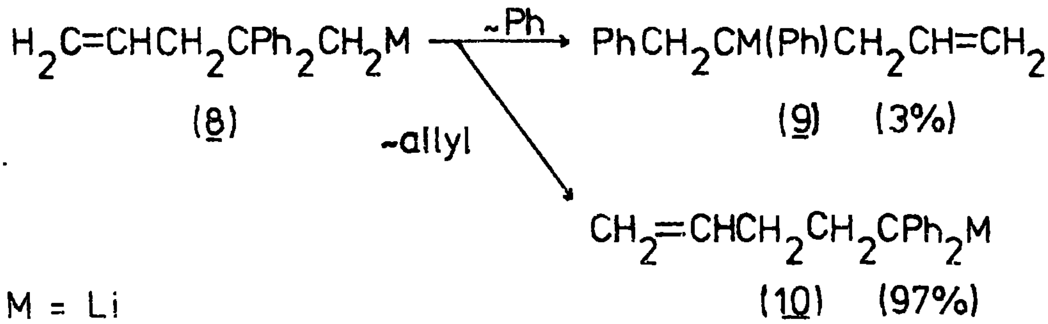


Scheme I.3.

Route (i) involves benzyl migration whilst (ii) results in phenyl migration. Low temperature conditions in solvents which are good for solvating cations (e.g. crown ethers) and small cations (e.g. Li^+, Na^+) were found to favour route (i) whilst higher temperatures, poorly solvating solvents and large alkali metal cations (K^+,Cs^+) promoted route (ii). This indicated the formation of "loose" or separated ion pairs in the case of benzyl migration (i) and "tight" or contact ion pairs for route (ii).

In a similar reaction Grovenstein[13] has shown the effect of varying the conditions mentioned on the competition between allyl and phenyl migration in 2,2-diphenyl-4-pentenyl-alkali metal compounds (8). Reaction of the corresponding chloro-compound with lithium metal in THF at -75°C yielded (8) ($M = Li$) and on warming to 0°C the following rearrangement occurred (equation I.4.).

I.4.



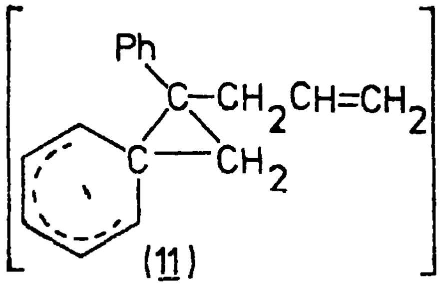
$$H_2C{=}CHCH_2CPh_2CH_2M \xrightarrow{\sim Ph} PhCH_2CM(Ph)CH_2CH{=}CH_2 \quad (9)\ (3\%)$$

$$H_2C{=}CHCH_2CPh_2CH_2M \xrightarrow{-allyl} CH_2{=}CHCH_2CH_2CPh_2M \quad (10)\ (97\%)$$

The addition of lithium tert-butoxide to the mixture exerted no catalytic effect at -75°C and appeared to retard rearrangement at 0°C. However, addition of potassium or caesium tert-butoxides catalysed rearrangement at -75°C and promoted phenyl migration over allyl (e.g. for Cs, (9) : (10) = 16 : 84). This latter is believed to occur by interchange of cations (equation I.5.)[12].

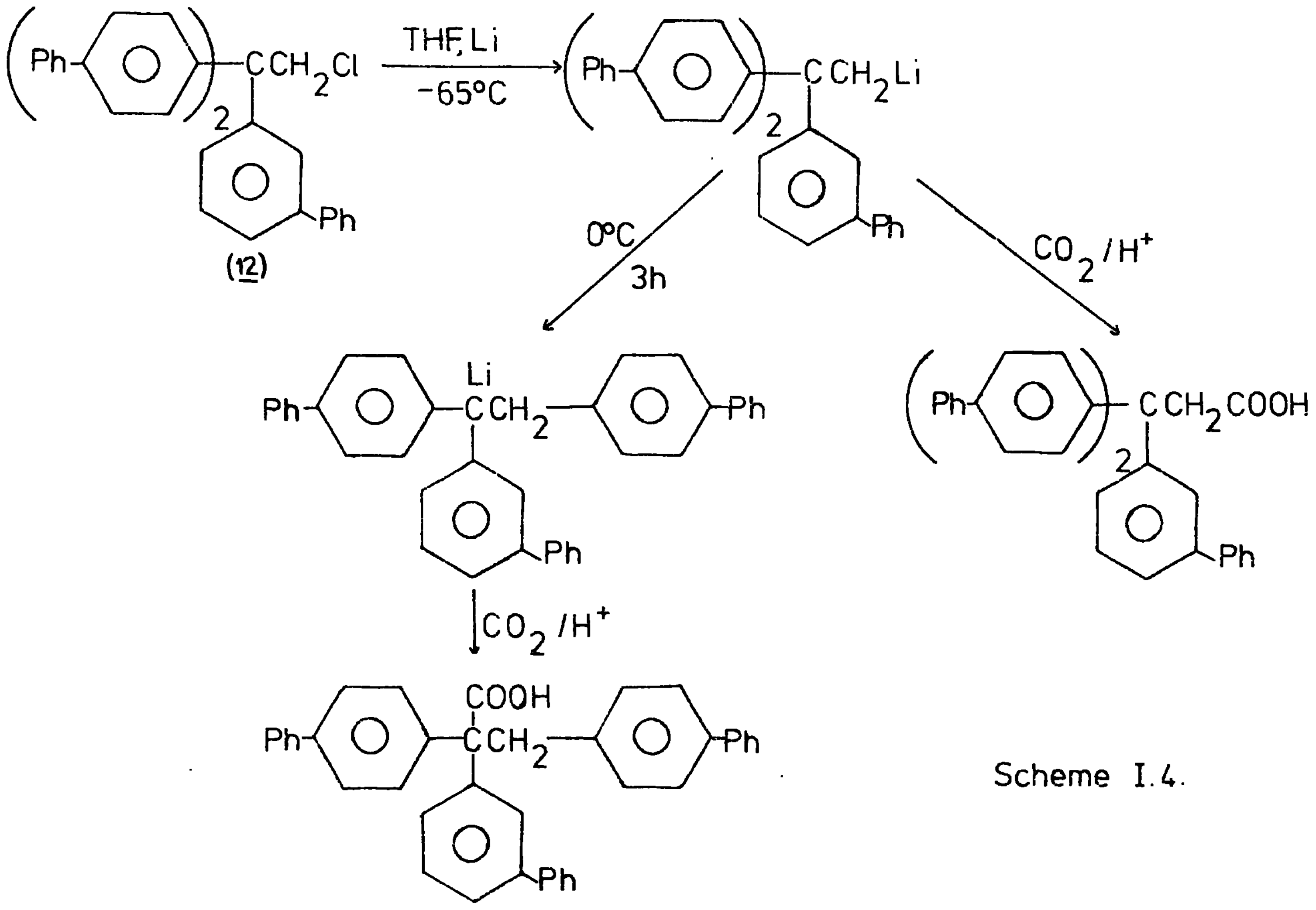
$$\text{I.5.} \qquad LiR + MOtBu \longrightarrow MR + LiOtBu$$

When 18-crown-6 was added to a mixture containing potassium tert-butoxide the amount of phenyl migration was reduced, owing to the efficient solvation of the metal ion which diminished the availability of suitable ligands about the metal ion for coordination with the organic moeity. As with the rearrangement of compound (7), the two routes for compound (8) have been described in terms of "loose" and "tight" ion pairs, phenyl migration once again resulting from a "tight" ion pair intermediate (e.g. (11), equation I.6.).

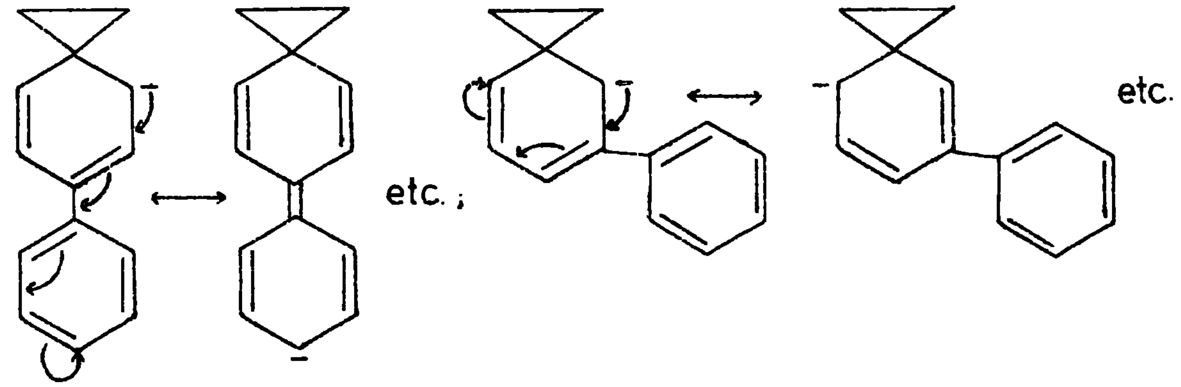
I.6. (8) $\longrightarrow$  M+ $\longrightarrow$ (9)

The allyl rearrangement is enhanced under conditions which promote the presence of loose ion pairs. The mechanisms described adequately account for observations made, but a radical mechanism was not dismissed at this stage, particularly from the allyl migration as it also could account for the data obtained.

Grovenstein and Wentworth have carried out studies[14] on the migratory aptitude of m- versus p-biphenylyl groups in the reaction of compound (12) with lithium in THF, in order to clarify the mechanism of rearrangement (Scheme I.4.). No evidence was observed for m-biphenylyl migration. Rearrangement of a 2,2,2-triarylethyllithium compound occurring via elimination of an aryl anion would require that a m-biphenylyl anion be eliminated a little more readily than a p-biphenylyl anion (from deuterium exchange experiments). In elimination and readdition, the unshared pair of electrons in the phenyl anion, or the unpaired electron in a phenyl radical is in an sp^2 orbital which is orthogonal to the aromatic π-orbitals of the migrating phenyl group, therefore the presence of a substituent at the m- or p-position of the phenyl group should not greatly affect the elimination of the group as an anion or a radical. However, if the intermediate is a spiroanion, the p-biphenylyl group should migrate more readily than a m-biphenylyl group because of greater charge delocalisation in the former:

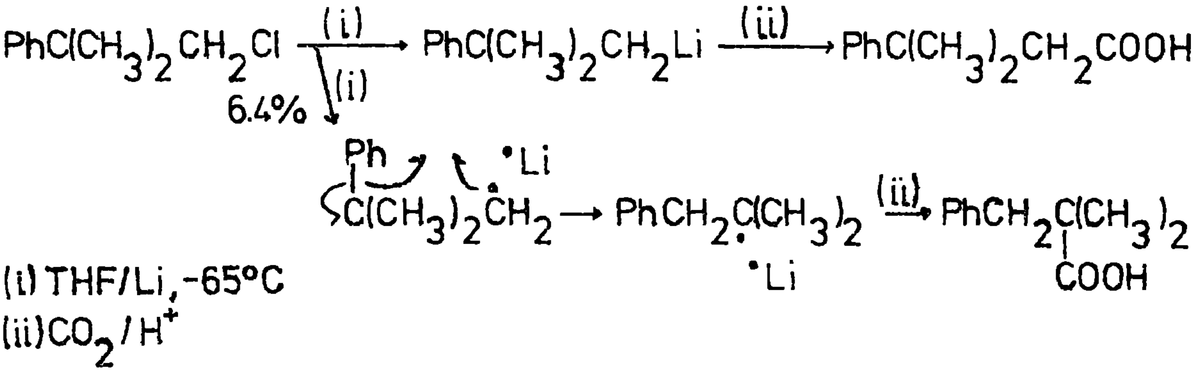


Scheme I.4.



In this case, therefore, the formation of a spiroanion intermediate is perfectly feasible whilst elimination - readdition or radical mechanisms seem unlikely.

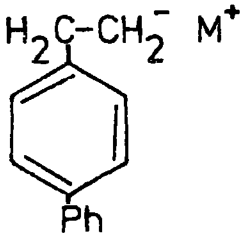
All of the reactions discussed so far have involved migration of an aryl group from a carbon atom which is substituted with at least one other large unsaturated group. This stabilises the system towards rearrangement by providing delocalisation of electrons in the transition state for rearrangement and also by providing release of steric strain in the transition state. In the reactions where these conditions do not hold, e.g. in the reaction of 1-chloro-2-methyl-2-phenylpropane with lithium[15] and in the reactions of phenyl substituted pentylmethane sulphonates with potassium or sodium in ammonia[16] very little rearrangement (<6%) was seen to occur. The former reaction is believed to involve rearrangement via a radical intermediate formed prior to the formation of the organolithium compound, since on warming up no rearrangement of the organolithium compound occurred (Scheme I.5.).



Scheme I.5.

The latter reaction is also believed to involve one electron transfer, in this case from the alkali metal to the phenyl group to produce a radical anion which is then believed to act as a powerful nucleophile to displace the methane sulphonate group. The resulting phenyl-bridged radical can then react with the metal atom and abstract a proton from the solvent to give the rearranged product.

1.2-Rearrangements in a simple arylethyl anionic system have been investigated by Grovenstein[17] in order to see if rearrangement could be effected with no stabilising groups present on the carbon atom from which migration should occur. In THF at -70°C with lithium, no rearrangement was observed with 1-chloro-2-(p-biphenylyl)ethane, neither was any observed when the mixture was warmed to 0°C. With caesium or potassium in refluxing THF, however, about a 50:50 mixture of rearranged to non-rearranged products was observed. tert-Butanol was used as a trap for anion (13) before rearrangement took place, since when the reaction was carried out in the presence of a small quantity of this, the amount of rearrangement was greatly reduced. This was also taken to imply little radical contribution to the rearrangement, since any radicals formed would have been expected to react much more readily with the solvent (THF) than with tert-butanol. The fact that rearrangement did not occur with



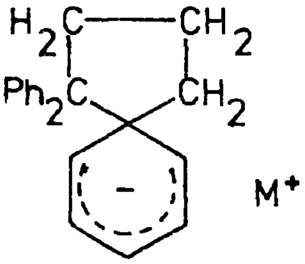
(13)

lithium but did with the more reactive metals implies that substitution of the carbon atom from which migration occurs is important with lithium but not very significant (if at all) with the more reactive cations.

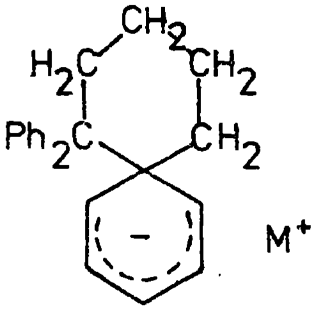
No examples have been observed of 1,2-aryl migrations from carbon atoms in organomagnesium compounds. This is probably due to the greater covalency of the carbon-magnesium bond[27].

I.1.C. Aryl Migrations other than to an adjacent carbon atom.

Investigations have also been carried out[18] into 1,4- and 1,5-migrations of aryl groups with 4-chloro-1,1,1-triphenylbutane and 5-chloro-1,1,1-triphenylpentane and alkali metals in order to determine whether any spiro-intermediates of the type (14) or (15) exist.

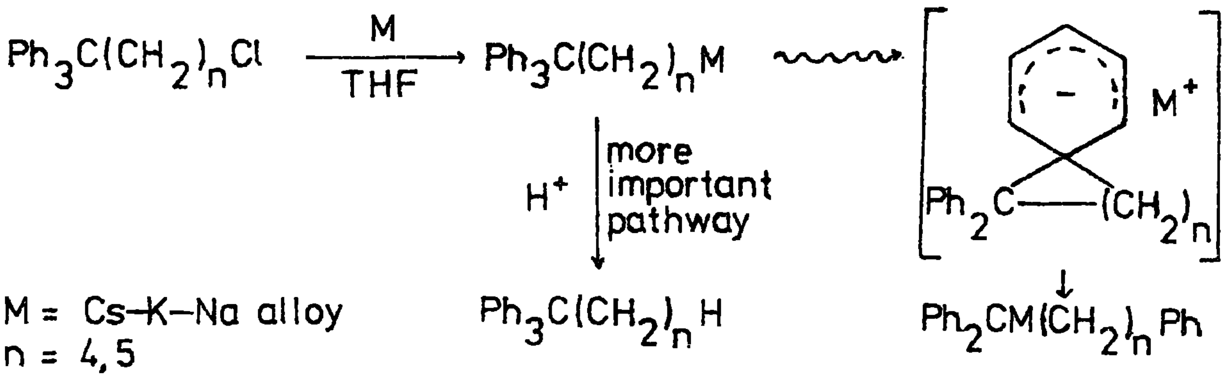


(14)



(15)

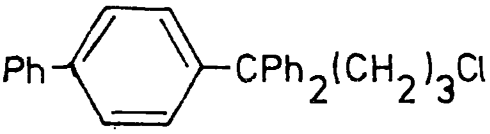
Rearrangements were observed with caesium alloys but only 10% of the total reaction was observed under any of the conditions studied (Scheme I.6.).



Scheme I.6.

Reactions where n = 1,3 have also been observed with lithium metal.

The reaction of 4-chloro-1-(*p*-biphenylyl)-1,1-diphenylbutane (16) with caesium-potassium-sodium alloy, potassium or sodium takes place via the intermediate (17) rather than by a radical mechanism, as has been shown by trapping experiments with *tert*-butanol. It has, however, been suggested that the reaction with lithium metal, which is much less facile, occurs via a radical mechanism, followed by reduction of the radical on the metal surface.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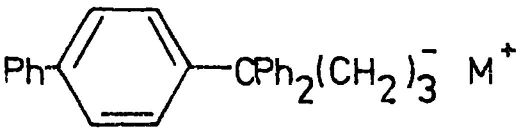
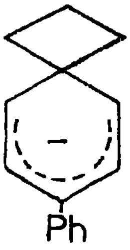
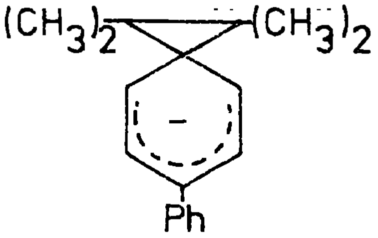

(17)

No 1,3-aryl migrations have been observed[2].

I.1.D. Recent Developments.

In many of the rearrangements cited above spiro-intermediates have been suggested where carbanionic pathways have been proposed. Grovenstein and co-workers[19] have prepared and characterised by carbonation spiroanions of the type (18) and (19) from 2- and 3-(*p*-biphenylyl)alkyl chlorides with caesium-potassium-sodium alloy.

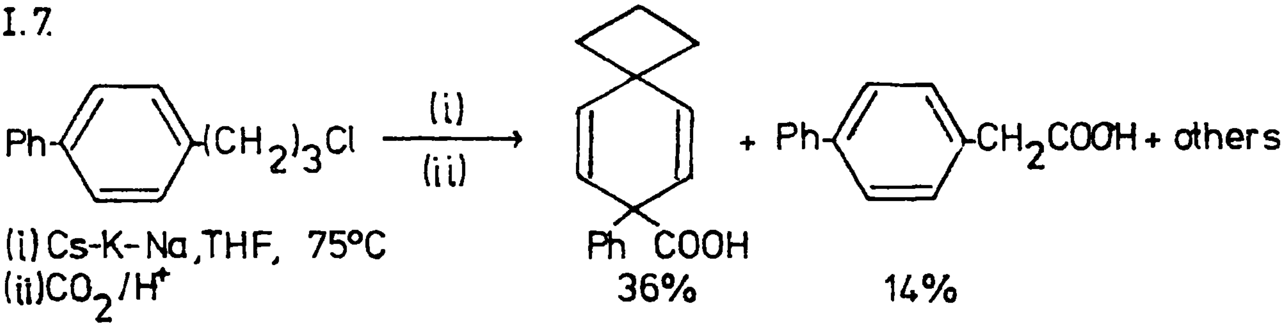

(18)


(19)

The fact that these can be formed indicates that they could well be intermediates, or transition states, in 1,2-aryl rearrangements under appropriate conditions.

Some evidence has, in fact, recently been found for the presence of spiroanions in a rearrangement of the type under review[20], the results of which are illustrated in equation I.7.

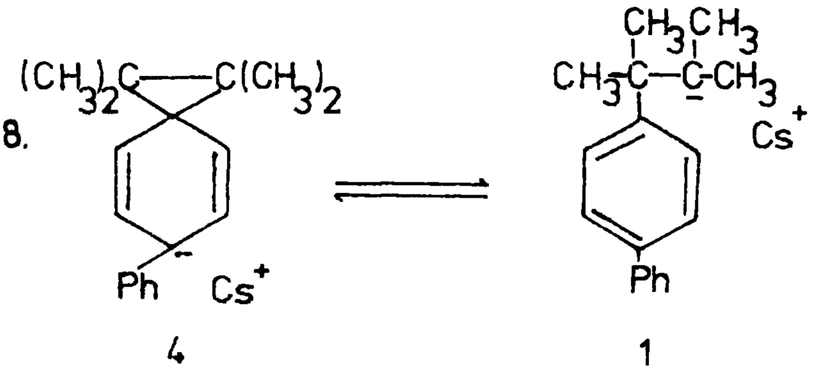
I.7



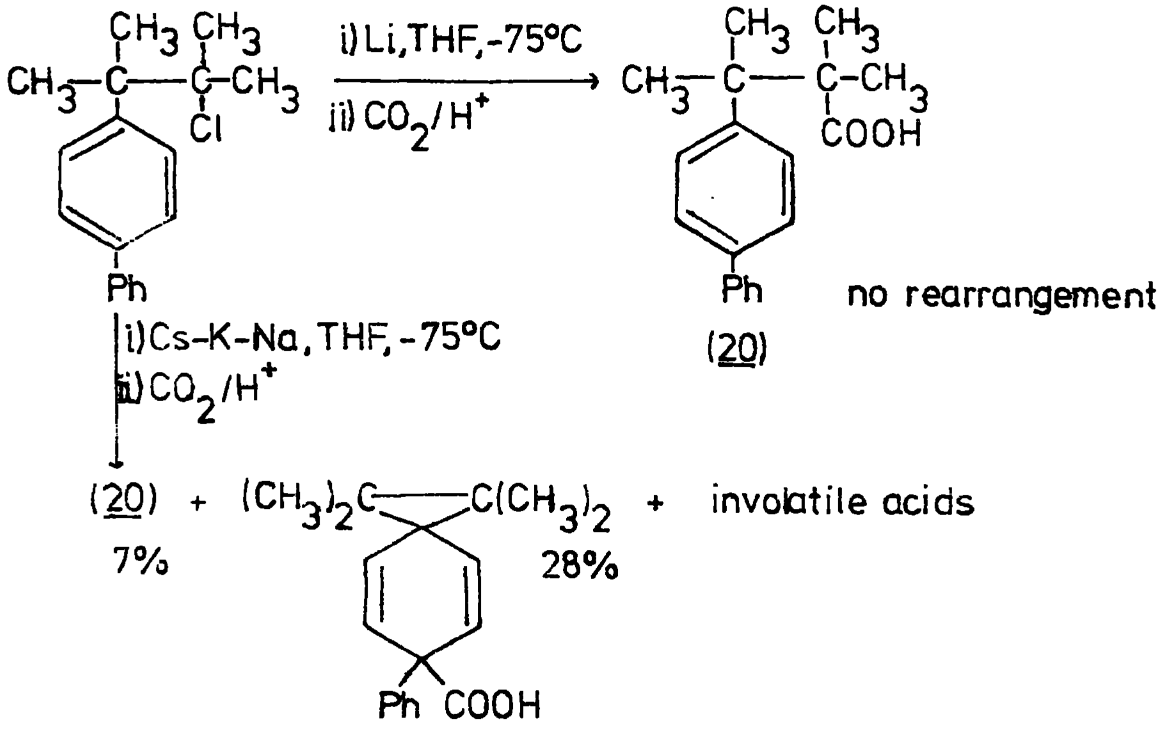
The yield of spiroacid decreased with time of the reaction and the amounts of spiroanion decreased on standing and with increased temperature. These data implied the intermediacy of a spiroanion. No appreciable amount of rearrangement was observed in a similar reaction involving lithium metal.

Unusually, however, less than 1% (if any) of a spiroanion was detected in the reaction of 2-(p-biphenylyl)-1-chloropropane under similar conditions, even although the total ring strains in the cyclopropyl and cyclobutyl rings produced would not be expected to be appreciably different[22]. A cyclopropyl spiroanion was detected[20] in a system where the ring was stabilised by geminal methyl groups[23]. This latter reaction is shown in Scheme I.7. together with further evidence of the effect of the nature of the cation on reaction pathways in these systems[20]. From labelling experiments and other evidence[20], the following equilibrium was believed to be set up (equation I.8.).

I.8.



With lithium as the counterion the localised open form of the anion was preferred, leading to the covalent lithium compound.



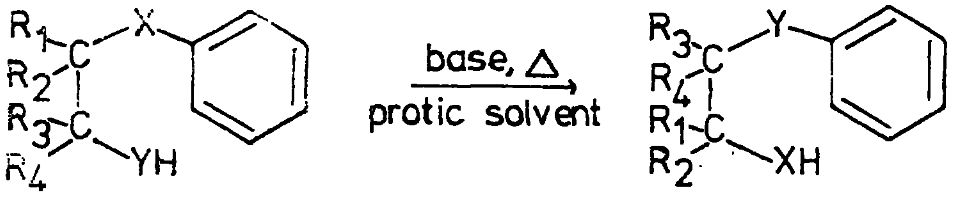
Scheme I.7.

I.1.E. Related Rearrangements.

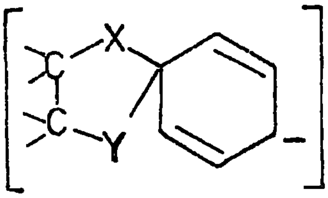
Several rearrangements analogous to those discussed above are known, which involve heteroatoms and which are believed to proceed, at least in part, via carbanionic mechanisms. Examples of these are given[3] but will not be discussed in detail.

The Smiles rearrangement is illustrated in equation I.9.[3a].

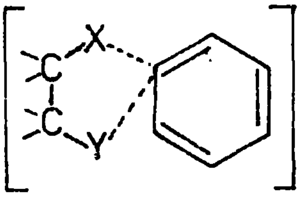
I.9



This is believed to involve nucleophilic attack of Y on the ring with elimination of X. The intermediate or transition state is believed to involve the aromatic ring, for example in the manner shown below:



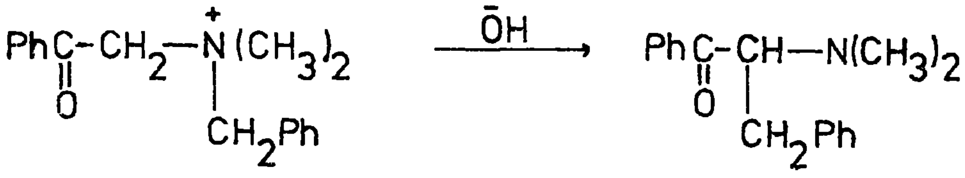
or



For rearrangement to occur readily Y must be strongly nucleophilic and X a good leaving group. Stabilisation of the ring by electron-withdrawing groups also aids rearrangement.

The Stevens rearrangement involves migration of an alkyl group from a tertiary ammonium group to an adjacent carbanionic centre (equation I.10.).

I.10.

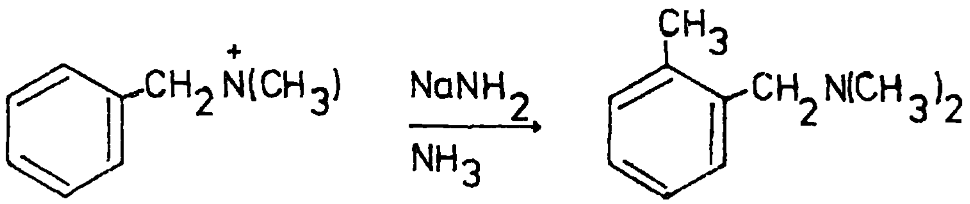


$$\mathrm{Ph\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{CH_2Ph}{|}}{\overset{+}{N}}(CH_3)_2} \xrightarrow{\bar{O}H} \mathrm{Ph\underset{\underset{O}{\|}}{C}-\underset{\underset{CH_2Ph}{|}}{C}H-N(CH_3)_2}$$

As with the rearrangements discussed above several mechanisms have been suggested to account for this reaction, including carbanionic mechanisms, but it has recently been found[24] that a radical process is involved.

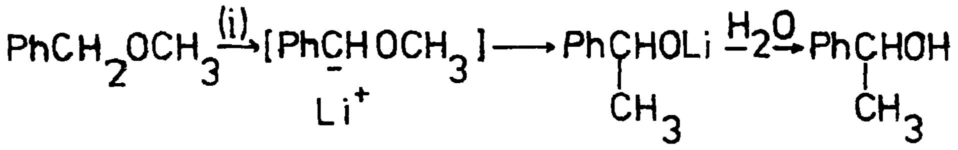
The Sommelet - Hauser rearrangement involves 1,4-migration of an alkyl group from a quaternary nitrogen in benzyltrimethylammonium salts (equation I.11.).

I.11.



The Wittig rearrangement involves 1,2-rearrangement of a benzyl or allyl ether in a strong base to give an alkoxide (equation I.12.).

I.12.



$$\mathrm{PhCH_2OCH_3} \xrightarrow{(i)} [\mathrm{Ph}\underset{\underset{\mathrm{Li^+}}{-}}{\mathrm{C}}\mathrm{HOCH_3}] \longrightarrow \mathrm{Ph}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HOLi} \xrightarrow{H_2O} \mathrm{Ph}\underset{\mathrm{CH_3}}{\mathrm{C}}\mathrm{HOH}$$

(i) = PhLi

In some of the above cases the mechanisms have not yet been fully elucidated.

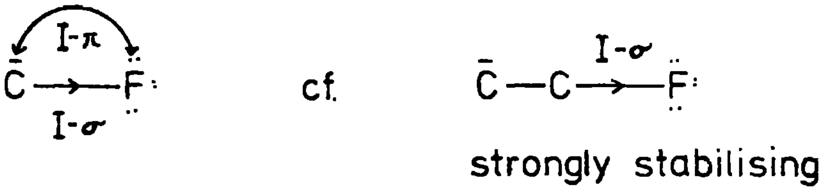
I.1.F. Conclusion.

Even at this stage very few firm conclusions can be drawn as to the mechanism of 1,2-aryl and related rearrangements. Obviously evidence in favour of spiroanion intermediates or transition states in many of these rearrangements is more concrete than previously and it is likely that these species are present in some instances. The difficulties involved in elucidating a mechanism are large owing to the critical dependence of reaction products on conditions such as temperature and time of reaction, the nature of the solvent and particularly the nature of the counter ion. With larger cations (caesium, potassium) the likelihood of rearrangement via a carbanionic mechanism involving a spiroanion intermediate or transition state is quite high. With smaller cations (e.g. lithium) rearrangement is more difficult to effect and species other than spiroanions may well be involved. Radical contributions must also be considered. Radical rearrangements have been observed during the formation of both lithium[20] and magnesium[21] compounds.

It should be stated, finally, that the practical difficulties involved in carrying out reactions of the type under review often make it difficult to achieve meaningful results.

I.2.A. The Effect of Fluorine on Carbanions.

Although fluorine as a substituent attached directly to a carbanionic centre may be destabilising because of the destabilising I - π effect competing with the stabilising I -σ effect:



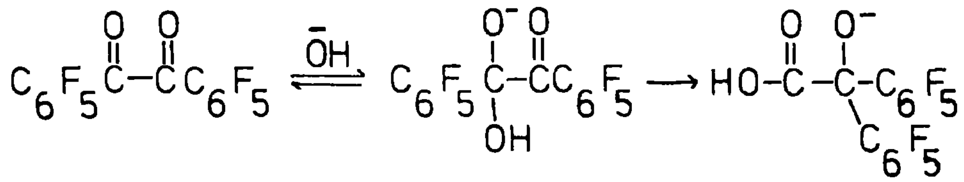
fluorine situated on a carbon atom adjacent to a carbanionic centre is strongly stabilising, presumably because of the inductive effect[25]. Thus fluorine, or fluorocarbon substituents attached to the carbon atom adjacent to an anionic site will stabilise the anion and enhance its formation.

I.2.B. The Pentafluorophenyl group as a substituent.

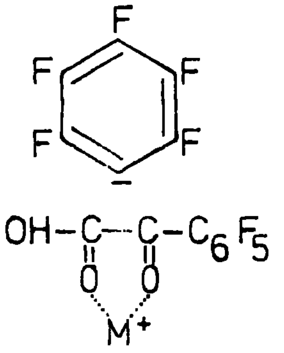
The pentafluorophenyl group differs from the phenyl group in the distortion of its electron density by the inductive withdrawal of the five fluorine atoms through the σ- framework. The effect of this is shown by the ease of nucleophilic attack on the ring and its stabilisation of carbanions. There may be slight counteraction of this σ - inductive effect by interaction of the lone pairs on the fluorine atoms and the π- framework of the ring [26] (cf. I.2.A. above).

The effect of fluorine atoms on the ring is illustrated by the benzil-benzilic acid rearrangement[27]. A rate enhancement of the rearrangement of decafluorobenzil over benzil was estimated at $\geqslant 10^5$. The activating influence of five fluorine atoms on the ring can be accommodated by assuming a transition state which is similar to the initial state (equation I.13.).

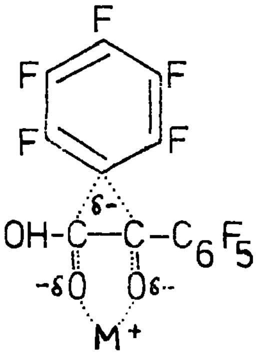
I.13.



However, the very large rate enhancement led Chambers and co-workers[27] to postulate a mechanism involving a tight ion pair intermediate or transition state (21), or a structure such as (22), which would more intimately involve the aryl group and more effectively account for the huge rate difference.



(21)



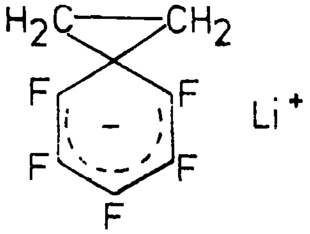
(22)

I.3. The β-Pentafluorophenylethyl anion.

Very little work appears to have been undertaken with this anion but for the reasons outlined below it would seem ideally suited to a study of 1,2-aryl migration with alkali metals.

Pentafluorophenyl groups have been shown to be super-mobile already in one instance[27] (benzil-benzilic acid rearrangement) and if this could be extended to other situations it seems reasonable to suppose that reactions of, for example, pentafluorophenylethylbromide with lithium or even magnesium could produce rearrangement. So far rearrangements of analogous systems have only been achieved with very highly reactive alkali metal alloys.

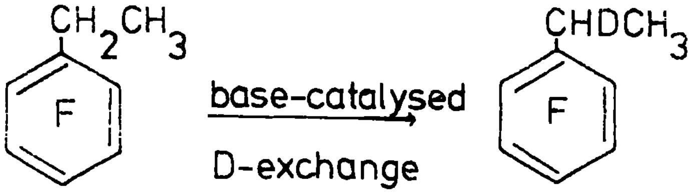
It is also possible that the stabilising influence of a pentafluorophenyl group would be sufficient to allow observation of stable intermediates in 1,2-rearrangement reactions. An intermediate such as (23) could be envisaged for this type of system and the effect of the fluorine atoms on this would be strongly stabilising and would promote its formation.



(23)

It would also be expected that the presence of the fluorine atoms on the phenyl ring would show up an unusual enhancement of acidity (equation I.14.) of the proton α to the ring.

I.14.



In view of the interesting possibilities concerned with 1,2-rearrangements in such a system, an investigation was undertaken and is the subject of the work discussed in this section of this thesis.

Chapter II

Discussion -

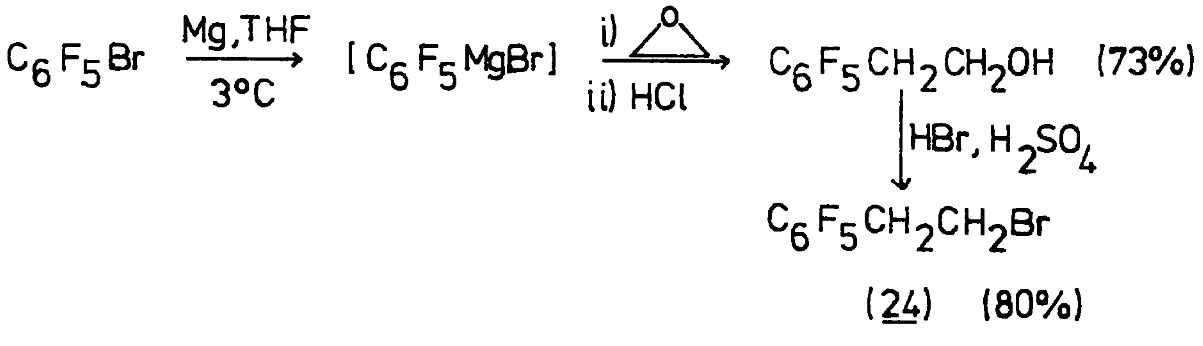
Reactions of 1-Bromo-2-Pentafluorophenylethane and Related Compounds.

II.1. Introduction.

In the following sections the reactions of 1-bromo-2-pentafluorophenylethane (<u>24</u>) with metals and organometallics under various conditions are discussed. The initial aim was to determine whether the pentafluorophenyl group was sufficiently mobile to undergo rearrangement with lithium or magnesium (which have not produced rearrangement in analogous, non-fluorinated systems) and if it was sufficiently stabilising of the intermediate in this rearrangement to allow observation and trapping.

II.2. Preparation of 1-bromo-2-pentafluorophenylethane.

This compound was prepared via the Grignard reagent formed from bromopentafluorobenzene according to a literature method[28]. The yields quoted in the following scheme are the maximum obtained during a series of reactions.



Scheme II.1.

II.3. Reactions of Compound (<u>24</u>) with Magnesium.

No 1,2-aryl rearrangements have yet been observed in reactions involving magnesium[29] but for the reasons indicated earlier the Grignard reaction of compound (<u>24</u>) was investigated and the products identified.

II.3.A. Products from the Grignard Reaction.

Compound (24) reacted readily with magnesium in diethyl ether at room temperature and yielded a single product on hydrolysis. Characterisation by spectral techniques and microanalysis identified this as pentafluorophenylethane (25) (equation II.1.).

$$\text{II.1.}\quad C_6F_5CH_2CH_2Br \xrightarrow[Et_2O]{Mg} [C_6F_5CH_2CH_2MgBr] \xrightarrow{H_3O^+} C_6F_5CH_2CH_3$$

(24) (25) (99%)

No evidence was obtained for any other species having been trapped. Reaction in THF also yielded greater than 99% conversion to (25). Attempts were made to prepare the Grignard reagent in other solvents but it proved impossible to get the same levels of yields as with ether and THF. This was because of solubility problems resulting in deposition of material (presumably magnesium bromide) on the metal surface which inhibited further reaction. Various different methods were tried with 1,4-dioxane but in no case was product obtained.

Nmr analysis of the Grignard complex was carried out to see if this would give any indication of its structure. The ^{19}F nmr spectrum was not very clear but the signals obtained were at identical chemical shifts and of similar intensities to those of the parent compound, indicating that the ring played no direct part in the reaction. Proton nmr signals for ether and THF masked the proton signals of the Grignard complex and as stated above no satisfactory reaction could be achieved with other solvents so no meaningful data could be obtained from the ^1H nmr spectrum.

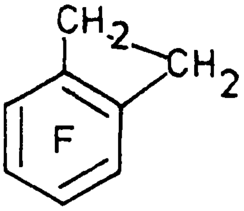
On carbonation of the Grignard reagent an acid, $C_6F_5CH_2CH_2COOH$, was obtained which was recrystallised from water (mp 92°C, lit.[30] 95-6°C).

Methylation of this and the reaction residues with methanol and concentrated sulphuric acid resulted in the formation of an ester which has not previously been reported. This was not isolated from ether solution but composite spectra were obtained and these indicated that the ester was $C_6F_5CH_2CH_2COOCH_3$. No other isomeric compounds were detected, either in the methylated acid or methylated residues.

The results above indicate that the pentafluorophenyl ring is largely unaffected in this reaction and therefore that no rearrangement occurs, the reaction giving the expected products. The results are consistent with the magnesium bond having a fairly large amount of covalent character and the pentafluorophenyl group not being sufficiently activating to produce rearrangement.

II.3.B. Decomposition of the Grignard Reagent.

The decomposition of the Grignard reagent described above was investigated to see whether the side chain would attack the ring to give a product such as compound (26) which would occur as a result of nucleophilic displacement of fluoride. Attempts were made to decompose the complex by replacing the solvent used in its formation (THF) by one of higher boiling point (o-xylene, bp 144°C). The products of hydrolysis of this showed one major signal on glc, and mass spectral data indicated that this was compound (25). The reaction was repeated in a sealed tube using THF as the solvent, the liquid above the magnesium surface being transferred to, and sealed in the Carius tube. After heating, the mixture was hydrolysed and glc and



(26)

tlc evidence showed that the volatile component contained two products. Analysis by MS-glc indicated that these were (25) (M^+ 196) and $C_6F_5CH{=}CH_2$ (M^+ 194). These materials were not isolated further. Comparisons can be drawn between this reaction and the decomposition of the corresponding lithium compound (Section II.5.D.).

II.4. Reactions of Compound (24) with n-Butyllithium.

The investigation was extended to consider the formation and possible rearrangement of 2-pentafluorophenylethyllithium (27). This was thought likely to enhance the possibility of rearrangement since the lithium-carbon bond is less covalent than the magnesium-carbon bond. Initial attempts to form (27) involved metal-halogen exchange between compound (24) and a solution of n-butyllithium in hexane.

II.4.A. Reaction Conditions.

The reaction of compound (24) with n-butyllithium solution was carried out under a variety of different conditions to find those most suitable for the study being considered. The results are summarised in Table II.1.

The following reaction would be anticipated for the straight-forward metal-halogen exchange reaction (equation II.2.).

$$\text{II.2.}\quad \underset{(24)}{C_6F_5CH_2CH_2Br} \overset{nBuLi}{\rightleftharpoons} C_6F_5CH_2CH_2Li \xrightarrow{H_3O^+} \underset{(25)}{C_6F_5CH_2CH_3}$$

The pentafluorophenylethane formed was detected by glc analysis of a hydrolysed aliquot of reaction mixture and comparison with a standard

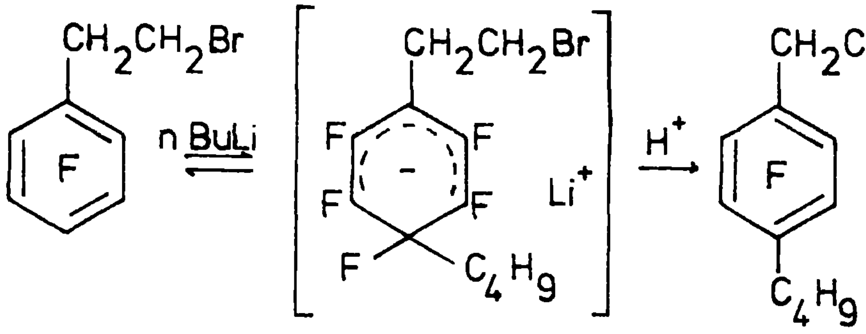
Table II.1. Reaction Conditions for the Metal-Halogen Exchange Reaction of Compound (<u>24</u>) with n-Butyllithium.

Solvent[1]	Temp. °C	(nBuLi)/(Substrate)[2]	Time h	Extent of Reaction %[3]
Hexane	-20	1	2	Small
Hexane	-20	2.1	1.5	Very small
Hexane	0	1	3	4
Ether	-78	1	2	3
Ether	-78	2	1	15
Ether	-20	1	1	5
Ether	-20	1.9	1	100[4]
Ether	-20	1.2	0.16	3
Ether	0	2.1	0.58	100[4]
THF	-78	1	1.75	55
THF	0	1	3	Small[4]

1. Solvent contains some hexane from nBuLi solution.
2. (reagent) means total stoichiometric concentration of the reagent.
3. Based on the disappearance of starting material observed on glc.
4. In these cases only involatile products were obtained.

sample. As can be seen from Table II.1. very little reaction was observed with hexane even under what may be considered fairly vigorous conditions for this type of reaction. Metal-halogen exchange reactions are known to be slow in hydrocarbon solvents[31] and this may explain the very small conversions. In other solvents the equilibrium in the reactions which give volatile products was largely found to be on the side of starting materials, rather than products, which is unexpected[31]. The most suitable conditions appeared to be those using THF as solvent at -78°C with equimolar amounts of n-butyllithium, when approximately 55% reaction was observed. The reaction with THF at 0°C appeared to be anomalous for two reasons. Firstly, the extent of reaction was very low relative to that observed at -78°C and secondly, the products formed were not those anticipated from equation II.2. i.e. bromobutane was observed but none of compound (25). A similar effect to this latter point was observed with ether at 0°C and so an excess of n-butyllithium was added. The initial transient pink colouration persisted, resulting in a pink-yellow colour just prior to hydrolysis of the bulk solution. All of the starting material was consumed but again none of (25) was observed, although a small amount of bromobutane was detected. An involatile product was separated on preparative thin layer chromatography, the infra-red spectrum of which was similar to that of the starting material but with ν_{max} 2875cm^{-1} (C-H stretch). Mass spectral data showed M^+ 312, with M+2 314 of similar intensity, indicating the presence of bromine and the fragmentation pattern indicated that an n-butyl group was also present. This would imply that n-butylation of the ring is very important under these conditions, the pentafluorophenyl ring being attacked in preference to metal-halogen exchange. Since the temperature used was high for this type of reaction (0°C) this pathway is consistent with other observations[31] (equation II.3.).

II.3.



(pink?) (28)

It is possible that the pink colouration observed was caused by an intermediate similar to that illustrated in equation II.3.

The bromobutane observed was almost certainly present as a result of metal-halogen exchange. The fact that no (25) was observed implies that the 2-pentafluorophenylethyllithium (27) formed by exchange underwent further reaction, possibly n-butylation. This possibility is discussed later.

In all of the cases where ether was the solvent, higher temperatures and excess n-butyllithium resulted in the formation of n-butylated species, and equimolar amounts of n-butyllithium gave very little reaction.

II.4.B. Metal-Halogen Exchange Reaction in THF.

This reaction was investigated further and attempts were made to enhance the equilibrium in favour of the lithium compound. The temperature was kept low (-78°C) to discourage n-butylation of the starting material. The reaction was monitored at various stages of n-butyllithium addition by hydrolysis and glc analysis of aliquots of material. The n-butyllithium was added fairly slowly since it had been observed that a pink colouration was only present with equimolar quantities of reagents when a localised excess was present because of rapid addition. The results are shown in Table II.2.

Table II. 2. Reaction of n-Butyllithium with Compound (24) in THF at -78°C.

(nBuLi)/(Substrate)[1]	Stirring time h	Time[4] h	%Reaction[2]	Products			
				nBuBr	(25)	Other	(24)
1	1.5	1.5	34	p	p	p	76%
1.4	1.8	3.3	80	i	d	d	20%
1.8	1	4.3	100	i	d	n	n[3]
1.8	2.5	6.8	100	unchanged from previous result.			

1. (reagent) means total stoichiometric concentration of the reagent.

2. Based on glc observations.

3. High boiling material observed in this reaction.

4. Cumulative time.

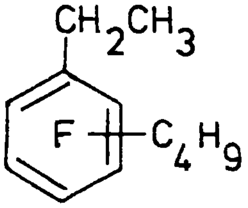
p present

i increased

d decreased

n none detected

It can be observed that initially the reaction follows the expected pathway (equation II.2.) but one other product was present as well as (25). On addition of more n-butyllithium the amount of reaction increased, as did the proportion of bromobutane to other products. This implies that exchange was occurring to give (27) (and hence bromobutane) but that this species was reacting further. The two volatile products disappeared gradually as more n-butyllithium was added and towards the end of the reaction very little volatile material was left although all of the starting material had been consumed. Mass spectral analysis of the higher boiling material showed M^+ 234 and a fragmentation pattern consistent with there being a butyl group present. Thus it was identified as compound (29).

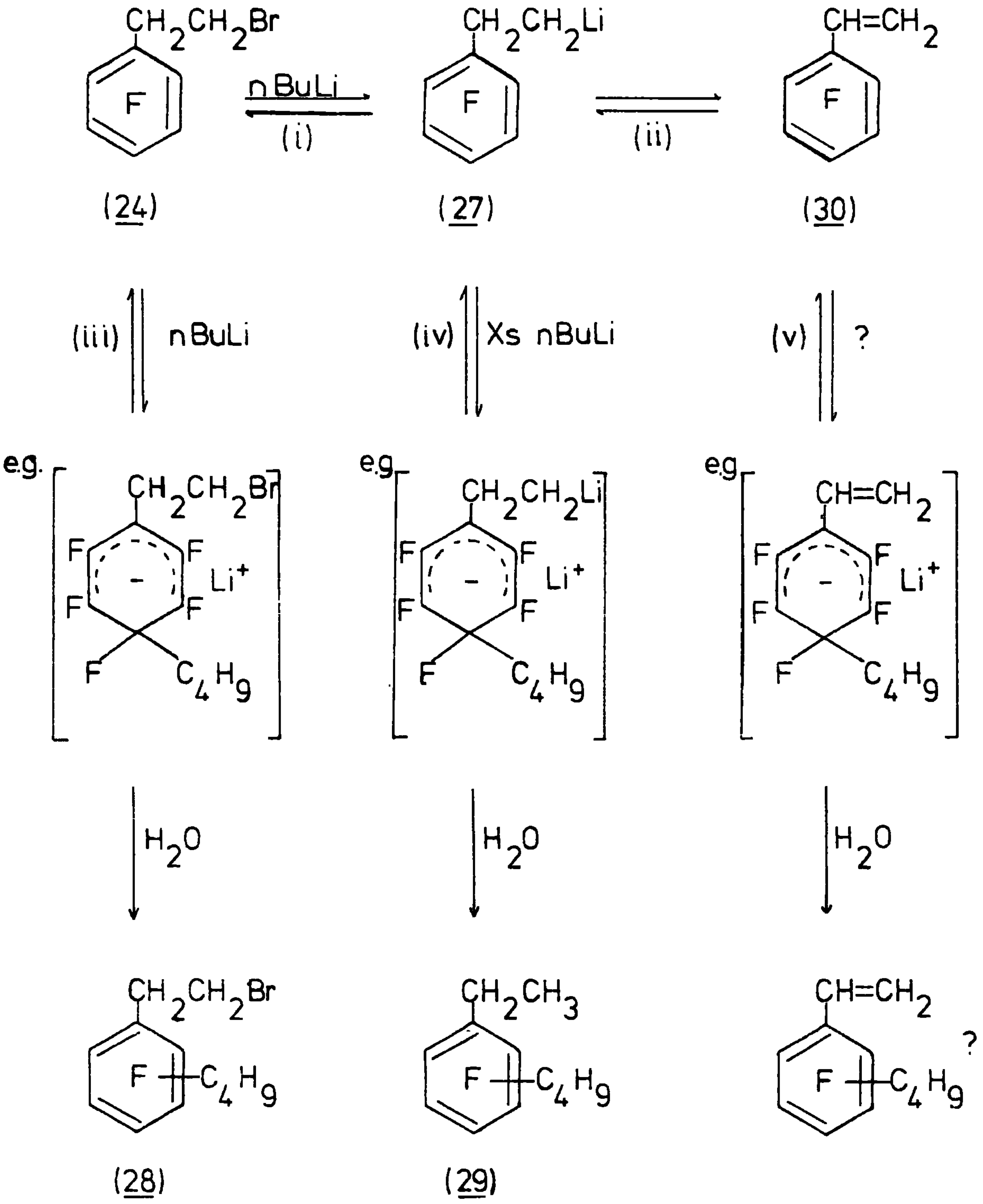


(29)

None of compound (28) was detected in this instance, implying that n-butylation of the starting material was not significant under those conditions, although in a reaction carried out on a larger scale and in which about 34% reaction occurred, some n-butylated starting material was observed.

Mass spectral analysis of the other volatile component showed M^+ 194, which is consistent with pentafluorophenylethene (30). No other identification was attempted at this stage (see Section II.5.D.). The reaction sequence would therefore appear to be as illustrated in Scheme II.2.

Routes (i), (iii) and (iv) are consistent with the products observed and are expected in this type of reaction. Pathway (ii) could occur via a variety of mechanisms, the most reasonable of


CH2CH2Br
F
nBuLi
(i)
CH2CH2Li
F
(ii)
CH=CH2
F
(24)
(27)
(30)
(iii)
nBuLi
(iv)
Xs nBuLi
(v)
?
e.g.
CH2CH2Br
F
F
F
F
F
Li+
C4H9
e.g.
CH2CH2Li
Li+
C4H9
e.g.
CH=CH2
Li+
C4H9
H2O
H2O
H2O
CH2CH2Br
F
C4H9
CH2CH3
F
C4H9
CH=CH2
F
C4H9
?
(28)
(29)

Scheme II. 2.

these being

a) decomposition of the lithium reagent (see later and ref.36)

or b) elimination of HBr by n-butyllithium.

The former possibility is discussed in Section II.5.D. and consideration of this will be left until then. The second possibility may well play a part in the mechanism but is probably not very significant. No attempts were made to collect the butane which would be formed in this case. Route (v) is presumed to occur because of the disappearance of compound (30) during the reaction although no product from this was identified. The ethenyl substituent would be expected to be more electron-withdrawing than an ethyl group and hence butylation would be expected to be faster. This is consistent with the observed disappearance of (30) relative to that of compound (25).

In view of the ease of n-butylation of both starting materials and products, even at low temperatures and also the fact that only a small amount of reaction could be effected (maximum 55%) without excess n-butyllithium, it was decided that this method was not the most satisfactory for observing compound (27), the 2-pentafluorophenylethyllithium reagent, and the reaction with lithium metal was therefore proposed.

II.5. Reactions of Compound (24) with Lithium metal.

II.5.A. Introduction.

In a similar manner to that described in the previous sections, reactions of lithium metal with an organic halide are very dependent upon the conditions used. In this instance not only is the nature of the solvent important but also the state and purity (or perhaps impurity!) of the metal and the nature of the halide are very significant in the ease of reaction and the pathway followed[32].

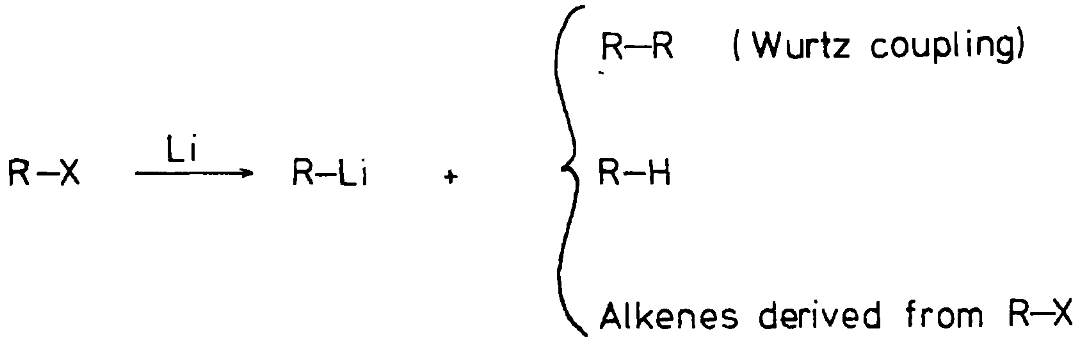
Obviously in any heterogeneous reaction the larger the surface area exposed the greater the extent of reaction and lithium can be obtained as a wire or as a dispersion for use in these reactions. It has been found[33] that pure lithium does not react with organic halides and that traces of sodium[33] and copper[34] often enhance the reactivity. Sodium is, in fact, often present in commercial supplies of lithium[32]. However, too much of these impurities promotes side reactions.

Reactions with lithium are carried out under an inert atmosphere, both to keep the metal surface clean and also to prevent reaction of the lithium reagents formed with oxygen from the air. Although nitrogen and lithium react to form lithium nitride, this reaction is sufficiently slow to allow nitrogen to be used as the inert atmosphere in many cases.

As stated above, organolithium compounds react with oxygen from the air to form alkoxides. These can also be formed by the reaction of organolithium compounds with ethers, which are frequently used as solvents. It is believed[32] that the presence of the alkoxides may enhance the reaction of lithium with organic halides, although little data are available. Also significant may be the presence of lithium halides formed during the reaction. The solubility of these compounds in different solvents varies and while the presence of dissolved halide may promote the reaction, insoluble halides would inhibit it by the deposition of material on the clean metal surface.

Each of the factors discussed above can affect the course of the reaction, which can give rise to several by-products (equation II.4.). The nature of these by-products indicates some sort of radical involvement in the reaction, although the mechanism is not clearly

II.4.



understood[32].

The results of attempts to form compound (27) from (24) and lithium metal under a variety of conditions are discussed below.

II.5.B. Reactions with a Lithium dispersion in Paraffin Wax.

It was decided to investigate the reaction of compound (24) with lithium dispersion in paraffin wax , as the metal in this form presented a greater surface area than wire. Investigations were carried out on the best methods of using the material under the conditions required, by carrying out standard reactions[35]. n-Butyllithium was prepared according to published procedures[35] and the extent of reaction assessed by hydrolysis and titration of the product with standard acid. The dispersion was easily handled and pentane or hexane were suitable solvents for removal of the wax. However, lithium bromide formed during the reaction is insoluble in hydrocarbon solvents and inhibition of the reaction was caused by deposition of this on the metal surface. Alleviation of this problem was achieved in part by vigorous agitation of the mixture. Using ethers as solvents resulted in the presence of undissolved paraffin wax which inhibited the reaction by reducing the amount of clean metal surface present.

Errors were obtained in the titration values as aliquots removed for titration often contained unreacted metal which tended to remain as a dispersion throughout the solution instead of settling on the surface. Some part of the titre was therefore due to the hydrolysed lithium. Various unsuccessful attempts were made to overcome this, including centrifuging and filtration of unreacted lithium. One other problem resulting from the size of the lithium particles was that on stirring in solvent they tended to "creep" up the sides of the vessel, thus reducing the contact with the substrate. Once these problems had been dealt with fairly good yields of lithium compounds could be obtained (55 - 66%) although these were not as high as those quoted for reactions carried out with, for example, lithium wire.

When this dispersion was reacted with (<u>24</u>) in hexane at -10°C and in THF/pentane at -10° and -78°C, very little reaction was observed (by monitoring the disappearance of starting material on glc). Sodium wire was added to the mixture to see if this effected any enhancement upon the extent of reaction but no reaction was observed in this experiment. This lack of reactivity was presumably due to the difficulties encountered in cleaning the metal surface and solubility problems of any lithium halide produced. Thus, although this form of the metal provided the greatest surface area, this was overshadowed by the other problems encountered in its use. It was therefore decided to use lithium wire.

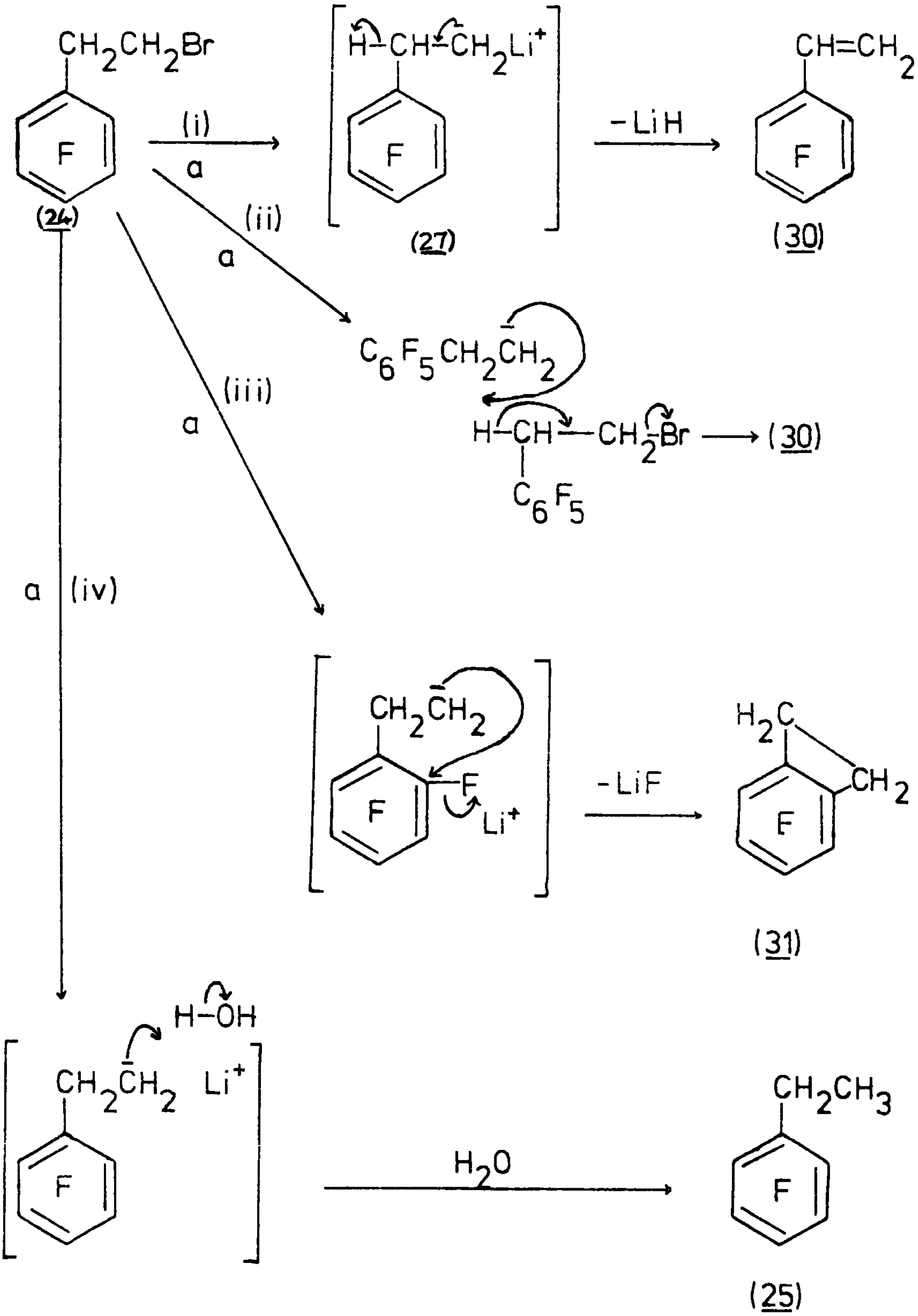
II.5.C. Reactions with Lithium Wire.

The wire used was known to have both copper and sodium impurities and it was chopped up in order to increase the surface area. This procedure not only dispensed with the presence of the paraffin wax but also more closely resembled the work of Grovenstein[17], where lithium-halogen exchange has been carried out successfully. The metal was activated with iodomethane and a small quantity of the organic halide before the bulk was added, to ensure that the surface was clean. It was observed that at -10°C in THF stirring for one hour resulted in only 3% conversion to products (determined by glc analysis of hydrolysed aliquots, assuming no involatile products were formed). In a similar reaction a longer reaction time (3 hours) gave a conversion of 62%. In other reactions, however, reproducible yields could not be obtained and from observation of the lithium metal, it appeared that this was non-homogeneous. Thus different portions were more difficult to activate, or less reactive than others. There was no means of knowing beforehand the exact composition of the strip of metal used and hence reproducibility could not be ensured. Obviously when higher temperatures were used for long periods decomposition of the solvent by the metal was to be expected.

II.5.D. Identification of Hydrolysis Products.

In a reaction carried out at 5°- 10°C for 22.5 hours about 53% reaction was observed after hydrolysis.The products were isolated and identified as (25) (16%)(by comparison of mass spectral data and glc retention time with those of an authentic sample), pentafluorophenylethene (30) (62%)(from mass spectral data) and a compound with M^+ 176 (22%). This latter is consistent with a structure (31). The proton nmr spectrum of the mixture gave shifts and coupling consistent with these products. These data lead to the postulation of the reaction scheme illustrated in Scheme II.3.

If pathway (ii) were the sole mechanism involved in formation of compound (30), the relative amount of (25) formed would be expected to be higher, thus implying that route (i) is at least partly involved. This has been suggested by other workers[36] as



a = Li, THF, 0°–10°C

Scheme II.3.

being the route taken on decomposition of a lithium reagent. No evidence was observed in this reaction for dimeric products (e.g. $C_6F_5(CH_2)_4C_6F_5$).

The low temperature ^{19}F nmr spectrum of the reaction mixture showed very little difference to that of the hydrolysed products. This implies that the majority of the lithium reagent is reacting (route (iii)) or decomposing (routes (i) and (ii)) soon after being formed.

These results reinforce the conclusions arrived at for the decomposition of the Grignard reagent (Section II.3.B.).

II.5.E. Reaction of Compound (24) with Lithium and quenched with Bromine in Pentane.

The object of this experiment was to corroborate the findings described in the previous section. If Scheme II.3. is correct, then quenching with bromine should lead to similar products, except that where (25) was observed, (24) should now be present. However, in this experiment the problems with inhomogeneity of composition of the metal, mentioned earlier, once more occurred and at -10°C in THF as solvent only two hours' reaction time was required before glc analysis of a hydrolysed aliquot indicated that no starting material was left. A substantial amount of red metal, presumably copper, was observed in the pieces of lithium used in this experiment. Glc analysis of the mixture after bromination showed five components, none of which corresponded to starting material (24) or any of the products observed so far in analogous reactions. It may be concluded from this that the influence of copper on this reaction was such as to greatly enhance the production of side reactions and although it speeded up the consumption of starting material it did not promote the reaction being studied here.

II.5.F. Reaction of Compound (24) with Lithium and quenched with *tert*-Butanol.

The reaction was carried out at about -10°C (± 5°C) in a mixture containing *tert*-butanol in order to determine whether the lithium compound (27) could be trapped prior to decomposition, in which case (25) should be the sole, or major product. The reaction went largely to completion within 3.5 hours and it appeared from glc analysis of the reaction mixture that the major product corresponded to compound (25). The other products were formed but in much lower proportions than previously observed. This is therefore consistent with the mechanism proposed in Scheme II.3.

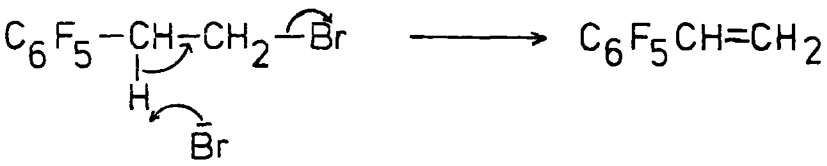
II.5.G. Reaction of Compound (24) with Lithium doped with Copper.

When the reaction was carried out with added copper powder many products were obtained, as in the case described in Section II.5.E., although in this instance some starting material was also left. Again, the copper must have promoted side reactions over the reaction under study.

II.5.H. Reaction of Compound (24) with anhydrous Lithium Bromide.

One other possibility for the formation of compound (30) is the action on starting material of lithium bromide formed during the reaction, to eliminate HBr. Halides are known to act as bases in this manner (equation II.5.).

II.5.

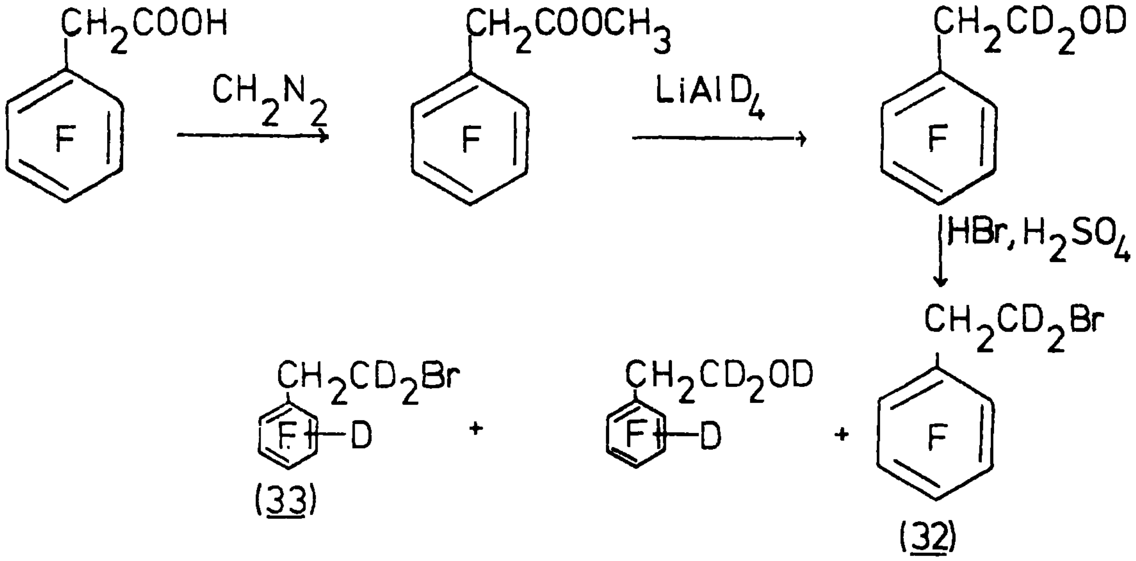


An attempt was made to test this possibility by reacting anhydrous lithium bromide with compound (<u>24</u>) under conditions similar to those used in the reactions with lithium metal. No reaction was observed and it is therefore reasonable to dismiss this possibility.

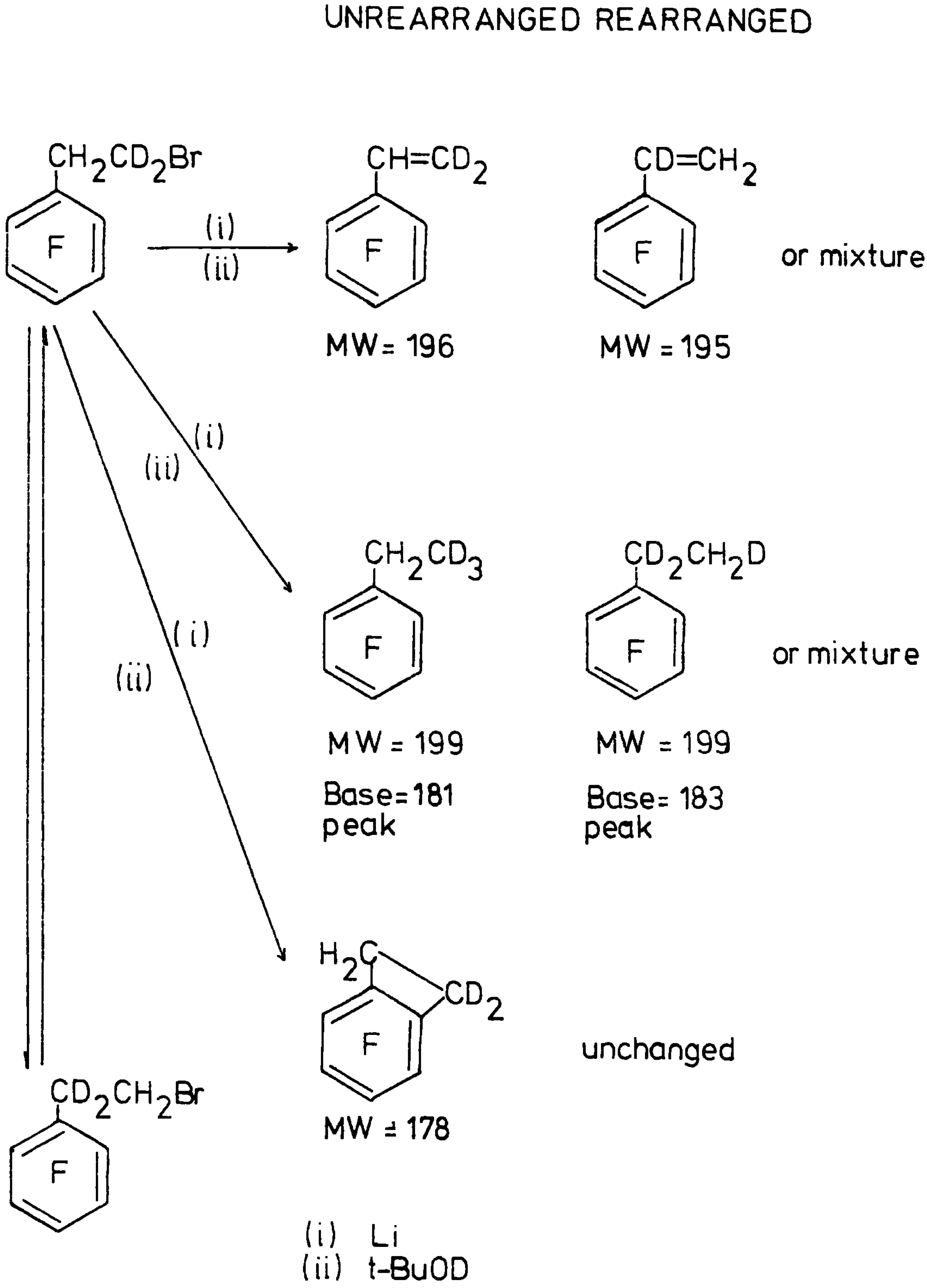
II.5.J. Reaction of 1-Bromo-2-pentafluorophenyl-[1,1-$^2H_2$]ethane with Lithium.

Having established the course of the reaction of compound (<u>24</u>) with lithium metal under normal conditions (Scheme II.3.) it was decided to label the substrate in order to discriminate between the two methylene positions to establish whether or not rearrangement was occurring during this reaction. 1-Bromo-2-pentafluorophenyl-[1,1-$^2H_2$]ethane ($C_6F_5CH_2CD_2Br$) (<u>32</u>) was used and the reaction envisaged is shown in Scheme II.4. It was hoped to identify the position of the deuterium label after reaction by mass spectral analysis of the reaction mixture.

Compound (<u>32</u>) was prepared according to Scheme II.5.



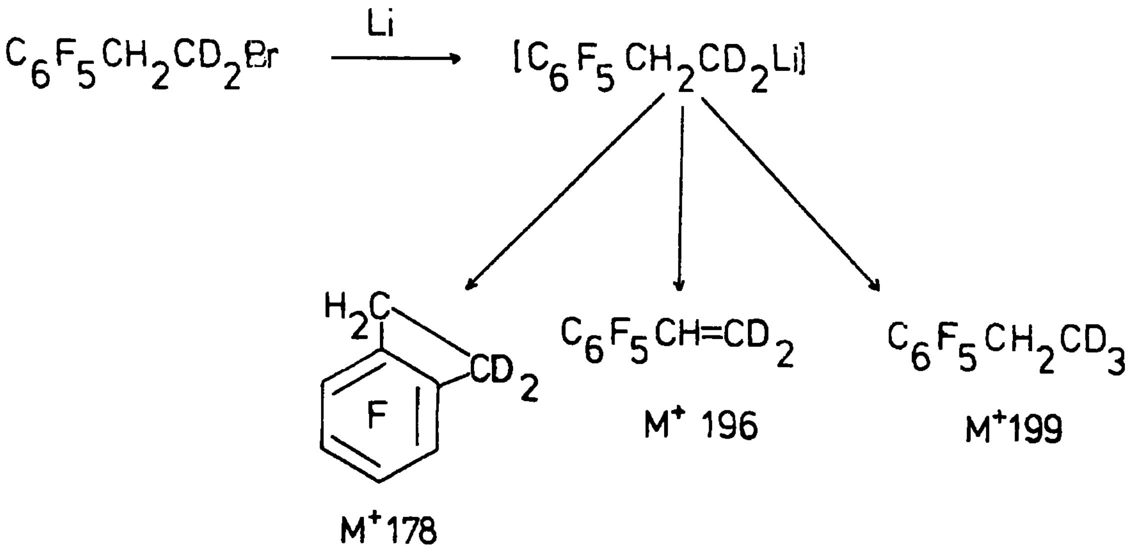
Scheme II.5.


UNREARRANGED REARRANGED
CH2CD2Br
F
(i)
(ii)
CH=CD2
MW= 196
CD=CH2
MW = 195
or mixture
CH2CD3
MW = 199
Base=181 peak
CD2CH2D
MW = 199
Base= 183 peak
or mixture
H2C
CD2
MW = 178
unchanged
CD2CH2Br
(i) Li
(ii) t-BuOD

Scheme II.4.

The product was obtained in 85% yield, an impurity , (33), being detected on mass spectral analysis (M^+ 259, M+2 261). Compound (32) was identified by comparison of data with those of compound (24) and from mass spectral and proton nmr evidence.

The reaction of (32) with lithium was carried out at 0°C for five hours, during which time a green colouration was observed, followed by the formation of a red-brown colour. After this time no starting material was detected on glc analysis of a hydrolysed aliquot. Analysis of the quenched material showed there to be three volatile components, which were separated from the solvent by preparative scale glc. Mass spectral data for the product mixture indicated that the following had occurred (Scheme II.6.).

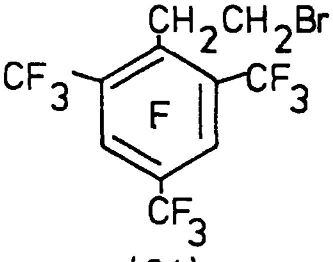


Scheme II.6.

The base peak in the mass spectrum of the pentafluorophenyl-[1,1,1-$^2H_3$]-ethane component of the mixture occurred at m/e 181, which corresponds to a very stable benzyl fragment $C_6F_5CH_2^+$, and no significant peak occurred at m/e 183. This indicates that no deuterium had been incorporated into the benzyl position of the molecule and therefore that no 1,2-rearrangement had occurred.

II.5.K. Conclusion.

Despite the difficulties involved in forming the compound (27) reproducibly, it seems clear that no 1,2-aryl rearrangement occurred in this system. Several factors are involved here. Obviously the pentafluorophenyl group itself is not sufficiently activating to produce rearrangements with magnesium or lithium and the carbon-metal bonds in the organometallic compounds formed are not sufficiently ionic. Coupled with these factors is the ease of decomposition of the organometallic once it has formed. Possibly the best solution for producing rearrangement would be to use a ring with strongly electron-withdrawing groups attached at the 2, 4, and 6 positions (e.g. (34)) as substrate and attempt similar reactions to those described above. This should be even more activating for a carbanion rearrangement than the pentafluorophenyl group. The addition of bulky groups at the 2-position of the ethyl group in compound (34) would further enhance rearrangement, by relief of steric strain.



(34)

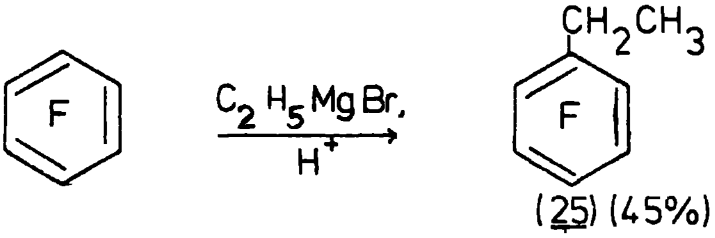
II.6. Reactions with Pentafluorophenylethane.

Several reactions were performed on pentafluorophenylethane to determine the effect of base upon it and the influence exerted by the β-pentafluorophenyl group in its reactions and to see whether any rearrangement occurred.

II.6.A. Preparation of Pentafluorophenylethane (25).

Compound (25) was prepared according to a literature method[37] (equation II.6.).

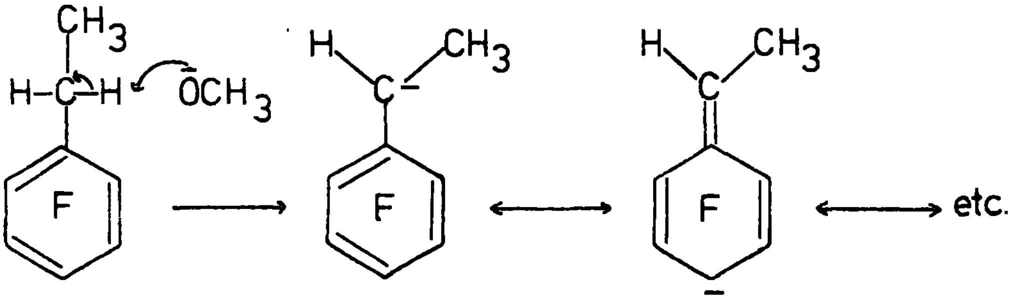
II.6.



II.6.B. Reaction of Compound (25) with Sodium Methoxide.

The object of this reaction was to observe whether sodium methoxide would remove an α-proton from the ethyl group and if so what form the resulting anion would assume, since benzilic anions can be regarded as analogues of bridged species (equation II.7.).

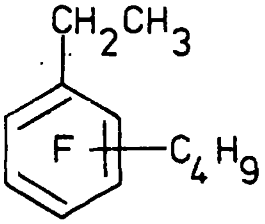
II.7.



Initial experiments indicated that no ring substitution occurred, even after 28 days at room temperature. In the presence of methanol - d_4 no deuterium incorporation was observed at room temperature. Presumably, therefore, the pentafluorophenyl group is not sufficiently electron-withdrawing to make the α-proton acidic enough to be removed by methoxide.

II.6.C. Reaction of Compound (25) with n-Butyllithium.

This reaction was carried out for a similar reason to that described in Section II.6.B., but using a stronger base. Compound (25) and n-butyllithium were stirred together for three hours at -70°C and the mixture was quenched with deuterium oxide. Two components were observed in the mixture - compound (25) with no deuterium incorporated and a higher boiling point liquid which was shown to be compound (29) from mass spectral data, which agreed with those found in Section II.4.B. This reaction illustrates the ease with which the pentafluorophenyl ring can be butylated.



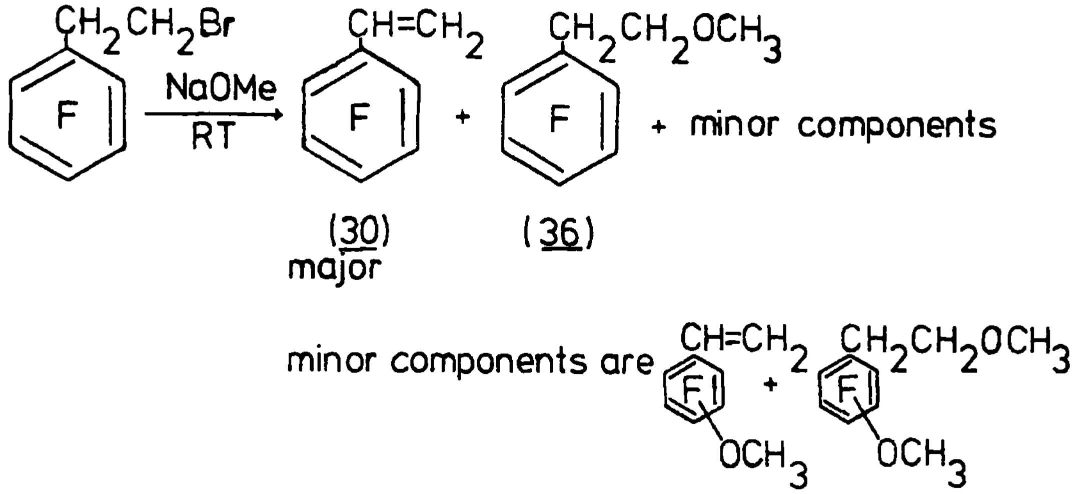
(29)

II.7. Miscellaneous Reactions.

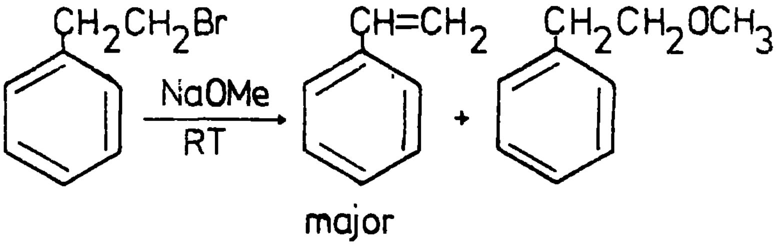
II.7.A. Reactions of Compound (24) and 1-bromo-2-phenylethane with Sodium Methoxide.

The object of these experiments was to compare the activity of pentafluorophenyl and phenyl groups as substituents in a base-induced elimination reaction. The reactions are shown in equations II.8. and II.9.

II.8.



II.9.

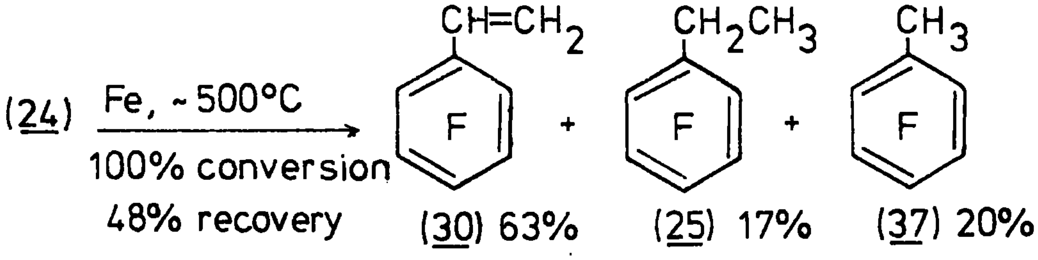


The products were identified from mass spectral evidence and comparison of data with those from authentic samples. It appears that the pentafluorophenyl ring does not exert any marked influence over phenyl in this reaction apart from its greater susceptibility to ring substitution. This is consistent with the results described in Section II.6.B., where no enhancement of acidity of the proton α to the ring was observed. Compound (36) and its non-fluorinated analogue are presumably formed by nucleophilic displacement of bromide.

II.7.B. Passage of Compound (24) over hot iron in a silica tube.

This reaction was carried out to determine whether Br and F could be removed from the molecule to give the very interesting benzo-cyclobutene - type compound discovered in the decomposition of compound (27) (see Scheme II.3., compound (31)). The reaction observed is shown in equation II.10.

II.10.

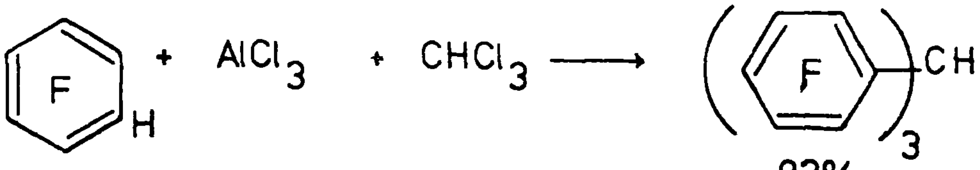


Compounds (30) and (25) have been prepared earlier. Compound (37) showed M^+ 182 in its mass spectrum and ^{19}F and ^1H nmr spectral data were consistent with the proposed structure. No benzocyclobutene-type compounds were detected in the reaction mixture.

II.7.C. Attempted Preparation of 1-Bromo-2,2,2-tris(pentafluorophenyl)-ethane.

As stated earlier, (Section II.5.K.), one reasonable suggestion for increasing the probability of 1,2-aryl rearrangement in a substituted ethyl system would be to increase the steric crowding of the molecule around the site from which rearrangement would occur. Accordingly, attempts were made to prepare compound (38) from pentafluorobenzene in a two-step process. Tris(pentafluorophenyl)methane was prepared in a literature Friedel-Craft type reaction[38] (equation II.11.). Attempts were made to determine whether the tris(pentafluorophenyl)methyl anion would react, under fairly vigorous

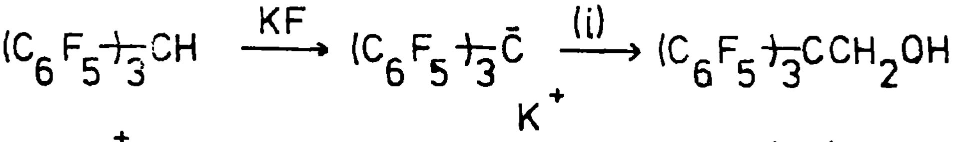
II.11.


93%

(m.p. 153-4°C,
lit.[38] 157-9°C)

conditions, with formaldehyde in order to produce 1-hydroxy-2,2,2-tris(pentafluorophenyl)ethane according to equation II.12.

II.12.


$$(C_6F_5)_3CH \xrightarrow{KF} (C_6F_5)_3\bar{C}\ K^+ \xrightarrow{(i)} (C_6F_5)_3CCH_2OH$$

(i) HCHO; H^+

(38)

However, although the anion was readily formed with potassium fluoride, very little, if any, reaction was observed, even after treatment with formaldehyde in a sealed tube at 170°C for 60 hours. The tris(pentafluorophenyl)methyl anion is obviously very stable presumably because of the shielding effect of the three large groups surrounding the anionic site and also because of the delocalisation which is possible throughout the three pentafluorophenyl rings.

Chapter III

Experimental Results for Chapter II.

III.1. Instrumentation.

Proton and fluorine nmr spectra were recorded at 40°C (standard probe temperature) on a Varian A 56/60D spectrometer, operating at 60 and 56.4 MHz respectively. Chemical shifts are quoted relative to external TMS and chlorotrifluoromethane. Infra-red spectra were recorded on a Perkin-Elmer 457 Grating Infra-red spectrophotometer using KBr plates or discs. Mass spectra were run using an AEI MS-9 instrument or a VG Micromass 12B spectrometer fitted with a Pye 104 gas chromatograph. Gas liquid chromatographic analyses were carried out on a Griffin and George D6 Gas Density Balance, Varian Aerograph Model 920 or Pye 104 Gas Chromatograph using columns packed with 30% silicone gum rubber SE-30 on chromosorb P (column O), 20% diisodecylphthalate on chromosorb P (column A) or 30% trixylenylphosphate on chromosorb P (column T). Preparative scale gas liquid chromatography was performed on a Varian Aerograph Model 920 using columns O and A.

III.2. Reagents and Solvents.

III.2.A. Reagents.

Bromopentafluorobenzene was supplied by Imperial Smelting Corporation Ltd..Lithium dispersion in wax was supplied by Pfizer Ltd. and had the following composition: lithium (37.5%), paraffin wax (60.5%) and oleic acid (2.0%). The particle size was 90% $< 30\mu$. Lithium wire, supplied as 3.2mm diameter wire packed under mineral oil from Alfa-Ventron, contained 0.02% sodium. n-Butyllithium was supplied in hexane solution, approximately 2M, by LithCoA. The assay of this solution is described in a subsequent section. Other reagents were used as supplied.

III.2.B. Solvents.

THF was supplied dry (distillation from lithium aluminium hydride and then potassium metal) by the Technical Services of this department.

1,4-Dioxane was purified by a standard procedure[39], peroxides having first been removed by passage down an alumina column.

Chloroform was also purified by a literature method[40].

All other solvents were sodium dried where appropriate.

III.3. Reactions.

III.3.A. Preparation of 1-Bromo-2-pentafluorophenylethane (<u>24</u>).

a) Preparation of 1-Hydroxy-2-pentafluorophenylethane[28].

In a typical reaction, magnesium (8.5g, 0.35mmol) and dry THF (100ml) were placed in a flask which had been purged with dry nitrogen. The reaction was carried out under nitrogen . The magnesium was activated with 1,2-dibromoethane, and bromopentafluorobenzene (39.3g, 0.16mol) was added slowly over 2.5h, the internal temperature being maintained at 2-3°C. The mixture was stirred for 1h, the temperature remaining below 6°C. Oxirane (18ml, 15.9g, 0.36mol) was added and the mixture was kept at room temperature for 15.5h. Hydrochloric acid (5M, 15ml) was added to the thick, black slurry, with cooling, and effervescence occurred. The organic layer was separated, the aqueous phase washed with ether and the organic phases then combined and dried over magnesium sulphate. After removal of the desiccant, ether and THF were distilled at atmospheric pressure. Distillation of the residue at reduced pressure yielded 1-hydroxy-2-pentafluorophenylethane (24.6g, 73%) b.p. 87-89°C at 8mm Hg. This was identified by comparison of the ir spectrum with that of an authentic sample[41].

b) Preparation of 1-Bromo-2-pentafluorophenylethane.

1-Hydroxy-2-pentafluorophenylethane (35.8g, 17mol), sulphuric acid (conc., 36ml) and hydrobromic acid (48%, 111ml) were refluxed for 19h. Water (100ml) was added, the organic phase was extracted with ether, dried and the solvent removed at atmospheric pressure to leave compound (<u>24</u>) (37.3g,80%). The product was distilled through a short column filled with glass helices b.p. 72-76°C at 8mm Hg and glc analysis (Pye 104, col. $O_{25\%}$, 120°C) indicated 98% purity.

III.3.B. Grignard Reaction of 1-Bromo-2-pentafluorophenylethane (<u>24</u>).

a) Hydrolysis.

In a typical reaction, magnesium (0.14g, 5mmol) was placed in ether (2.5ml) in a flask fitted with a reflux condenser and previously purged with dry nitrogen. The reaction was carried out in an atmosphere of nitrogen. The magnesium was activated with 1,2-dibromoethane. Compound (<u>24</u>) (0.91g, 3mmol) was added dropwise over 2.5h at room temperature. The mixture was stirred for 1h at 15°C. Hydrochloric acid (5M, 2.3ml) was added, the organic layer was separated and dried. Glc analysis (GDB, col.O, 120°C) indicated one product. The extent of reaction based on disappearance of starting material calculated from glc was ~ 98%. The product was isolated by preparative scale glc (col. O, 132-133°C) and vacuum transferred from phosphorus pentoxide. This was identified as pentafluorophenylethane (<u>25</u>) (Found: C, 49.2; F, 47.9; H, 2.6%. $C_8F_5H_5$ requires C, 49.0; F, 48.5; H, 2.5%). Nmr spectrum no.1, ir spectrum no.1.

Reactions using THF as solvent were carried out in an analogous manner.

Attempts were made to carry out this reaction in 1,4-dioxane, monoglyme, tetraglyme and benzene but in no case could the magnesium be successfully activated since insoluble material coated the surface.

b) Carbonation.

The Grignard reagent was prepared as in (a) above using magnesium (1.1g, 45mmol), compound (<u>24</u>) (3.05g, 11mmol) and THF (16ml). Glc of a hydrolysed aliquot (Pye 104, col.O, 150°C) showed that no starting material was present. Carbon dioxide was sublimed from solid through a drying tower (calcium chloride) and into the reaction mixture for 0.5h. The mixture was kept overnight and then acidified (11M hydrochloric acid) to destroy the magnesium. The organic layer was extracted with ether and washed (2M sodium hydroxide solution, 3x15ml). The aqueous layer was separated, acidified and extracted with ether (2x30ml). After drying (magnesium sulphate), the desiccant and solvent were removed from the organic layer to leave a yellow - brown solid. This was recrystallised from hot water, an insoluble yellow oil being left. White crystals separated and were dried in vacuo. The ir spectrum of the oil agreed with that of the crystals (ir spectrum no. 2). The oil was sublimed, 70°C at 1mm Hg, to give white crystals. The total yield of 3-pentafluorophenylpropanoic acid obtained was 0.77g (29%), m.p. 94.5°C, lit.[30] 95-96°C. Glc analysis of the original organic layer showed a very small trace of compound (<u>25</u>).

c) Methylation of the Carboxylic acid.

3-Pentafluorophenylpropanoic acid (0.1g, 0.42mmol), methanol (1ml, excess) and sulphuric acid (conc., 4 drops) were refluxed for 8.5h. Water was added to remove the acid and methanol, and the organic phase was extracted with ether and dried. Glc of the ethereal solution (GDB, col. O, 120°C) showed one product peak. The ir spectrum of this in ether (contact film) showed $\nu_{max} = 1740\text{cm}^{-1}$ (ester C=O stretch) and no acid O-H stretch. The residue from crystallisation was also refluxed with methanol and after work-up showed a similar product to that described above.

d) Decomposition of the Grignard Reagent.

i) The Grignard reagent was formed as described above, in THF, but the temperature was maintained at reflux temperature (65°C) for 3h before hydrolysis. Glc analysis of the products showed only compound (25). In another experiment, THF was distilled from the Grignard reagent, o-xylene was added to the mixture and the whole was refluxed for 1h (144°C). Hydrolysis and glc analysis showed a similar product to that obtained in the previous experiment.

ii) The Grignard reagent was formed as described above, in THF, and when it had formed (observed by glc of a hydrolysed aliquot) the liquid above the magnesium was syringed into a Carius tube which was then sealed. After heating at 130°C for 22h the tube was opened and the products separated (GDB, col. O, 210°C). Two products were observed, MS data showed M^+ 196 ($C_6F_5CH_2CH_3$) and M^+ 194 ($C_6F_5CH{=}CH_2$).

III.3.C. Reaction of Compound (24) with n-butyllithium.

a) Assay of n-Butyllithium.

The solution of n-butyllithium in n-hexane (1ml) was assayed by reaction with water (20ml), all lithium reacting to give lithium hydroxide, which was then titrated with 0.1M hydrochloric acid using phenolphthalein indicator. In order to determine the exact n-butyllithium content (free from alkoxide impurity) the double titration method was used[42]. A second aliquot of n-butyllithium solution (1ml) was added to redistilled benzyl chloride (2-3ml) b.p. 61-62°C at 8mm Hg, in anhydrous ether (10ml). After a fairly vigorous reaction in which a faint transient yellow colouration was observed (owing to the presence of benzyllithium formed in the reaction with n-butyllithium) and a white precipitate was seen (lithium chloride?), the mixture was reacted with water and titrated as before. The difference in titres was due to the n-butyllithium present. The molarity of the solution used was initially 1.2M. After a period of approximately 5 months the molarity had risen to 1.7M owing to solvent evaporation.

b) Reaction with n-Butyllithium.

In a typical reaction, compound (<u>24</u>) (0.25g, 0.9mmol) was placed in ether (5ml) under nitrogen and the solution was cooled to -70°C in a carbon dioxide - acetone bath. n-Butyllithium solution (0.75ml, 0.9mmol) was added dropwise, the temperature being kept below -65°C. The mixture was stirred at this temperature for 2h, when water (1ml) was added and the mixture was allowed to attain room temperature. The organic layer was separated, dried and analysed by glc.

In other reactions using different temperatures, solvents or scale, the procedure was the same.

c) Reaction in Ether at 0°C.

Compound (<u>24</u>) (0.58g, 2.1mmol) was placed in dry ether (5ml). n-Butyllithium (2.55ml, 4.3mmol) was added over 0.3h at 0°C and the mixture was stirred for a further 0.16h. A transient pink colouration was observed, then a yellow colour.After hydrolysis (water, 4ml) the organic layer was separated, dried and analysed by glc (GDB, col. 0, 120°C). No starting material was detected and little or no volatile material. Tlc of the mixture ($CHCl_3$:C_6H_{14}, 50:50) showed a single spot R_f= 0.71, which did not correspond to n-bromobutane. Isolation was effected by preparative scale thin layer chromatography. Mass spectral evidence was as follows: m/e M^+312, M+2, 341, of similar intensity ($C_6F_4(C_4H_9)CH_2CH_2Br$), 219 ($C_6F_4(C_4H_9)CH_2^+$), 190 ($C_6F_4(C_2H_5)CH_2^+$), 189 ($C_6F_4(C_2H_4)CH_2^+$), 177 ($C_6F_4(CH_3)CH_2^+$), 176 ($C_6F_4(CH_3)CH_2^+$), 163 ($C_6F_4HCH_2^+$). Nmr spectrum no.2. These data clearly indicate a structure (<u>28</u>).

d) Reaction in THF at -74°C.

Compound (<u>24</u>) (1.05g, 3.8mmol) was placed in THF (10ml) and cooled to -74°C. n-Butyllithium (2.15ml, 3.65mmol) was added slowly over 0.16h to the stirred mixture. On addition, a pink colouration was observed and when all of the n-butyllithium had been added the colour was intense. This faded to a yellow-green colour after 0.08h. A sample (1ml) was removed and hydrolysed after 1.5h. A further addition of n-butyllithium (0.9ml, 1.5mmol, giving total (nBuLi) 5.3 mmol) was made over 0.3h. Again a pink colouration was observed, which faded slowly. After stirring for 1.5h a second aliquot was removed and hydrolysed. A final portion of n-butyllithium solution (1ml, 1.7mmol, giving total (nBuLi) 7.0mmol) was added over 0.5h. The pink colour appeared on addition and remained. A third aliquot was removed after 0.5h. The bulk solution was hydrolysed after a further 2.5h and on addition of water the colour disappeared. Glc analysis (Pye 104, col. O, 150°C) of the samples was carried out and the following was observed; (Cumulative time, extent of reaction, components detected); 1.5h, 34%, bromobutane, (25), unknown, (24); 3.3h, 80%, bromobutane (increased), (25) and unknown (decreased), (24); 4.3h, 100%, bromobutane, (25) (very small amount), higher boiling material; 6.8h, other data unchanged. MS-glc data were obtained for the volatile material and the residue, and were as follows:

Volatile material: m/e M^+ 196 ($C_6F_5CH_2CH_3$) and 181 ($C_6F_5CH_2^+$); m/e M^+ 194 ($C_6F_5CH{=}CH_2$). These data and glc retention times suggested that the volatile component of the mixture contained compound (25) and pentafluorophenylethene (30). Involatile material: m/e M^+234 ($C_6F_4(C_4H_9)CH_2CH_3$), 191 ($C_6F_4(C_2H_5)CH_2^+$), 177 ($C_6F_4(CH_3)CH_2^+$), 163 ($C_6F_4HCH_2^+$), 162 ($C_6F_4CH_2^+$). These data are consistent with structure (29). Ir spectrum no. 3.

III.3.D. Experiments with Lithium in wax.

a) In a typical reaction to observe the conditions required for using this material, lithium (0.4g, 1.06g in wax, 58mmol) was placed in pentane (10ml) and the mixture was stirred to remove the wax coating from the metal. 1-Bromobutane (3.14g, 23mmol) in pentane (10ml) was added to the refluxing mixture over 2.5h and the mixture was stirred for a further 1h. Aliquots (1ml) were removed, hydrolysed (degassed water) and titrated with standard acid. Lithium metal contamination of this aliquot was minimised by allowing the metal to settle before removal of the solution. Calculated yield of n-butyllithium from hydrolysis of an aliquot of material was 64%. The liquid was filtered from unreacted lithium under nitrogen, the metal was hydrolysed and the lithium hydroxide formed was titrated with standard acid. This corroborated the earlier figure and indicated that ~65% reaction had occurred. Table III.1. illustrates the effect of conditions upon yield.

Solvent	Temp. °C	Time h [1]	% Yield nBuLi[2]	Comments
Hexane	30	3	26	Very little agitation. Inhibition at the metal surface - by metal halide?
Pentane	37	2	55	Increased agitation.
Pentane	37	3.5	66	Increased agitation and increased addition time.

1. Time for addition of 1-bromobutane.
2. Determined by titration with standard acid.

Table III.1.

b) Reaction of Compound (<u>24</u>) with Lithium in Wax.

In a typical reaction, lithium (0.17g, 0.46g in wax, 25mmol) was placed in pentane (20ml) to remove the wax. The majority of this solvent was removed and THF (6ml) was added. The mixture was cooled to -10°C and compound (<u>24</u>) (1.64g, 5mmol) was added over 1.3h. The mixture was stirred at -10°C (± 5°C) for 2.5h. Water (20ml) was added to hydrolyse the lithium and the organic phase was separated and dried. Glc analysis (GDB, col. O, 120°C) indicated that $<1\%$ reaction had occurred.

The reaction was repeated with added sodium wire but this appeared to have no effect.

III.3.E. Reaction of Compound (<u>24</u>) with Lithium Wire.

In the reactions carried out with lithium wire the reaction conditions and times vary widely. This was due to the difficulty experienced in activating the metal and in some cases to the inhomogeneity of its composition. The technique involved was the same in all cases and experiments are quoted only where some variation is significant.

a)Hydrolysis.

Lithium (1.35g, 193mmol, as wire cut into small pieces) was placed in THF (15ml) in apparatus which had been purged with nitrogen. The mixture was cooled to -10°C (± 5°C) and methyl iodide (0.5ml) and (<u>24</u>)(20 drops) in THF (1-2ml) were added to activate the metal. The mixture was stirred for 1h, a green colouration being observed, and an exothermic reaction being detected. The remainder of the halide (<u>24</u>) (total 5.14g, 18.7mmol) was added over 0.5h at -5°C, and stirring at this temperature was continued. After 2h glc analysis of a hydrolysed aliquot showed only a small conversion to products. The temperature was raised to 0°C and more methyl iodide was added, whence a vigorous reaction occurred. Aliquots were removed and hydrolysed at intervals and the reaction was allowed to proceed for 22.6h. The lithium was removed and destroyed (ethanol) and the reaction mixture quenched with water. Glc analysis of the mixture indicated 53% conversion to products. The organic layer was extracted (ether), dried, and the desiccant and solvent were removed. Glc analysis (GDB, col. A, 120°C) showed three volatile components and a small amount of involatile material. The volatile materials were identified by MS-glc data as pentafluorophenylethane (25) (16%) m/e M^+ 196 ($C_6F_5CH_2CH_3$) and 181 ($C_6F_5CH_2^+$); pentafluorophenylethene (30)(62%) m/e M^+ 194 ($C_6F_5CH{=}CH_2$); the third component (22%) m/e M^+176, consistent with loss of HF and hence structure (31). ^{1}H Nmr spectral data of the mixture showed the following: δ 1.48ppm, triplet, $-CH_3$; 2.09ppm, quartet, $-\underline{CH_2}-CH_3$; 3.94ppm, multiplet, $-CH_2-CH_2-$; 6.45ppm, multiplet, $-CH{=}CH_2$. No meaningful integration values could be obtained since a mixture was being investigated but the positions and coupling of the signals are consistent with the proposed structures.

b) Quenching with Bromine.

The reaction was carried out in a similar manner to that described earlier but bromine in pentane was added to quench it. Water was added after the mixture had attained room temperature. The organic layer was separated and dried, excess bromine being removed with copper powder. The mixture was analysed by glc.

c) Quenching with tert-Butanol.

The reaction was carried out in the usual manner at -10°C (±5°C) except that tert-butanol was added with the halide (24). A green colouration was observed initially and just prior to hydrolysis the mixture was a dark red colour. Most of the starting material had been consumed after ~3.5h. Hydrolysis of the mixture after the lithium had been removed and destroyed caused effervescence to occur.

Glc analysis of the mixture (GDB, col. T, 150°C) showed (25) as the major product, with some pentafluorophenylethene (30).

d) Reaction of Lithium doped with Copper.

In this reaction, a small amount of copper powder was added to the reaction mixture. Incomplete conversion to products occurred, even after several hours, and many components were observed in the volatile fraction after hydrolysis, both those expected and several others. No products were isolated.

III.3.F. Reaction of Compound (24) with anhydrous Lithium Bromide.

Lithium bromide (0.31g. 3.9mmol) was placed in dry THF (20ml) in which only a small amount dissolved. The mixture was cooled in an ice-salt bath to ~ 0°C. Compound (24) (1.01g, 3.7mmol) was added and the mixture stirred at 0°C for 4.5h. Glc analysis of the organic layer showed that no reaction had occurred.

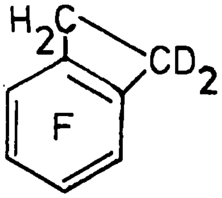
III.3.G. Preparation of 1-Bromo-2-pentafluorophenyl-[1,1-$^2H_2$]-ethane.

Potassium hydroxide (6.06g, 108mmol) was dissolved in water (10ml) and ethanol (35ml) and ether (10ml) were added. p-Tolylsulphonylmethylnitrosamide (21.64g, 101mmol) was dissolved in ether (125ml), and ether (10ml and 35ml respectively) was placed in two traps cooled in ice-salt. The p-tolylsulphonylmethylnitrosamide solution was added to the warmed base over 0.75h and the diazomethane solution so formed was collected in the traps. A further portion of ether (35ml) was added to the reaction mixture and was distilled to wash through all of the diazomethane. When the distillate appeared colourless the distillation was stopped and the ethereal solution of diazomethane was poured into a solution of pentafluorophenylacetic acid (10g, 44mmol) in ether (35ml) until a permanent yellow colouration was observed. The excess diazomethane was removed by distillation, the residual solution was dried ($MgSO_4$), filtered and the total volume of ethereal product was ~275 ml. Dry ether (double dried with sodium, 105ml) and lithium aluminium deuteride (10g, 239mmol) were placed in a flask to which the ester was added fairly rapidly. An exothermic reaction ensued and reflux was maintained for 1.25h after addition. The excess lithium aluminium deuteride was destroyed with ethylacetate in ether and dilute hydrochloric acid was added to the mixture. The organic layer was separated and washed with water. The aqueous layer was extracted with ether and the combined organic layers were dried ($MgSO_4$). A dark brown liquid was left after removal of solvent. This crude material was refluxed with hydrobromic acid (40ml, 48%) and sulphuric acid (conc., 12ml) for 17h. Water was added and the organic layer ether extracted. After removal of solvent the product was distilled at reduced pressure, 78°C, 10-11mm Hg, to give 1-bromo-2-pentafluorophenyl-[1,1-$^2H_2$]-ethane (9.16g, 75%). A second fraction (1.34g, 11%) was obtained b.p. 80-83°C, 10-11mm Hg. The ir spectra of the two fractions were identical (no. 4), nmr spectrum no. 3., m/e M^+276, M + 2 278, of similar intensity, ($C_6F_5CH_2CD_2Br$), 197 ($C_6F_5CH_2CD_2^+$), 181 ($C_6F_5CH_2^+$). A small amount of an impurity was observed at m/e 259,261 which could have been due to $C_6F_4(D)CH_2CD_2Br$.

III.3.H. Reaction of Compound (32) with Lithium.

Lithium wire (1.00g, 143mmol) was placed in dry THF (20ml) and activated at -3°C with a few drops of iodomethane. Compound (32) (~ 30 drops) was added and the mixture stirred for 0.5h. A green colouration was observed. The remainder of compound (32) (total 4.20g, 15.3mmol) was added slowly over 1h and resulted in a brown colouration of the mixture. This was stirred at -5°C (± 5°C) until glc analysis of a hydrolysed aliquot showed no starting material. The lithium was removed and destroyed after ~ 4.5h and tert-butanol-d_1 was added

(2.5ml). The mixture was allowed to attain room temperature and was kept overnight. After extraction and drying, the majority of the solvent was removed by distillation and the volatile material was vacuum transferred. The solvent was further removed by preparative scale glc and the product mixture (three peaks) was analysed by MS-glc to give: pentafluorophenyl-[1,1,1-$^2H_3$]-ethane m/e M^+ 199 ($C_6F_5CH_2CD_3$), and 181 ($C_6F_5CH_2^+$). Loss of $-CD_3$ to give $C_6F_5CH_2^+$ proves that no exchange of the pentafluorophenyl group occurred. 2-pentafluorophenyl-[1,1-$^2H_2$] -ethene m/e M^+196 ($C_6F_5CH{=}CD_2$) (major product) and the third component, m/e 178, which is consistent with the structure illustrated below. No further isolation procedure was



carried out.

III.3.J. Reactions of Pentafluorophenylethane (25).

a) Preparation of Pentafluorophenylethane.

This was carried out according to a literature method[37], with the following isolation procedure. The majority of the solvent (pentane and THF) was removed by distillation through a 2ft column filled with glass helices, with a take off rate of 1:10 and the liquid remaining was distilled on a Fischer Spaltrohr concentric tube apparatus. The fraction b.p. 130-133°C was collected. The residue remaining in the distillation vessel was purified by vacuum transference and glc analysis (GDB, col. O, 120°C) showed that this also contained the required product. The total yield of pentafluorophenylethane was 45%. The ir spectrum agreed with that of an authentic sample (III.3.B.).

b)Reaction of Compound (25) with sodium methoxide in methanol.

Pentafluorophenylethane (0.6g, 3.1mmol), sodium methoxide (0.08g, 3.5mmol) and dry methanol (0.5ml) were mixed in an nmr tube and the ^{19}F nmr spectrum was run at intervals (1h, 4days and 28days). No change was observed after this time.

c)Reaction of Compound (25) with sodium methoxide in methanol-d_4.

Compound (25) (0.39g, 1.98mmol) was added to benzene (176 μl internal integration standard) and methanol-d_4 (0.6ml) was added. This solution was divided equally into two nmr tubes, one to act as a control. Sodium (0.07g, 3.0mmol) was added to methanol-d_4(~ 3ml) to make ~ 10% solution of sodium methoxide. This (0.7ml) was added to the mixture in one of the nmr tubes and the proton nmr spectra were compared at varying intervals over a period of six days. No change was observed over this time.

d)Reaction of Compound (25) with n-Butyllithium.

Compound (25) (0.94g, 4.8mmol) was placed in a flask which had been purged with nitrogen, dissolved in THF (8ml) and cooled to -70°C. n-Butyllithium (3.9ml, 4.7mmol) was added slowly and the mixture was stirred for 3h, after which time it had assumed a yellow-brown colour. D_2O (0.5ml, 99.8%) in THF (3ml) was added and the mixture allowed to attain room temperature. The now colourless crude reaction mixture was was analysed by glc (GDB, col. 0,120°C). This indicated the presence of starting material as well as a less volatile component. These were separated by preparative scale glc (col. 0, 150°C) and each was analysed by its mass spectrum and nmr data. These data indicated that no deuterium had been incorporated into either component. The mass spectral data for the higher boiling material gave m/e M^+ 234 ($C_6F_5(C_4H_9)CH_2CH_3$). These data indicated a structure (29) (see Section III.3.C.(d) for comparison).

III.3.K. Reaction of Compound (24) with sodium methoxide in methanol.

Methanol (10ml) and sodium (0.26g, 11mmol) were mixed together When the reaction had subsided compound (24) (3.1g, 11mmol) was added over a few minutes and the mixture was stirred at room temperature for 21h. Water was added and a white colouration was observed. The lower layer was separated (1.8g), dried ($MgSO_4$) and the volatile components were vacuum transferred in two fractions - at room temperature (1.1g) and on heating. The first fraction contained one major component m/e M^+ 194($C_6F_5CH{=}CH_2$). The glc retention time was similar to that of pentafluorophenylethane, which is consistent with this identification. Ir spectrum no. 5. The minor component was not identified. On standing in the light the sample gradually solidified to give a colourless polymer. The second fraction contained several components each present in very small amounts. The MS data are as follows: m/e M^+ 194 ($C_6F_5CH{=}CH_2$); m/e M^+ 206 ($C_6F_4(OCH_3)CH{=}CH_2$) and 191 (loss of $-CH_3$); m/e M^+274,276 ($C_6F_5CH_2CH_2Br$); m/e 224 ($C_6F_5CH_2CH_2OCH^+$); m/e M^+ 286,288 ($C_6F_4(OCH_3)CH_2CH_2Br$). A further component was not identified. There was insufficient of any of these to isolate.

III.3.L. Reaction of 1-Bromo-2-Phenylethane with sodium methoxide in Methanol.

The reaction was carried out in an analogous manner to that described above using the following conditions: 1-bromo-2-phenylethane (2.69g, 14.5mmol), sodium (0.34g, 16.8mmol) in methanol (10.5ml), reacted at room temperature for 25h. Work-up was effected in the same manner as described above, to give 1.16g of material. The most volatile fraction contained two components - starting material and phenylethene m/e M^+ 104. The second fraction contained phenylethene together with 1-methoxy-2-phenylethane m/e M^+ 136 ($C_6H_5CH_2CH_2OCH_3$), 104 ($C_6H_5CH_2CH^+$), and 92 ($C_6H_5CH_2^+$).

III.3.M. Passage of Compound (24) over Iron.

Compound (24) (3.97g, 14.4mmol) was dripped into a silica tube containing iron filings and heated to 490 - 500°C. It was carried over the metal surface in a slow stream of nitrogen (flow rate ca. $50cm^{-1}$). When all of the halide (24) had been passed over the metal surface the trapped material (1.35g) was analysed by glc (GDB, col. A, 140°C) No starting material was found to be present, but three products had been formed. These were separated by preparative scale glc. Two of the components were identified as compound (25), pentafluorophenylethane (17%) and pentafluorophenylethene (30) (63%) by comparison of spectral data with those of authentic samples prepared earlier. The most volatile component was lost before ir data could be obtained but other data indicated that it was pentafluorophenylmethane $C_6F_5CH_3$, (20%), m/e M^+ 182 and 181 ($C_6F_5CH_2^+$). ^{19}F nmr spectral data exhibited signals consistent with a pentafluorophenyl group and the proton nmr spectrum showed a singlet at δ 1.86ppm.

III.3.Na)Preparation of tris(pentafluorophenyl)methane.

This was carried out according to a literature method[38] to give 93% crude yield of material, which gave white crystals m.p. 153-4°C, lit.[38] 157-9°C, after purification.

b) Reaction of tris(pentafluorophenyl)methane with potassium fluoride and formaldehyde.

i) tris(Pentafluorophenyl)methane (1.92g, 3.3mmol), potassium fluoride (0.33g, 5.7mmol) and paraformaldehyde (0.18g, 6mmol) were heated to 60°C in monoglyme for 21h. Yellow and then purple colourations were observed. Thin layer chromatography of the mixture showed one spot which had a similar R_f value to that of the starting material ($CHCl_3$:hexane; 5:95). A colouration was observed at the origin. MS data on the mixture were identical with those of the starting material. The ir spectra were also identical.

ii) tris(Pentafluorophenyl)methane (1.34g, 2.3mmol), potassium fluoride (0.32g, 5.5mmol) and paraformaldehyde (0.18g, 6mmol) were sealed in a Carius tube with monoglyme (~7ml) and heated at 170°C for 60h. Some purple colouration was observed in the tube. After opening, the liquid was filtered from a brown solid and the volatile material (monoglyme) was pumped off to leave solid material (1.34g). Hydrochloric acid (1.25M) was added and the product was washed with water and extracted with ether. Removal of ether left a brown-orange solid which showed as starting material on tlc, with a purple spot at the origin. The starting material was sublimed from the solid but the ir spectrum of the residue indicated that starting material was the only component present. It was concluded from this that only a very small amount of reaction (if any) could have occurred.

II. REACTIONS OF PERFLUORO-3,4-DIMETHYL-3-HEXENE AND RELATED COMPOUNDS.

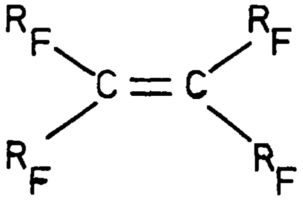
Chapter IV

Introduction -

Preparation and Reactions of Internal Fluoroalkenes.

IV.1. Introduction.

Many different types of fluoroalkene are known at the present time, from the simplest ($CF_2{=}CF_2$) to highly complex branched compounds. The aim of this chapter is to give a brief summary of the preparation and general reactions of internal alkenes. For the purposes of this review the term internal fluoroalkene is taken to mean structures such as (39) where the R_F groups are perfluoroalkyl or perfluorocycloalkyl groups. There are relatively few examples of this type of compound compared with less-highly substituted analogues.

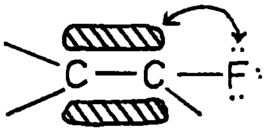


(39)

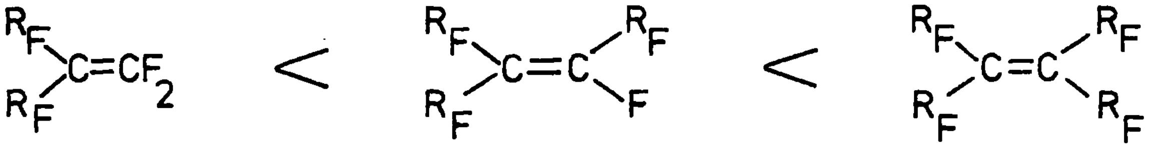
IV.2. The Effect of Fluorine on Alkenes.

Substitution of a hydrogen atom by fluorine in an alkene does not significantly affect the geometry of the system but the nature of the reactions is greatly altered. Thus, hydrocarbon alkenes have an extensive electrophilic chemistry while fluorocarbon analogues are largely susceptible to nucleophilic attack because of the electron-withdrawing effect of fluorine and perfluoroalkyl groups[44].

Compounds containing a fluorine atom attached directly to the double bond are less stable than those in which the double bond is surrounded by, for example, perfluoroalkyl groups. This is most probably due to destabilisation by repulsive interaction of the lone pairs on the fluorine atom with the π-electrons of the double bond.



The order of stability is therefore:



Fluoroalkenes containing vinylic fluorine atoms are readily isomerised, for example in the presence of fluoride ion, to the more stable internal alkenes[44].

IV.3. Preparation of Internal Fluoroalkenes.

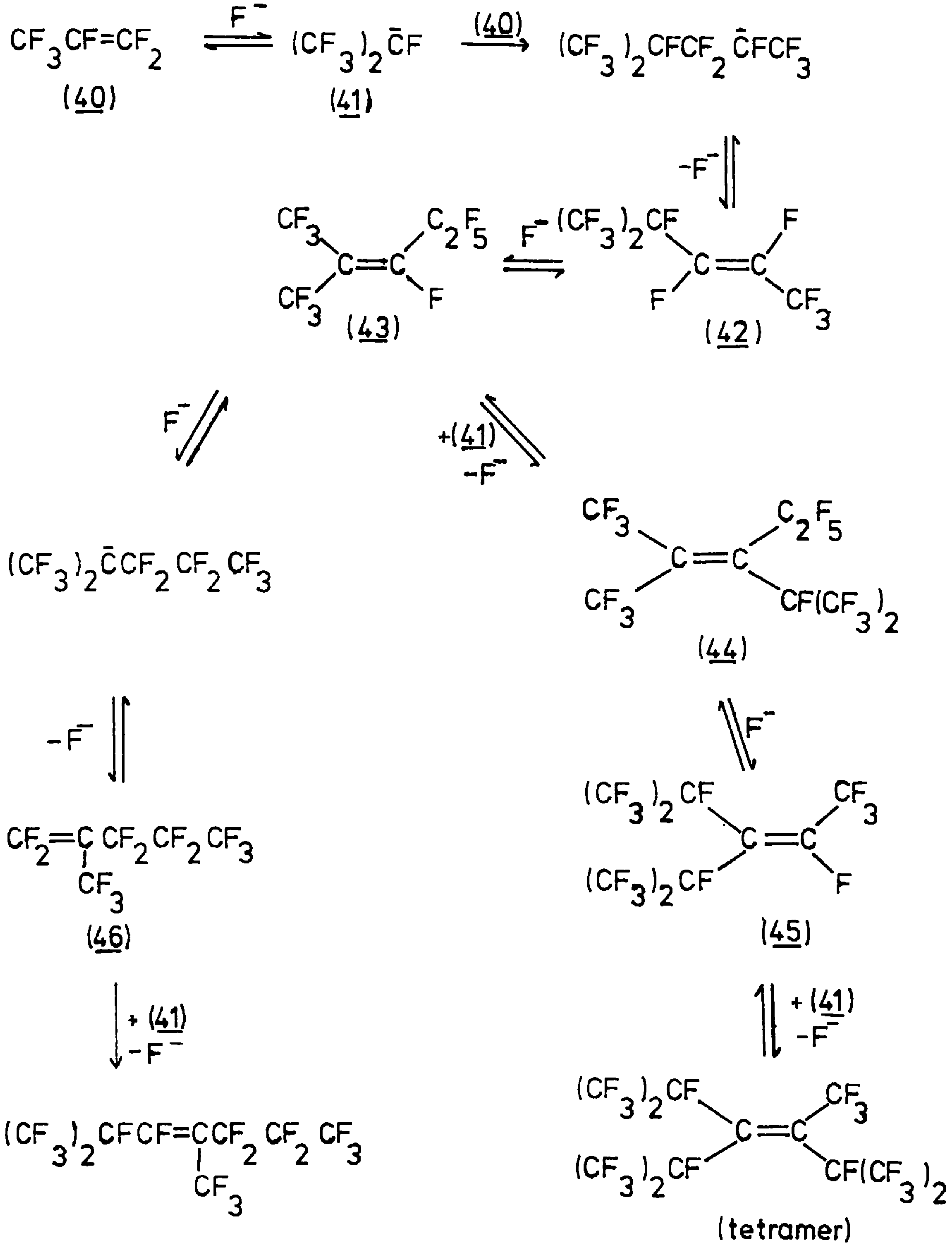
IV.3.A. Anionic Oligomerisation.

Anionic oligomerisation is the most useful method for preparing internal fluoroalkenes although cationic processes are also known. Free radical reactions result in the formation of high molecular weight material, not simple oligomers.

The general method can be illustrated by consideration of the oligomerisation of hexafluoropropene, for example (Scheme IV.1.). From this it can be seen that there are three stages in the process:

i) formation of the carbanion from the alkene (initiation),

ii) reaction of the carbanion and the alkene to give a larger



Scheme IV.1.[45]

carbanion (propagation) and
iii) loss of fluoride ion, often accompanied by isomerisation to a more stable alkene (termination).

Several factors affect the product distribution in these systems. Firstly, the catalyst is important. Very often fluoride ion is used (as tetraalkylammonium or alkali metal fluorides), although in principle anything which would give fluoride ion by reaction with the alkene may be used[46]. Fluorides with large cations (e.g. $(C_2H_5)_4N^+$, Cs^+) are more active than those with smaller cations (e.g. KF). Tertiary amines are frequently used. A change of catalyst usually gives merely a change in the proportions of the products formed - with hexafluoropropene fluoride ion produces mainly dimers and trimers, whereas tetramers and higher oligomers are produced in greater proportions when amines are used - but in the oligomerisation of perfluorocyclobutene the use of caesium fluoride or pyridine (see Table IV.1.) produces different trimers, not merely different proportions of the same trimer. With hexafluoropropene very active catalysts (e.g. caesium fluoride) enhance the formation of dimer (<u>43</u>) by promoting the equilibrium (<u>42</u>) $\rightleftharpoons$ (<u>43</u>), whilst use of potassium fluoride results in the production of good yields of dimer (<u>42</u>), since this is a less active catalyst and not so efficient in promoting the equilibrium[50].

The second important factor which determines the nature and distribution of products is the solvent, Usually polar aprotic solvents (e.g. dimethylformamide, glymes etc.) are used. Both amine and fluoride ion catalysts are soluble in these solvents and since the fluoride ion is not solvated it acts as a strong nucleophile. In polar protic solvents (methanol, water etc.) the fluoride ion is highly solvated and hence a weak nucleophile, therefore these solvents are not frequently used. If the fluoride ion and alkene are sufficiently active a solvent need not be used and hexafluoropropene, for example, can be oligomerised with caesium fluoride in the presence or absence of solvent[47-49]. In some cases for very nucleophilic solvents (e.g. dimethylsulphoxide) a catalyst need not be used[46].

The final factor involved in these systems is the temperature. Thus for example, trimers (44) and (45) which are in equilibrium are formed at low temperatures, but higher temperatures enhance the formation of (46)[47].

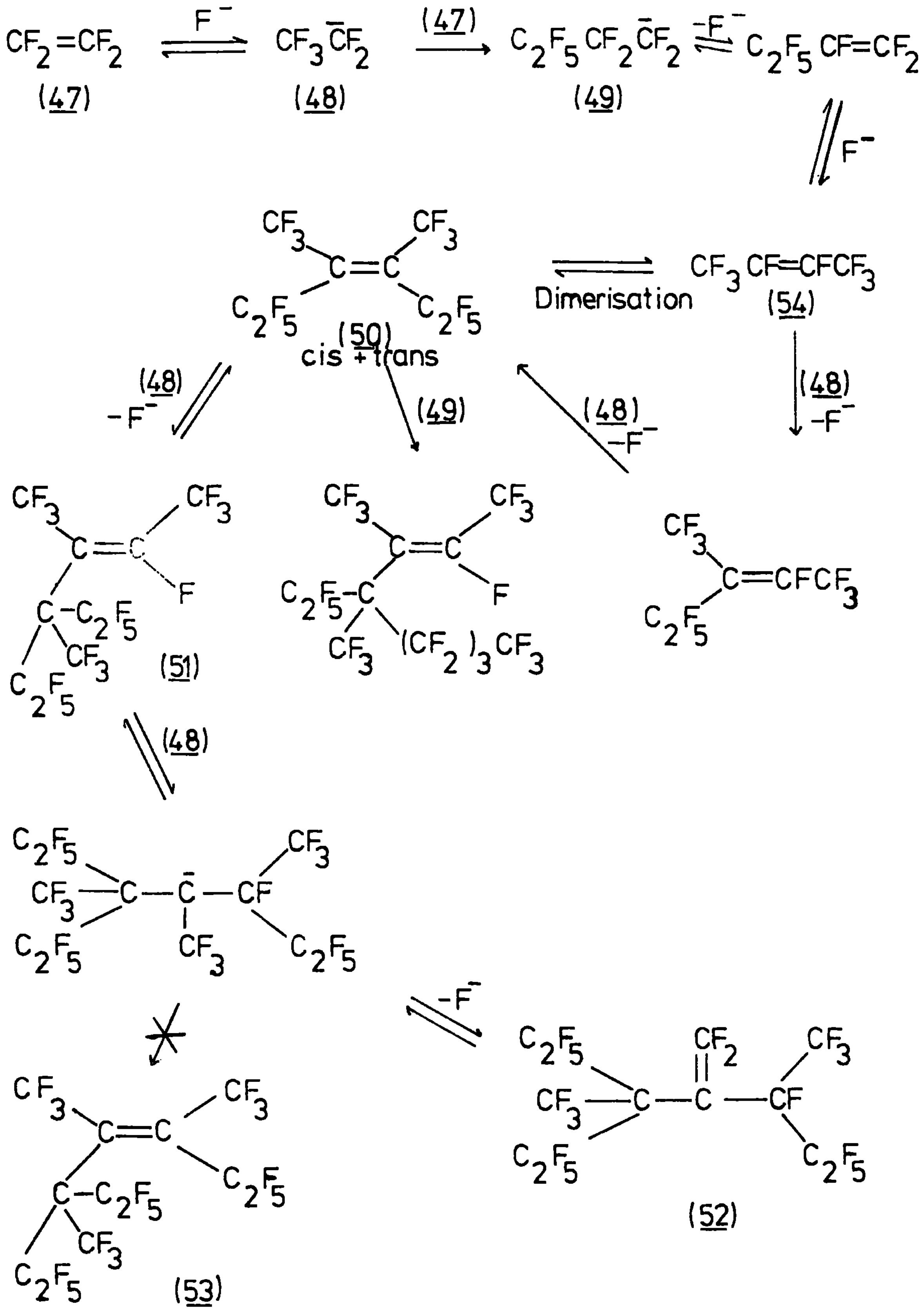
Trimer (44) and the corresponding tetramer (see Scheme IV.1.) are internally unsaturated alkenes producedin the oligomerisation of hexafluoropropene.

Tetrafluoroethylene is much less readily oligomerised than hexafluoropropene.[52] The product distribution is less susceptible to reaction conditions than is that of hexafluoropropene. The general reaction to be expected is illustrated in equation IV.1.

$$\text{IV.1.} \quad \begin{array}{ccccccc} CF_2{=}CF_2 & \xrightarrow[F^-]{DMF} & C_8F_{16} & + & C_{10}F_{20} & + & C_{12}F_{24} \quad [53] \\ & & (\underline{50})\ 15\% & & (\underline{51})\ 65\% & & 10\% \end{array}$$

The pentamer (51) is the major component under most conditions used but the product distribution will alter slightly depending upon the conditions[52,54,55]. Higher molecular weight oligomers are obtained in greater yield when high pressures are used[54,55]. The fluoroethyl anion reacts with the solvents used and so in these instances the yield of oligomers is usually less than 70%[53].

A possible mechanism which accounts for the products is shown in Scheme IV.2.[51]. Interestingly, hexamer (52) is formed in preference to compound (53) which would be expected to be the more stable isomer.



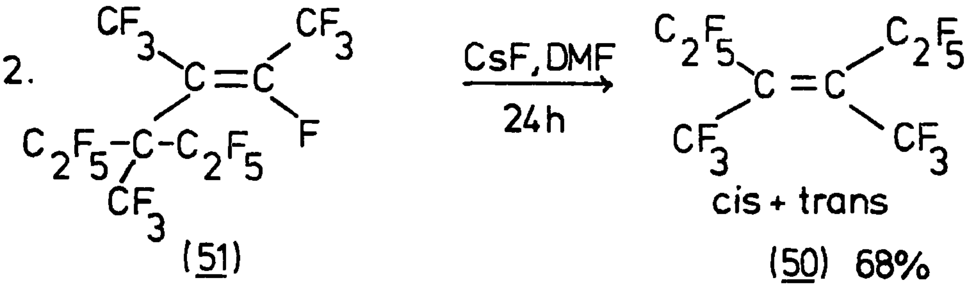
CF2=CF2
(47)
F⁻
CF3CF2⁻
(48)
(47)
C2F5CF2CF2⁻
(49)
-F⁻
C2F5CF=CF2
F⁻
CF3CF=CFCF3
(54)
Dimerisation
cis + trans
(50)
(48)
-F⁻
(49)
(48)
-F⁻
(48)
-F⁻
(51)
(48)
-F⁻
(52)
(53)

Scheme IV. 2.

It is believed that this occurs because of steric crowding in the product, or because of kinetic preference for loss of F^- from the $-CF_3$ group in the carbanion.

Tetramer (<u>50</u>) is known[54] to be a mixture of <u>cis</u> and <u>trans</u> isomers and can be produced by degradation of the higher oligomers of tetrafluoroethylene since the reactions are reversible (e.g. equation IV.2.).

IV. 2.



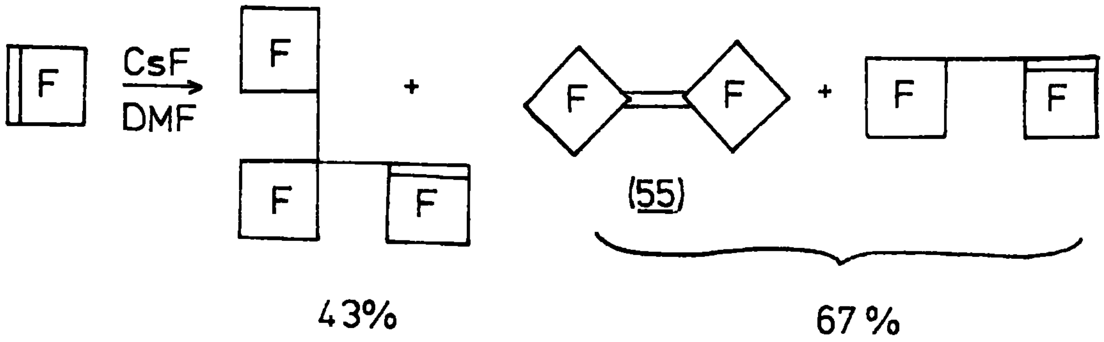
[56]

It has also been obtained by dimerisation of perfluoro-2-butene[57,58].

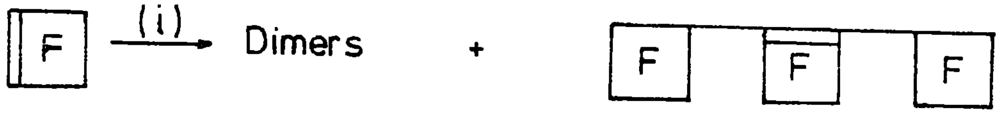
$$\text{IV.3.}\quad \underset{(\underline{54})}{CF_3CF{=}CFCF_3} \xrightarrow[\text{sulpholane}\ 24h]{CsF,\ 100°C} \underset{62\%}{(\underline{54})} + \underset{33\%}{(\underline{50})} \qquad [57]$$

$$\text{IV.4.}\quad (\underline{54}) \xrightarrow[45°C\ 89h]{CsF,\ DMF} \underset{80\%}{(\underline{50})} + \underset{14\%}{\text{trimers}} \qquad [58]$$

Cyclic alkenes will oligomerise in the presence of fluoride ion, cyclobutene readily but higher analogues require more vigorous conditions. Some examples of such oligomerisations which result in the formation of internal fluoroalkenes are illustrated in Table IV.1.

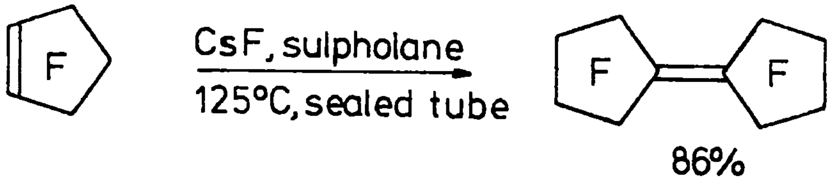


[59]



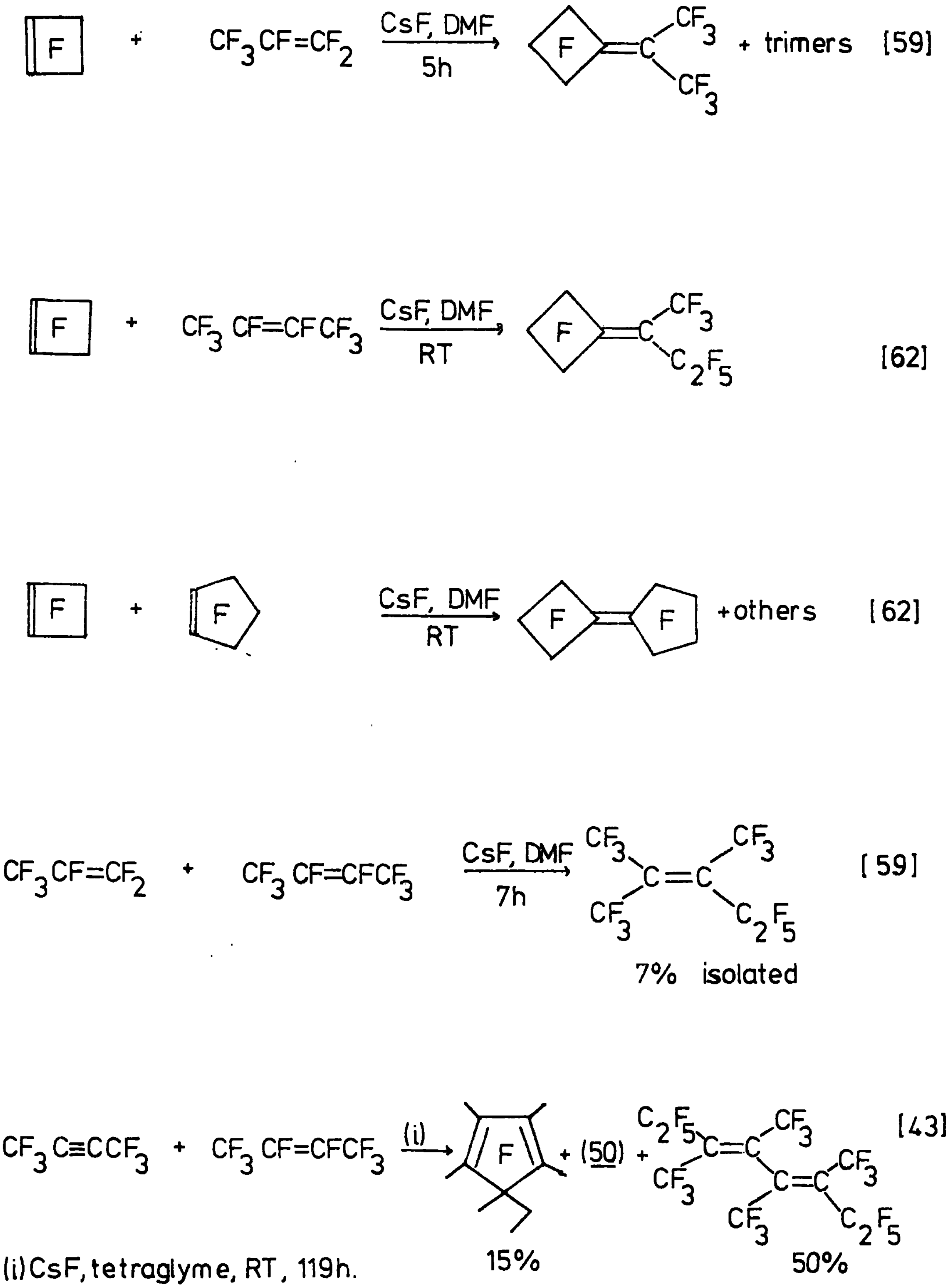
[60]

(i) pyridine



[61]

Table IV.1.



(i)CsF, tetraglyme, RT, 119h.

Table IV.2.

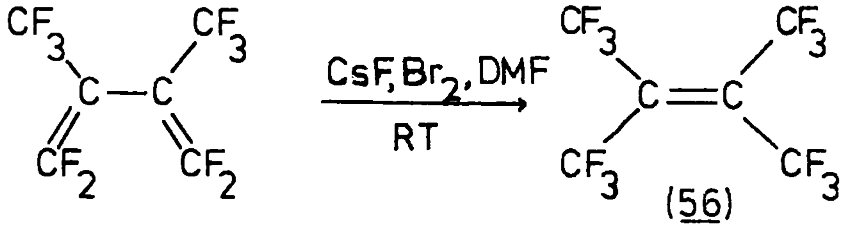
Internal alkenes can also be prepared by co-oligomerisations. Again, a variety of conditions can be used but care must be taken to avoid independent oligomerisation. Several examples are shown in Table IV.2.

Other co-oligomers have been prepared in the Durham laboratories[43, 62].

IV.3.B. Other Methods.

Although oligomerisation is probably the major source of internal fluoroalkenes, other methods are known for their preparation.

IV.5.

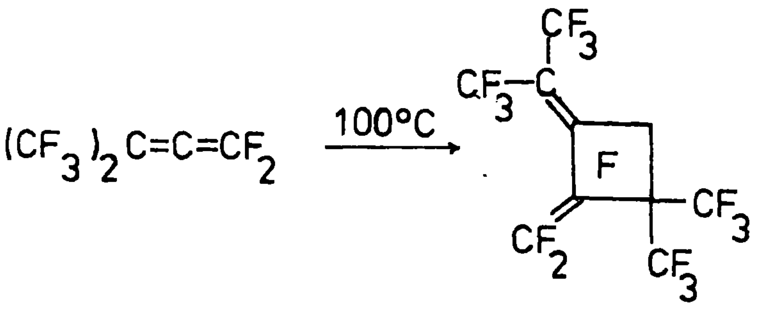


[43]

In this case the anion formed with fluoride ion can be trapped with bromine, further reaction with fluoride ion producing the perfluoro-2,3-dimethyl-2-butene (56). Other examples are illustrated below.

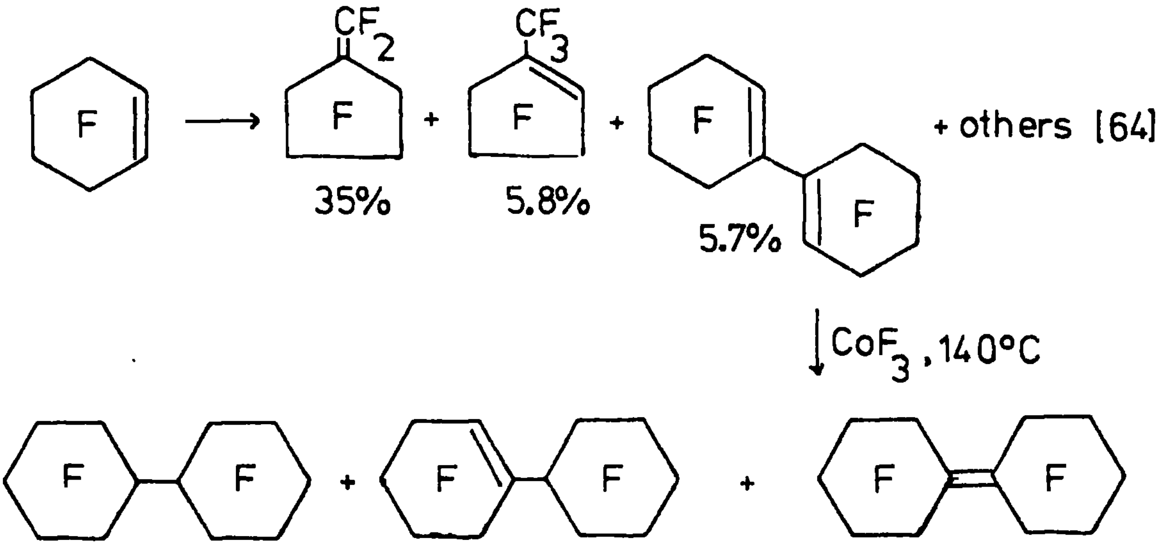
IV.6. $$CF_3I + CF_3C\equiv CCF_3 \xrightarrow[350^\circ C]{5\ days} (CF_3)_2C{=}C(CF_3)_2$$ autoclave (56) 73% [63]

IV.7.

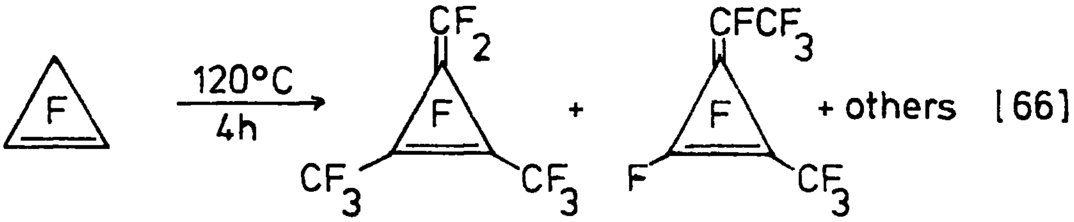


[65]

IV. 8.



IV. 9.



IV.4. Reactions of Internal Fluoroalkenes.

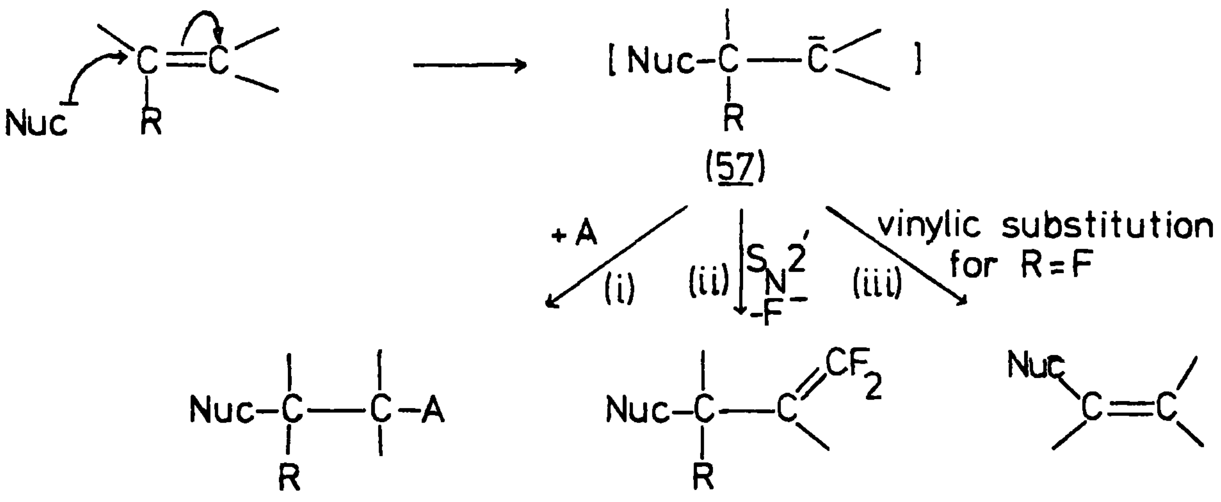
Internal fluoroalkenes can undergo reactions with nucleophiles and addition reagents and can partake in photochemical and thermal reactions.

No attempt will be made here to give an exhaustive list of these reactions - the salient points will be illustrated by a selection of examples.

IV.4.A. Reaction with Nucleophiles.

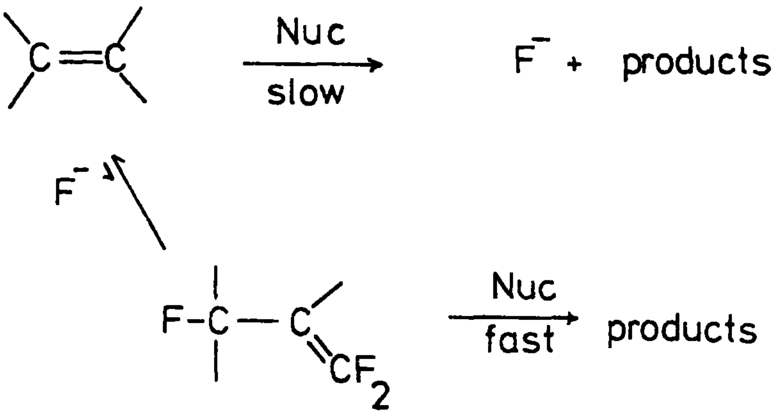
Since this aspect is the one most closely investigated by the author it will be discussed in rather more detail than the other reactions.

In general there are three types of reaction which may occur between a fluoroalkene and a nucleophile[67] (Scheme IV.3.).



Scheme IV.3.

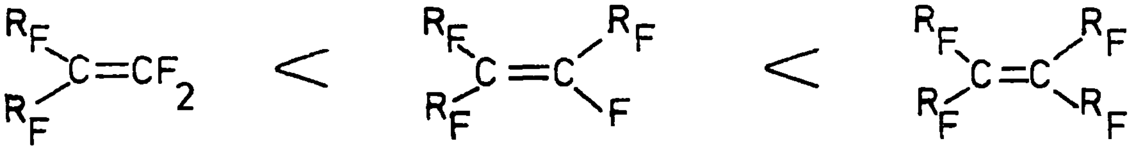
For an alkene with no vinylic fluorine atoms route (iii) is not possible and so the chemistry of nucleophilic attack on internal alkenes is interesting in that only allylic displacement of fluorine (ii) or addition across the double bond (i) can occur. The intermediate anion (57) may be transient or long-lived (Chambers and Taylor[60,62] have observed several stable anions in the reactions of cyclic alkenes with fluoride ion) and whether route (ii) occurs via a concerted reaction, or an addition-elimination process cannot always be elucidated. In some cases the internal alkene may react initially to give fluoride ion which can then initiate rearrangement to a less stable (more reactive) terminal alkene, which may then undergo fast reaction with the nucleophile (Scheme IV.4.).



Scheme IV.4.

IV.4.A.1. Factors Affecting Nucleophilic Reactions.

As described in Section IV.2. the order of stability of fluoroalkenes is



Thus internal fluoroalkenes being most stable would be expected to be the least reactive of the three types. As shown in Table IV.3. for example, this is in fact the case, but a balance of several factors must be taken in considering the reactivity with nucleophiles.

Reaction of an internal alkene with a nucleophile will not result in the formation of a more stable alkene as it would for a less substituted compound (by loss of vinylic fluorine atoms) so there will be no driving force of this nature. Internal alkenes are usually fairly large and branched and so the steric hindrance to attack will also reduce their reactivity relative to less substituted alkenes.

One factor which will enhance nucleophilic attack is the stabilisation of the intermediate developing carbanion ((57) in Scheme IV.3.) because of the I -σ effect of perfluoroalkyl groups. Where attack occurs to give a carbanion at a fluorine-bearing carbon atom, the I -σ stabilisation is in competition with I -π repulsion of the negative charge with the lone pairs on the fluorine atom. Clearly, in this case comparison of reactivity depends very much on the site of attack.

Some reactions of internal fluoroalkenes with nucleophiles are discussed below.

IV.4.A.2. Reactions.

The reactivity of internal alkenes can be clearly compared with that of less substituted alkenes in their reactions with methanol (Table IV.3.).

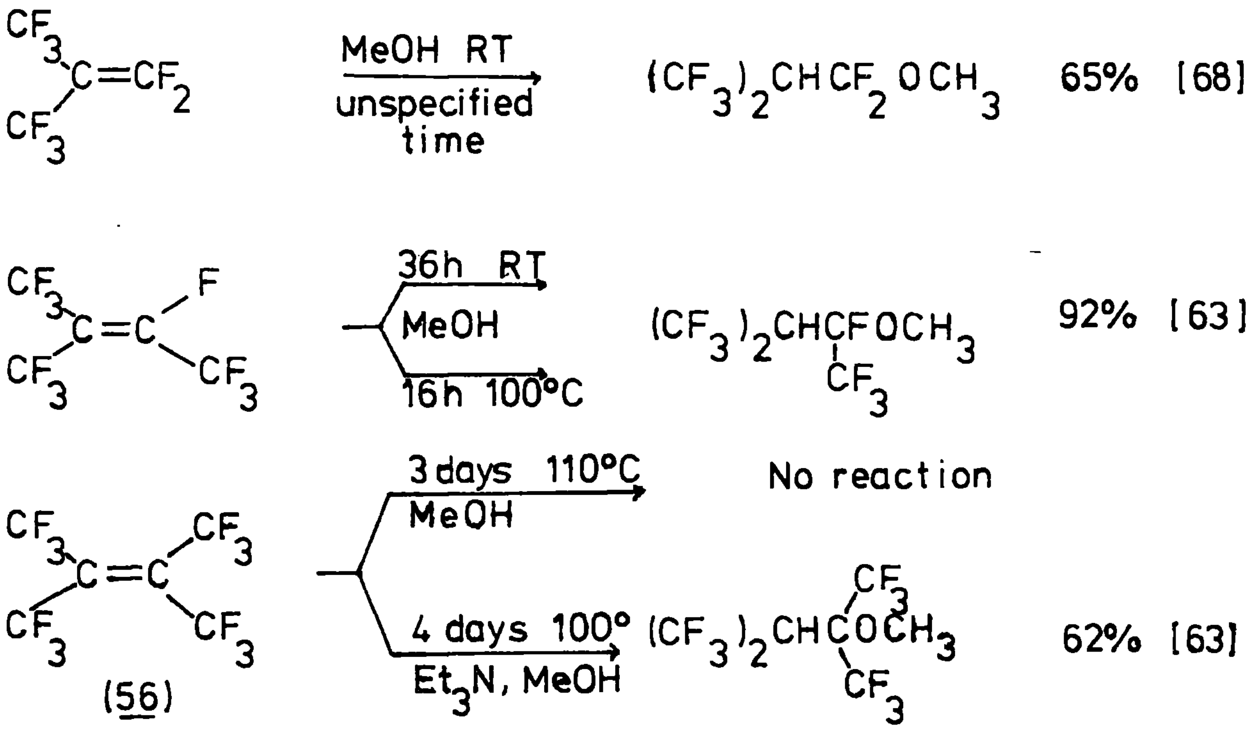


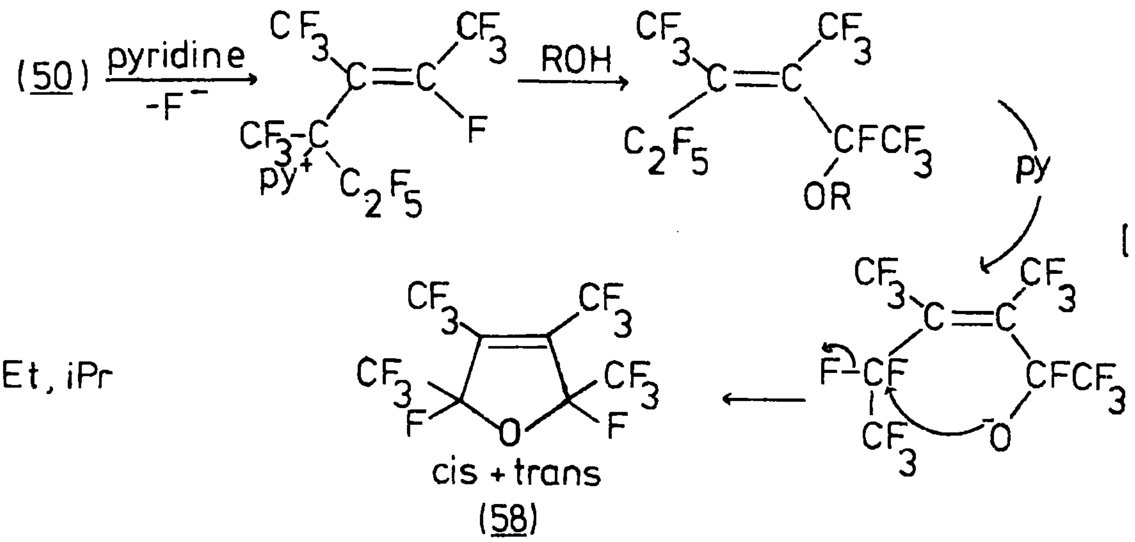
Table IV.3.

As illustrated, the tetraalkyl substituted alkene only reacts with neutral methanol in the presence of base under fairly vigorous conditions. General reactions with oxygen nucleophiles are shown in Table IV.4.

Several points emerge from these data. Firstly, the majority of the reactions can be explained by S_N2' processes (either concerted, or addition-elimination processes) followed by vinylic substitution, or by subsequent S_N2' reactions. Where no allylic fluorine atoms exist (as in compound (56)) then the carbanion must pick up an electrophile. Compound (50) in its reaction with caesium fluoride illustrates the process outlined in Scheme IV.4. Compound (55) is more reactive than analogous internal fluoroalkenes and this has been rationalised in terms of the angle strain present in the compound[62].

One further interesting reaction of compound (50) is shown in equation IV.10.

IV.10.



[71]

Here is an example of nucleophilic attack on a saturated $-CF_2-$ group, to give a cyclic product. Compound (58) is a precursor of the furans described in Chapter VI.

Detailed discussion of the reactions of internal fluoroalkenes with nitrogen and carbon nucleophiles will be found in Chapter V

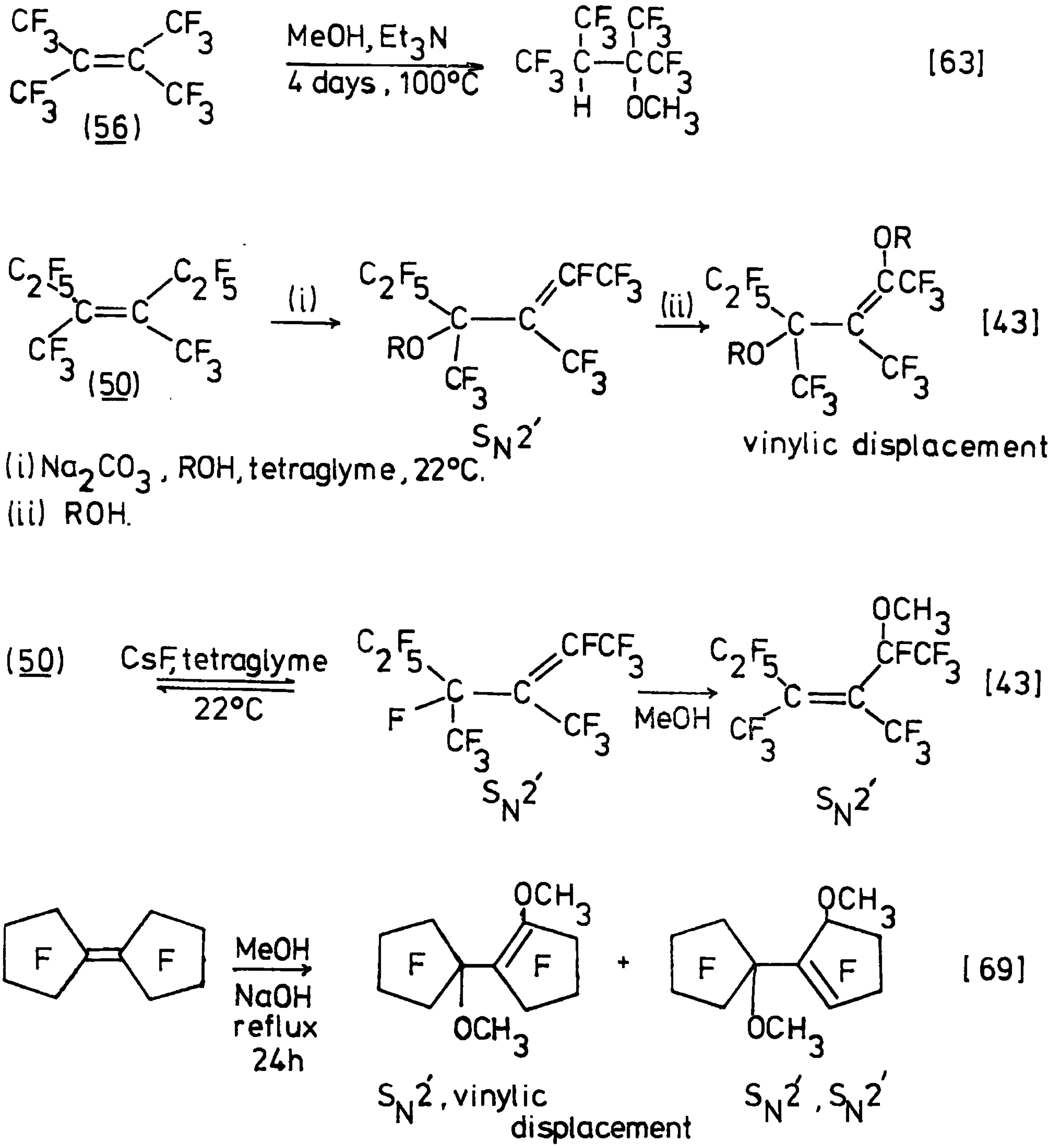
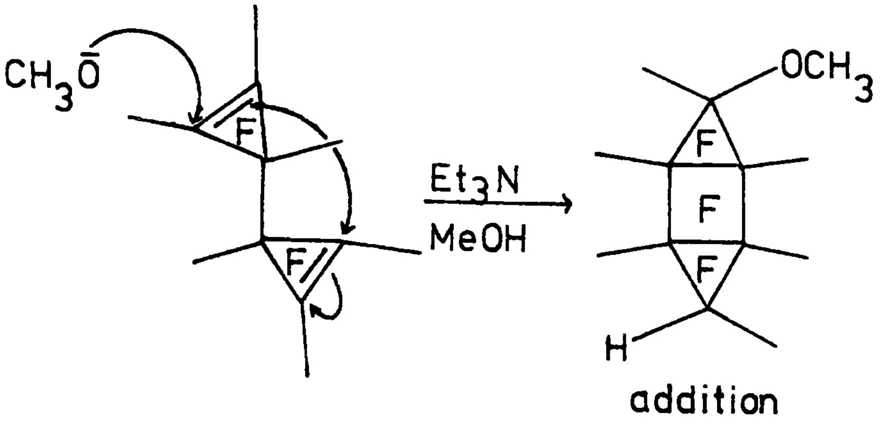
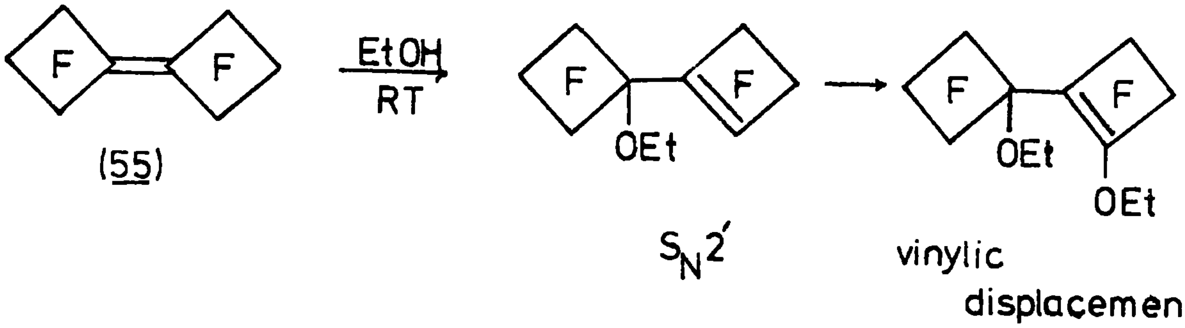

(56)
MeOH, Et$_3$N
4 days, 100°C
[63]
(50)
(i)
(ii)
S_N2'
vinylic displacement
[43]
(i) Na$_2$CO$_3$, ROH, tetraglyme, 22°C.
(ii) ROH.
(50)
CsF, tetraglyme
22°C
MeOH
S_N2'
S_N2'
[43]
MeOH
NaOH
reflux
24h
S_N2', vinylic displacement
S_N2', S_N2'
[69]

Table IV.4.



[70]



[62]

Table IV. 4. contd.

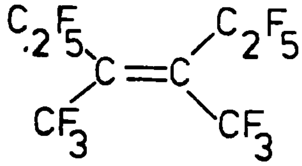
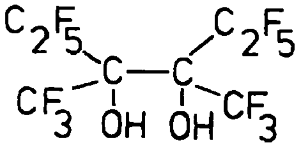
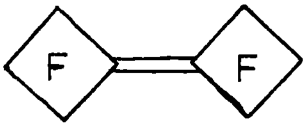
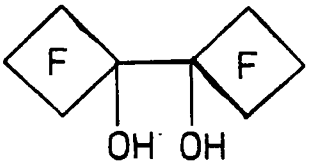
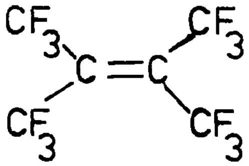
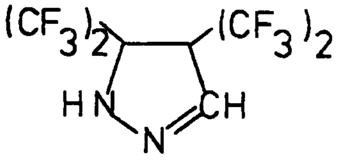
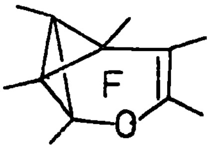
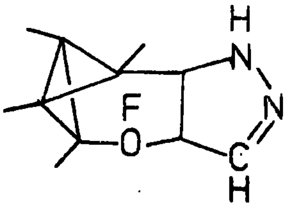
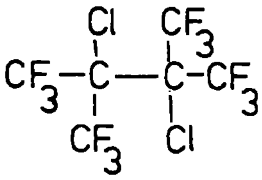
	KMnO$_4$ acetone		65%	[71]
	KMnO$_4$		90%	[62]
	CH$_2$N$_2$,Et$_2$O RT			[62] [63]
	CH$_2$N$_2$			[73]
(<u>56</u>)	Cl$_2$, hν 4 days		92%	[63]
(<u>50</u>)	Br$_2$	No reaction		[62]

Table IV.5.

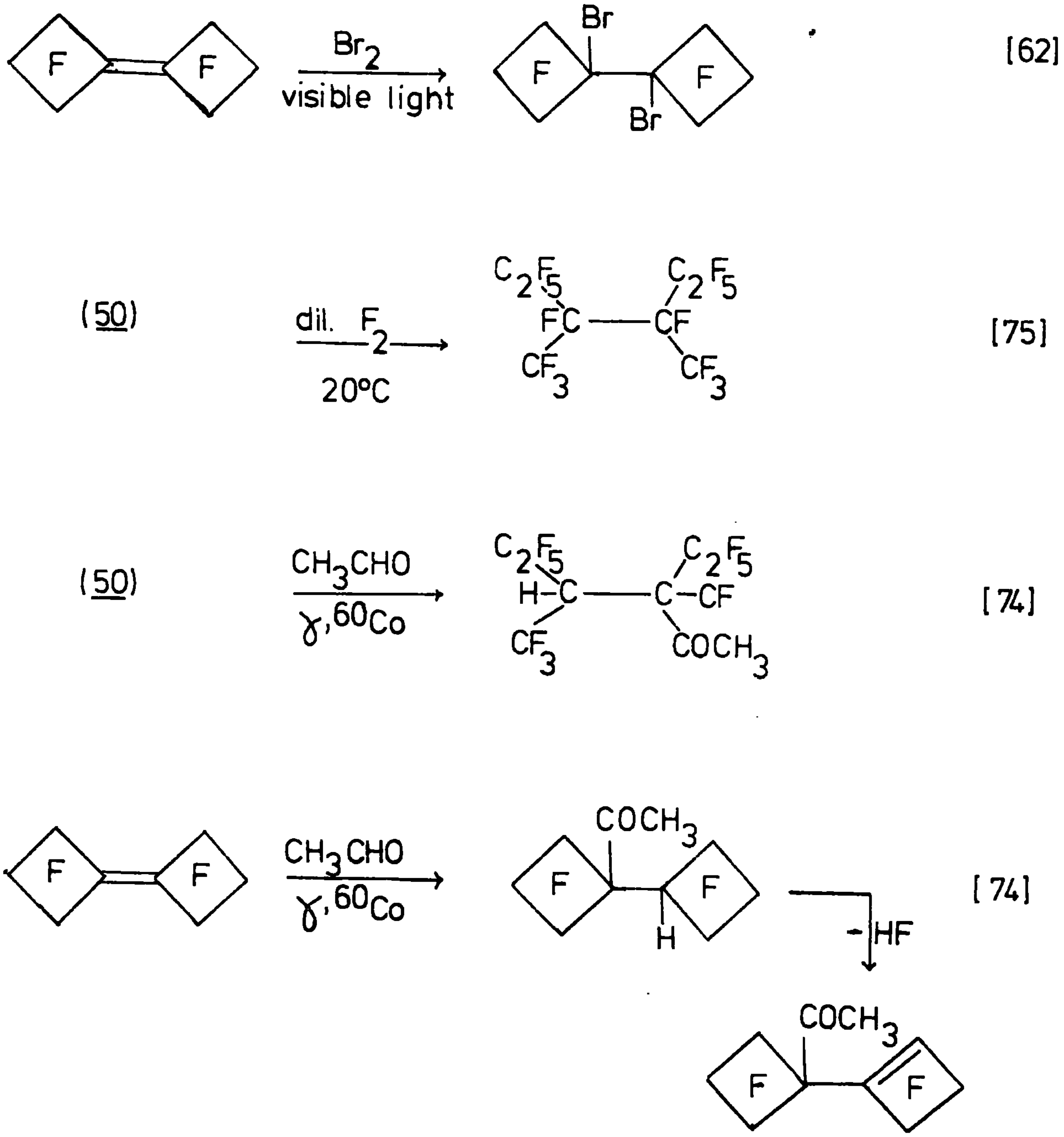


Table IV. 5. contd.

as these concern the work discussed in this part of the thesis. In many cases the reactions observed are similar to those of oxygen nucleophiles (see for example refs. 62,63 and 72).

Tertiary amines do not give stable compounds with internal fluoroalkenes, because the amine group is readily displaced by fluoride ion or other nucleophile, hence they are used as bases or oligomerisation catalysts.

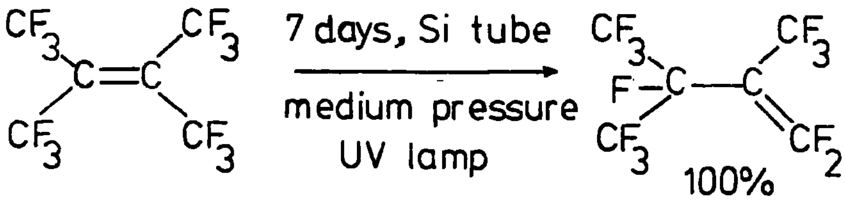
IV.4.B. Addition Reactions.

There are no examples of electrophilic addition to internal alkenes, although addition to less substituted fluoroalkenes is known (see e.g. ref. 43). This is not unreasonable since the generation of a positive charge on a carbon atom attached to an electron-withdrawing group ($-R_F$) would not be favourable. Other addition reactions are illustrated in Table IV.5.

IV.4.C. Photochemical Reactions.

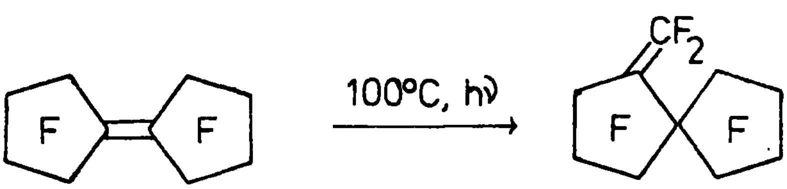
Photochemical rearrangements occur more readily with internal fluoroalkenes than with their less substituted analogues[76], to give less highly substituted isomers.

IV.11.



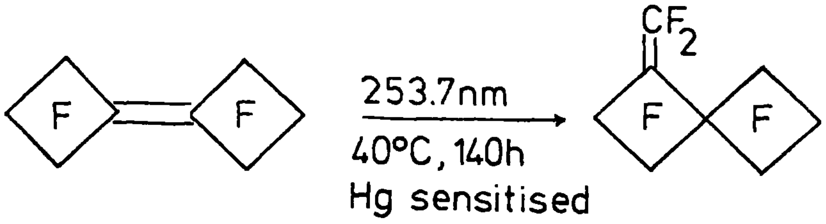
[76]

IV.12.



[77]

IV.13.



[62]

These products arise from 1,3-allylic shifts of fluorine or fluoroalkyl groups[77].

IV.4.D. Thermal Reactions.

Three types of reaction can be expected on thermolysis of a fluoroalkene:

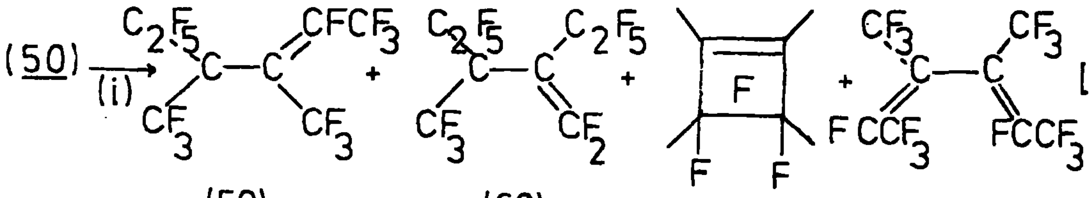
i) isomerisation

ii) defluorination and

iii) fragmentation.

In flow systems the exact nature of the reaction depends mainly upon the inert surface used (e.g. platinum, iron, caesium fluoride etc.) and the temperature. Examples of each of these processes are shown below.

IV.14.



[78]

(i) Fe, 540°C

(59)
cis + trans

(60)

isomerisation

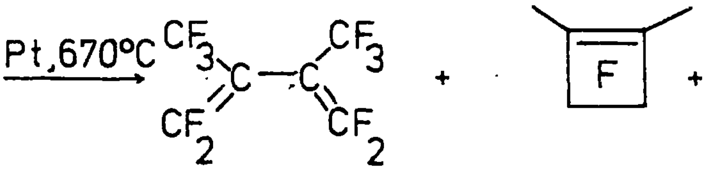
defluorination

IV.15. (50) $\xrightarrow{\text{Pt, 540°C}}$ (50) + (59) + (60) [43]

70% 25% 5%

(cis + trans) isomerisation

IV.16. (50)



+ others [79]

59% 14%

fragmentation

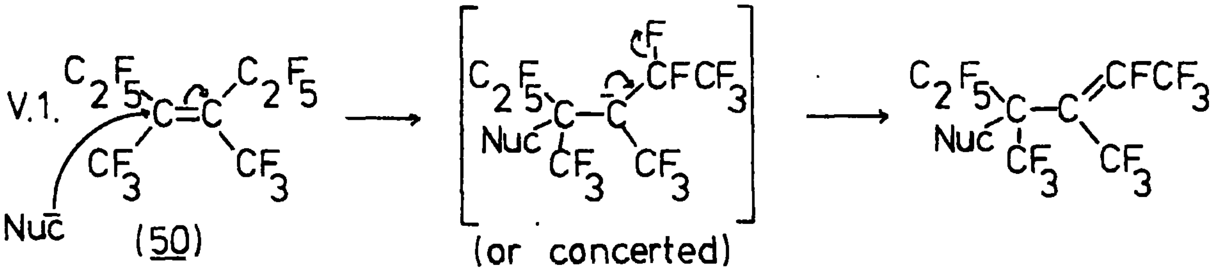
Chapter V

Discussion -

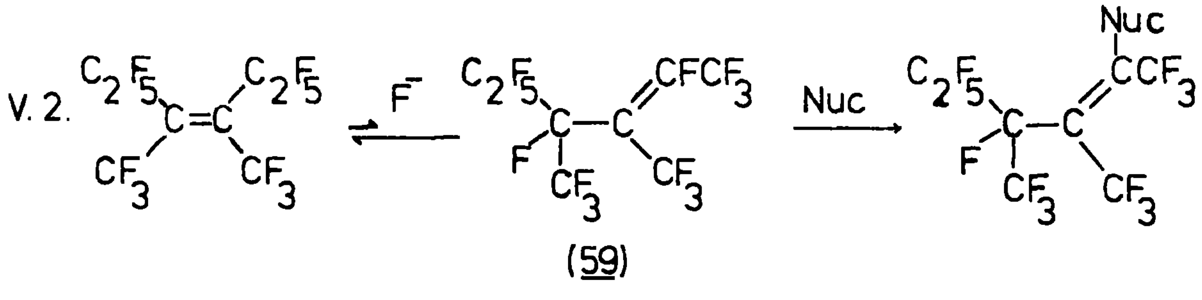
Reactions of Perfluoro-3,4-dimethyl-3-hexene.

V.1. Introduction.

The work discussed in this chapter is a continuation of work begun in these laboratories[43,80]. The interesting chemistry of internal fluoroalkenes has been discussed in Chapter IV and the work carried out by the author has extended this by further investigation into the reactions of <u>cis</u>, <u>trans</u>-perfluoro-3,4-dimethyl-3-hexene (<u>50</u>). This compound is particularly interesting because it can undergo S_N2' reactions with nucleophiles (equation V.1.) by displacement of an allylic fluorine atom and also because it can isomerise to a less highly substituted alkene prior to reaction (see Scheme IV.4., Table IV.4. and equation V.2.).



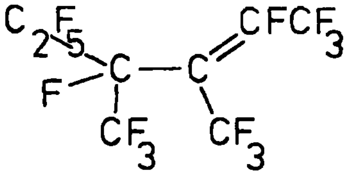
eg.



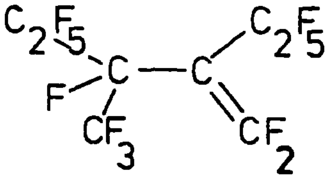
V.2. Reactions with Nitrogen Nucleophiles (with A.A. Lindley).

This study was carried out in collaboration with another worker in these laboratories[43].

It has been shown[43] that compound (<u>50</u>) reacts with oxygen nucleophiles to give products arising from (<u>50</u>) and isomer (<u>59</u>) (see Table IV.4.) but no products from isomer (<u>60</u>) were observed.



(59)



(60)

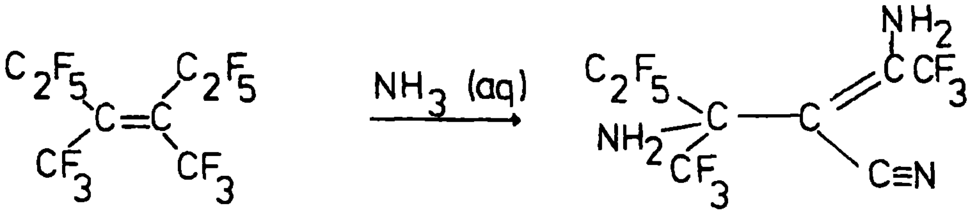
The reactions of compound (50) with various amines and nitrogen nucleophiles was therefore investigated to observe the manner in which reaction occurred and to see if products arising from isomer (60) could be detected. Amines of varying size and basicity were used.

V.2.A. Ammonia.

i) Aqueous Ammonia.

Compound (50) was found to react with excess aqueous ammonia to give compound (61) (equation V.3.).

V.3.



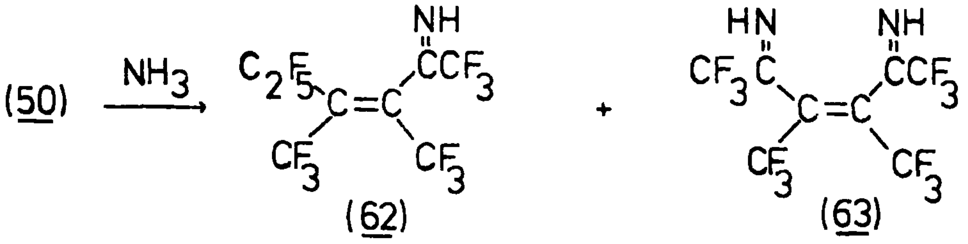
(50) (61)

This was identified by mass spectral analysis which showed a parent peak and the ir spectrum which showed a characteristic absorption at ν_{max} = 2220cm^{-1} (C≡N stretch). ^{19}F nmr spectral data were consistent with there being four types of fluorine present $-\underline{CF_3}CF_2-$ (81.4ppm), $\underline{CF_3}C$ (75.1ppm), $\underline{CF_3}C=$ (70.1ppm) and $CF_3\underline{CF_2}-$ (121.2ppm) (see Table V.1.).

ii) Anhydrous Ammonia.

It has been reported[81] that two components ((62) and (63)) are formed when anhydrous ammonia is bubbled through alkene (50) (equation V.4.).

V.4.

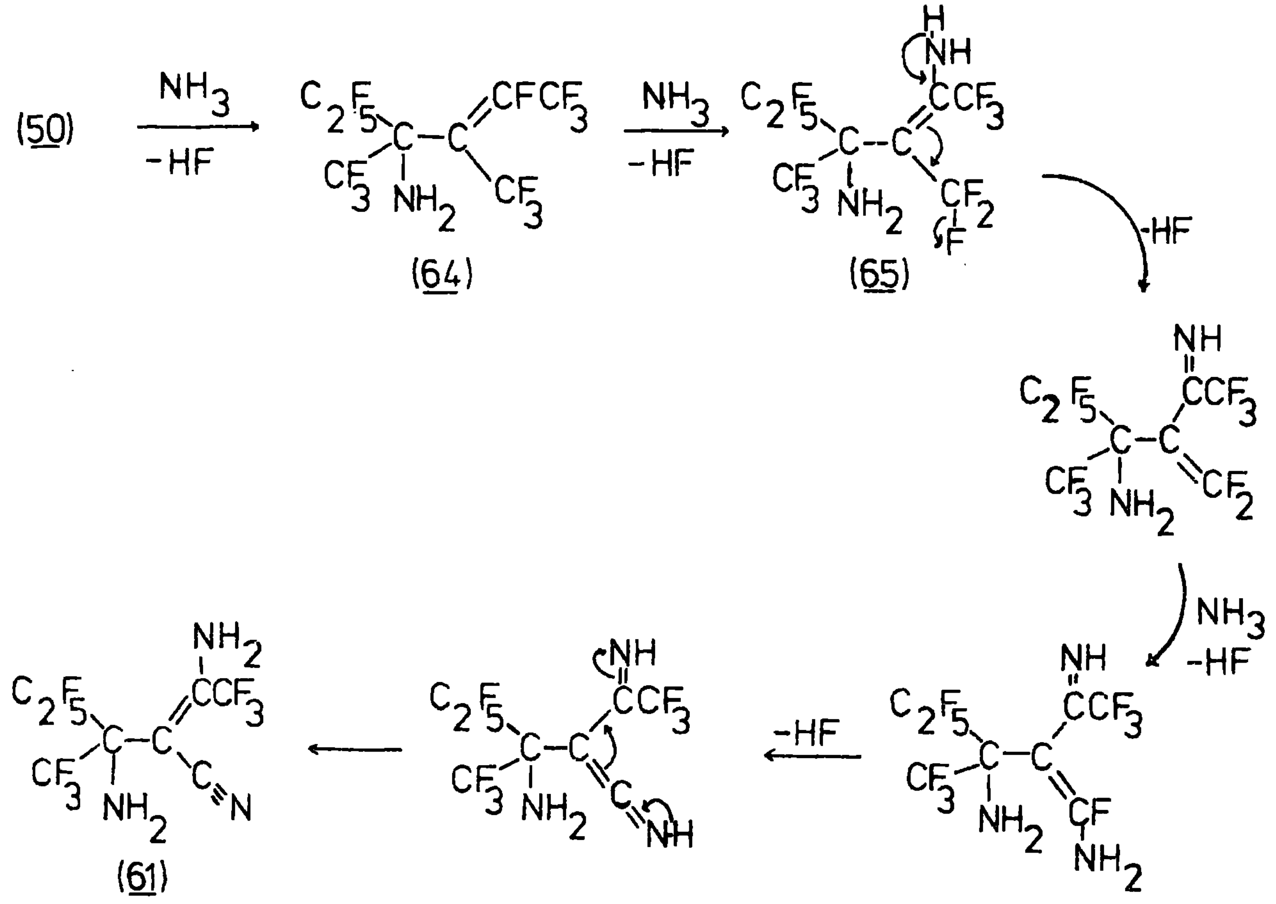


[81]

When this reaction was repeated under similar conditions, in all cases tried some of compound (61) was observed (detected by the characteristic ir absorption at 2220cm^{-1} and MS-glc analysis of the reaction mixture). Glc analysis showed other components to be present in the mixture which MS-glc data indicated could be $C_8F_{15}NH_2$ and $C_8F_{14}(NH_2)_2$.In a series of reactions the proportions of the components varied according to the amount of ammonia passed. During the reaction a solid was precipitated which was subsequently found to be water-soluble. This was presumably ammonium fluoride.

When excess ammonia was bubbled through a sample of the reaction mixture the proportion of (61) increased at the expense of the other components. A similar effect was observed when aqueous ammonia was added to a sample of the reaction mixture. This implies that the intermediate products in the reaction react with excess ammonia to give compound (61). To verify this and to eliminate any possibility of loss of material by evaporation as the gas was bubbled through the solution, the reaction was carried out in a sealed system at room temperature, excess dry ammonia being allowed to diffuse from a bladder into the alkene. After stirring for several days, greater than 97% of the product was compound (61).

These data are consistent with the reactions under both aqueous and anhydrous conditions following the mechanism outlined in Scheme V.1.



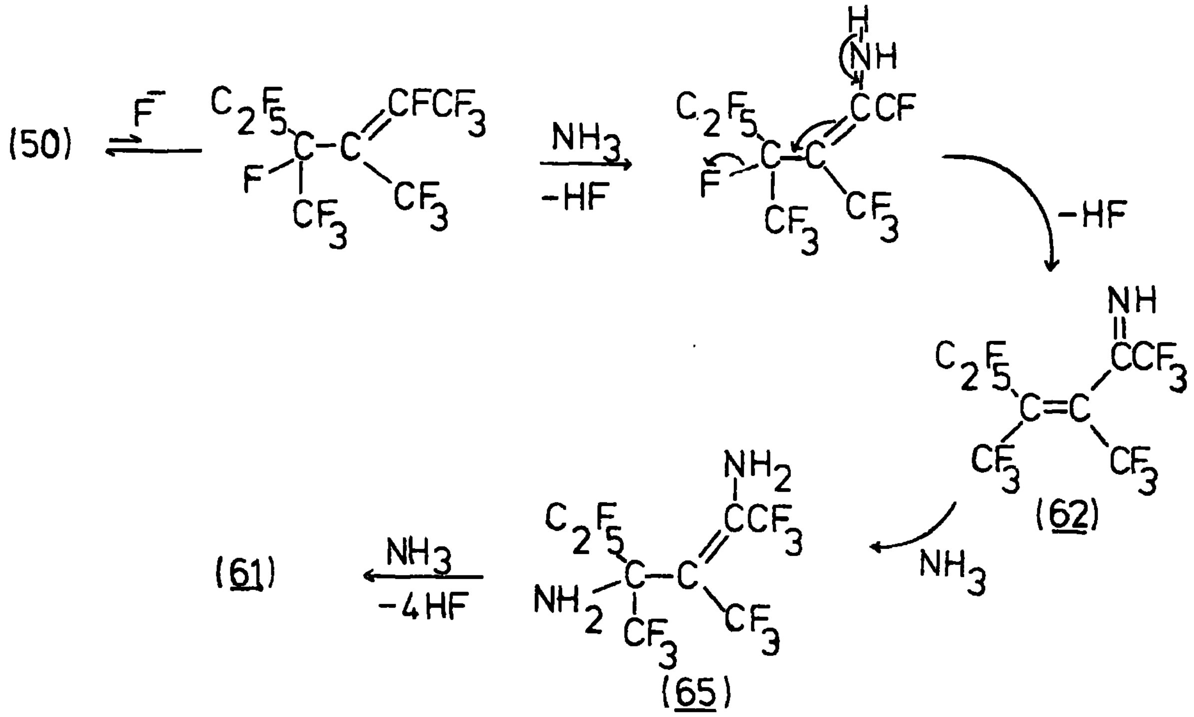
Scheme V.1.

Structures (64) and (65) are consistent with the data observed for the intermediates in the reaction with anhydrous ammonia. The reaction therefore occurs by direct attack on isomer (50) and S_N2' displacement of fluoride, followed by ~~a series of~~ vinylic substitutions and maximum loss of HF.

In these reactions, no evidence was obtained for the presence of compounds (62) and (63) observed by Fielding[81]. Attempts were made to obtain these compounds, one of which involved the addition of caesium fluoride to the reaction to see if the promotion of the equilibrium between (50), (59) and (60) would result in the production of (62) or (63). The results are discussed below.

iii) Anhydrous Ammonia in the presence of Caesium Fluoride.

The reaction was carried out in an open system in a similar manner to that described earlier but with the addition of a small quantity of caesium fluoride. Compound (61) was still found to be present but MS-glc analysis of the mixture indicated that as well as this and $C_8F_{14}(NH_2)_2$ (65), a compound with formula $C_8F_{14}NH$ was present. Structure (62) is consistent with this. Scheme V.2. shows a mechanism for its formation.



Scheme V. 2.

Excess ammonia and loss of the maximum amount of HF lead to the formation of (61). No evidence was obtained for the presence of compound (63) and no products deriving from isomer (60) were observed.

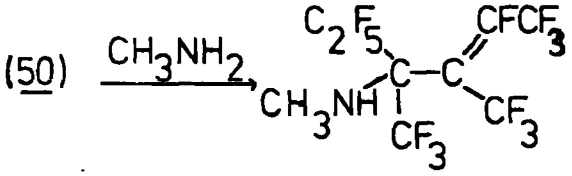
V.2.B. Conclusion.

Both aqueous and anhydrous ammonia react with compound (50) to give products which arise from direct attack on this isomer. Under normal conditions no products are observed which arise from attack on isomers (59) or (60). This is presumably because the ammonium fluoride produced during the reaction is precipitated and hence does not promote the equilibrium between the isomers. This is borne out by the fact that when added active fluoride ion is present a product from reaction with isomer (59) is observed.

V.2.C. Methylamine.

In a similar manner to the reactions of compound (50) with ammonia, both anhydrous and aqueous methylamine gave products arising from direct attack on isomer (50). When anhydrous methylamine was bubbled into compound (50) an exothermic reaction occurred which resulted in approximately 60% reaction and the formation of compound (66) as the major product. Insufficient of the minor component was obtained to allow identification. Clearly compound (66) must be formed by direct attack on (50) (equation V.5.).

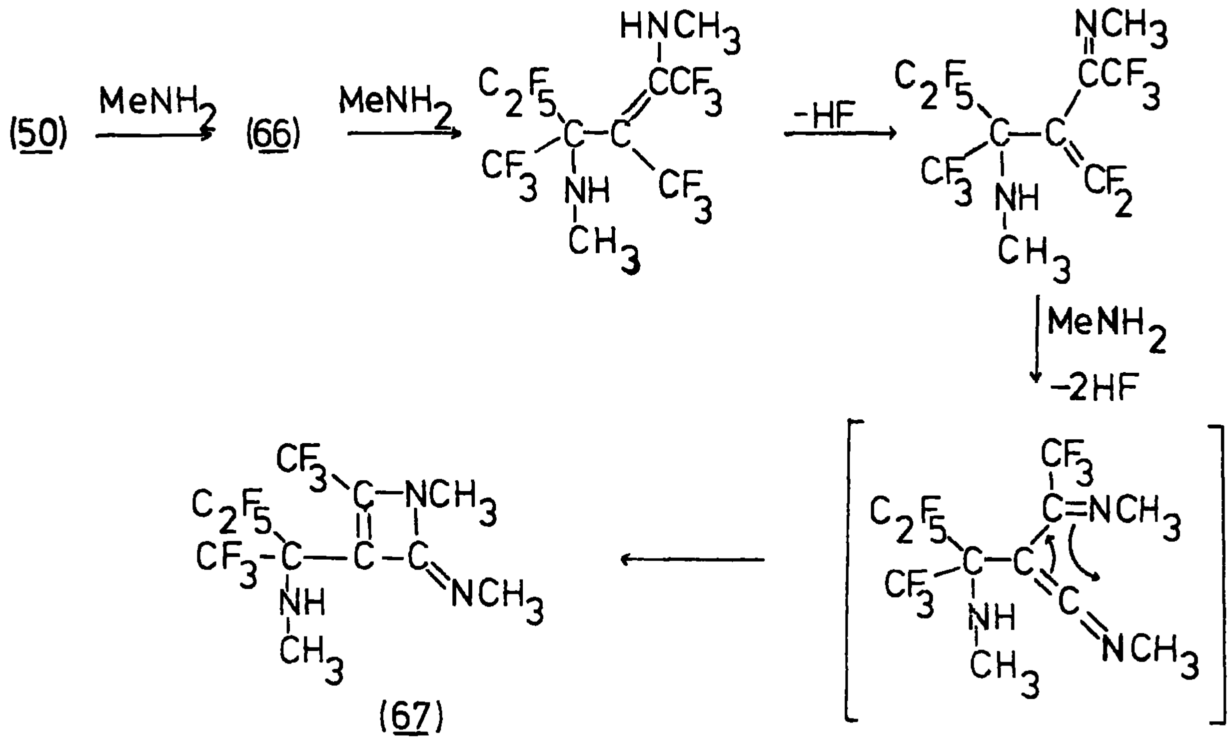
V.5.



(66)

Under aqueous conditions the major component was identified as azetine (67), formed by initial S_N2' attack, followed by a series of vinylic substitutions of fluorine and maximum loss of HF (Scheme V.3.).

Compounds (66) and (67) were identified from their mass spectra as both showed parent peaks, and from their nmr spectra. The ^{19}F nmr spectrum of (66) was assigned by comparison with that of compound (50) (see Table V.1.) and the $C{=}C\begin{smallmatrix}\diagup F \\ \diagdown CF_3\end{smallmatrix}$ group was observed at 95.4ppm. The ir spectrum showed a doublet at 3460cm^{-1}, 3410cm^{-1} (N-H), broad signals at 2960cm^{-1} and 2840cm^{-1} (C-H) and a doublet at 1700cm^{-1} (C=C).

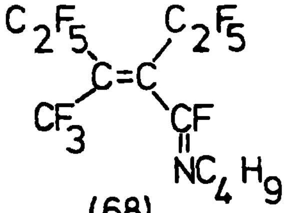


Scheme V. 3.

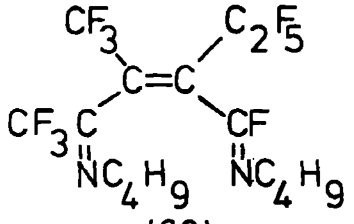
The ^{19}F nmr spectrum of (67) showed clearly the presence of three types of $-CF_3$ group and one $-CF_2-$ group. ($\underline{CF}_3-C=C-$, 66.6ppm; $\underline{CF}_3-C\equiv$, 70.1ppm; $\underline{CF}_3-CF_2-$, 82.2ppm and $CF_3-\underline{CF}_2-$, 116.0ppm). The ^1H nmr spectrum showed the presence of three methyl groups at similar chemical shift (2.4-2.7ppm, $N-\underline{CH}_3$) and one N-H proton.

V.2.D. tert-Butylamine.

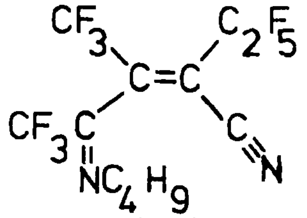
This reaction has been carried out previously[43] and is reported to give (68) with equimolar amounts of anhydrous amine and (50) and (69) with excess amine.



(68)



(69)



(70)

The reactions were repeated in this work under a variety of conditions. In all cases these reactions took much longer than those with methylamine and ammonia.

i) Excess anhydrous amine.

The major component in this reaction was identified as (69) (70%). Preparative scale glc resulted in decomposition on the hot filament to release butyl fluoride and leave compound (70). Preparative scale thin layer chromatography also resulted in decomposition, this time to give many components. Low temperature-reduced pressure transference only achieved enrichment of (69) but never its isolation as a pure compound.

ii) Excess anhydrous amine with ether.

The presence of ether in the reaction mixture appeared to make little difference to the reaction products.

iii) Equimolar amounts of amine and compound (50).

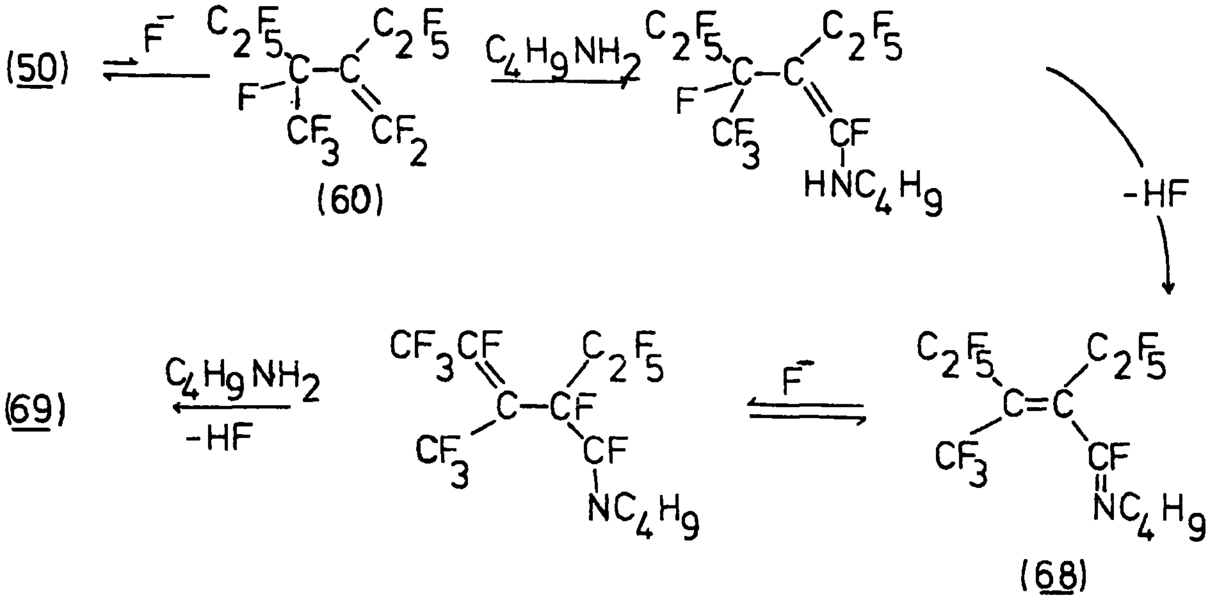
When approximately equimolar proportions of amine and compound (50) were reacted the major component in the mixture was found to be unreacted (50) (73%) with (69) (18%) also present. The remainder of the mixture contained several more-volatile components which were not identified.

The products observed in these reactions do not arise from attack on isomer (50) but must derive from isomer (60) (Scheme V.4.).

Compound (68) presumably isomerises to provide a less crowded site for attack by excess amine, to give (69).

iv) Aqueous tert-butylamine.

This reaction was carried out because under these conditions any fluoride ion produced would be solvated and hence be a weak nucleophile and the equilibrium between (50), (59) and (60) could not be set up. With excess amine the reaction went to completion but only 9% of the recovered material was volatile and this was



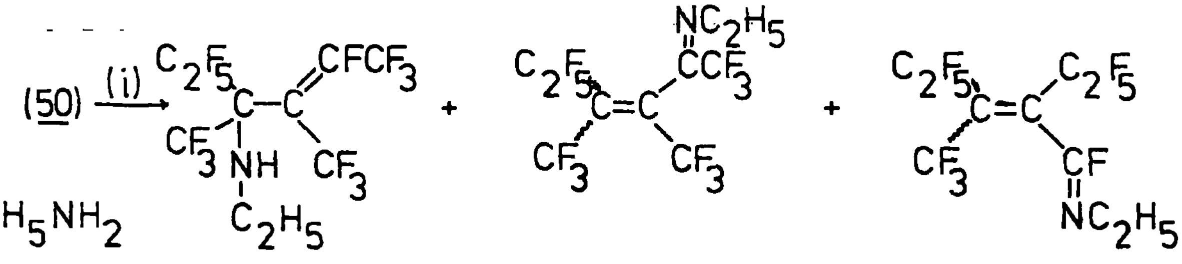
Scheme V. 4.

shown by glc to contain at least six components which were not examined. With an equimolar amount of amine very little reaction was observed.

V.2.E. Conclusion.

Studies on the reaction of compound (50) with anhydrous ethylamine have been reported[43] to give products which derive from each of the isomers (50), (59) and (60) (equation V.6.).

V.6.



(i) $C_2H_5NH_2$

Taking account of the data obtained in the reactions of nitrogen nucleophiles with compound (50) it is obvious that products are obtained from reaction with all three isomers, unlike reactions with oxygen nucleophiles which only give products arising from reaction with (50) and (59). Several reasons may be considered to account for this.

Initially base strength was believed[43] to direct the position of attack. The more basic the amine the more free the fluoride ion in the hydrofluoride and hence the greater the likelihood of isomer formation. However, the values of pK_a for the amines used (Table V.2.) bear no simple relationship to the observed reactions.

The nature of the fluoride ion is, of course, very important in directing the reaction. Where the hydrofluorides are precipitated and the fluoride ion is removed from solution (e.g. in the reactions with ammonia) or under aqueous conditions where the fluoride ion is highly solvated and hence a weak nucleophile, no equilibrium will be set up. In these cases direct attack on isomer (50) occurs. In the cases of tert-butylamine and ethylamine the fluoride ion is soluble, or at least partially so and not solvated and hence the equilibrium between the alkene isomers can be set up and the products deriving from these will be formed.

However, another factor must be considered. The steric requirements of the nucleophile are significant in directing the position of attack. Hence the bulky tert-butyl group only gives products arising from the least hindered isomer ((60)), and none of the expected products under aqueous conditions where only direct attack on (50) is possible.

The reactions of compound (50) with nitrogen nucleophiles can therefore be considered to be dependent upon the steric requirements of the nucleophile and the nature of the hydrofluoride produced, and under the correct conditions products from all three isomers of compound (50) can be obtained.

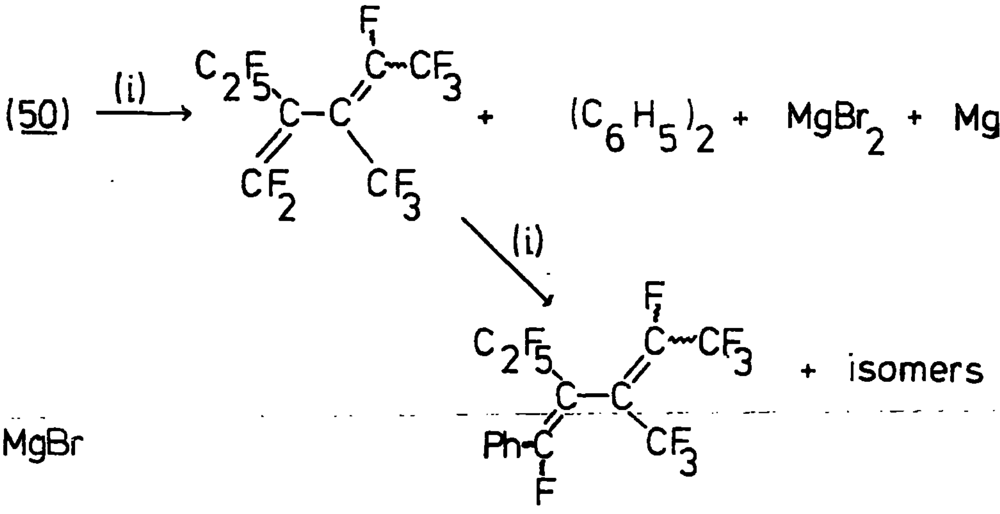
Amine	pK_a	Relative Basicity [95]
Ammonia	9.25	1
Methylamine	10.657	26
Ethylamine	10.807	36
tert-Butylamine	10.83	38

Table V.2.

V.3. Reactions with Carbon Nucleophiles.

The reaction of (50) with phenylmagnesium bromide has already been investigated[43] and has not been found to give products from direct nucleophilic attack but an initial defluorination followed by vinylic displacement of fluoride by phenyl (equation V.7.).

V.7

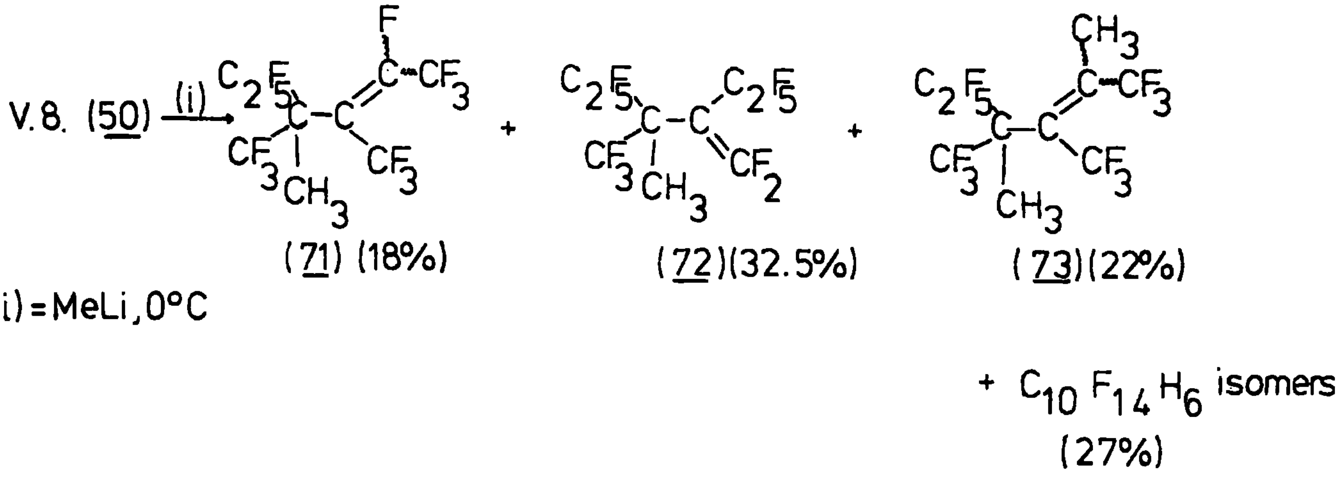


[43]

(i)=PhMgBr

V.3.A. Methyllithium.

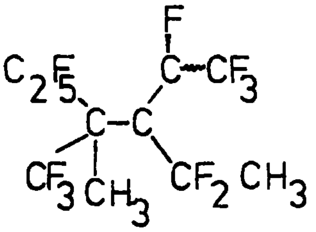
Compound (50) reacted vigorously with methyllithium at 0°C. Four products were formed which were isolated by preparative scale glc (equation V.8.)

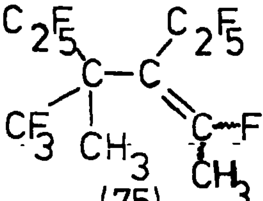

V.8. (50) → (71) (18%) + (72) (32.5%) + (73) (22%) + $C_{10}F_{14}H_6$ isomers (27%)

(i) = MeLi, 0°C

During the course of the reaction a white suspension was observed, which was presumably lithium fluoride.

Production of compounds (71) and (73) is easily explained in terms of S_N2' displacement of fluoride (for (71)) followed by vinylic substitution (for (73)). The fourth component was found to be a mixture of $C_{10}F_{14}H_6$ isomers which are presumably formed by attack of methyllithium on compound (72). The most likely products would be expected to be structures such as (74) and (75) but the components were not isolated (see Section V.3.C.).


(74) (S_N2' displacement)


(75) (vinylic substitution)

It is interesting that the major product (72) was formed by a displacement of fluoride from a trifluoromethyl group, rather than from a difluoromethylene group to produce a terminal alkene - the least stable of the substituted fluoroalkenes (see Chapter IV.). This effect has been observed during the formation of the hexamer of tetrafluoroethylene (Scheme IV.2.)[82]. In this case the pentamer (51) is thought to react to give a carbanion which eliminates fluoride to give (52) in preference to the more stable (53). This was explained as being due to the alleviation of steric effects either in the carbanion or in the product. None of compound (53) was observed.

In the reaction of (50) with methyllithium both isomers are formed ((71) and (72)). It would therefore seem that here the loss of fluoride from the $-CF_3$ group is kinetically slightly more favoured, possibly for steric reasons, than loss of fluoride from the $-CF_2-$ group.

The reaction was also carried out using a deficiency of methyllithium since (72) was thought to be the initial product formed and the conditions under which that was produced (large excess of (50)) were simulated. In this instance, however, many components were detected by glc. Reactions of impurities in the methyllithium (e.g. alkoxides) were presumably becoming significant under these conditions and so the reaction was not pursued further.

V.3.B. Reaction of Potassium Fluoride with the Product Mixture from V.3.A.

It is reasonable to assume that compound (72) will isomerise in the presence of fluoride ion to give (71), since the latter is the more stable isomer. Under the reaction conditions which formed these compounds, the fluoride ion produced (as lithium fluoride) was deposited and hence would be unable to catalyse isomerisation. The reaction mixture was therefore stirred with potassium fluoride in tetraglyme at room temperature and the reaction monitored by ^{19}F nmr spectral data and glc analysis. As expected, the mixture was now shown to have compound (71) as its major component. The equilibrium $(72) \rightleftharpoons (71)$ was therefore catalysed by fluoride ion and lay largely to the right.

V.3.C. Structural Assignments.

Most of the compounds discussed in this section have been identified by comparison of their ^{19}F nmr and ir spectra with those of model compounds. Table V.1.a. shows the general areas in which chemical shifts may be expected to occur and Table V.1.b. shows several examples of the models used.

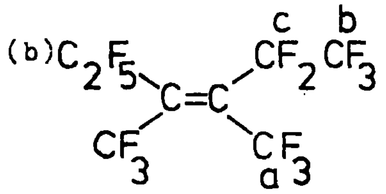
Compound ($\underline{71}$) showed a P - 19 peak in the mass spectrum. The ir spectrum showed two C=C stretches, at 1650 and 1690 cm^{-1}, indicating that the compound was a mixture of *cis* and *trans* isomers. This was confirmed by the fine structure in the ^{19}F nmr spectrum, which was assigned by comparison with data from model compounds. The presence of the $CF_3\text{-}CF_2\text{-}C\leqq CF_3$ moeity was confirmed by signals at 82.2ppm, 114.2ppm ($CF_3\text{-}CF_2\text{-}$) and 67.9ppm ($CF_3\text{-}C\text{-}$). The vinylic fluorine atom was detected by its nmr signal at 86.5ppm, whilst the two $-CF_3$ groups attached to the double bond gave signals at 56.7ppm ($\underline{CF}_3\text{-}\underset{|}{C}=$) and 69.7ppm ($\underline{CF}_3\text{-}CF=$). The proton nmr spectrum showed a broad signal at 1.17ppm.

Compound ($\underline{72}$) gave a parent peak in its mass spectrum and showed a strong C=C ir absorption at 1690 cm^{-1}. The proton nmr spectrum showed a broad signal at 1.35ppm. ^{19}F nmr spectral data indicated the presence of two C_2F_5- groups (86.6, 117.6ppm and 88.7, 106.6ppm), a $\geqq C=C\underline{F}_2$ moeity (56.7, 59.6ppm) and a $\underline{CF}_3\text{-}C\leqq$ group (71.9ppm).

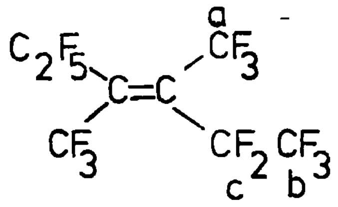
The dimethyl compound ($\underline{73}$) also showed a parent peak in its mass spectrum and showed a strong C=C absorption at 1695 cm^{-1}. The ^{19}F nmr spectrum was assigned by comparison with those of models and that of compound ($\underline{71}$), the indication being that a mixture of *cis* and *trans* isomers was present. Two $-CH_3$ signals were observed in the proton nmr spectrum (1.8ppm, vinylic $-CH_3$ and 1.4ppm, tertiary $-CH_3$), the signals for the two isomers being superimposed upon one another.

(a) Group	^{19}F Chemical Shift^{43,83} (wrt external $CFCl_3$, ppm)	ir (cm^{-1}) C=C
$\underline{CF}_3C\leq$	60 - 70	
$\underline{CF}_3-C=C<$	50 - 70	1670 - 1620
$\underline{CF}_3-C\leq F$	70 - 80	
$\underline{CF}_3-CF_2$	75 - 90	
$>C=\underline{CF}_2$	60 - 80	1740 - 1760
$-CF_2-$	100 - 140	
$CF_3-C\underline{F}$	98 - 105	1670 - 1715
$-CF<$	160	

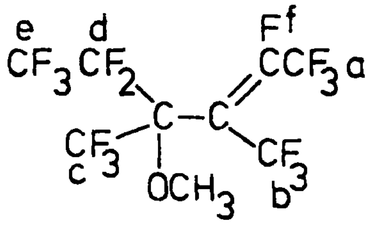
(b)



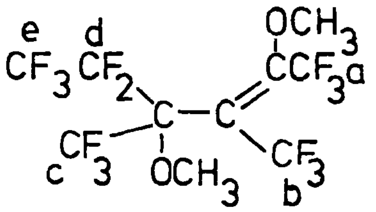
58.0	a			
74.5	b		1650	[43]
99.8	c			



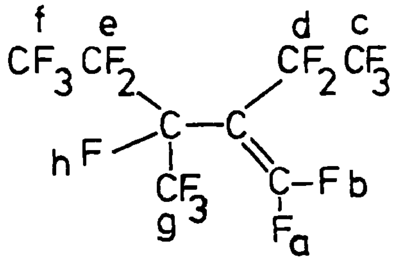
57.7	a			
74.5	b			[43]
99.8	c			



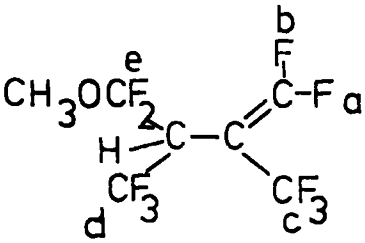
54.3	b			
65.7	c			
68.8	a	D(J_{ab}= 2) of Q(J_{ab}= 15)		
81.0	e		1660	[43]
92.1	f			
119.0	d			



53.0	b			
63.1	a	Q(J_{ab}=17)		
64.4	c		1620	[43]
80.6	e			
118.5	d			



62.3	a				
68.1	b				
75.6	g		119.7	e	[43]
83.0	f	D	183.0	h	
88.3	c				
109.1	d				

Group	^{19}F Chemical Shift (wrt external $CFCl_3$, ppm)	ir (cm^{-1})
	59.4 broad b 63.2 broad D(J_{dc} 19) c 67.2 broad d 69.0 Q a 77.3 broad e	

D doublet

Q quartet

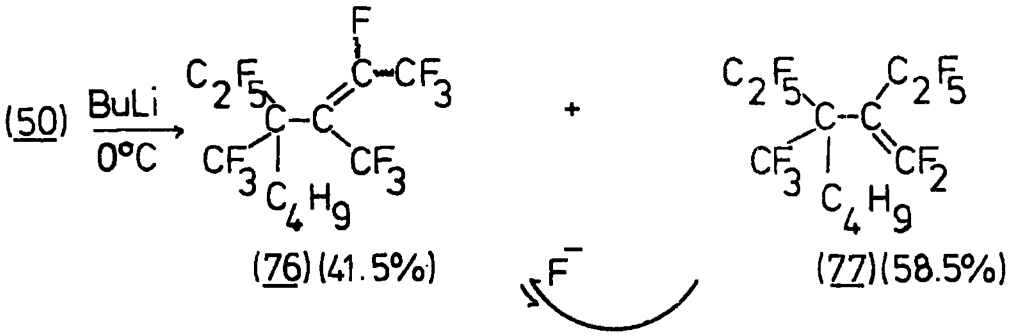
Table V.1.

The fourth component in this mixture analysed to $C_{10}F_{14}H_6$ and parent peaks were observed in the MS-glc spectra. The ^{19}F nmr spectrum was too complex to assign satisfactorily but the characteristic CF_3-CF=C frequency in the ir spectrum was observed at 1640 cm^{-1}. This is consistent with the mixture containing compounds such as (<u>74</u>) and (<u>75</u>) but no further identification could be achieved.

V.3.D. n-Butyllithium.

Compound (<u>50</u>) was reacted with n-butyllithium to observe the effect of a larger nucleophile on the product distribution. Once again the reaction was vigorous and two isomeric products were isolated from the reaction mixture, (<u>76</u>) and (<u>77</u>) (equation V.9.).

V.9.

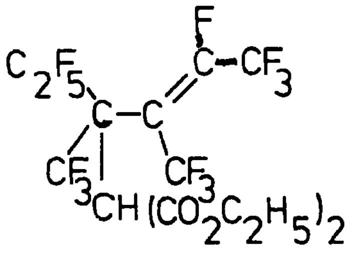


As with the methyl derivatives, addition of potassium fluoride in tetraglyme to the reaction mixture resulted in the isomerisation of (<u>77</u>) to (<u>76</u>). The effect of the larger nucleophile seems to have little effect on the product type or distribution. No dibutyl compounds were detected.

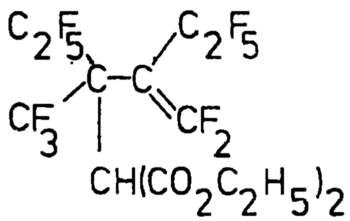
These compounds were identified by comparison with their methyl analogues. The data were similar, with the addition of C-H stretches (2880, 2940, 2965 cm^{-1}) in the ir spectra. Satisfactory analyses were not obtained.

V.3.E. Sodium Diethylmalonate.

From the reactions observed above it would be expected that sodium diethylmalonate would react with (50) in a similar manner to give products such as (78) and (79).



(78)



(79)

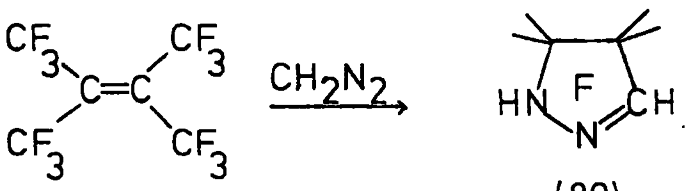
These would be very interesting compounds because of the extra functionality provided by the diethylmalonate groups. Attempts were made to form these compounds by reacting sodium diethylmalonate (prepared in situ from sodium hydride and diethylmalonate) in tetraglyme with (50) at room temperature. The product (*ca.* 37% yield by glc) was isolated by preparative scale glc but was found from MS-glc analysis to be a mixture of compounds. Comparison of the ^{19}F nmr spectrum of the mixture with those of model compounds indicated that the *trans* isomer of (78) was probably present. Insufficient time was available to repeat this reaction to isolate pure products.

V.4. Miscellaneous Reactions.

V.4.A. Reaction with Diazomethane.

Diazomethane is known to add to internal fluoroalkenes. Perfluoro-2,3-dimethyl-2-butene reacts to give (80)[62,63] (equation V.10.).

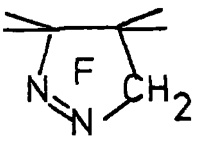
V.10.



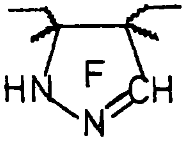
(80)

This was initially identified as structure (80a)[63] but it was seen from ^{1}H nmr spectral data[62] (which shows N-H 11.0ppm and C-H 7.2ppm) and the ir spectrum (N-H, 3350 cm^{-1}) that structure (80) was most consistent with these data.

Alkene (50) also reacts with diazomethane at room temperature to give a mixture of geometrical isomers of the 2-pyrazoline (81).



(80a)



(81)

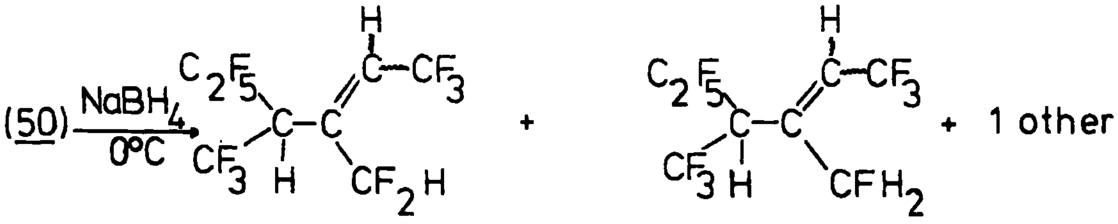
Presumably the 1-pyrazoline is formed initially and then undergoes a 1,3-proton shift to give (81).

This compound was identified by comparison with the data for compound (80). A parent peak was observed in the mass spectrum. Two sets of signals were observed in the proton nmr spectrum, which were of similar intensity. These were due to the N-H and C-H protons in each of the geometrical isomers. The ^{19}F nmr spectral assignments follow from comparison with those of compounds (80) and (50). The ir spectrum shows an absorption at 3265 cm^{-1} (N-H) and another at 2900 cm^{-1} (C-H). Only very weak absorptions were observed at 1640 cm^{-1} where the C=N stretch would be expected.

V.4.B. Reaction with Sodium Borohydride.

Alkene (50) reacted with excess sodium borohydride in tetraglyme at 0°C to give three products, the major two of which were separated by preparative scale glc and were identified as (82) and (83) (equation V.11.).

V.11.



(82) (83)

The reaction to give these products can be explained simply as a series of S_N2' and vinylic substitutions of fluoride by hydride.

Identification followed by comparison with model compounds and both products showed parent peaks in their mass spectra. Ir spectra showed C=C absorptions at 1740 and 1680 cm^{-1} for (82) and (83) respectively.

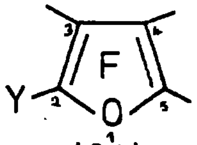
Chapter VI

Discussion -

Preparation and Reactions of Fluorinated Furans.

VI.1. Preparation of Furans.

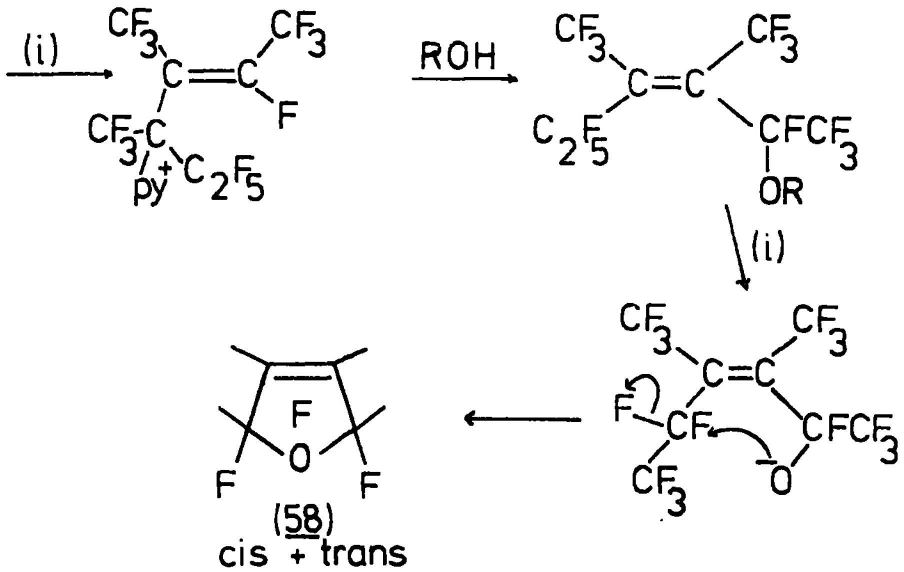
Work in this laboratory[71,79] has illustrated the connection between internal fluoroalkenes (oligomers of tetrafluoroethylene) and fluorinated furans of type (84) (equations VI.1. and VI.2., and Table VI.1.).



(84)

For consistency, the numbering shown has been maintained throughout this discussion.

VI.1. (50)

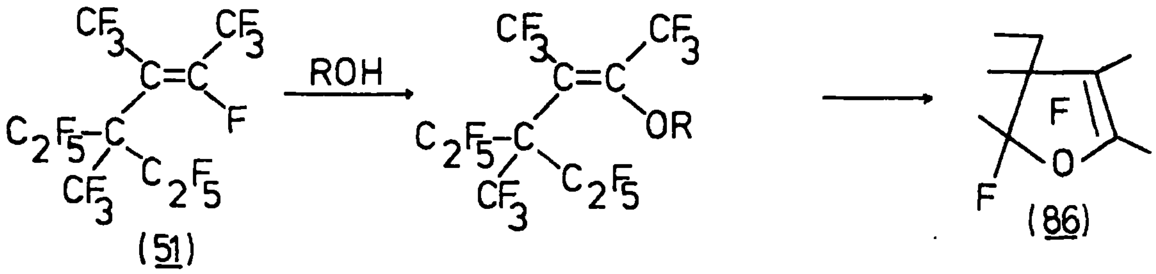


[71]

(i) = pyridine

R = Me, Et, iPr

VI.2.



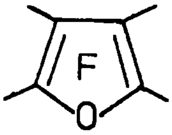
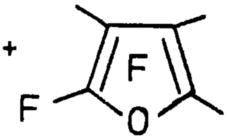
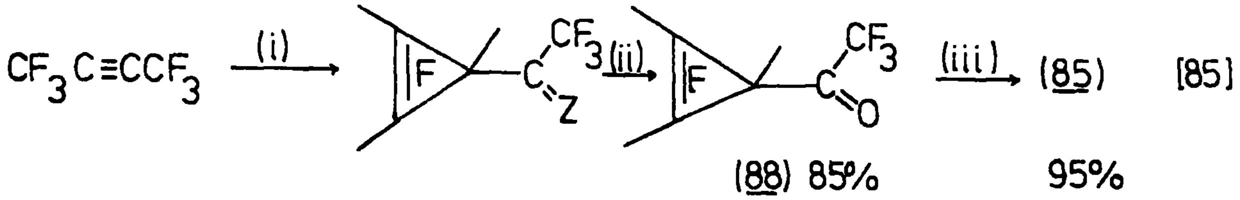
(58)	$\xrightarrow[\text{80\% conversion}]{\text{Fe, 580°C}}$	 (85)	79%	[71]
(58)	$\xrightarrow[\text{tetraglyme}]{Et_3N}$	(85)	41%	[71]
(86)	$\xrightarrow[\text{100\% conversion}]{\text{Fe, 470°C}}$	(85) + (58) +  (87) 75%		[79]
(86)	$\xrightarrow[\text{100\% conversion}]{\text{Pt, 570°C}}$	(87) + C_4F_{10} + others 85%		[79]

Table VI.1.

Other recently reported methods for the preparation of fluorinated furans are shown in Table VI.2.



(i) = $C_6H_{11}NCO$

(ii) = $3\text{-}ClC_6H_4CO_3H$; $1,2,4\text{-}Cl_3C_6H_3$

(iii) = Br_2, 250°C, 13h

Z = $CN\text{-}C_6H_{11}$

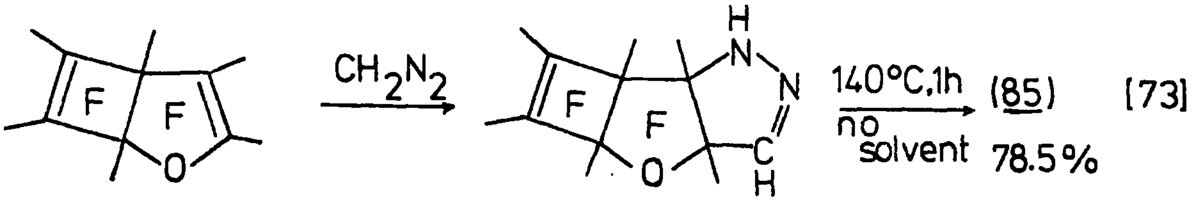
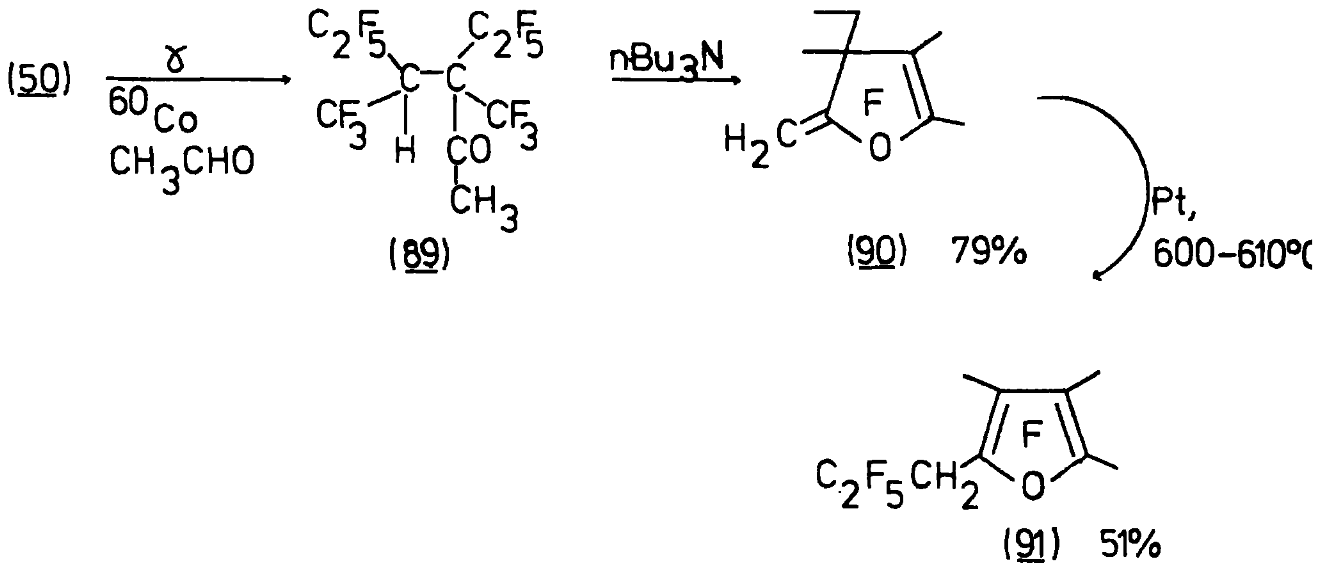


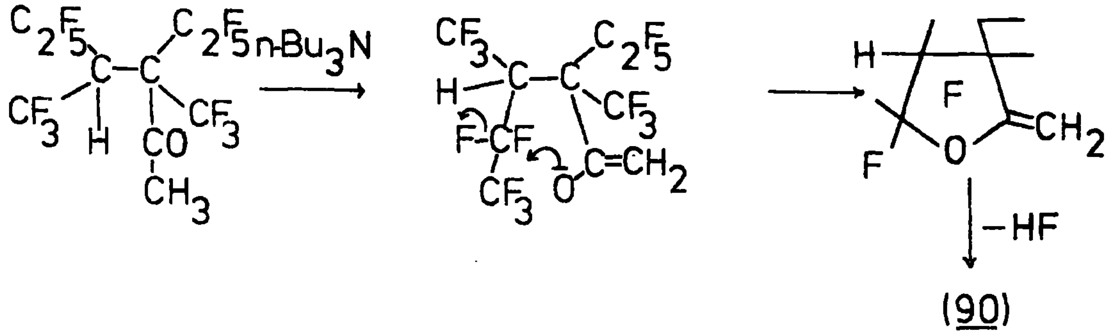
Table VI.2.

A completely different method for preparing compound (84) with $Y = CH_2C_2F_5$ has been discovered by a worker in these laboratories[74] and has been repeated by the author. The reaction is outlined in Scheme VI.1. This provides another link between internal fluoroalkenes and fluorinated furans. Compound (50) underwent free radical addition to give compound (89) which, under the influence of base, rapidly cyclised with the loss of HF to give compound (90). This process involves nucleophilic attack on a saturated perfluoromethylene position (equation VI.3.), which has been observed in several other instances (e.g. equations VI.1. and VI.2.).



Scheme VI.1.

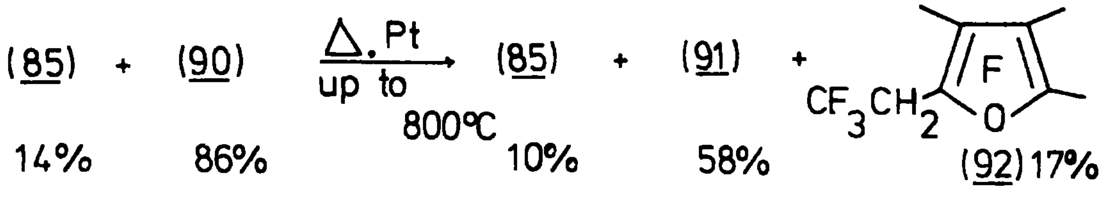
VI.3.



Passage of compound (<u>90</u>) over platinum at 600°C in a flow system effected a 1,3-migration of a-C_2F_5 group, resulting in the formation of compound (<u>91</u>) in fairly good yield.

In another reaction carried out in the same manner, an impurity (1·4%) in the second stage of the scheme ((<u>89</u>)⟶(<u>90</u>)) was identified as compound (<u>85</u>). When the reaction mixture was pyrolysed at a higher temperature to that used in Scheme VI.1. (up to 800°C) three components were identified from the recovered material. These were found to be unchanged (85), (91) and a different furan, (92), (equation VI.4.).

VI.4.



VI.2. Reactions of Fluorinated Furans.

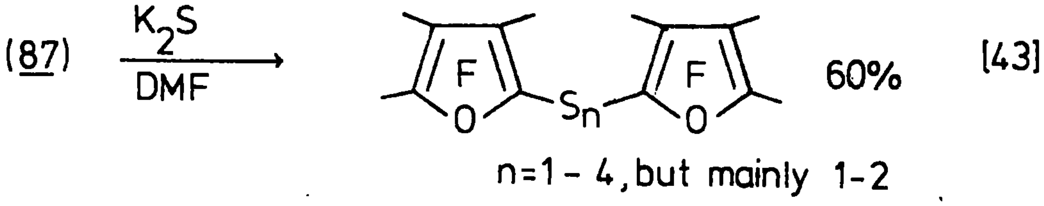
There are two major areas of interest in the reactions of fluorinated furans - nucleophilic attack and their photochemistry.

VI.2.A. Nucleophilic Attack.

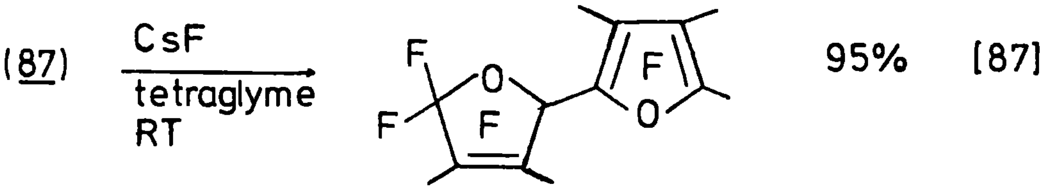
The double bonds of the furans (type (84)) should be susceptible to nucleophilic attack because of the electron withdrawing effect of the perfluoroalkyl substitutents. These systems are also aromatic.

For Y = F (compound (87)) some nucleophilic reactions have previously been observed (e.g. equations VI.5 and VI.6.).

VI.5.



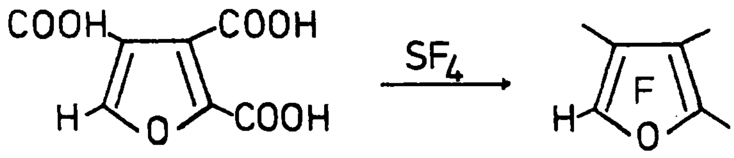
VI.6.



This compound has a fluorine atom attached directly to a double bond and hence this should be easily replaced. The reactions with this compound have been pursued with other nucleophiles and a series of furans with a variety of substitutents (Y) have been prepared. The results are shown in Table VI.3.

Compound (93) has been prepared by an alternative method by Russian workers[86] (equation VI.7.).

VI.7.



(93) 76%

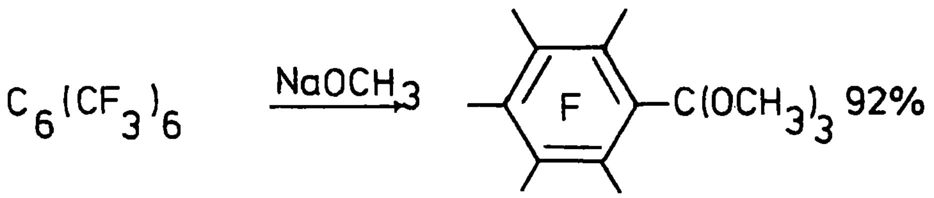
[86]

Compounds (95) and (96) have also been prepared previously by a worker in these laboratories[87].

Reactions have also been pursued with compound (85), perfluorotetramethylfuran. Surprisingly this compound is completely inert to a variety of reagents. No reaction was observed with methanol or sodium methoxide and even under more forcing conditions, when heated to 100°C for 67 hours in a sealed tube with caesium fluoride and methanol, there was no detectable reaction.

An analogous system - perfluorohexamethylbenzene - has been reported to undergo reaction with methoxide[96] (equation VI.8.).

VI.8.



92%

[96]

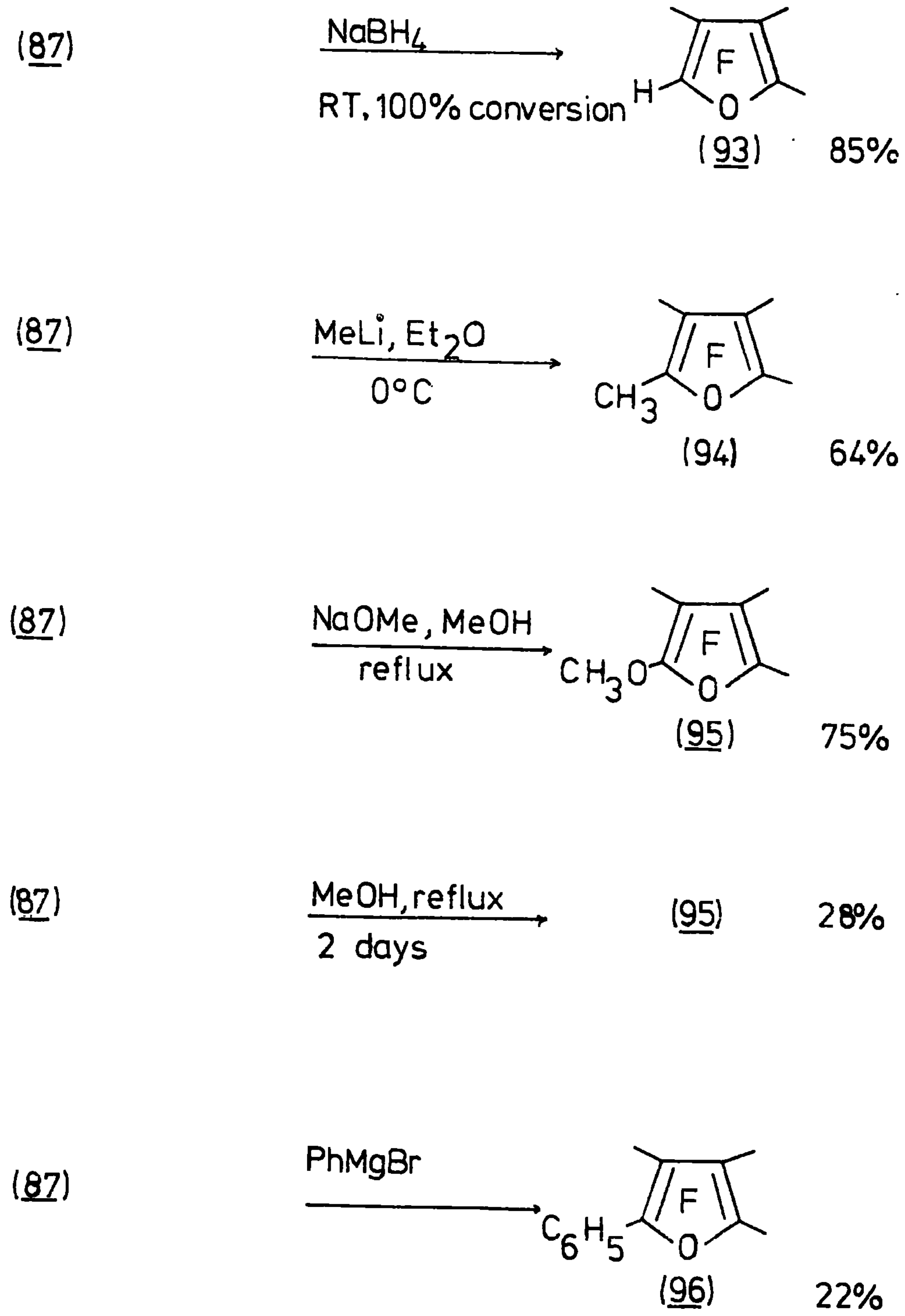
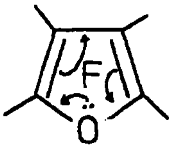
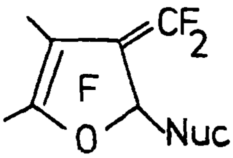

(87)
NaBH$_4$
RT, 100% conversion
H
F
O
(93)
85%
(87)
MeLi, Et$_2$O
0°C
CH$_3$
F
O
(94)
64%
(87)
NaOMe, MeOH
reflux
CH$_3$O
F
O
(95)
75%
(87)
MeOH, reflux
2 days
(95)
28%
(87)
PhMgBr
C$_6$H$_5$
F
O
(96)
22%

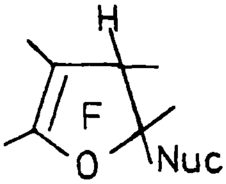
Table VI.3.

Two factors account for the lack of reaqtivity of perfluorotetramethylfuran. Firstly, it is presumably a π-electron rich system and therefore resistant to attack by nucleophiles in the ring or side chain and secondly the aromatic system of the ring would have to be disrupted to give nucleophilic substitution or addition at a ring carbon.





Nucleophilic substitution



Addition

VI.2.B. Addition Reactions.

The conclusions reached in the last section are borne out by the lack of reactivity of compounds (85) and (87) with addition reagents. Neither compound reacted with diazomethane. Compound (85) did not react with methanol on irradiation with a γ-ray ^{60}Co source, even after prolonged exposure. This compound did, however, react with potassium permanganate in acetone but the products were not isolated. It seems reasonable to assume that they were either gaseous or water-soluble, and hence not detected.

VI.2.C. Structural Assignments.

The structures of the furans formed above follow simply from a comparison with ^{19}F nmr and ir spectral data of model compounds, shown in Table VI.4. Each of the furans prepared gave a parent peak in its mass spectrum.

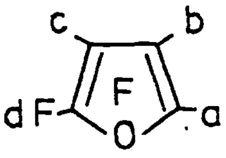
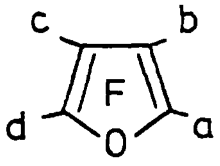
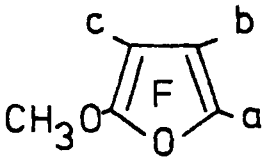
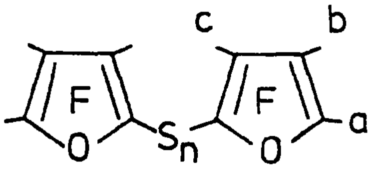
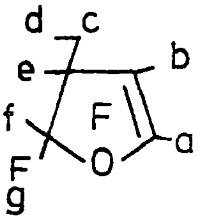
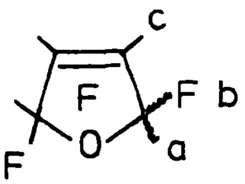
Compound	^{19}F Chemical Shift[43] (wrt external $CFCl_3$, ppm)	ir (cm^{-1})
	60.2 m b,c 60.5 64.5 D(J_{ad}=2.5) of Q(J_{ab}= 8.3) a 103.7 Q(J_{cd}= 15) of Q d	1610 1635 C=C 1681 1465 C-O
	60.0 a,d 65.6 b,c	1640 C=C 1440 C-O
	58.7 Q(J_{bc}= 7) c 59.6 septet b 63.3 Q(J_{ab}= 8.5) a	1610 1650 C=C 1480 1430 C-O 1380
	59.0 broad S b,c 64.0 broad Q(J=7) a	1810 w 1620 1540 C=C 1422 C-O
	58.3 m b 68.32 m a 71.06 m e 79.4 D(J_{fg}=35) f 80.64 m d 105.6 m c 116.98 m g	
	Isomer A 63.3 m c 85.0 m a 122.6 broad m b Isomer B 62.9 m c 83.4 m a 112.2 broad m b	

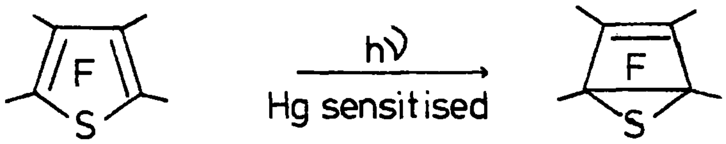
Table VI.4.

VI.3. Photochemistry.

The second major area of interest of fluorinated furans is that of their photochemistry.

Valence bond isomers have been discovered in recent years for six carbon π-systems and also one example of a five atom π-system was discovered on the irradiation of perfluorotetramethylthiophene[88,89] (equation VI.9.).

VI.9.

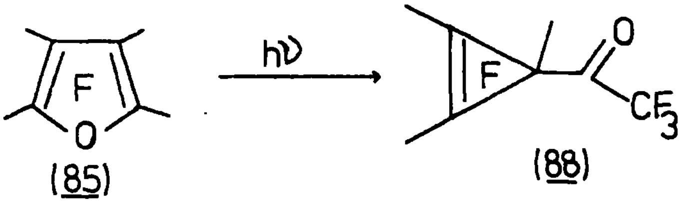


[88]

It was therefore of interest to discover whether the corresponding oxygen analogues could be formed from perfluorinated furans and the compounds described in the previous section provide a very useful probe for this investigation.

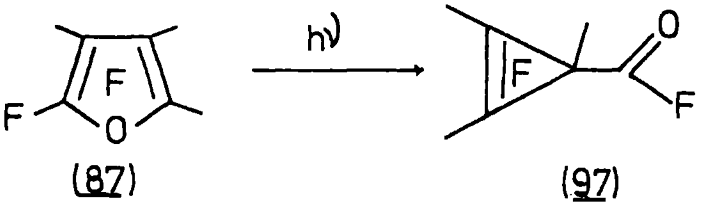
The photolyses of perfluorotetramethylfuran and perfluoro-3,4,5-trimethylfuran were successfully carried out by workers in these laboratories[87] although in concurrent studies other workers were unable to do this[73]. In both of these reactions the expected ring opening reaction occurred rather than the formation of a Dewar furan (equations VI.10 and VI.11.).

VI.10.



[87]

VI.11.



In both cases the reactions were carried out under transference conditions where the volatile products transferred out of the photolysis vessel and were collected in a cold trap[91]. It was found that unless the initial photolysis products were removed in this way further reaction occurred to give a multicomponent mixture[43]. A fairly low yield (ca. 20%) of products was obtained in each reaction.

An interesting aspect of the reaction with compound (87) was the highly specific nature of the ring opening.

The photochemistry of various substituted furans was therefore investigated for the evidence of formation of a Dewar isomer and also to see whether other substituents influenced the mode of ring opening in a specific manner. All reactions were carried out under transference conditions.

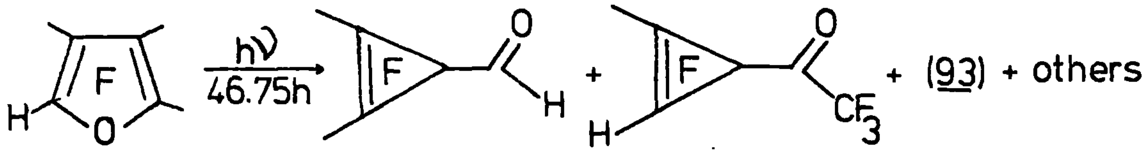
VI.3.A. Photolysis of Perfluoro-3,4,5-trimethylfuran (87).

This reaction was repeated but again no evidence was obtained for any other than the single acylfluoride (97). The reaction gave a 32% conversion to products after 18 hours photolysis.

VI.3.B. Photolysis of 3,4,5-Tris(trifluoromethyl)furan (93).

In this reaction only 13% conversion to products was observed, with 29% recovery of volatile material. The involatile material was found to contain many components and was not investigated further. The reaction proceeded according to equation VI.12.

VI.12.



(93) (98) (99)

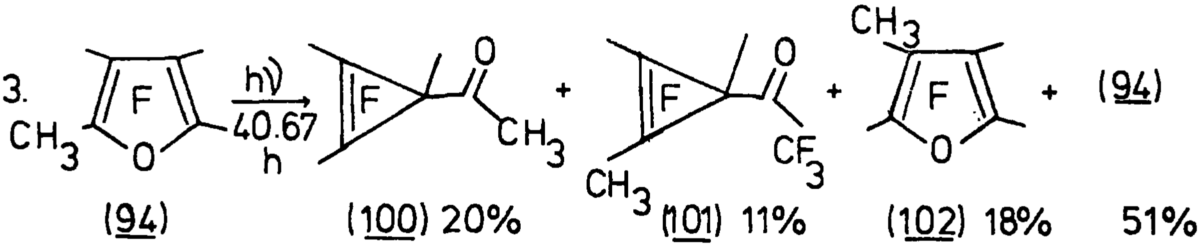
10% 19% 54%

Compounds (<u>98</u>) and (<u>99</u>) were the only identified components of the mixture, although there were other very minor components present. In this case, therefore, there is little specificity in ring opening, products from both modes of opening being observed.

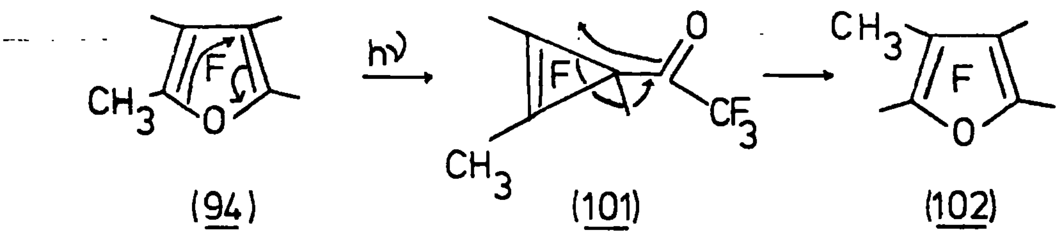
VI.3.C. Photolysis of 2-Methyl-3,4,5-<u>tris</u>(trifluoromethyl)furan (<u>94</u>).

The reaction observed with this compound is shown in equation VI.13.

VI.13.



In this case 40% recovery of volatile material was obtained with 19.75% conversion to products. Again, products from both modes of opening have been observed ((<u>100</u>) and (<u>101</u>)) as well as compound (<u>102</u>). This latter is very interesting, as compounds formed in a similar manner were not observed in the other photolysis reactions tried. It seems most likely that compound (<u>102</u>) is formed as a result of ring opening of compound (<u>101</u>) (Scheme VI.2.).

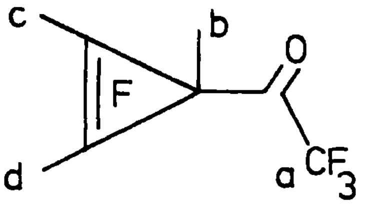


Scheme VI.2.

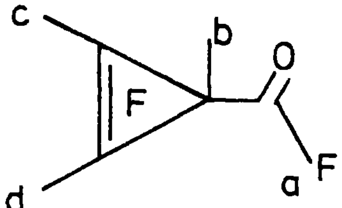
The other possibility to explain the presence of (<u>102</u>) is the occurrence of some type of ring walk mechanism. Photolysis of compound (<u>101</u>) on its own is required to clarify this situation.

VI.3.D. Structural Assignments.

The photolysis products were identified by comparison with ^{19}F nmr and ir spectral data from compounds (88) and (97) shown in Table VI.5.



(88)



(97)

Compound	^{19}F nmr (ppm wrt ext. $CFCl_3$)[43]			ir (cm^{-1})
(88)	63.1	singlet	c,d	1775
	69.3	singlet	b	1295
	76.9	singlet	a	
(97)	-29.7	quartet(J_{ba} = 10)of m($J \leq 1$)	a	
	63.6	singlet	c,d	1860
	70.4	doublet	b	1310

Table VI.5.

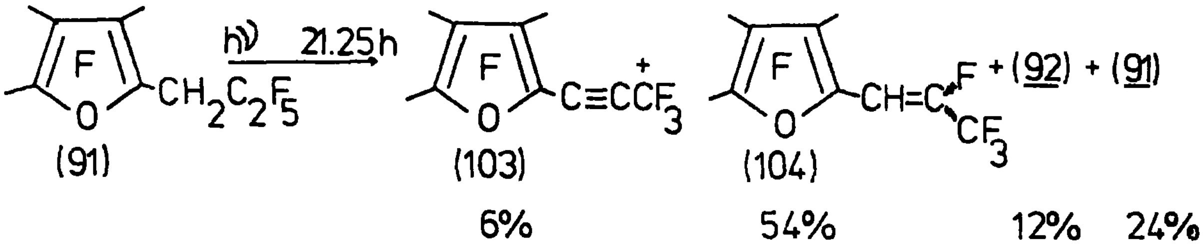
Compound (98) was identified by its ^{19}F nmr spectrum (which showed $CF_3-C{=}C-CF_3$ and $>C-CF_3$ groups present) and its mass spectrum which showed a P - 29 peak (loss of CHO). Since only very small quantities of pure compounds were obtained this was the only identification possible. Compound (99) showed a parent peak in its mass spectrum. ^{19}F nmr and ir spectral data were consistent with the structure indicated. Insufficient material was obtained to get analyses of these compounds. Compounds (100) and (101) were identified by comparison with spectra of model compounds and (100) showed a small parent peak, P- 19 (loss of F) and P - 43 (loss of CH_3CO) peaks in its mass spectrum. Analyses were not obtained for these compounds. Furan (102) was identified by comparison with data shown in Table VI.4. A parent peak was observed in the mass spectrum and there was no

C=O stretch in the ir spectrum, but a characteristic C-O absorption was observed at 1435cm^{-1}.

VI.3.E. Photolysis of Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-propane (91).

The photolysis of this compound provided an interesting reaction not similar to those recorded earlier. Unlike the other compounds, this furan was photolysed using a medium pressure uv lamp. The reaction observed is illustrated in equation VI.14.

VI.14.



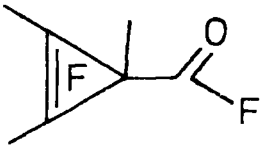
The recovery of volatile material was good in this instance (82%). The presence of compound (92) in the reaction mixture can most reasonably be accounted for as an initial impurity in the starting material which did not show up on glc analysis, since the retention times are similar. Obviously in this reaction the loss of HF from the side chain is the most facile process, as only compounds where this had occurred were identified. In the other systems photolysed no such route was available.

Compounds (103) and (104) were identified by comparison of data with those shown in Table VI.4. Compound (103) showed a characteristic ir stretch at 2370cm^{-1} (C≡C) and a parent peak in its mass spectrum. Furan (104) also showed a parent peak in its mass spectrum. ^{19}F nmr spectral data showed that a cis and trans isomer mixture was present.

VI.3.F. Conclusion.

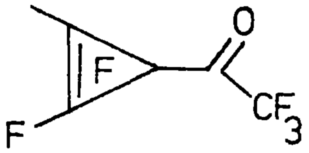
Although the furans used were found to photolyse readily, in small yield, no Dewar species was observed in any of the cases tried. This difference between perfluorothiophene and perfluorofurans is presumably due to the greater strength of the C=O than the C=S bonds.

It also emerges from the reactions described above that whilst furans containing substituents other than fluorine in the 2-position open on photolysis with little selectivity, perfluoro-3,4,5-trimethylfuran opens to give exclusively the acid fluoride (97). This is probably due to the destabilising influence of a fluorine atom directly attached to a C=C group (see Chapter IV.) and compound (97) would be expected to be more stable than the isomer containing a vinylic fluorine atom (105).



(97)

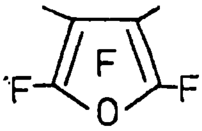
more stable than



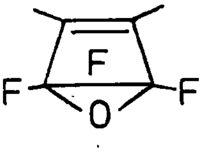
(105)

The stabilising influence of CF_3 groups on small rings[85,92] may also influence the mode of ring opening and in fact a combination of these two factors is probably involved.

In view of the specificity exhibited only by compound (87), the photolysis of compound (106) would seem very suitable for enhancing the formation of a Dewar furan. Photolytic ring opening of this compound in either sense would produce an unstable species and therefore if photolysis were to occur the possibility of forming a compound (107) would be quite reasonable.



(106)



(107)

No attempts were made to sensitise the photolyses discussed above, but this is another possible route for the enhancement of the formation of a Dewar furan.

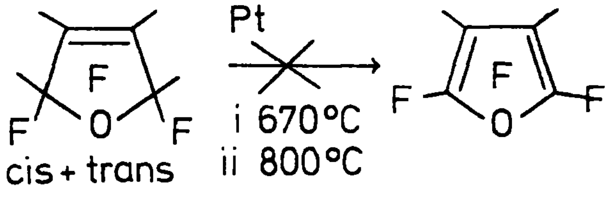
VI.3.G. Attempted Preparation of Compound (106).

Attempts were made to prepare compound (106) by passage of compound (58) over platinum at 670°C and 800°C but in the first instance very little reaction was observed, (giving several products), and at the higher temperatures mainly decomposition occurred (equation VI.15).

VI.3.H. Related Reactions - Attempted Formation of Compound (103).

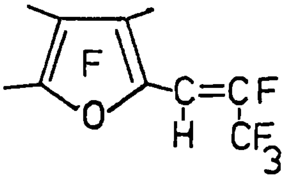
In an attempt to form the acetylene (103) by an alternative route to photolysis, furan (91) was reacted with base in order to remove HF. In one reaction, (91) was passed over potassium fluoride at 580-630°C in a flow system but no products were collected, the majority of the material being observed to tar up on the surface of the potassium fluoride. The elimination of HF was therefore attempted using triethylamine, this base being chosen to minimise the possibility of nucleophilic attack on any products formed. The reaction occurred rapidly at room temperature and the ^{19}F nmr spectrum of the product mixture taken one hour after mixing showed that compound (104a) was formed and was the major component in the mixture. This was identified as the trans isomer because of the trans H-F coupling observed (35 Hz) which is known to be greater than cis H-F coupling[94]. A small amount of starting

VI.15.



(58) (106)

material was also present.



(104a)

The mixture was heated to 50°C for several hours but no change was observed. Thus only one mole of HF could be removed from the side chain of furan (91) and the acetylene could not be obtained by this method.

Chapter VII

Experimental Results for Chapter V.

VII.1. Instrumentation.

The instrumentation described in Chapter III also applies to this section of work. In addition, distillations were carried out on Fischer Spaltrohr concentric tube systems MMS 200 and HMS 500. Carbon, hydrogen and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analyses for fluorine were carried out as described in the literature[84]. Boiling points were determined by Siwoloboff's method and are not corrected for changes in atmospheric pressure. Glc analyses were carried out on a Varian Aerograph model 920 machine unless otherwise stated.

VII.2. Reagents and Solvents.

VII.2.A. Reagents.

Methyllithium was supplied as a solution in ether, approximately 1.7M, by LithCoA or the Ethyl Corporation. The solution was not standardised prior to use.

Perfluoro-3,4-dimethyl-3-hexene (50) (supplied by I.C.I, Mond Ltd.) (500ml) was obtained as a mixture of cis and trans isomers. It was washed with acid (hydrochloric acid, 3M, 2x200ml) to remove amines, and water (3x200ml) and dried over magnesium sulphate. The resulting liquid was distilled through a 2 ft. column filled with glass helices, b.p. 90-91°C. ^{19}F nmr data agreed with those of an authentic sample[43]. A small impurity was present ($<5\%$, 3-methyl-3-trifluoromethyldecafluoropentane) and this was not removed before use, nor has adjustment been made for it in the quantities used. Compound (50) was used throughout as a mixture of cis and trans isomers.

Potassium fluoride (reagent grade) was dried by heating under vacuum for several hours and was stored under dry nitrogen.

All other reagents were used as supplied, or as previously described.

VII.2.B. Solvents.

Tetraglyme was purified by stirring with sodium at 95°C for 24h followed by fractional distillation under vacuum, the middle fraction being collected over dry molecular sieve (type IVA) and then stored under dry nitrogen.

VII.3. Reactions with Nitrogen Nucleophiles (with A.A. Lindley).

VII.3.A. Reactions with Ammonia.

i) Aqueous Ammonia.

Compound (50) (2.4g, 6mmol) in ether (2ml) was mixed with aqueous ammonia (0.88M, 3ml) and stirred overnight. A yellow colouration was observed and the reaction was initially slightly exothermic.
Glc analysis (col. O, 195°C) showed that the major product was trans-2,4-diamino-3-cyano-4-trifluoromethyloctafluoro-2-hexene (61). This was characterised by A.A. Lindley and identification was carried out by spectral comparisons.

ii) Anhydrous Ammonia.

a) Open System.

Compound (50) (8.17g, 20.4mmol) was transferred under vacuum from P_2O_5 to ensure that no water was present and was mixed with dry ether. Ammonia (anhydrous) was bubbled through the solution at a flow rate of approximately $20 cm.min^{-1}$. A solid was deposited during the reaction. When-passage of the gas had ceased, glc analysis (col. O, 190°C) showed two products as well as compound (50) and ether. In a series of similar reactions the proportions of products varied, presumably depending upon the amount of ammonia passed. Ir spectral data of the mixture showed $\nu_{max}^{film} = 2220 cm^{-1}$ (C≡N stretch). MS-glc data was as follows: 1. (Found: M^+ 378 (P - 19), $C_8F_{15}NH_2$ requires M^+ 397); 2. (Found: M^+ 375 (P - 19), $C_8F_{14}(NH_2)_2$ requires M^+ 394); 3. (Found: M^+ 352, $C_8F_{11}H_4N_3$ requires M^+ 352), also identified by comparison of data with those of an authentic sample of (61).

b) Addition of Excess Ammonia to Products from (a).

Ammonia (anhydrous) was bubbled through a sample of the reaction mixture obtained from (a) and aliquots were analysed by glc at intervals. As more ammonia was passed the proportion of fraction 3 (compound (61)) increased, whilst the proportions of the other components decreased. When an aqueous solution of ammonia was added to a sample of the reaction mixture from (a) similar effects were observed on glc analysis.

c) Sealed System.

Compound (50) (6.32g, 15.8mmol) was placed in a flask fitted with a bladder containing anhydrous ammonia. The gas was allowed to diffuse into the liquid, the bladder being refilled as necessary. After stirring at room temperature for several days the mixture was completely solid and was dissolved in ether to mobilise it. Glc analysis (col. O, 180°C) of an ethereal solution of the reaction mixture showed that $>97\%$ of the product was compound (61). ^{19}F nmr and ir spectral data confirmed this.

iii) Anhydrous Ammonia in the presence of Caesium Fluoride.

Compound (50) (7.88g, 19.7mmol) and a small quantity of caesium fluoride were mixed, and anhydrous ammonia was passed through the mixture, with stirring, for 0.75h at a flow rate of ca. 50 $cmmin^{-1}$. A solid yellow mass was obtained which was diluted with dry ether. Glc analysis of the solution showed that some of compound (50) was still present and so ammonia was passed for a further period of time. The mixture was filtered and the solid washed with ether. The ir spectrum of the crude mixture showed $\nu_{max}^{film} = 2220\ cm^{-1}$ ($C\equiv N$). MS-glc data was as follows: 1. (Found:M^+ 358 (P - 19), $C_8F_{15}.NH$ requires M^+ 377); 2. (Found:M^+ 375 (P - 19), $C_8F_{14}(NH_2)_2$ requires M^+ 394); 3. (Found: M^+ 352, $C_8F_{11}H_4N_3$ requires M^+ 352), also identified by comparison of data with those of an authentic sample of (61).

VII.3.B. Reactions with Methylamine.

i) Aqueous Methylamine.

Compound (50) (9.68g, 24.6mmol), methylamine (20ml, 25-30% aq) and ether (10ml) were stirred together in an exothermic reaction which produced a yellow solution. After 4 days at room temperature, water (50ml) and ether (50ml) were added. The organic layer was separated, washed (water, 2x50ml) and dried (magnesium sulphate). After removal of desiccant, and solvent at reduced pressure, the volatile material was vacuum transferred (8.53g) and distilled on a concentric tube apparatus. Glc analysis (col. O, 150°C) of the initial fractions b.p. 60-70°C, 26mm Hg, (2.27g) showed a mixture of at least two components. Later fractions b.p. 91°C, 17mm Hg, (1.43g) also contained two volatile components together with a less volatile component not contained in earlier fractions. Vacuum transference of the pot residue (3.11g) was shown to yield one component (col. O, 200°C), identified as <u>2-trifluoromethyl-3-(2'-methylaminooctafluoro-2'-butyl)-4-methylimino-N-methyl-2-azetine</u> (67). (Found: C, 33.6; F, 53.5; H, 2.7; N, 10.8%, M^+ 393. $C_{11}F_{11}H_{10}N_3$ requires C, 33.6; F, 53.1; H, 2.6; N, 10.7%, M^+ 393). Nmr spectrum no. 4, ir spectrum no. 6, MS no. 1.

The more volatile fractions were found to contain at least two major components which could not be separated by distillation. In another experiment attempts were made to separate the components of the reaction mixture by preparative scale glc but decomposition of the mixture occurred. Low temperature vacuum transference was also unsuccessful in obtaining separation.

ii) Anhydrous Methylamine.

Methylamine (g, 2.6g 83.8mmol) was passed into compound (50) (6.5g, 16mmol) in an exothermic reaction. Ether (10ml) was added during the reaction as a diluent to prevent blockage by the white solid which was formed. Aliquots of reaction mixture were removed at intervals and analysed by glc (col. A, 108°C). When a substantial amount of reaction had occurred (product mixture 39% (50), 61% products, determined by glc) water was added and the organic layer was ether extracted. A white solid (0.55g) insoluble in both ether and water was isolated but not identified. After removal of ether at atmospheric pressure the volatile material was vacuum transferred (2.96g). This was separated into three components by preparative scale glc, the major of which was identified as trans-4-methylamino-perfluoro-3,4-dimethyl-2-hexene (66). (Found: C, 26.5; F, 69.0; H, 1.3; N, 3.7%, M^+ 411. $C_9F_{15}H_4N$ requires C, 26.3; F, 69.3; H, 1.0; N, 3.4%, M^+ 411). Nmr spectrum no. 5, ir spectrum no. 7, MS no. 2.

Insufficient material was obtained to allow identification of the minor component.

VII.3.C. Anhydrous tert-Butylamine.

i) Excess Anhydrous Amine.

Compound (50) (1.16g, 2.9mmol) and tert-butylamine (anhydrous, 1.87g, 25.6mmol) were stirred together in an exothermic reaction which immediately produced a white solid. The mixture was stirred for 7 days at room temperature. Water was added and a yellow lower layer was separated (0.85g). Glc analysis (col. A, 137°C) showed there to be at least five components, the major one constituting about 70% of the mixture. ^{19}F nmr data was consistent with compound (69). Since attempts to isolate this compound by preparative scale glc led to its decomposition, alternative purification methods were sought. Preparative thin layer chromatography (pentane) resulted in the isolation of four fractions (R_f= 0.75, 0.55, 0.14, Origin). Glc analysis of these after removal from the silica (ether) showed many peaks, implying that decomposition had occurred on the silica. Low temperature - reduced pressure transference only led to enrichment, never complete isolation of pure material.

ii) Excess Anhydrous Amine with Ether.

This reaction was carried out as in (i) above. Analysis of the product mixture by ^{19}F nmr spectral and glc techniques showed that it was similar to that formed in (i).

iii) Equimolar Amounts of Amine and Compound (50).

Compound (50) (2.04g, 5.1mmol) and *tert*-butylamine (anhydrous, 0.36g, 4.9mmol) were stirred together for 7 days. A white solid was formed. After addition of water a lower layer was recovered (1.73g). Glc analysis (col. A, 140°C) and ^{19}F nmr spectral data showed that compound (50) was the major component (73%) with a small amount of (69) (18%), plus other, more-volatile components.

VII.3.D. Aqueous *tert*-Butylamine.

i) Excess Amine.

Compound (50) (9.53g, 23.8mmol), *tert*-butylamine (14.79g, 202mmol) and water (50ml) were stirred together at room temperature for 15 days. A yellow lower layer was separated (7.22g) and the volatile fraction was vacuum transferred (0,66g). Glc analysis of the volatile fraction (col. O, 200°C) showed at least six components, with no (50) and no (69) present. The ^{19}F nmr spectrum of the residue was very complex.

ii)Equimolar Amounts of Amine and Compound (50).

Compound (50) (1.99g, 4.9mmol), *tert*-butylamine (0.37g, 5.1mmol) and water (1.5ml) were stirred at room temperature for 7 days. The lower layer was separated (1.50g) and glc analysis and ^{19}F nmr data indicated that (50) was the major component in the mixture ($>$90%), with two very minor volatile components also present. No (68) was present.

VII.4. Reactions with Carbon Nucleophiles.

VII.4.A. Reactions with Methyllithium.

i) Compound (50) (10.5g, 26.25mmol) in ether (20ml) was cooled to 0°C. Methyllithium (15ml, ca. 1.7M in ether, 25mmol) was added over 20min. and spitting was observed, together with the formation of a white colouration. The mixture was stirred at 0°C for 1.6h and then at room temperature for a further 2.6h. Water was added and the mixture was kept overnight. The organic layer was separated, dried (magnesium sulphate) and the ether was removed at atmospheric pressure. The residue was vacuum transferred (7.41g). Glc analysis (col. O, 90°C) showed four products which were separated by preparative scale glc (col. O, 85-150°C) and were identified as follows in ascending order of retention times: cis,trans-4-methyl-perfluoro-3,4-dimethyl-2-hexene (71) (18%) (Found: C, 27.2; F, 71.7; H, 0.7%, M^+ 377 (P - 19). $C_{12}F_{15}H_3$ requires C, 27.3; F, 71.9; H, 0.8%, M^+ 396). Nmr spectrum no. 6, ir spectrum no. 8. 3-methyl-perfluoro-2-ethyl-3-methyl-1-pentene (72) (32.5%) (Found: C, 27.4; F, 71.5; H, 0.7%, M^+ 396. $C_{12}F_{15}H_3$ requires C, 27.3; F, 71.9; H, 0.8%, M^+ 396). Nmr spectrum no. 7, ir spectrum no. 9. cis, trans-2,4-dimethyl-perfluoro-3,4-dimethyl-2-hexene (73) (22%) (Found: C, 30.6; F, 68.1; H, 1.4%, M^+ 392; $C_{10}F_{14}H_6$ requires C, 30.6; F, 67.8; H, 1.5%, M^+ 392). Nmr spectrum no. 8, ir spectrum no. 10, MS no. 3. The fourth fraction was shown by ^{19}F nmr spectral data to be a mixture of at least two isomeric components (27%) (Found: C, 30.4; F, 67.8; H, 1.3%, M^+ 392. $C_{10}F_{14}H_6$ requires C, 30.6; F, 67.8; H, 1.5%, M^+ 392).

In another reaction carried out for a shorter time the proportions of ((71) + (72)) to the less volatile components was 72% to 28%, with (72) again being the major product.

ii) Reaction with Methyllithium using excess Compound (50).

Compound (50) (4.77g, 11.9mmol) in ether (10-11ml) was cooled to 0°C. Methyllithium (3.75ml, ca. 1.7M in ether, ca. 7mmol) was added fairly rapidly. A white colouration was observed. The mixture was stirred for 4.5h at room temperature. Water was added and the organic layer extracted (ether) and dried (magnesium sulphate). Glc analysis (col. O, 90°C) showed there to be many other components in the mixture as well as those expected for the reaction. The reaction was not pursued further.

VII.4.B. Reaction of Potassium Fluoride with Product Mixture from VII.4.A.

The reaction mixture from VII.4.A. above (1.06g) and potassium fluoride (0.12g, 2.1mmol) were stirred together in tetraglyme at room temperature. A yellow colouration was observed immediately. After 4 days the ^{19}F nmr spectrum was taken of the crude mixture and the signals were similar to those of compound (71). Glc analysis (col. O, 95-100°C) showed that the major volatile component was (71), not (72) as in the original mixture.

VII.4.C. Reaction with n-Butyllithium.

Compound (50) (8g, 20mmol) in dry ether (15ml) was cooled to 0°C. n-Butyllithium (12ml in hexane) was added over 0.5h and a vigorous reaction ensued leaving a yellow-coloured solution. The mixture was stirred at room temperature for 1h and water was added, the organic layer was separated and dried (magnesium sulphate) and the ether removed at atmospheric pressure. Glc analysis of the residue (4.84g) (Pye 104, col. O, 100°C) showed that no (50) was left and that two products were formed. These were separated from the mixture by preparative scale glc (col. O, 195°C) to give cis, trans-4-butyl-perfluoro-3,4-dimethyl-2-hexene (76) (Found: M^+ 417 (P - 21); $C_{12}F_{15}H_9$ requires M^+ 438). Nmr spectrum no. 9, ir spectrum no. 11. and 3-butyl-perfluoro-2-ethyl-3-methyl-1-pentene (77) (Found: M^+ 417

(P - 21); $C_{12}F_{15}H_9$ requires M^+ 438). Nmr spectrum no. 10, ir spectrum no. 12.

VII.4.D. Reaction of Potassium Fluoride with Product Mixture from VII.4.C.

Crude reaction mixture from VII.4.C. above (1.06g) was stirred at room temperature with a small amount of potassium fluoride in tetraglyme. Soon after mixing a yellow colouration was observed. After several hours the ^{19}F nmr spectrum showed the mixture to consist largely of compound (76) , rather than an approximately equal mixture of (76) and (77), as originally.

VII.4.E. Reaction with Sodium Diethylmalonate.

Sodium hydride (50% dispersion in oil) was added to diethylmalonate (1.57g, 9.8mmol) in tetraglyme (5ml) until no more effervescence was observed. Compound (50) (4.07g, 10.2mmol) was added in one portion at room temperature to give initially a two phase system. A yellow colouration began to develop and after several hours' stirring at room temperature the volatile material was vacuum transferred to give two layers of colourless liquid (5.14g). Water was added to the involatile residue but no lower layer was observed. The lower (fluorocarbon) layer of the volatile fraction was separated (3.45g) and shown by glc analysis (col. O, 240°C) to contain diethylmalonate, (50) and one product (59% by glc, ca. 37% yield). A sample of this was separated by preparative scale glc (col. O, 195°C). MS-glc analysis of the product indicated that it was a mixture of two components with M^+ 512 (P - 28) (loss of CO). This is consistent with $C_{15}F_{15}H_{11}O_4$. Comparison of the composite ^{19}F nmr spectrum with model compounds suggested that a compound (78) is present.

VII.5. Miscellaneous Reactions.

VII.5.A. Reaction with Diazomethane.

An ethereal solution of diazomethane (prepared as in Section III.3.G.) was added to compound (50) (4.81g, 12mmol) at room temperature until the yellow colour of diazomethane persisted. The mixture was kept at room temperature for several hours and then the ether was removed at atmospheric pressure. Glc analysis (col. O, 100° C) showed a small amount of compound (50) together with a less volatile component. This was purified by preparative scale glc (col. O, 100°C) to give perfluoro-4,5-diethyl-4,5-dimethyl-3-H-2-pyrazoline (81) (Found: C, 24.2; F, 69.0; H, 0.2; N, 6.7%, M^+ 442. $C_9F_{16}H_2N_2$ requires C, 24.4; F, 68.8; H, 0.4; N, 6.3%, M^+ 442). Nmr spectrum no. 11, ir spectrum no. 13, MS no. 4.

VII.5.B. Reaction with Sodium Borohydride.

Sodium borohydride (1.23g, 32.4mmol) was stirred in tetraglyme (14ml) for 35min. at 0°C. Compound (50) (6.90g, 17.25mmol) was added over 20min. against a counter current of nitrogen. The mixture was stirred at 0°C for 25min. and then at room temperature for 17.75h. The volatile material was vacuum transferred (3.96g). Glc (Pye 104, col. O, 48°C) showed three components and no starting material. Water was added to the residue, which was completely soluble and therefore contained no fluorocarbon. The volatile components were separated by preparative scale glc (col. O, 90°C) to give cis, trans-3-difluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (82) (Found: C, 27.8; F, 71.6; H, 0.9%, M^+ 346. $C_8F_{13}H_3$ requires C, 27.8; F, 71.4; H, 0.9%, M^+ 346). Nmr spectrum no. 12, ir spectrum no. 14, MS no. 5 and cis, trans-3-monofluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (83) (Found: C, 29.5; F, 69.2; H, 0.9%, M^+ 328. $C_8F_{12}H_4$ requires C, 29.3; F, 69.5; H, 1.2%, M^+ 328). Nmr spectrum no. 13, ir spectrum no. 15, MS no. 6. The third component was not characterised.

Chapter VIII

Experimental Results for Chapter VI.

VIII.1. Instrumentation.

The instrumentation used in this section of work is as described earlier (Chapters III and VII).

VIII.2. Reagents and Solvents.

Perfluoro-2-hydro-3-ethyl-2,3,4,5-tetramethylfuran was supplied by I.C.I, Mond, Ltd.. It was purified by washing with dilute hydrochloric acid (to remove triethylamine used in its preparation) then several times with water. The fluorocarbon layer was separated and dried (magnesium sulphate). ^{19}F nmr spectral data agreed with those of an authentic sample[93].

All other reagents and solvents were used as supplied, or as previously described.

VIII.3. Preparation of Furans.

VIII.3.A. Preparation of Perfluoro-2,5-dihydrotetramethylfuran (58).

This was prepared according to a literature method[71]. From glc analysis (col. O, 60°C) it was shown that 71% conversion was obtained and 46% yield. The product mixture distilled on a concentric tube apparatus to give (58) (26.5%) b.p. 83-85°C.

VIII.3.B. Preparation of Perfluorotetramethylfuran (85).

Perfluoro-2-hydro-3-ethyl-2,3,4,5-tetramethylfuran (86) (87.4g, 183mmol) was passed in a stream of nitrogen (flow rate ca. 50cm.min^{1}) through a tube packed with iron filings. The products were collected in a cold trap (55.4g). Glc analysis (col. O, 60°C) of the product mixture showed it to contain compound (85) (71%) (identified by comparison of retention time with that of an authentic sample[93]). Distillation on a concentric tube apparatus left (85) as the residue (22.9g, 37.8%). ^{19}F nmr spectral data agreed with those of an authentic sample[93].

VIII.3.C. Preparation of 3,4,5-Tris(trifluoromethyl)furan (87).

Compound (86) (56.6g, 118mmol) was heated to 60°C and passed in a flow of nitrogen (flow rate ca. 50cm.min^{-1}) through a silica tube lined with platinum and filled with platinum pieces, at 655-660°C. The products were collected in a cold trap (34.8g). The volatile material was vacuum transferred (33.8g). Glc analysis (col. A, 50°C) showed that 100% conversion to products had occurred and that at least 88% of the mixture was (87) (by comparison of retention time with that of an authentic sample[93]) which gave 86% yield. Unless otherwise stated the material was not further purified before use. Account is taken of this.

VIII.3.D. Preparation of Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-propane (91).

a) Irradiation of Compound (50) with Acetaldehyde.

Compound (50) (35.84g, 89.6mmol) and acetaldehyde (10.9g, 247.7mmol) were separately degassed and mixed in a sealed tube which was irradiated for 846h at 5cm from ^{60}Co γ-ray source with a dose rate of 2.436x10^{4}radh^{-1} (2.06x10^{7}rad). When the tube was opened some tarry material was observed and the clear homogeneous mixture was distilled on a concentric tube distillation apparatus to remove the volatile material. Glc analysis of the residue (col. O, 77°C) showed there to be mainly one component left. This was vacuum transferred and identified as (89) (35.05g, 88%) (by comparison of retention time with that of an authentic sample[74]).

b) Reaction of Compound (89) with Tri-n-butylamine.

Compound (89) (19.3g, 43.4mmol) was mixed with tri-n-butylamine (30.04g, 162.4mmol) in tetraglyme (23ml) and the mixture was stirred overnight, although a single layer had formed within 8 min. of addition. The mixture was washed with dilute hydrochloric acid (2M, 2x50ml) to remove excess amine and then water (2x50ml) and finally dried over magnesium sulphate. After removal of desiccant the volatile material was vacuum transferred (14.4g) and glc analysis (col. O, 120°C) showed this to be one component ($>$96%). This was identified as compound (90) by comparison of ^{19}F nmr data with those of an authentic sample. The yield of (90) was 79%.

In another experiment carried out on a larger scale and worked-up in a similar manner the volatile material recovered was shown to be 86% pure. MS-glc analysis of the impurity in the mixture showed m/e M^+ 340 ($C_8F_{12}O$) and a fragmentation pattern consistent with perfluorotetramethylfuran (85). ^{19}F nmr data of the mixture also showed signals consistent with this (δ -60.8ppm and 66.05ppm of equal intensity).

c)Pyrolysis of Compound (90).

Compound (90) (12.1g, 28.75mmol) was passed through a tube containing platinum at 600-610°C in a stream of nitrogen (flow rate ca. 60cm.min^{-1}), the products of the reaction being collected in a cold trap. A large amount of tarry material was observed on the platinum surface and also in the recovered material. Vacuum transference yielded volatile material (6.33g) giving a recovery of 49%. Glc analysis (col. O, 120°C) showed that the major product was over 94% pure (51% yield). By comparison of nmr data[74], this compound was identified as perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-propane (91) (Found: C, 29.5; H, 0.22%, M^+ 404. $C_{10}F_{14}H_2O$ requires C, 29.7; H, 0.49%, M^+ 404). MS no. 10.

In another experiment, the mixture containing (90) (86%) and (85) (14%) (35.01g) was reacted in a similar manner to that described above except that during the experiment the temperature of the tube rose to 800°C. Volatile material (11.49g) was recovered from the cold traps. Glc analysis (col. T, 110°C) of this mixture showed there to be four major components present. These were separated by preparative scale glc (col. T, 80°C) and identified as follows: (85) (9.7% of mixture), identified by comparison of ^{19}F nmr, ir and mass spectral data and glc retention times with those of an authentic sample[93]; the second fraction (15.4% of mixture) was obtained as a mixture of components and was not further separated; (91) (57.7% of mixture) identified by comparison of ^{19}F nmr, ir and mass spectral data and glc retention time with those of an authentic sample prepared earlier; perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-ethane (92) (17% of mixture) (Found: C, 30.7; F, 64.7; H, 0.3%, M^+ 354. $C_9F_{12}H_2O$ requires C, 30.5; F, 64.4; H, 0.6%, M^+ 354). Nmr spectrum no. 16, ir spectrum no. 19, MS no. 11. B.p. 133.5°C.

VIII.4. Reactions of Furans.

VIII.4.A. Reaction of Compound (87) with Sodium Borohydride.

Sodium borohydride (0.41g, 10.7mmol) was added to tetraglyme (10ml) and stirred at ice-salt temperature for 50min.. Perfluoro-3,4,5-trimethylfuran (87) (3.01g, 9.1mmol) was added dropwise against a counter-current of nitrogen. On addition effervescence occurred slowly and a yellow colouration was observed. After addition (1h) the mixture was allowed to warm up to room temperature and stirring was continued for a further 2h. The volatile components were vacuum transferred (2.11g). Glc analysis (cols. O and A, 100-120°C) showed a single component to be present. The residue from vacuum transference was destroyed over a long period with water. 3,4,5-Tris(trifluoromethyl)furan (93) was formed in 85% yield (100% conversion of starting material) (Found: C, 31.0; F, 62.5; H, 0.3%, M^+ 272. C_7F_9HO requires C, 30.9; F, 62.8; H, 0.4%, M^+ 272). Nmr spectrum no. 14, ir spectrum no. 16, MS no. 7,

λ_{max}^{MeOH} 216nm (3.82). B.p. 101.5°C.

VIII.4.B. Reaction of Compound (87) with Methyllithium.

Methyllithium (9.5ml, ~16mmol) was added dropwise to compound (87) (4.54g, 13.7mmol) at 0°C. A vigorous reaction occurred and after addition the mixture was stirred at 0°C for a further 25 min. and at room temperature for 2.5h. Water was added to the bulk and the organic phase was ether extracted. The ether layer was separated, dried (magnesium sulphate) and the ether removed by distillation. The residue (2.51g) was shown by glc analysis (Pye 104, col. O, 70°C) to contain a single component, 2-methyl-3,4,5-tris(trifluoromethyl)furan (94) (Found: C, 33.6; F, 60.1; H, 0.7%, M$^+$ 286. $C_8F_9H_3O$ requires C, 33.6; F, 59.8; H, 0.7%, M$^+$ 286). Nmr spectrum no. 15, ir spectrum no. 17, MS no. 8. A yield of 64% was obtained, which was probably low because of the difficulty of separating the emulsion formed after hydrolysis of the reaction mixture.

VIII.4.C. Reaction of Compound (87) with Sodium Methoxide.

Sodium (0.68g, 29mmol) was added to excess methanol (14-15ml) and compound (87) (3.54g, 10.7mmol) was added slowly. After stirring for 31h at room temperature a yellow colouration was observed and ^{19}F nmr spectral data indicated that the main component in the mixture was starting material. The mixture was then heated under reflux (65°C) for 27h. A lower layer separated on cooling. The volatile material was vacuum transferred and the majority of the methanol was distilled at atmospheric pressure. The volatile material was vacuum transferred once more to leave a residue (1.49g) which contained 2-methoxy-3,4,5-*tris*(trifluoromethyl)furan (95) (42% by glc, col. O, 130°C, 0. 9g), the remainder being methanol. The volatile fraction contained a small amount of (95) (5.4%, 0.49g). Compound (95) was identified by comparison of data with those of an authentic sample[43]. The yield, according to glc, was *ca.* 75%. The material was not isolated further.

VIII.4.D. Reaction of Compound (87) with Neutral Methanol.

Compound (87) (2.32g, 7mmol) and dry methanol (6ml) were stirred at room temperature for 24h. Glc analysis (col. O, 100°C) showed there to be only starting materials present in the mixture after this time. Refluxing for three hours produced no reaction but after 2 days at this temperature, glc analysis showed that ~28% of the fluorocarbon present was compound (95).

VIII.4.E. Reaction of Compound (87) with Phenylmagnesium bromide.

Magnesium (0.62g, 25.8mmol) in dry ether (10ml) was activated with 1,2-dibromoethane. Bromobenzene (3.32g, 21mmol) was added at such a rate that reflux was maintained and the mixture was then heated for a further 0.5h to ensure complete reaction. Compound (87) (5.86g, 18mmol) in ether (5ml) was added dropwise at a rate to maintain reflux. A slightly exothermic reaction occurred and a certain amount of intractable material was formed. After addition, the mixture was heated for 1.16h, then quenched with acid and ice. The organic layer was extracted with ether and dried over magnesium sulphate. The ether was distilled through a small column at atmospheric pressure and the residue was vacuum transferred. A white solid appeared on transference, together with a colourless liquid. Glc analysis (Pye 104, col. O, 209°C) of this liquid showed it to contain one major product as well as compound (87) and minor components. No bromobenzene or benzene were observed. ^{19}F nmr spectral data indicated that the major component was 2-phenyl-3,4,5-*tris*(trifluoromethyl)furan (96) (by comparison with an authentic sample) and this was separated by preparative scale glc (col. 0, 210°C) (1.34g, 22%). Tlc of the tarry residue ($CHCl_3$:C_6H_{14}; 5:14) showed that compound (96) was present but could not easily be extracted. λ_{max} 252nm (4.25), MS no. 9.

VIII.4.F. Reaction of Perfluorotetramethylfuran (85) with Methoxide.

a) Sodium (0.69g, 30mmol) was dissolved in methanol (14-15ml) and compound (85) (7.39g, 20mmol) was added. An exothermic reaction ensued. The mixture was left stirring for 31h at room temperature but ^{19}F nmr spectral data indicated only the presence of starting material after this time. The mixture was heated to reflux for 27h and again ^{19}F nmr spectral data, as well as glc analysis (col. 0, 106°C) indicated that no reaction had occurred.

b) Compound (85) (1.44g, 4.23mmol), methanol (2.47g, excess) and caesium fluoride (1.26g, 9.5mmol) were placed in a Carius tube and degassed and the tube was sealed. After heating at 100°C for 67h the volatile material was pumped from the tube and glc and MS-glc analyses indicated that no reaction had occurred.

VIII.4.G. Reactions of Compounds (85) and (87) with Diazomethane.

Compound (87) (2.71g, 9.3mmol) in ether was reacted with diazomethane in ether (prepared as described in Section III.3.G.). White fumes were observed and a small amount of gassing. The mixture was coloured yellow from the beginning of addition of diazomethane. After standing at room temperature overnight, the ether was distilled and the residue was vacuum transferred. Glc analysis (col. 0, 62°C) showed that no reaction had occurred. This was confirmed by ^{19}F nmr spectral data. The bubbling observed was presumably due to decomposition of the diazomethane on the surface of the vessel or the stirrer.

The reaction with compound (85) (3.23g, 2.9mmol) was carried out in exactly the same manner as described above and again in this case only starting material was recovered.

VIII.4.H. Irradiation of Compound (85) with Methanol on a ^{60}Co Source.

Compound (85) (0.7g, 2.1mmol) was mixed with methanol (0.4g, 12.5mmol) and the mixture was sealed in an nmr tube. The ^{19}F nmr spectrum was run prior to irradiation. After irradiation for 1571h at 8cm from the source (dose = 1.38×10^7rad) the ^{19}F nmr spectrum was run again. No change was observed in the two spectra.

VIII.4.J. Reaction of Compound (85) with Potassium Permanganate in Acetone.

Potassium permanganate (3.0g, 19mmol) was dissolved in dry acetone (50ml) under nitrogen. Compound (85) (4.15g, 12.2mmol) was added slowly at room temperature against a counter-current of nitrogen. An exothermic reaction was observed. After addition was complete the mixture was kept stirring at room temperature for a further 5.5h. Water (30ml) was added to the brown coloured mixture. Sulphur dioxide was bubbled through the mixture to decolourise it and two layers resulted. The top layer was red and the lower one colourless. A white solid was also present. Ether and water were added to the mixture, the ether layer was separated and washed with water and the aqueous layer was washed with ether. The combined ether extracts were dried (magnesium sulphate) and the ether was removed at atmospheric pressure. A small amount of a brown residue was left. Little information could be obtained about the structures of components in this residue. No starting material was detected in any of the product mixtures. It is assumed that the products were either gaseous or water-soluble and hence not observed.

VIII.5. Photochemistry of Furans.

The photolyses were carried out according to the general method described in the literature[91] using a high pressure uv lamp except in the case of compound (91) when a medium pressure uv lamp was used. Solid carbon dioxide was used as the coolant for trapping the products.

VIII.5.A. Photolysis of Perfluoro-3,4,5-trimethylfuran (87).

Compound (87) (8.96g, 27.2mmol) was placed in the transference apparatus and degassed. The system was evacuated and a partial pressure of nitrogen (1.5 cm Hg) was allowed in. The liquid phase was shielded and the vessel was irradiated for 18h 5min.. Some involatile material was observed in the reaction vessel and a clear liquid had transferred (4.98g). From glc analysis (col. O, 70°C) two components were detected- product (58%) and unchanged (87) (42%). The reaction resulted in 71% recovery of volatile material and 32.3% conversion to products. The components of the mixture were separated by preparative scale glc (col. O, 70°C). The product was identified as perfluoro-1,2,3-trimethylcyclopropenylacyl fluoride (97), by comparison of ^{19}F nmr and ir spectra with those of an authentic sample[43].

VIII.5.B. Photolysis of 3,4,5-Tris(trifluoromethyl)furan (93).

Compound (93) (8.05g, 29.6mmol) was placed in the transference vessel and the liquid was degassed. The pressure of the system was regulated to 1cm Hg with dry nitrogen. The liquid phase was shielded and the system was irradiated for 46.75h. A clear liquid had transferred (2.32g, 29% recovery) and glc analysis (col. A, 55°C) showed there to be 13% conversion to products. Three major components were separated by preparative scale glc (col. A, 55°C) to give the following: 1,2,3-tris(trifluoromethyl)cyclopropenyl aldehyde (98) (Found: M^+ 243 (P - CHO). C_7F_9HO requires M^+ 272). Nmr spectrum no. 24. 1,3-bis(trifluoromethyl)-2-H-cyclopropenyltrifluoromethylketone (99) (Found: M^+ 272 C_7F_9HO requires M^+ 272). Nmr spectrum no. 17, ir spectrum no. 22. 3,4,5-tris(trifluoromethyl)furan (93) (unchanged starting material).

VIII.5.C. Photolysis of 2-Methyl-3,4,5-tris(trifluoromethyl)furan (94).

Compound (94) (5.21g, 18.2mmol) was placed in the transference vessel and degassed. The pressure in the vessel was adjusted to 4mm Hg pressure with dry nitrogen and the system was irradiated for 40h 40min.. A colourless liquid was collected in the trap (2.10g, 40% recovery). Glc analysis (col. A, 80°C) showed there to be four components present. The fractions were separated by preparative scale glc (col. A, 100°C) to give: 1,2,3-tris(trifluoromethyl)cyclopropenylmethylketone (100) (20%) (Found: M^+ 286, $C_8F_9H_3O$ requires M^+286). Nmr spectrum no. 18, ir spectrum no. 23, MS no. 13; 3-methyl-2,4,5-tris(trifluoromethyl)furan (102) (18%) (Found: M^+286, $C_8F_9H_3O$ requires M^+ 286). Nmr spectrum no. 19, ir spectrum no. 18; 2-methyl-1,3-bis(trifluoromethyl)-1-cyclopropenyl-trifluoromethylketone (101) (11%) (Found: M^+ 267 (M - 19). $C_8F_9H_3O$ requires M^+ 286). Nmr spectrum no. 20, ir spectrum no. 24, MS no. 14; compound (94) (51%) (unchanged starting material).

VIII.5.D. Photolysis of Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-propane (91).

Compound (91) (5.73g, 14mmol) was placed in the transference vessel, degassed and the pressure was adjusted to 0.06 mm Hg with dry nitrogen. The liquid phase was shielded and the vessel was irradiated for 21.25h with a medium pressure uv lamp. A high recovery of volatile material was obtained in the cold trap (4.72g, 82.4% recovery). Glc analysis of this (col. T, 100°C) indicated the presence of five major components in the mixture and these were separated by preparative scale glc to give the following: the first fraction was found to contain a mixture of components which were not separated further; 3,4,5-tris(trifluoromethyl)furyltrifluoromethylacetylene (103) (Found: C, 32.7; F, 62.3%, M$^+$ 364. $C_{10}F_{12}O$ requires C, 33.0; F, 62.4%, M$^+$ 364). Nmr spectrum no. 21, ir spectrum no.20; cis, trans-perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene (104) (Found: C, 31.0; H, 0.0%, M$^+$ 384. $C_{10}F_{11}HO$ requires C, 31.3; H, 0.3%, M$^+$ 384). Nmr spectrum no. 22, ir spectrum no. 21, MS no. 12; compound (91) (unchanged starting material); perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-ethane (92) identified by comparison with spectral data of an authentic sample prepared by an alternative method (Section VIII.3.D.c).

VIII.6. Related Reactions.

VIII.6.A. Reaction of Compound (91) with Triethylamine.

Compound (91) (0.17g, 1.42mmol) and triethylamine (0.19g, 1.88mmol) were placed in an nmr tube to give two layers initially. Soon after mixing only one layer was present. ^{19}F nmr spectral data, obtained after 1h 5min., showed that trans-perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene was present. (Nmr spectrum no. 23) Comparison of glc retention time with that of compound (104) confirmed this identification.

When the mixture was heated no change was observed in the ^{19}F nmr spectrum.

VIII.6.B. Reaction of Compound (91) with Potassium Fluoride.

Compound (91) (0.88g, 2.2mmol) was heated to 60-70°C and passed through a silica tube containing potassium fluoride at 580-630°C in a stream of nitrogen (flow rate ca. 50cm.min^{-1}). The products were trapped in a cold trap. Much tarry material was observed on the potassium fluoride surface and very little material was collected in the trap. This indicated that the furan had either tarred up on the fluoride surface or some perhaps had broken up to give gaseous products which were not trapped.

VIII.6.C. Passage of Compound (58) over Platinum.

Compound (58) (3.01g, 7.9mmol) was heated to 40-60°C and passed in a stream of nitrogen (flow rate ca. 50cm.min^{-1}) through a silica tube packed with platinum pieces heated to 650-670°C. A liquid (2.04g) was recovered in a cold trap and the volatile material (1.94g) was vacuum transferred. Glc analysis of this material (Pye 104, col. O, 210°,110°C; col. A, 110°C) showed that only a very small amount of reaction had occurred. ^{19}F nmr spectral data confirmed that the material was largely starting material.

The reaction was repeated at a higher temperature (805-810°C), with a lower flow rate of nitrogen and without heating the material initially. Only a small amount of a tarry material was trapped in this experiment.

APPENDIX I

Nmr Spectra

1. Pentafluorophenylethane (24).
2. 1-Bromo-2-butyltetrafluorophenylethane (28).
3. 1-Bromo-2-pentafluorophenyl-[1,1-$^2H_2$]-ethane (32).
4. 2-Trifluoromethyl-3-(2'-methylaminooctafluoro-2'-butyl)-4-methylimino-N-methyl-2-azetine (67).
5. Trans-4-methylamino-perfluoro-3,4-dimethyl-2-hexene (66).
6. Cis,trans-4-methyl-perfluoro-3,4-dimethyl-2-hexene (71).
7. 3-Methyl-perfluoro-2-ethyl-3-methyl-1-pentene (72).
8. Cis, trans-2,4-dimethyl-perfluoro-3,4-dimethyl-1-pentene (73).
9. Cis, trans-4-butyl-perfluoro-3,4-dimethyl-2-hexene (76).
10. 3-Butyl-perfluoro-2-ethyl-3-methyl-1-pentene (77).
11. Perfluoro-4,5-diethyl-4,5-dimethyl-3-H-2-pyrazoline (81).
12. Cis, trans-3-difluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (82).
13. Cis, trans-3-monofluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (83).
14. 3,4,5-Tris(trifluoromethyl)furan (93).
15. 2-Methyl-3,4,5-tris(trifluoromethyl)furan (94).
16. Perfluoro-(3',4',5'-trimethylfuryl)-1-H-1-H-ethane (92).
17. 1,3-Bis(trifluoromethyl)-2-H-cyclopropenyltrifluoromethylketone (99).
18. 1,2,3-Tris(trifluoromethyl)cyclopropenylmethylketone (100).
19. 3-Methyl-2,4,5-tris(trifluoromethyl)furan (102).
20. 2-Methyl-1,3-bis(trifluoromethyl)-1-cyclopropenyltrifluoromethylketone (101).
21. 3,4,5-Tris(trifluoromethyl)furyltrifluoromethylacetylene (103).
22. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene (104) (cis,trans).
23. Trans-perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene (104a).
24. 1,2,3-Tris(trifluoromethyl)cyclopropenylaldehyde (98).

The following abbreviations are used in the nmr tabulations:

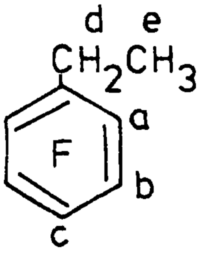
D	doublet
T	triplet
Q	quartet
S	singlet
m	multiplet

The ^{19}F shifts are quoted in ppm upfield from external $CFCl_3$ and the ^{1}H shifts are quoted in ppm downfield from external TMS.

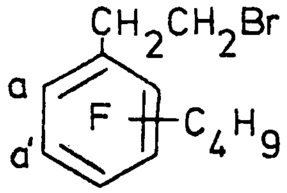
1. Pentafluorophenylethane (<u>24</u>).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
148.47	m	2	b
162.22	T(J=20)	1	c
166.86	m	2	a

^1H δ 1.3, (T),e, 2.75, (Q), d.



(<u>24</u>)



(<u>28</u>)

2. 1-Bromo-2-butyltetrafluorophenylethane (<u>28</u>).

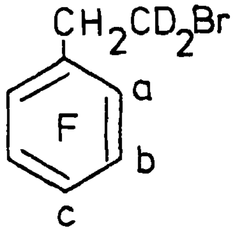
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
146.45	S broad		a,a'

^1H δ 1.35 - 3.54, (m).

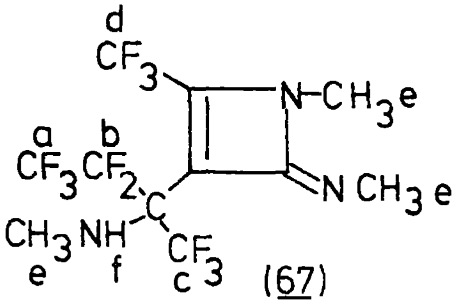
3.1-Bromo-2-pentafluorophenyl-[1,1-$^2H_2$]-ethane (32).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
146.13	m	2	b
161.03	T (J = 20)	1	c
165.64	m	2	a

^1H δ 3.65 (S)



(32)



(67)

4.2-Trifluoromethyl-3-(2'-methylaminooctafluoro-2'-butyl)-4-methylimino-N-methyl-2-azetine (67).

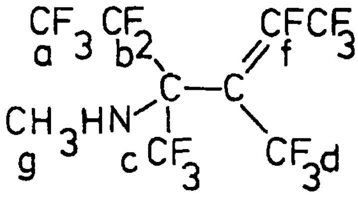
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
66.63	m(broad)	3	d
70.09	Q (J = 10)	3	c
82.23	S	3	a
116.01	m (J = 11)	2	b

^1H δ 2.38, 2.7 ,(m , 9H), e, 7.22 (m, 1H), f.

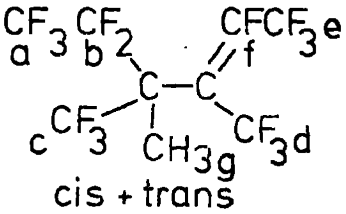
5. *Trans*-4-methylamino-perfluoro-3,4-dimethyl-2-hexene (66).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
54.79	m	3	d
65.07	m	3	c
69.70	Q (J = 16) of D(J = 2)	3	e
81.31	S	3	a
95.39	m	1	f
118.44	m	2	b

^{1}H δ 2.89 (m, g) (sample too small to observe N-H proton).



(66)



(71)

6. *Cis*, *trans*-4-methyl-perfluoro-3,4-dimethyl-2-hexene (71).

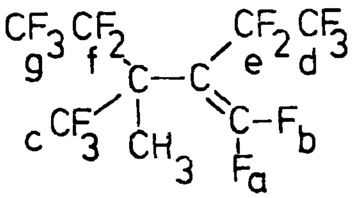
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
56.75	broad	3	d
67.89	Q(J = 17) of D(J = 2)	3	c
69.72	m	3	e
82.18	S	3	a
86.45	m	1	f
114.15	m	2	b

^{1}H δ 1.17 (S)

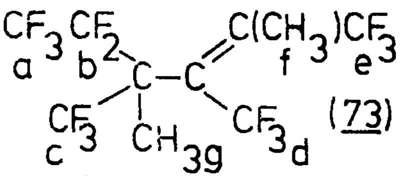
7. 3-Methyl-perfluoro-2-ethyl-3-methyl-1-pentene (72).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
56.72	Q(J = 40)	2	a
59.64	m		b
71.88	D(J = 40)	3	c
86.59	S	3	f
88.72	D(J = 15)	3	d
106.63	m	2	e
117.62	m	2	g

^{1}H δ 1.35 (S)



(72)



(73)

cis + trans

8. Cis,trans-2,4-dimethyl-perfluoro-3,4-dimethyl-1-pentene (73).

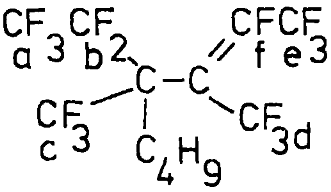
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
54.49	m	3	d
63.16	m(J = 14)	3	e
64.27	m	3	c
81.27	m	3	a
110.23	m	2	b

^{1}H δ 1.42 (m, 1H), g, 1.80 (m, 1H), f

9. <u>Cis</u>, <u>trans</u>-4-butyl-perfluoro-3,4-dimethyl-2-hexene (<u>76</u>).

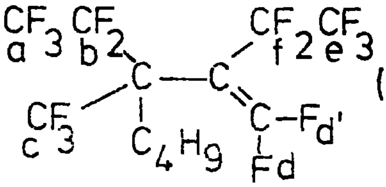
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
53.94	m	3	d
61.31	m	3	c
69.61	m	3	e
81.58	m	3	a
92.59	very broad	1	f
114.91	m	2	b

^{1}H δ 0.84 (overlapping multiplets)



cis + trans

(<u>76</u>)



(<u>77</u>)

10.3-Butyl-perfluoro-2-ethyl-3-methyl-1-pentene (<u>77</u>).

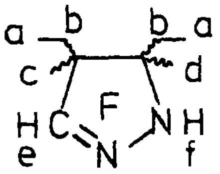
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
55.92	m	2,3	d,d'
60.46	m		c
79.79	m	3	a
80.6	m	3	e
101.10	m	2	f
103.62	m		
114.0	m	2	b

^{1}H δ 0.84 (overlapping multiplets)

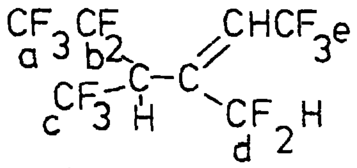
11. Perfluoro-4,5-diethyl-4,5-dimethyl-3-H-2-pyrazoline(<u>81</u>).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
62.73	m	3	d
68.40	m	3	c
81.03	m	6	a
106.6	m	4	b

^1H δ 4.35, 4.60 , (m, 1H), e, 7.91, 8.56, (m, 1H), f.



(<u>81</u>)



cis + trans

(<u>82</u>)

12. <u>Cis</u>, <u>trans</u>-3-difluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (<u>82</u>).

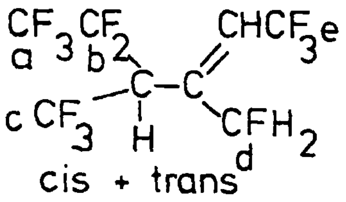
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
67.37	S broad	3	c
69.95	S broad	3	e
80.32	S broad	2	d
88.21	S	3	a
120.92	S broad	2	b

^1H δ 1.25 - 3.75, (m), 2.1 (Q (J =10)).

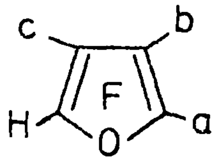
13. *Cis*, *trans*-3-monofluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (83).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
65.74	S broad	3	c
68.49	m	3	e
83.74	D(J=70) of T(J=22)	3	a
87.29			
119.2	m	1,2	d,b

^1H δ 1.33 - 7.83 (m)



(83)



(93)

14. 3,4,5-*Tris*(trifluoromethyl)furan (93).

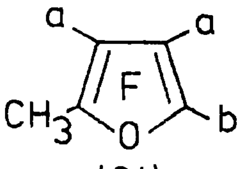
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
59.63	m(J=7)	3	c
62.34	m	3	b
65.48	m	3	a

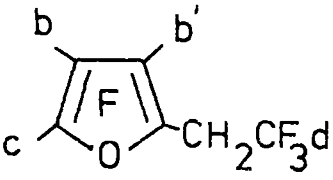
^1H δ 8.3 (m)

15. 2-Methyl-3,4,5-tris(trifluoromethyl)furan (94).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
60.30	m	6	a
65.23	m	3	b

^{1}H δ 1.97 (m)


(94)


(92)

16. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-ethane (92).

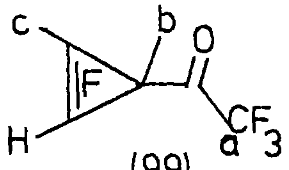
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
60.42	m	3	b
60.94	m	3	b'
65.65	m	3	c
68.49	T (J=10) of Q(J=2)	3	d

^{1}H δ 3.32 (Q, J = 9.5Hz)

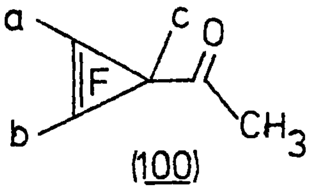
17. 1,3-*Bis*(trifluoromethyl)-2-H-cyclopropenyltrifluoromethylketone (99):

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
63.56	m broad	3	c
68.17	m broad	3	b
70.57	m	3	a

^{1}H δ 5.77, (D(J=8) of m).



(99)



(100)

18. 1,2,3-*Tris*(trifluoromethyl)cyclopropenylmethylketone (100).

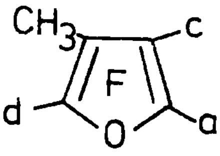
Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
65.46	S	6	a,b
70.60	S	3	c

^{1}H δ 1.75, (m).

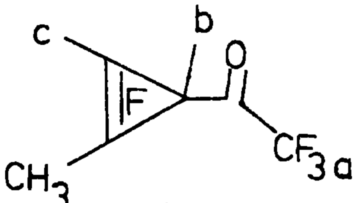
19. 3-Methyl-2,4,5-tris(trifluoromethyl)furan (102).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
61.06	m(J = 40)	3	c
65.67	m(J = 40)	3	d
65.94	m	3	a

^{1}H δ 2.0 (m)



(102)



(101)

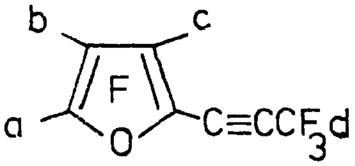
20. 2-Methyl-1,3-bis(trifluoromethyl)-1-cyclopropenyltrifluoromethyl-ketone (101).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
64.09	S	3	c
70.03	S	3	b
78.19	S	3	a

^{1}H δ 2.3 (m)

21. 3,4,5-Tris(trifluoromethyl)furyltrifluoromethylacetylene (103).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
56.12	S	3	d
60.21	septet(J = 8)	3	b
61.79	Q(J = 8)	3	a
65.71	Q(J = 8)	3	c



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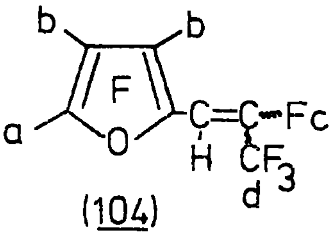


(104)

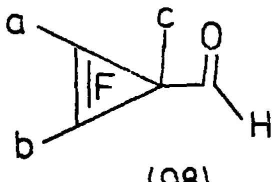
22. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene (104) (cis, trans).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
58.44	m	6	b
63.67	m	3	a
70.59	m	3	d(cis isomer)
75.02	m		d(trans isomer)
111.1	m	1	c(cis isomer)
117.66	D(J = 35) of m		c(trans isomer)

^{1}H δ 8.46 (D(J = 7), 1H, trans isomer), 8.86 (D(J = 4), 1H, cis isomer)

23. *Trans*-perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene (104a).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
62.14	m	6	b
65.69	m	3	a
76.77	m	3	d
120.26	D(J=30)	1	c



(98)

24. 1,2,3-*Tris*(trifluoromethyl)cyclopropenylaldehyde (98).

Shift (ppm)	Fine structure Coupling constants in Hz	Relative Intensity	Assignment
64.52	m	6	a,b
70.92	m	3	c

APPENDIX II

Infra-red Spectra

1. Pentafluorophenylethane (25). Contact film.
2. 3-Pentafluorophenylpropanoic acid. KBr disc.
3. Butyltetrafluorophenylethane (29). Contact film.
4. 1-Bromo-2-pentafluorophenyl-[1,1-$^{2}H_2$]-ethane (32). Contact film.
5. Pentafluorophenylethene (30). Contact film.
6. 2-Trifluoromethyl-3-(2'-methylaminooctafluoro-2'-butyl)-4-methylimino-N-methyl-2-azetine (67). Contact film.
7. Trans-4-methylamino-perfluoro-3,4-dimethyl-2-hexene (66). Contact film.
8. Cis, trans-4-methyl-perfluoro-3,4-dimethyl-2-hexene (71). Contact film.
9. 3-Methyl-perfluoro-2-ethyl-3-methyl-1-pentene (72). Contact film.
10. Cis, trans-2,4-dimethyl-perfluoro-3,4-dimethyl-1-pentene. (73). Contact film.
11. Cis, trans-4-butyl-perfluoro-3,4-dimethyl-2-hexene (76). Contact film.
12. 3-Butyl-perfluoro-2-ethyl-3-methyl-1-pentene (77). Contact film.
13. Perfluoro-4,5-diethyl-4,5-dimethyl-3-H-2-pyrazoline (81). Contact film.
14. Cis, trans-3-difluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (82). Contact film.
15. Cis, trans-3-monofluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (83). Contact film.
16. 3,4,5-Tris(trifluoromethyl)furan (93). Contact film.
17. 2-Methyl-3,4,5-tris(trifluoromethyl)furan (94). Contact film.
18. 3-Methyl-2,4,5-tris(trifluoromethyl)furan (102). Contact film.

19. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-ethane (92).

Contact film.

20. 3,4,5-Tris(trifluoromethyl)furyltrifluoromethylacetylene (103).

Contact film.

21. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene (104).(cis,trans).

Contact film.

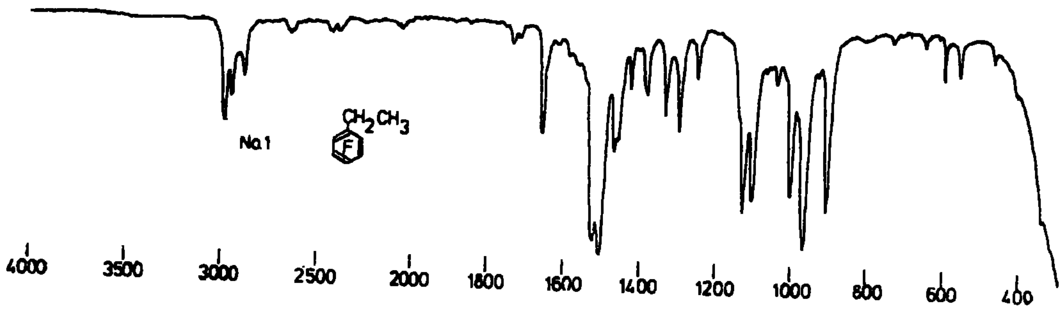
22. 1,3-Bis(trifluoromethyl)-2-H-cyclopropenyltrifluoromethylketone (99).

Contact film.

23. 1,2,3-Tris(trifluoromethyl)cyclopropenylmethylketone (100).

Contact film.

24. 2-Methyl-1,3-bis(trifluoromethyl)-1-cyclopropenyltrifluoromethylketone (101). Contact film.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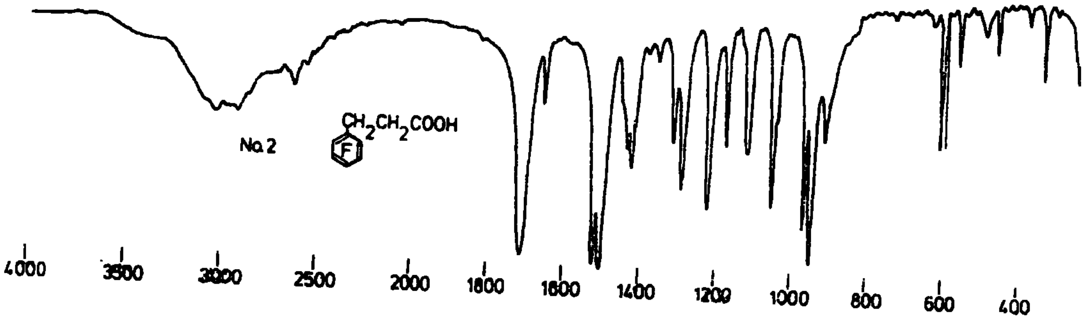
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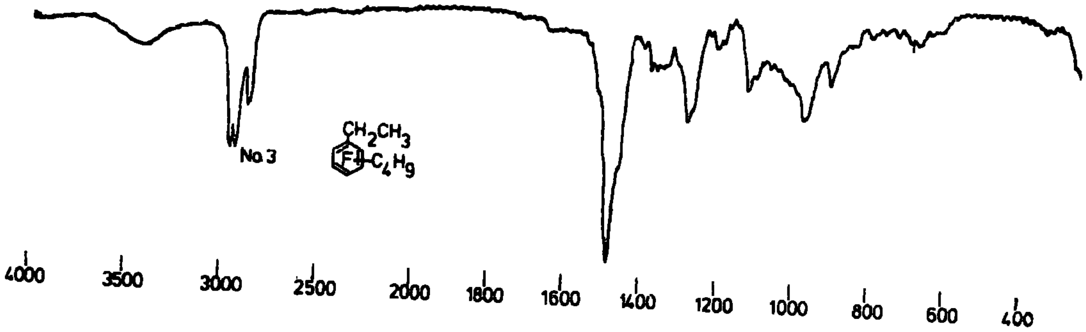
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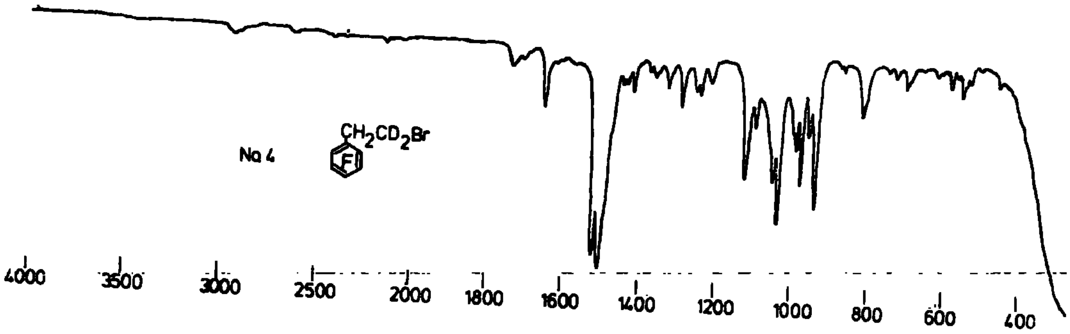
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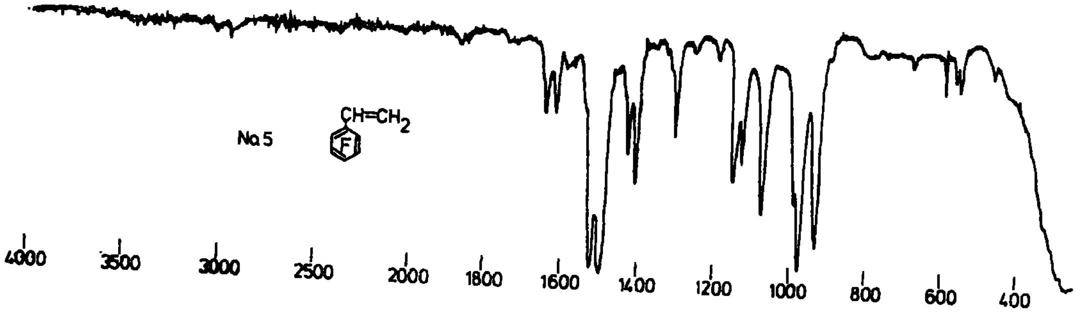
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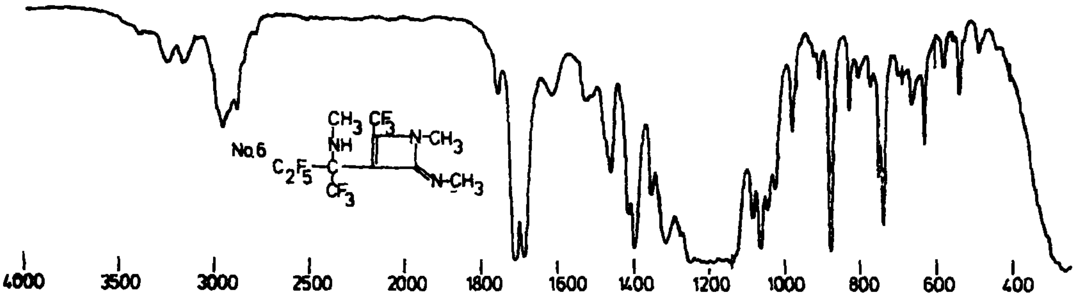
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CH3 CF3
NH
N-CH3
C2F5-C
CF3
N-CH3
4000
3500
3000
2500
2000
1800
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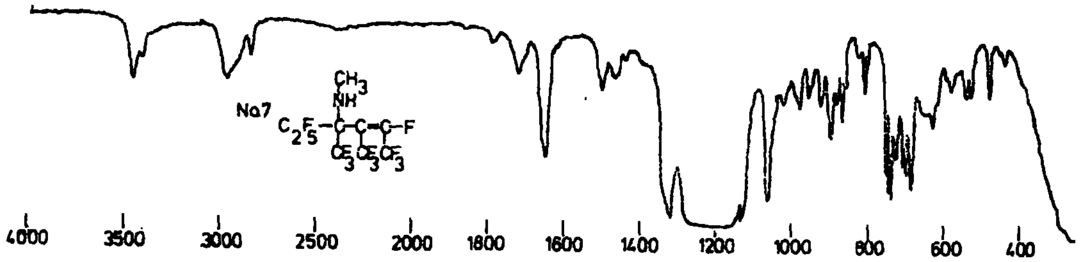
1400
1200
1000
800
600
400


No.7
CH3
NH
C2F5-C-C=C-F
CF3 CF3 CF3
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3500
3000
2500
2000
1800
1600
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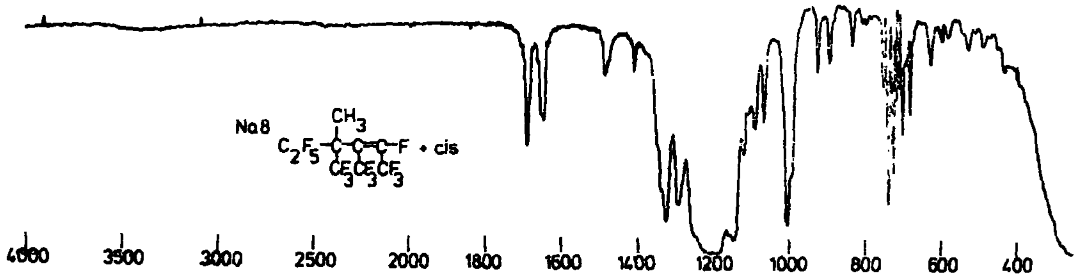
1200
1000
800
600
400


No.8
CH3
C2F5-C-C=C-F + cis
CF3 CF3 CF3
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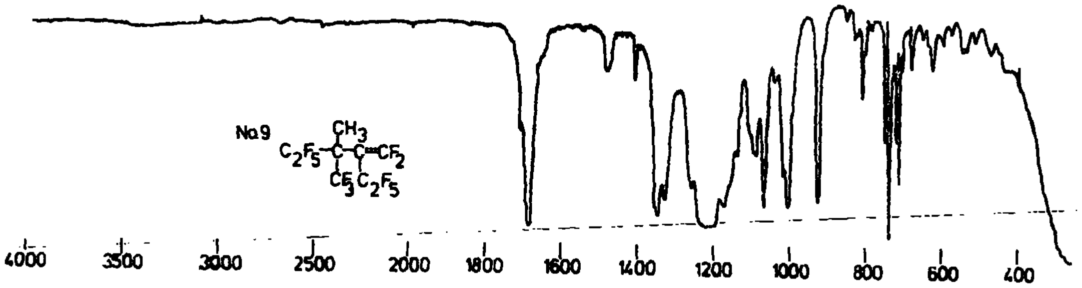
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


No.9
CH3
C2F5-C-C=CF2
CF3 C2F5
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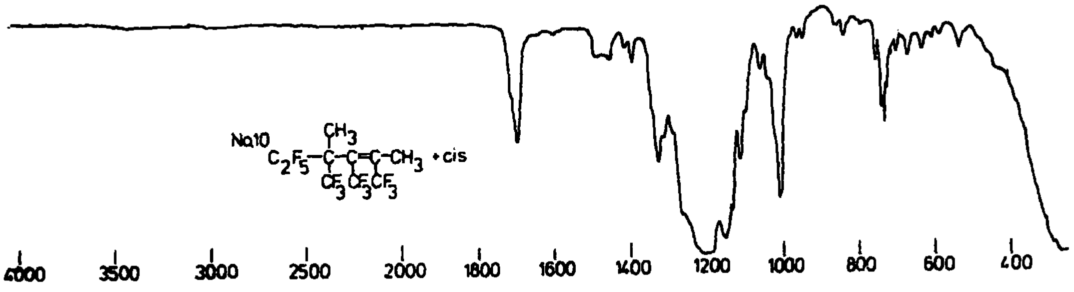
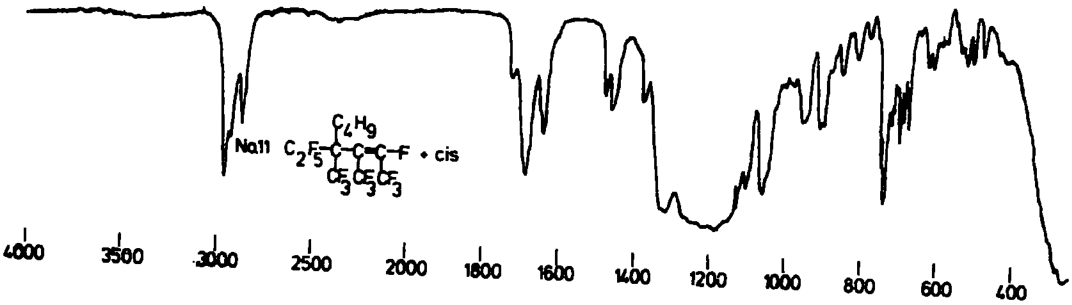
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


No.10
CH3
C2F5-C-C=C-CH3 + cis
CF3 CF3 CF3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


No11
C2F5–C(C4H9)(CF3)–C(CF3)=C(CF3)–F + cis
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3500
3000
2500
2000
1800
1600
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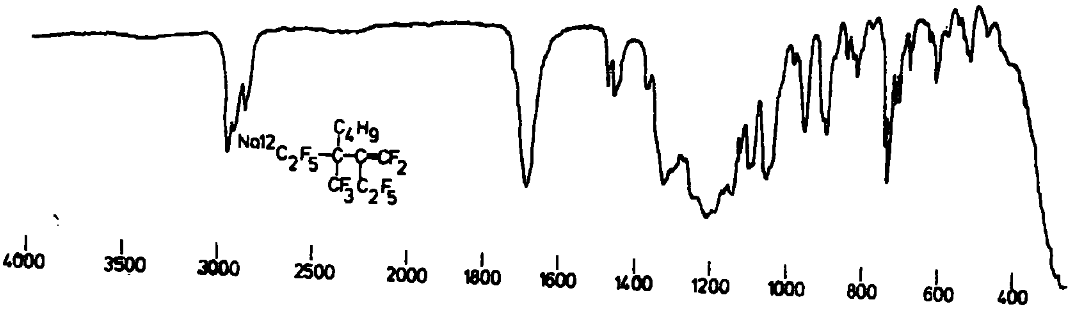
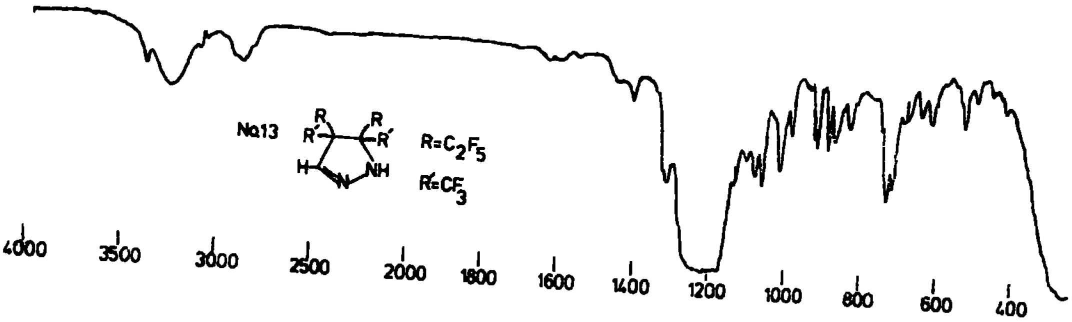
1200
1000
800
600
400


No12
C2F5–C(C4H9)(CF3)–C(C2F5)=CF2
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


No13
R
R'
R
R'
H
N
NH
R=C2F5
R'=CF3
4000
3500
3000
2500
2000
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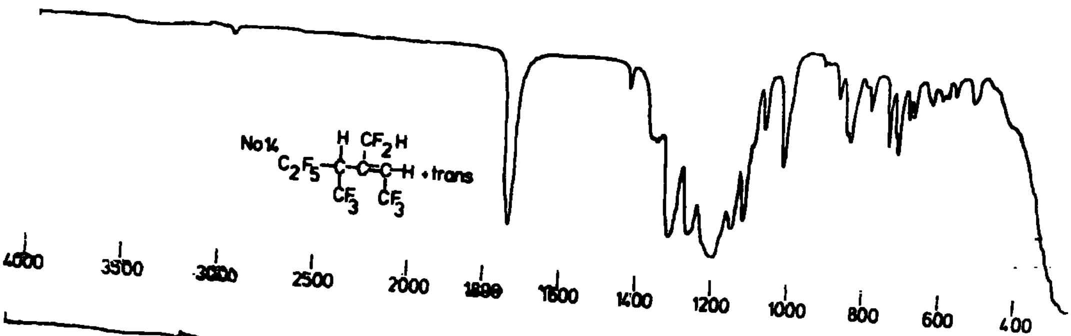
1400
1200
1000
800
600
400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C2F5–C(H)(CF3)–C(CF2H)=C(CF3)–H + trans
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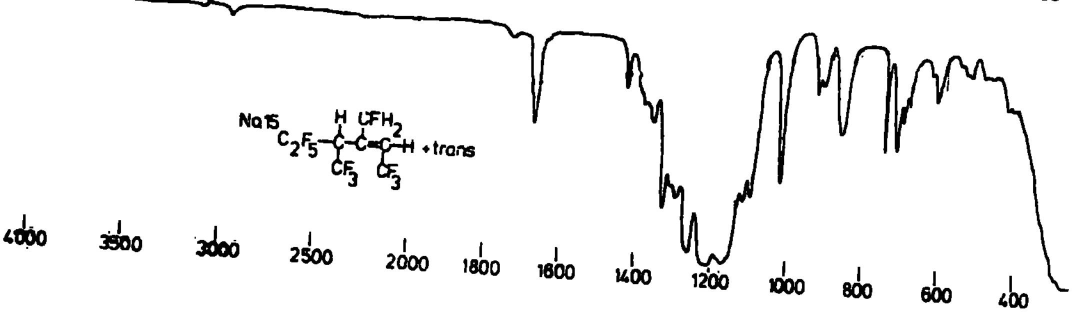
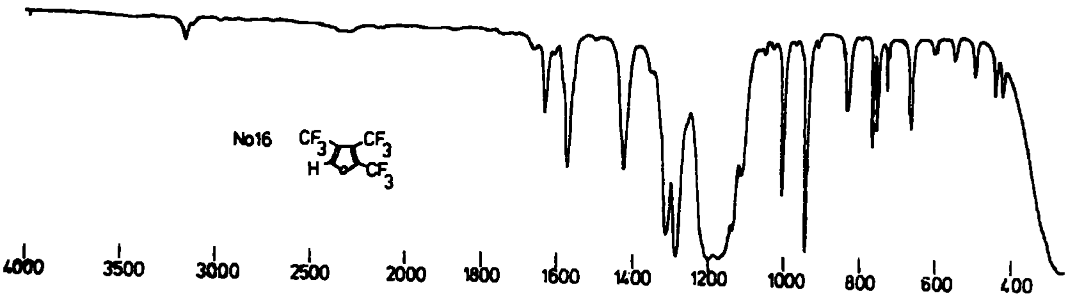
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


No15
C2F5–C(H)(CF3)–C(CFH2)=C(CF3)–H + trans
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400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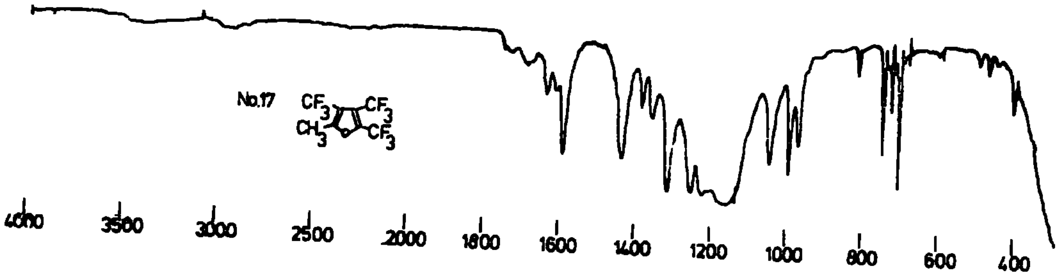
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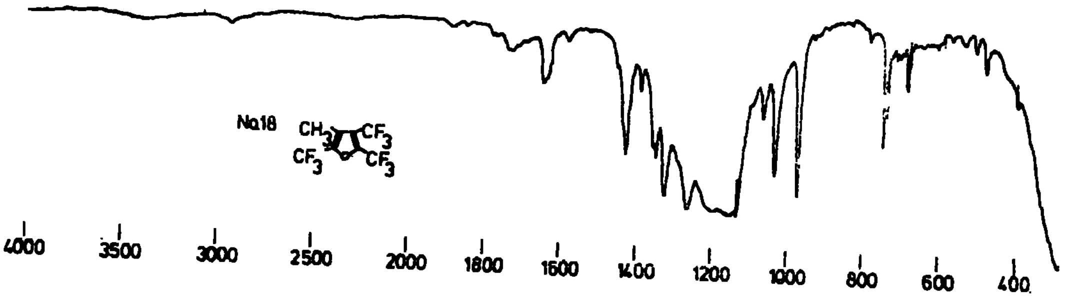
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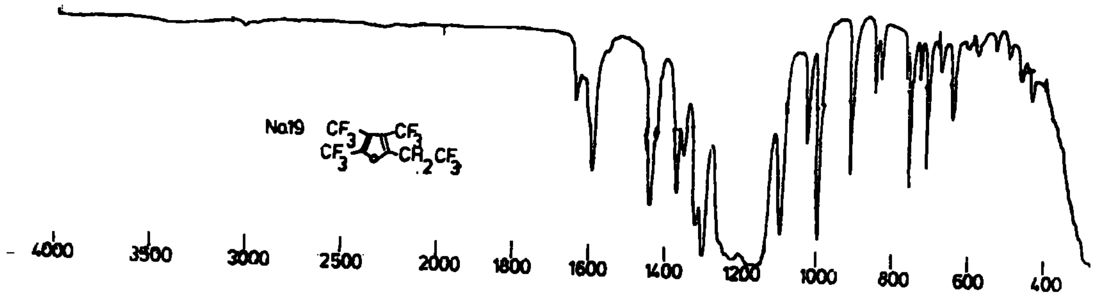
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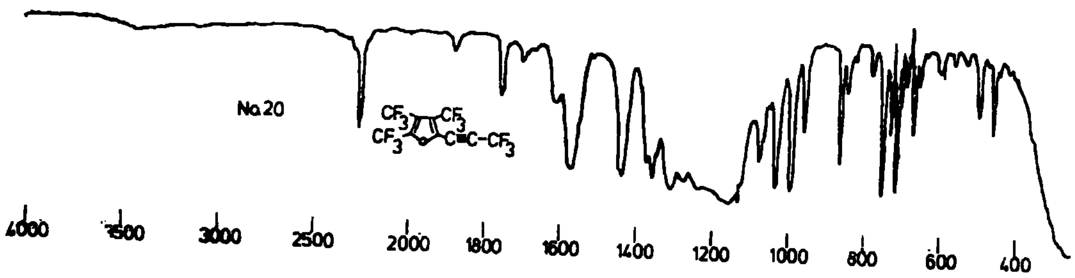
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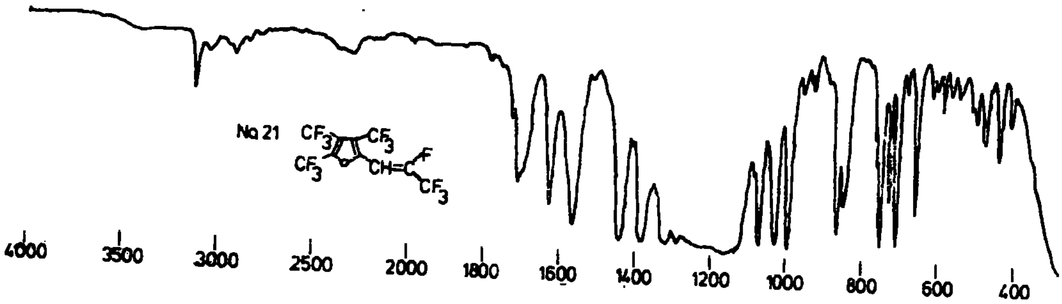
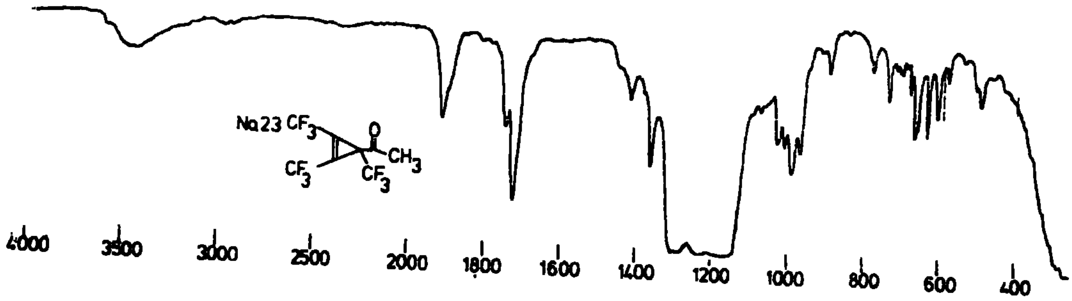

No 21
CF3
CF3
CF3
CH=C
F
CF3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


No 22
CF3
H
O
CF3
CF3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400


No 23
CF3
CF3
O
CH3
CF3
4000
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3000
2500
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1800
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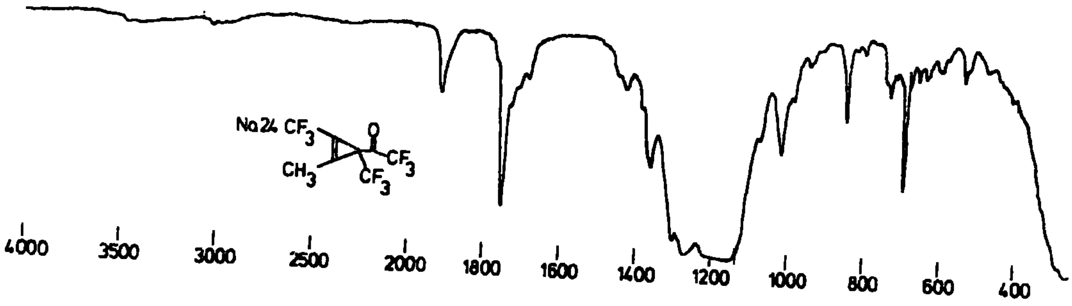
1200
1000
800
600
400


No 24
CF3
CH3
O
CF3
CF3
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400

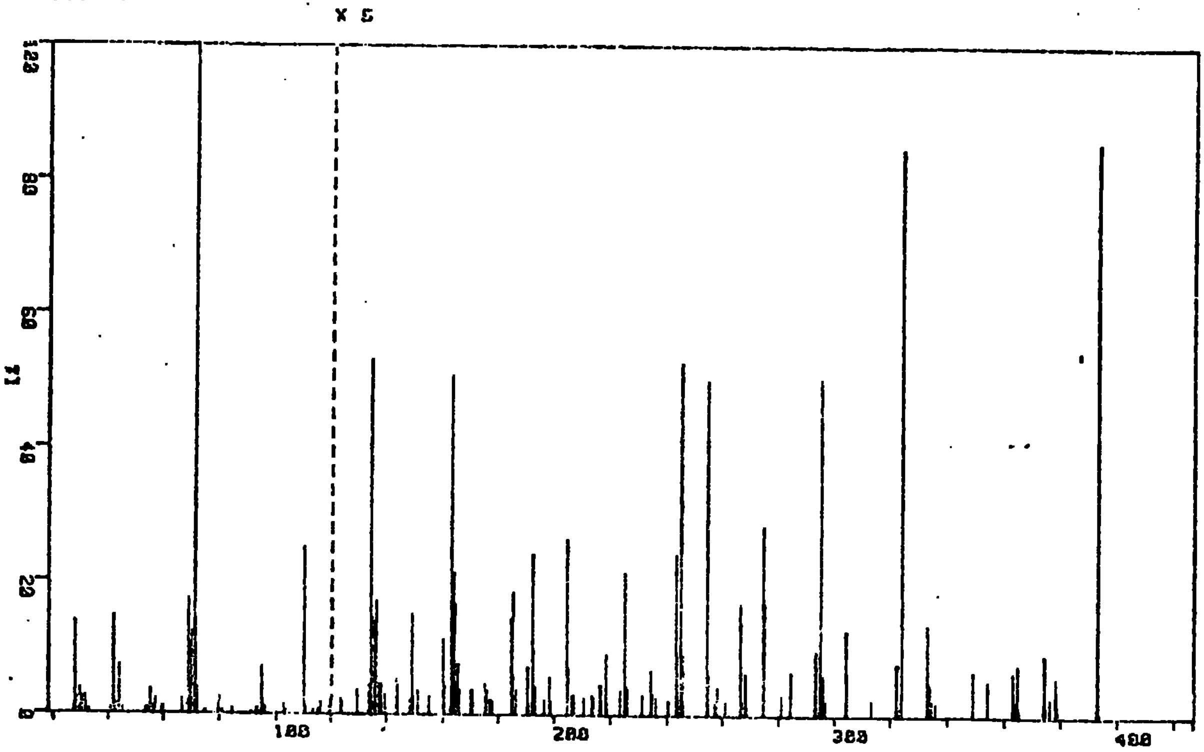
APPENDIX III

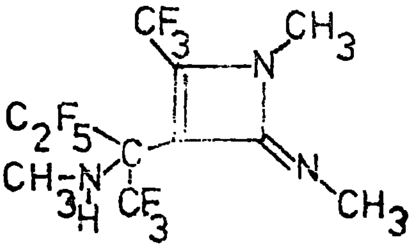
Mass Spectra

The data accompanying each spectrum relate to the most significant peaks.

1. 2-Trifluoromethyl-3-(2'-methylaminooctafluoro-2'-butyl)-4-methylimino-N-methyl-2-azetine (67).
2. *Trans*-4-methylamino-perfluoro-3,4-dimethyl-2-hexene (66).
3. *Cis*, *trans*-2,4-dimethyl-perfluoro-3,4-dimethyl-1-pentene (73).
4. Perfluoro-4,5-diethyl-4,5-dimethyl-3-H-2-pyrazoline (81).
5. *Cis*, *trans*-3-difluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (82).
6. *Cis*, *trans*-3-monofluoromethyl-4-trifluoromethyloctafluoro-2-H-4-H-2-hexene (83).
7. 3,4,5-*Tris*(trifluoromethyl)furan (93).
8. 2-Methyl-3,4,5-*tris*(trifluoromethyl)furan (94).
9. 2-Phenyl-3,4,5-*tris*(trifluoromethyl)furan (96).
10. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-propane (91).
11. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-H-ethane (92).
12. Perfluoro-1-(3',4',5'-trimethylfuryl)-1-H-1-propene (104).
13. 1,2,3-*Tris*(trifluoromethyl)cyclopropenylmethylketone (100).
14. 2-Methyl-1,3-*bis*(trifluoromethyl)-1-cyclopropenyltrifluoromethylketone (101).

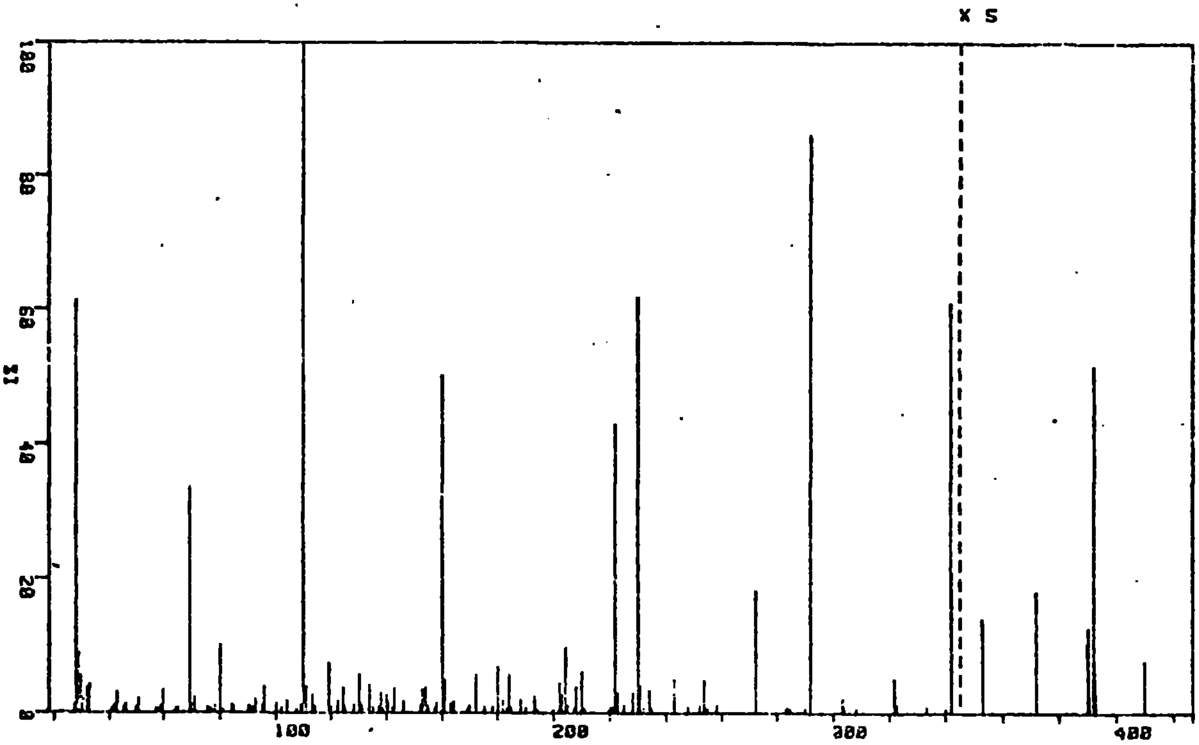
No. 1



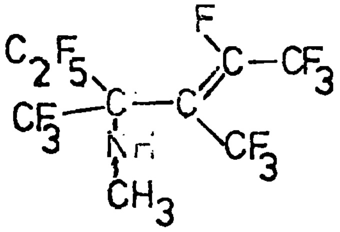


PEAK NO.	MASS	% INT BASE
2	28.05	13.91
3	28.95	2.39
4	29.79	3.96
5	30.84	2.62
6	31.94	2.74
9	42.04	14.61
11	44.16	7.28
15	55.14	3.67
17	57.11	2.39
20	66.13	2.44
23	69.02	17.40
24	69.97	12.51
25	71.04	100.00
26	72.09	4.07
30	79.97	2.62
36	95.14	7.16
40	109.94	25.09
46	119.95	2.39
51	134.06	10.65
52	135.08	2.85
53	136.08	3.43
59	147.04	3.03
63	159.78	2.33
65	163.07	10.19
66	164.07	4.31
74	184.04	2.71
75	185.04	3.73
79	192.07	4.83
84	204.05	5.30
94	225.07	4.31
102	243.06	4.83
104	245.09	10.54
106	254.96	10.01
111	266.07	3.38
114	274.13	5.70
115	275.06	3.38
118	293.02	1.98
119	295.04	10.13
122	304.02	2.50
126	324.23	17.00
127	333.04	2.74
132	354.06	1.11
133	362.97	1.28
134	364.00	0.52
135	365.01	1.57
136	374.04	1.80
137	376.05	0.58
138	378.03	1.16
139	392.97	17.17

No. 2



PEAK NO.	MASS	% INT BASE
2	28.05	61.29
3	28.94	8.89
4	29.79	5.54
6	31.93	3.77
7	33.05	4.32
21	68.96	33.60
28	79.93	9.98
37	96.04	3.83
43	109.92	100.00
44	110.97	3.90
47	118.95	7.43
50	124.04	3.77
53	129.95	5.72
56	134.03	4.20
64	142.98	3.71
67	153.00	3.47
68	154.02	3.77
72	159.92	50.21
73	160.95	4.99
78	171.97	5.66
81	179.96	6.82
85	184.00	5.66
92	201.97	4.56
94	203.99	9.80
97	207.96	3.96
98	209.93	6.15
102	221.97	42.97
106	229.92	61.90
107	230.94	4.08
111	242.94	5.05
114	253.54	4.93
117	272.12	18.32
122	291.99	86.24
126	321.93	5.17
130	341.99	61.17
131	352.94	2.86
132	371.88	3.65
133	389.88	2.56
134	392.04	10.35
135	407.90	1.58



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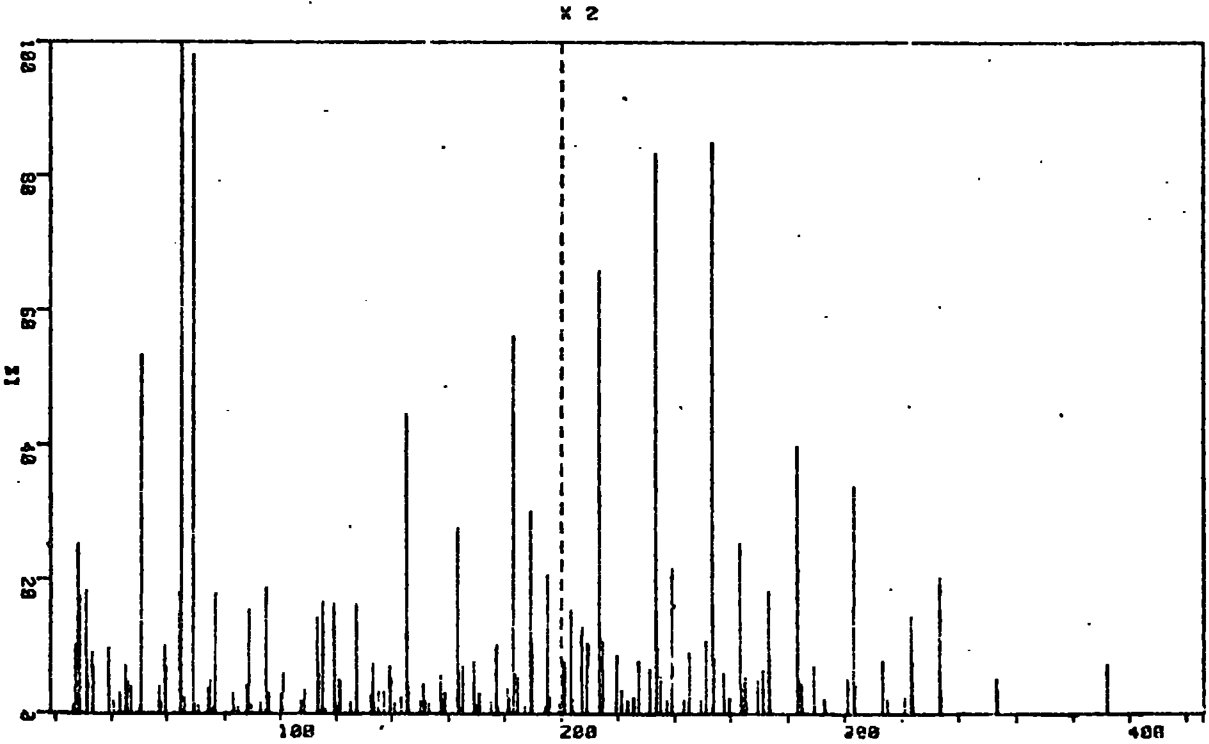
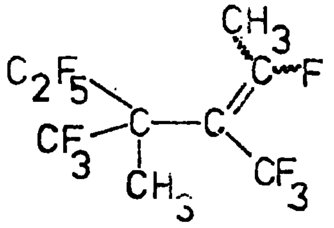
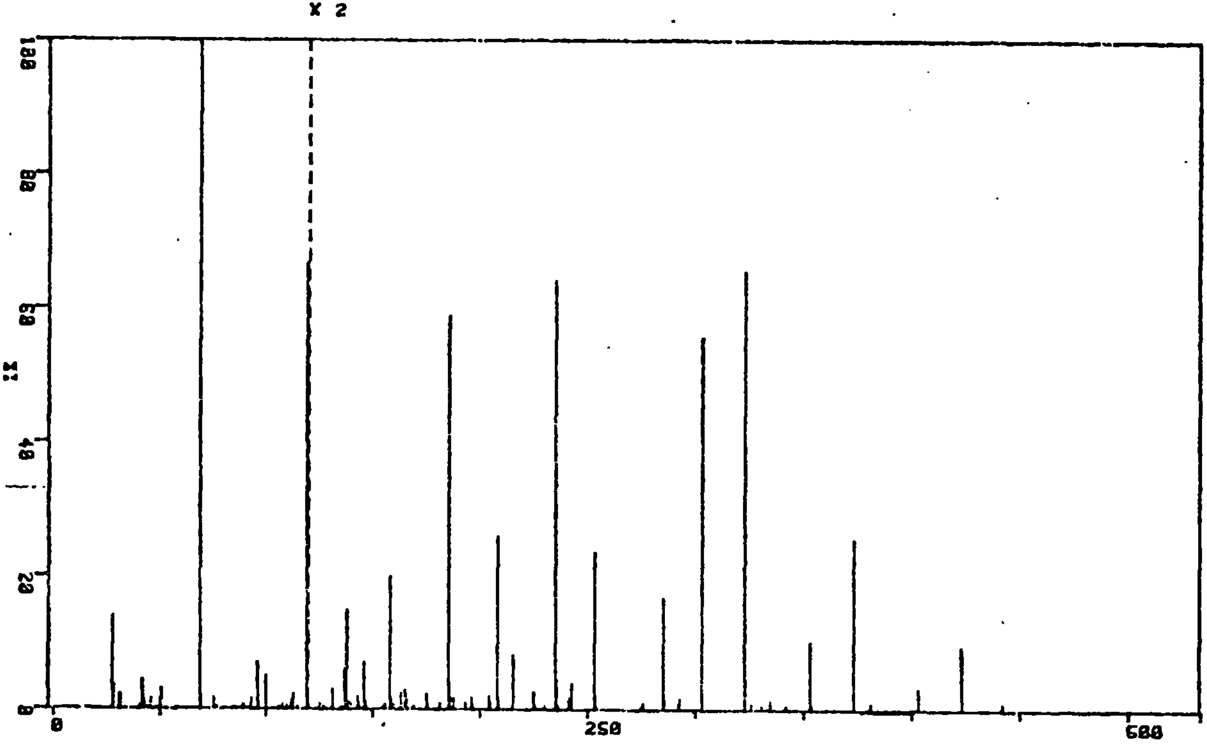


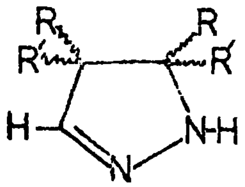


PEAK NO.	MASS	% INT BASE
2	27.17	10.16
3	28.05	25.21
4	28.95	17.44
5	30.84	18.28
6	31.94	5.62
7	33.06	9.20
8	38.97	9.68
11	45.15	7.05
14	50.94	53.29
16	59.01	10.16
17	64.10	18.28
18	65.09	100.00
20	68.96	98.09
24	75.08	4.90
26	77.06	17.80
31	88.98	15.53
34	95.06	18.76
37	100.99	5.97
41	113.02	14.46
42	114.07	5.97
43	115.07	16.61
45	118.99	16.37
47	121.00	5.14
49	127.05	16.37
51	133.06	7.41
55	137.01	7.17
58	145.07	44.56
64	157.03	5.73
67	163.05	27.72
68	164.07	5.97
69	165.09	6.93
70	169.02	7.77
74	177.06	10.39
78	183.07	56.03
79	184.08	5.97
80	185.09	5.38
82	189.02	30.23
85	195.06	20.67
90	203.07	7.77
92	207.06	6.57
93	209.03	5.38
94	213.07	32.97
95	214.55	5.62
102	233.08	41.70
103	234.08	4.90
106	239.03	10.87
110	251.06	5.38
111	253.07	42.53
115	263.08	12.78
120	273.05	9.20
121	283.07	19.95
127	303.03	16.97
132	323.07	7.29
133	333.08	10.16
136	392.04	3.70

NO. 4



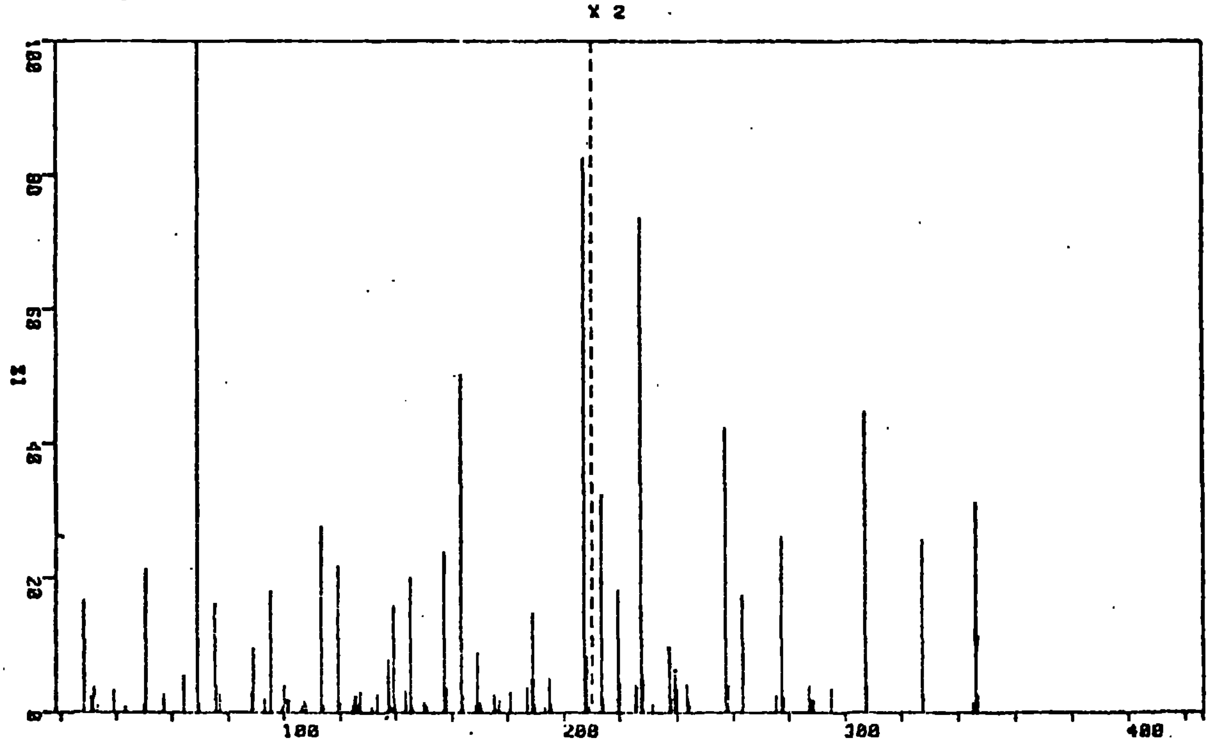
PEAK NO.	MASS	% INT BASE
2	28.05	13.84
3	28.93	3.96
4	30.83	2.38
5	31.94	2.38
7	42.02	4.34
13	50.93	3.03
15	68.97	100.00
25	96.06	7.13
27	99.93	5.06
33	113.03	2.44
35	118.97	66.64
41	137.04	3.06
42	138.02	7.44
47	146.05	3.48
51	158.01	9.95
61	185.06	29.47
70	203.00	12.94
73	216.04	4.10
77	235.05	32.01
78	236.05	2.31
82	253.03	11.84
86	284.99	8.40
90	303.09	27.92
91	323.13	32.74
96	352.96	5.16
97	353.97	0.48
98	373.07	12.81
99	390.99	0.48
100	402.99	1.62
101	423.07	4.75
102	441.97	0.52

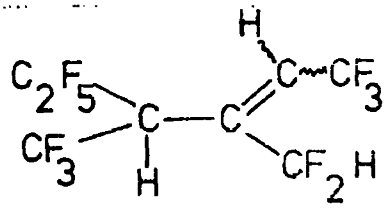


$R = C_2F_5$

$R' = CF_3$

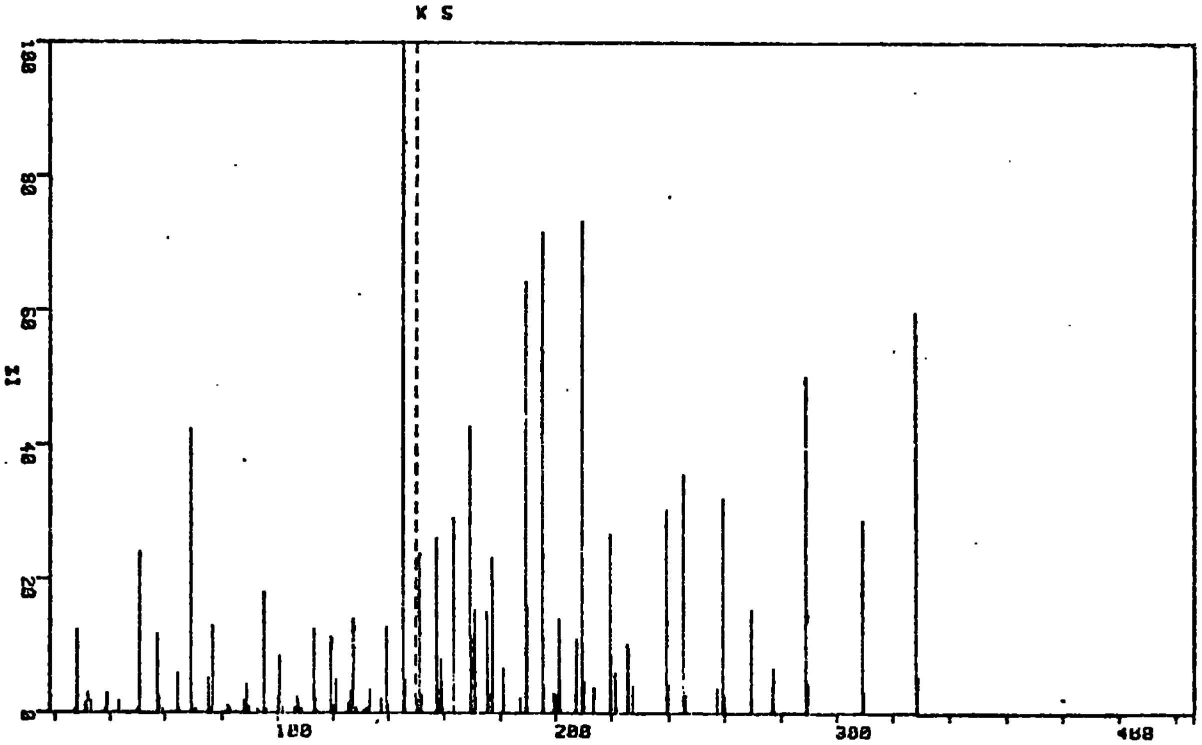
No. 5

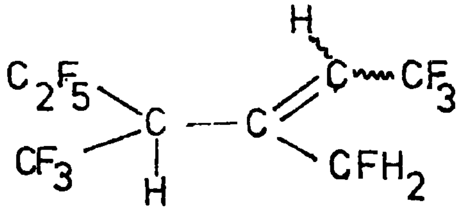




PEAK NO.	MASS	% INT BASE
1	28.05	16.68
2	30.84	2.45
3	31.95	3.67
5	38.97	3.41
8	50.95	21.22
9	57.09	2.71
10	64.11	5.50
11	68.99	100.00
13	75.10	16.33
14	76.08	3.84
15	77.07	2.79
16	88.03	2.97
17	88.98	9.61
18	93.03	2.01
19	95.06	17.99
21	99.93	4.10
26	113.03	27.69
28	119.00	21.83
31	125.07	2.53
33	127.06	3.06
35	133.05	2.71
36	137.05	7.86
38	139.02	15.81
40	143.05	3.23
42	145.07	20.09
46	157.04	23.84
47	158.03	3.50
48	163.04	50.22
49	164.06	2.45
51	169.04	8.91
53	175.09	2.62
55	177.09	1.72
56	181.02	3.14
57	187.06	3.76
58	188.91	14.76
61	195.06	5.07
62	207.06	82.53
63	208.05	8.56
65	213.07	16.24
67	219.05	9.08
69	225.08	2.10
70	227.08	36.86
71	228.06	2.45
73	237.06	4.80
75	239.05	3.32
76	243.07	2.18
77	257.09	21.22
78	258.09	2.01
79	263.08	8.73
81	277.11	13.10
83	287.08	2.01
87	307.05	22.36
88	308.05	2.10
89	327.11	12.84
92	346.05	15.63

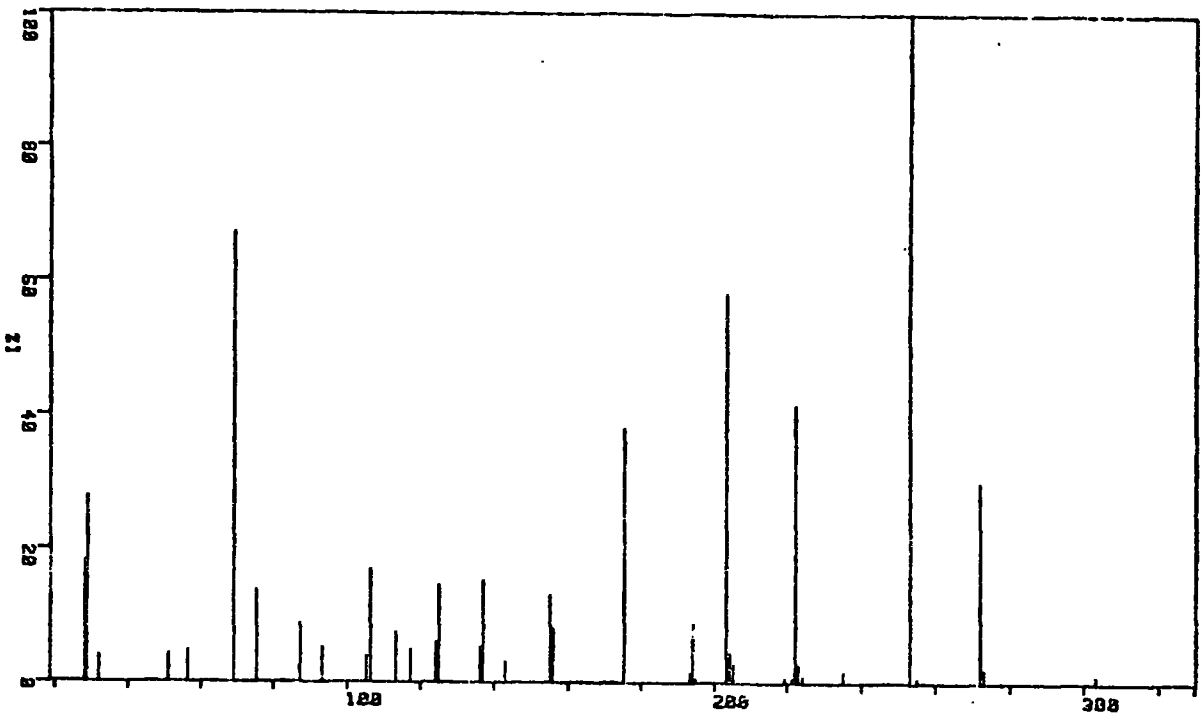
No. 6



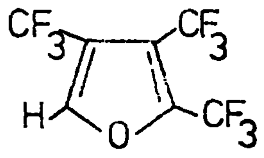


PEAK NO.	MASS	% INT BASE
2	28.05	12.27
4	31.95	3.07
7	38.97	2.95
10	50.95	23.99
11	57.09	11.79
12	58.05	2.47
14	64.10	5.83
16	68.96	42.39
19	75.08	5.23
21	77.06	13.05
25	88.98	4.33
28	95.06	17.98
30	99.93	2.53
32	100.97	8.48
35	107.04	2.53
38	113.02	12.51
40	118.99	11.36
42	121.01	5.11
44	126.06	3.25
45	127.05	13.89
49	133.04	3.49
50	137.04	2.22
51	139.01	12.81
53	145.05	100.00
54	146.05	4.81
55	149.99	1.98
56	151.02	4.75
58	157.04	5.23
61	163.03	5.83
62	169.02	8.60
63	170.02	2.22
64	171.05	3.07
65	175.07	3.01
67	177.06	4.63
70	189.02	12.87
71	190.01	3.25
72	195.05	14.37
76	201.03	2.83
77	207.04	2.22
78	209.01	14.67
81	219.04	5.35
84	225.06	2.10
86	239.03	6.07
88	245.06	7.16
91	259.03	6.43
93	269.06	3.07
95	289.04	10.04
97	309.05	5.77
99	328.09	11.97

No. 7



PEAK NO.	MASS	% INT BASE
1	28.05	17.89
2	28.93	25.99
4	31.94	3.82
9	50.95	3.82
10	56.11	4.47
13	68.99	65.00
16	75.10	13.48
21	87.04	8.10
24	89.90	2.66
26	93.03	5.38
29	105.06	4.21
30	106.05	15.55
32	113.03	7.39
34	115.06	2.33
35	117.04	5.12
39	124.05	6.03
40	125.06	14.32
45	136.06	4.73
46	137.05	14.32
49	143.04	3.24
54	155.04	12.77
55	156.06	8.23
59	172.04	2.01
60	174.06	2.46
61	175.07	38.24
62	176.09	2.01
66	194.04	9.01
68	203.04	56.90
69	204.05	4.21
70	205.06	2.40
73	222.04	40.89
74	223.06	2.53
77	253.13	100.00
78	271.99	28.65
79	273.00	2.27



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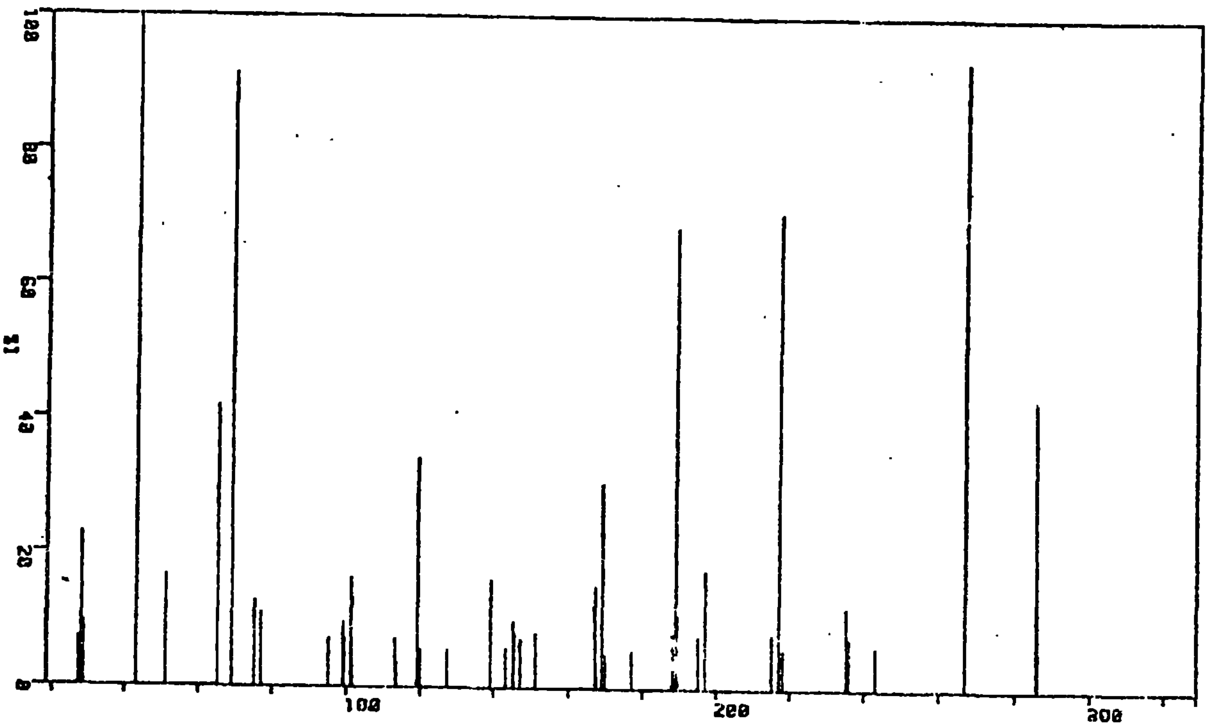
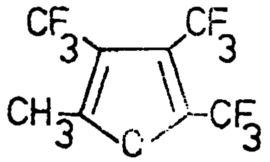


PEAK NO.	MASS	% INT BASE
2	27.17	7.29
3	28.05	22.76
4	28.95	9.60
11	43.09	100.00
17	50.95	16.53
25	65.12	41.87
27	68.96	91.29
30	75.07	12.89
32	77.06	11.20
42	95.06	7.38
45	98.97	9.78
47	101.00	16.36
54	113.03	7.38
59	118.99	34.04
60	119.97	5.69
64	127.07	5.69
73	139.01	16.18
75	143.03	5.96
76	145.08	9.87
78	147.05	7.29
82	151.03	8.27
93	167.05	15.20
95	169.03	30.49
96	170.01	5.24
100	177.07	5.60
107	188.04	7.73
108	189.03	68.53
112	195.07	7.73
114	197.04	17.60
125	215.08	8.27
127	217.05	70.67
128	218.06	5.96
137	235.08	12.27
138	236.06	7.64
141	243.03	6.58
151	267.01	93.42
157	285.87	43.20



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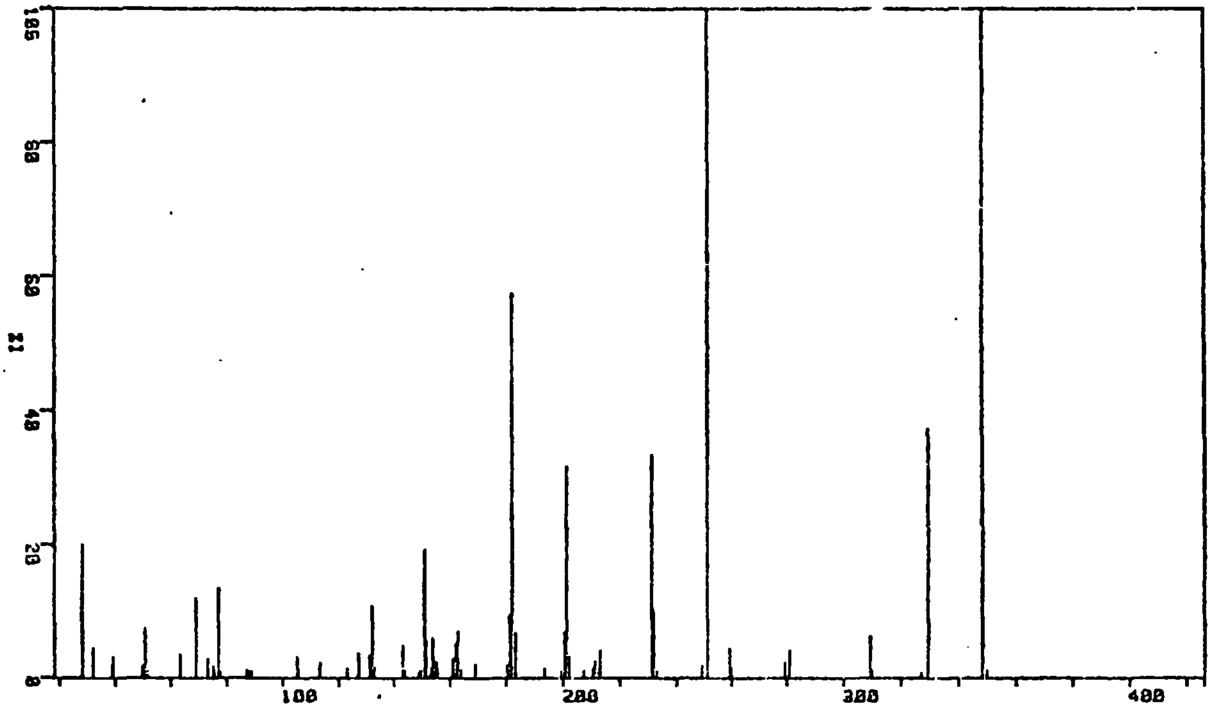
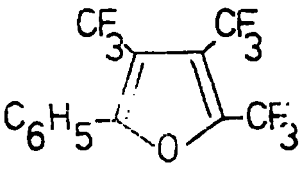


PEAK NO.	MASS	% INT BASE
1	28.05	19.98
2	31.94	4.35
3	38.97	3.00
5	50.96	7.45
7	63.09	3.52
8	68.99	11.90
9	73.12	2.90
12	77.10	13.35
17	105.08	3.21
19	113.06	2.28
21	127.07	3.62
22	131.02	3.42
23	132.05	10.77
25	143.06	4.76
29	151.04	19.25
30	152.06	3.42
32	154.09	6.00
33	155.07	2.48
35	161.00	2.90
36	162.05	5.07
37	163.07	6.94
39	169.05	2.07
40	180.02	1.97
41	181.03	9.42
42	182.06	57.45
43	183.08	6.33
46	200.01	6.83
47	201.03	31.68
48	202.06	3.31
51	211.03	2.48
53	213.08	4.14
54	231.05	33.44
55	232.07	10.14
58	251.12	99.90
59	259.02	4.35
61	279.06	2.28
62	281.04	4.04
63	309.02	6.31
66	329.17	37.37
67	348.08	100.00
68	349.99	1.14



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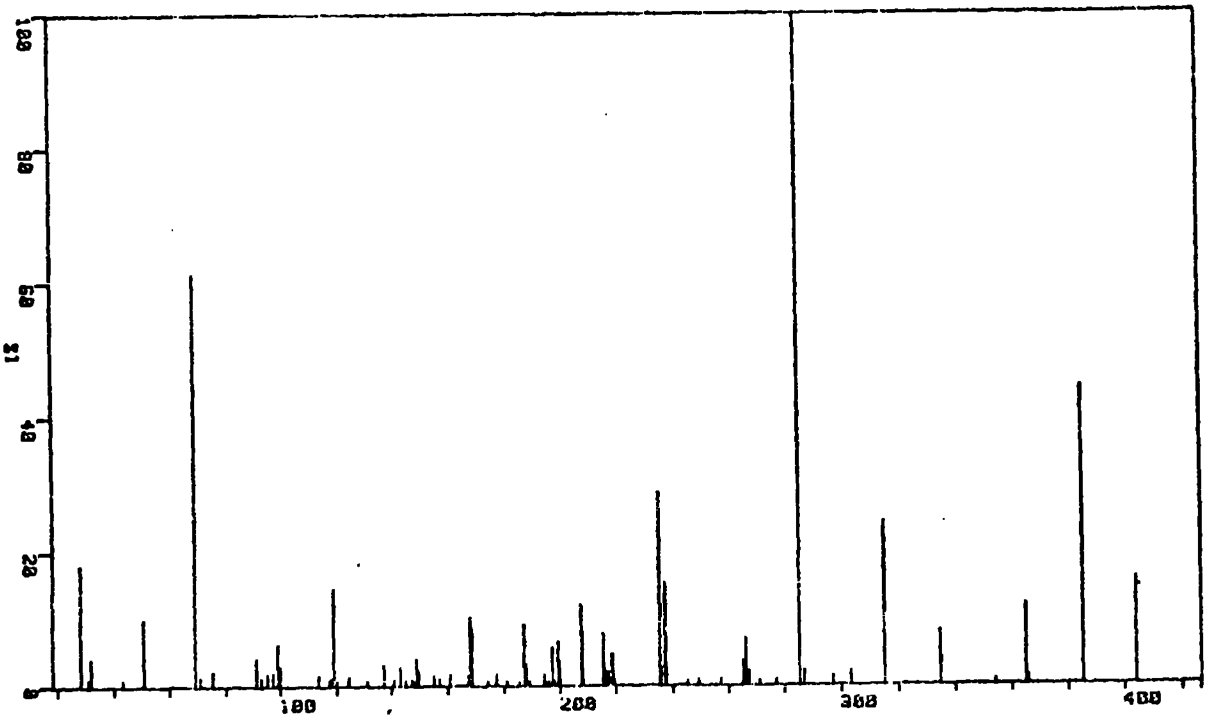
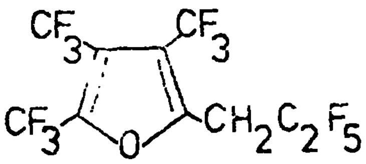


PEAK NO.	MASS	% INT BASE
1	28.05	18.09
3	31.95	4.13
5	50.94	9.91
6	68.98	61.24
8	75.10	2.33
9	90.97	4.22
12	97.04	2.07
13	99.00	6.29
14	99.95	2.93
18	119.01	14.47
22	137.07	3.27
24	143.06	2.84
28	149.04	4.05
29	150.01	2.24
34	168.06	10.16
35	169.05	8.53
40	187.06	9.04
41	188.06	3.27
46	197.11	5.77
48	199.05	6.63
50	207.10	12.14
52	215.11	7.84
53	216.07	1.90
54	217.08	2.24
55	218.05	4.74
57	235.06	28.85
58	236.07	2.76
59	237.07	15.33
64	265.08	3.70
65	266.11	6.98
66	267.08	2.33
69	285.12	100.00
70	287.02	2.33
72	303.01	2.07
73	315.13	24.20
74	334.40	8.10
75	353.97	0.86
76	364.98	11.97
77	365.99	1.38
78	385.00	44.36
79	404.07	15.76



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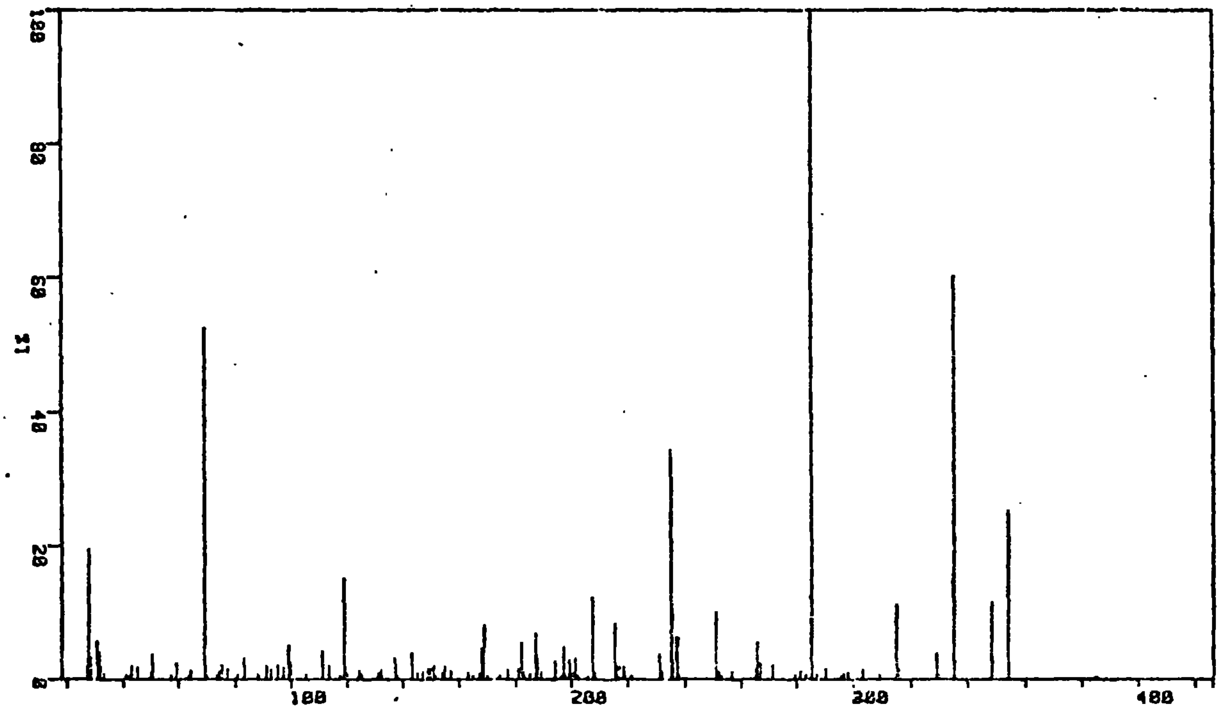
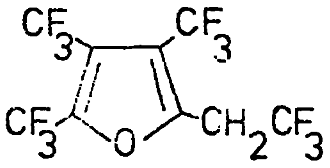


PEAK NO.	MASS	% INT BASE
1	27.17	2.11
2	28.05	19.42
3	28.95	3.33
4	30.84	5.79
5	31.94	4.15
9	43.09	2.05
12	50.95	3.68
14	59.02	2.46
17	68.98	52.46
21	75.10	2.16
24	83.07	3.22
26	90.97	2.05
28	95.08	2.22
30	98.99	5.09
33	110.99	4.21
34	113.05	2.05
37	119.01	14.97
43	137.06	3.33
45	143.06	3.80
50	151.05	2.05
53	168.04	4.68
59	169.05	8.13
64	182.09	5.50
67	187.06	6.84
68	188.04	3.57
70	193.82	2.75
72	197.10	4.85
74	199.07	2.92
76	201.10	3.22
79	207.09	12.28
81	215.09	8.36
82	216.09	2.05
87	231.05	3.68
89	235.06	34.33
90	236.06	3.04
91	237.04	6.43
93	251.06	10.00
99	266.05	5.61
100	267.05	2.51
101	271.02	2.16
105	285.12	100.00
113	315.03	11.17
115	329.06	3.86
117	335.11	60.23
118	348.11	11.52
119	354.00	25.26
120	384.97	0.53



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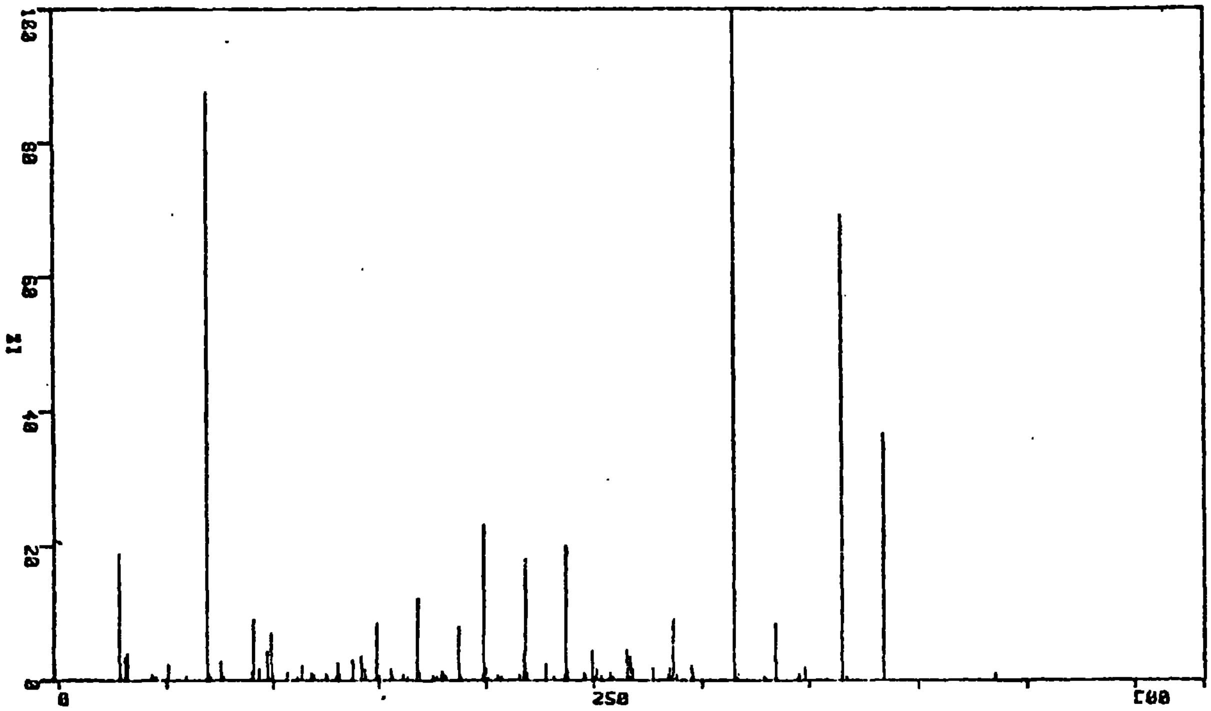
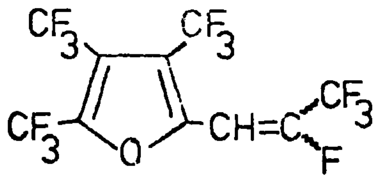


PEAK NO.	MASS	% INT BASE
1	28.05	18.75
3	30.84	3.38
4	31.94	3.98
7	50.95	2.35
9	68.99	87.64
12	75.10	2.83
15	90.97	8.98
17	97.04	4.46
18	99.00	7.05
22	113.06	2.29
29	129.99	2.59
31	137.06	3.13
32	141.01	3.56
35	149.03	8.50
41	167.07	2.65
42	168.06	12.24
50	187.08	7.96
53	199.02	23.15
59	217.07	3.92
60	218.05	18.08
62	227.08	2.47
65	237.05	20.07
69	249.05	4.46
76	265.06	4.52
78	267.04	3.56
80	277.06	1.99
84	287.06	9.22
86	295.06	2.23
88	315.14	100.00
71	334.30	8.44
94	365.02	69.02
95	366.95	0.54
96	384.06	36.71
97	435.02	1.02



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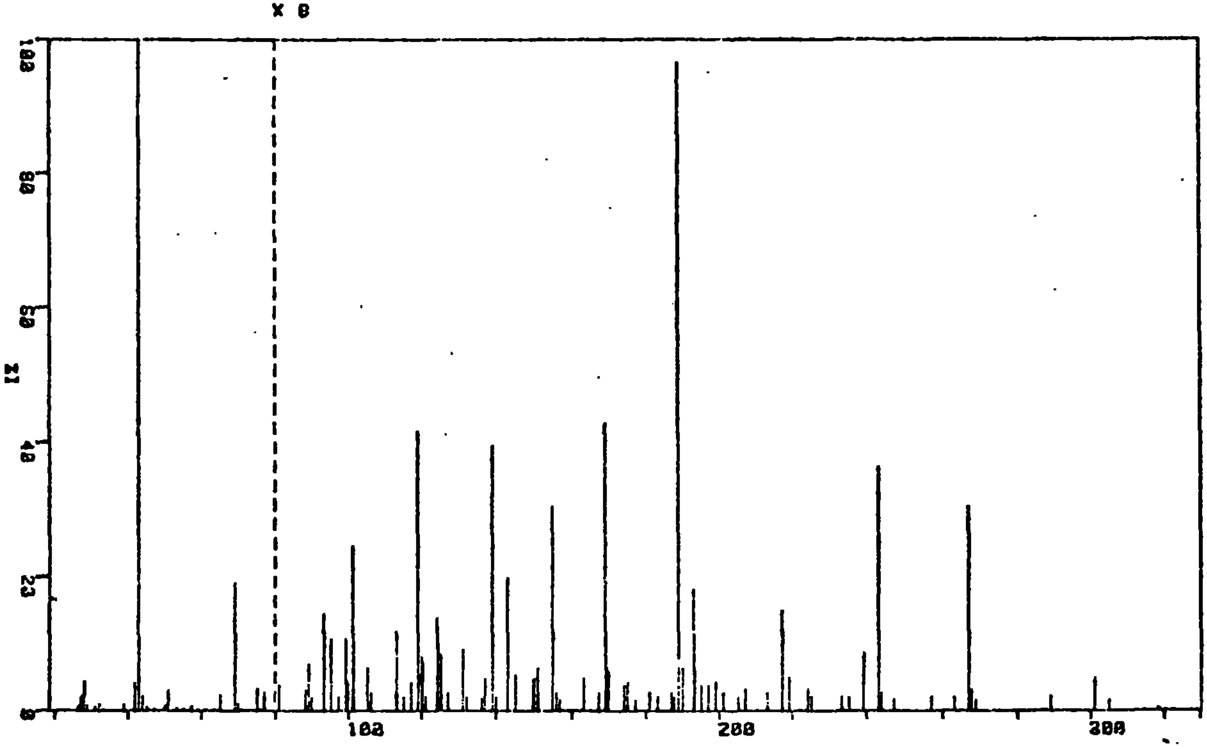
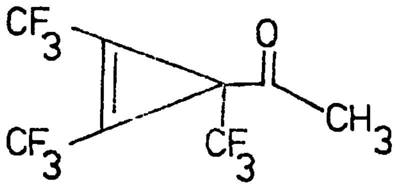


PEAK NO.	MASS	% INT BASE
2	27.17	2.16
3	28.05	4.35
10	42.02	4.18
11	43.09	100.00
12	44.13	2.25
16	50.95	3.11
24	65.12	2.39
25	68.96	19.00
29	75.07	3.37
31	77.05	2.74
41	100.97	3.08
47	118.96	5.21
57	138.98	4.98
59	143.00	2.51
63	155.01	3.86
68	168.99	5.36
77	188.97	12.12
79	192.98	2.27
94	242.97	4.58
99	267.01	3.83



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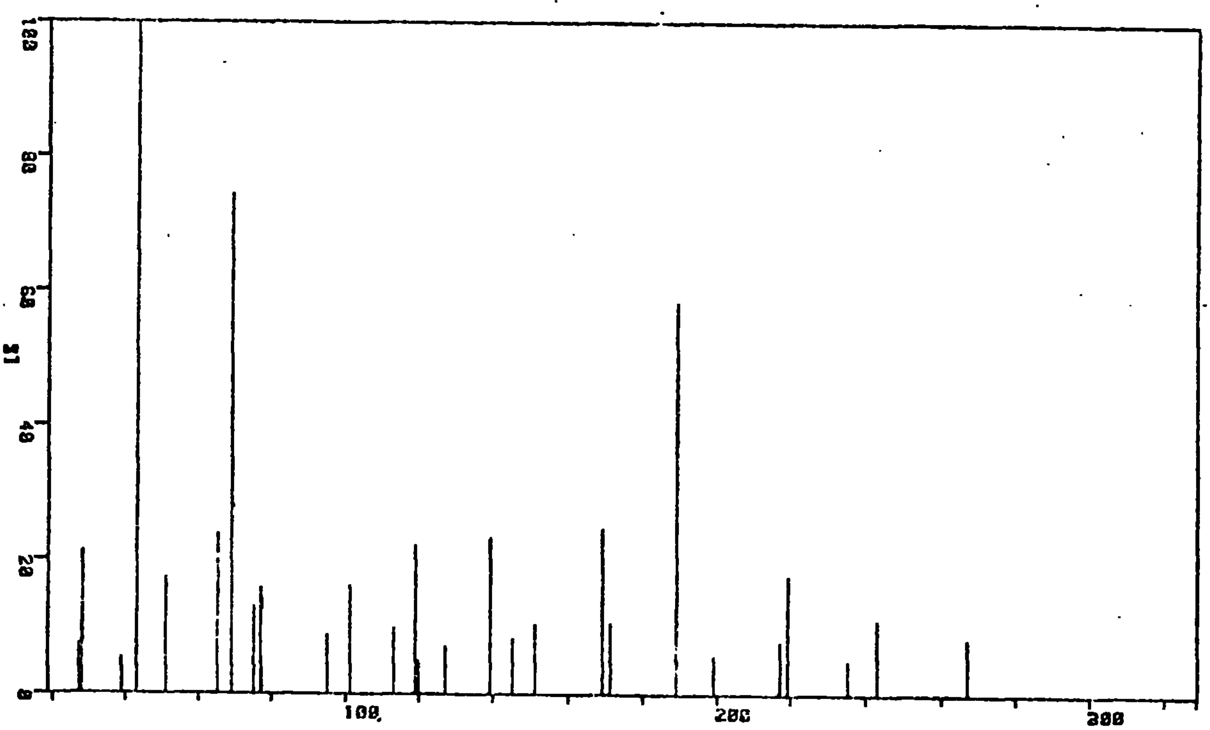
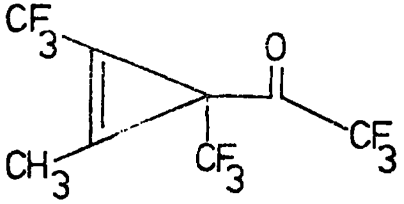


PEAK NO.	MASS	% INT BASE
2	27.17	7.57
3	28.05	21.27
9	38.97	5.39
12	43.09	100.00
18	50.95	17.38
28	65.11	24.64
30	68.95	74.38
33	75.07	13.03
35	77.06	15.81
46	95.05	8.84
51	100.98	16.33
59	113.02	9.31
62	118.99	22.25
63	119.96	5.09
69	127.05	7.19
75	139.00	23.30
79	145.06	8.31
84	151.01	10.49
95	169.01	24.72
97	171.03	10.64
109	189.00	58.28
117	199.01	5.77
125	217.04	7.37
127	219.03	17.75
135	235.06	5.07
139	243.01	11.16
151	267.06	8.39



APPENDIX IV

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing

a) all research colloquia, research seminars and lectures (by external speakers) arranged by the Department of Chemistry since 1st October 1976, and

b) all research conferences attended and papers read out by the author of the thesis, during the period when the research was carried out.

Research Colloquia, Seminars and Lectures.

1. University of Durham Chemistry Colloquia.

1976-77

* 20th Oct. Professor J.B. Hyne (University of Calgary), "New Research on an Old Element - Sulphur".

* 10th Nov. Dr. J.S. Ogden (Southampton University), "The Characterisation of High Temperature Species by Matrix Isolation".

* 17th Nov. Dr. B.E.F. Fender (University of Oxford), "Familiar but Remarkable inorganic Solids".

* 24th Nov. Dr. M.I. Page (Huddersfield Polytechnic), "Large and Small Rate Enhancements of Intramolecular Catalysed Reactions".

* 8th Dec. Professor A.J. Leadbetter (University of Exeter), "Liquid Crystals".

* 26th Jan. Dr. A. Davis (ERDR), "The Weathering of Polymeric Materials".

2nd Feb. Dr. A.M. Falk (NRC Canada), "Structural Deductions from the Vibrational Spectrum of Water in Condensed Phases".

* 9th Feb. Professor R.O.C. Norman (University of York), "Radical Cations; Intermediates in Organic Reactions".

23rd Feb. Dr. G. Harris (University of St. Andrews), "Halogen Adducts of Phosphines and Arsines".

25th Feb. Professor H.T. Dieck (University of Frankfurt), "Diazadienes- New Powerful Low-valent Metal Ligands".

* 2nd Mar. Dr. F. Hibbert (Birkbeck College, London), "Fast Reaction Studies of Slow Proton Transfers Involving Nitrogen and Oxygen Acids".

4th Mar. Dr. G. Brink (Rhodes University, R.S.A.), "Dielectric Studies of Hydrogen Bonding in Alcohols".

* 9th Mar. Dr. I.O. Sutherland (University of Sheffield), "The Stevens Rearrangement: Orbital Symmetry and Radical Pairs".

* 18th Mar. Professor H. Bock(University of Frankfurt), "Photoelectron Spectra and Molecular Properties: A Vademecum for the Chemist".

* 30th Mar. Dr. J.R. McCallum (University of St. Andrews), "Photoxidation of Polymers".

* 20th Apr. Dr. D.M.J. Lilley (G.D. Searle, Research Div.), "Tails of Chromatin Structure - Progress towards a Working Model".

* 27th Apr. Dr. M.P. Stevens (University of Hartford), "Photocycloaddition Polymerisation".

4th May Dr. G.C. Tabisz (University of Manitoba), "Collision Induced Light Scattering by Compressed Molecular Gases".

* 11th May Dr. R.E. Banks (UMIST), "The Reaction of Hexafluoropropene with Heterocyclic N-Oxides".

18th May Dr. J. Atwood (University of Alabama), "Novel Solution Behaviour of Anionic Organoaluminium Compounds: the Formation of Liquid Clathrates".

* 25th May Professor M.M. Kreevoy (University of Minnesota), "The Dynamics of Proton Transfer in Solution".

1st June Dr. J. McCleverty (University of Sheffield), "Consequences of Deprivation and Overcrowding on the Chemistry of Molybdenum and Tungsten".

6th July Professor J. Passmore (University of Brunswick), "Adducts between Group 5 Pentahalides and a Postscript on S_7I^+".

1977-78

* 27th Sept. Dr. T.L. Broxton (La Trobe University, Australia), "Interaction of Aryldiazonium Salts and Arylazoalkyl Ethers in Basic Alcoholic Solvents".

* 19th Oct. Dr. B. Heyn (University of Jena, D.D.R.), "σ-Organo Molybdenum Complexes as Alkene Polymerisation Catalysts".

* 27th Oct. Professor R.A. Filler (Illinois Institute of Technology, U.S.A.), "Reactions of Organic Compounds with Xenon Fluorides".

2nd Nov. Dr. N. Boden (University of Leeds), "Nmr Spin-Echo Experiments for Studying Structure and Dynamical Properties of Materials Containing Interacting Spin-½ Pairs".

* 9th Nov. Dr. A.R. Butler (University of St. Andrews), "Why I lost Faith in Linear Free Energy Relationships".

7th Dec. Dr. P.A. Madden (University of Cambridge), "Raman Studies of Molecular Motions in Liquids".

14th Dec. Dr. R.O.Gould (University of Edinburgh), "Crystallography to the Rescue in Ruthenium Chemistry".

* 25th Jan. Dr. G. Richards (University of Oxford), "Quantum Pharmacology".

* 1st Feb. Professor K. J. Irvin (Queen's University, Belfast), "The Olefin Metathesis Reaction: Mechanism of Ring Opening Polymerisation of Cycloalkenes".

* 3rd Feb. Dr. A. Hartog (Free University, Amsterdam), "Surprising Recent Studies in Organo-magnesium Chemistry".

* 22nd Feb. Professor J.D. Birchall (Mond Division, I.C.I. Ltd.), "Silicon in the Biosphere".

* 1st Mar. Dr. A. Williams (University of Kent), "Acyl Group Transfer Reactions".

* 3rd Mar. Dr. G. van Koten (University of Amsterdam), "Structure and Reactivity of Arylcopper Cluster Compounds".

* 15th Mar. Professor G. Scott (University of Aston), "Fashioning Plastics to Match the Environment".

* 22nd Mar. Professor H. Vahrenkamp (University of Frieburg, Germany), "Metal-Metal Bonds in Organometallic Complexes".

19th Apr. Dr. M. Barber (UMIST), "Secondary Ion Mass Spectra of Surfaces and Absorbed Species".

16th May Dr. P. Ferguson (C.N.R.S., Grenoble), "Surface Plasma Waves and Adsorbed Species on Metals".

* 18th May Professor M. Gordon (University of Essex), "Three Critical Points in Polymer Science".

* 22nd May Professor D. Tuck (University of Windsor, Ontario), "Electrochemical Synthesis of Inorganic and Organometallic Compounds".

24th & 25th May Professor P. von R. Schleyer (University of Erlangen Nurnberg),

* I "Planar Tetra-coordinate Methanes, Perpendicular Ethenes and Planar Allenes".

* II "Aromaticity in Three Dimensions".

*III "Non-Classical Carbocations".

21st June Dr. S.K. Tyrlik (Acad. of Sci., Warsaw), "Dimethylglyoxime-cobalt Complexes - Catalytic Black Boxes".

23rd June Professor W.B. Pearson (University of Florida), "Diode Laser Spectroscopy at 16μm".

30th June Professor G. Mateescu (Cape Western Reserve University), "A Concerted Spectroscopy Approach to the Characterisation of Ions and Ion-pairs: Facts, Plans and Dreams".

1978-79

8th Sept. Dr. A. Diaz (I.B.M., San Jose, California), "Chemical Behaviour of Electrode Surface Bonded Molecules".

15th Sept. Professor W. Siebert (Marburg, W. Germany), "Boron Heterocycles as Ligands in Transition Metal Chemistry".

22nd Sept. Professor T. Fehlner (Notre Dame U.S.A.), "Ferroboranes: Synthesis and Photochemistry".

* 12th Dec. Professor C.J.M. Stirling (University of Bangor), "Parting is such Sweet Sorrow - the Leaving Group in Organic Reactions".

* 31st Jan. Professor P.D.B. de la Mare (University of Auckland, New Zealand), "Some Pathways Leading to Electrophilic Substitution".

14th Feb. Professor B. Dunnell (University of British Columbia), "The Application of Nmr to the Study of Motions of Molecules in Solids".

16th Feb. Dr. J. Tomkinson (Institute of Laue-Langevin, Grenoble), "Studies of Adsorbed Species".

* 14th Mar. Dr. J.C. Walton (University of St. Andrews), "Pentadienyl Radicals".

* 28th Mar. Dr. A. Reiser (Kodak ltd.), "Polymer Photography and the Mechanism of Cross-Link Formation in Solid Polymer Matrices".

* 25th Apr. Dr. C.R. Patrick (University of Birmingham), "Chlorofluorocarbons and Stratospheric Ozone: an Appraisal of the Environmental Problem".

* 1st May Dr. G. Wyman (European Research Office, U.S. Army), "Excited state Chemistry of Indigoid Dyes".

* 2nd May Dr. J.D. Hobson (University of Birmingham), "Nitrogen-centred Reactive Intermediates".

8th May Professor A. Schmidpeter (Inst. of Inorg. Chem., University of Munich), "Five-membered Phosphorus Heterocycles Containing Dicoordinate Phosphorus".

* 9th May Professor G. Maier (Lahn Giessen University), "Tetra-tert-butyltetrahedrane".

9th May Dr. A.J. Kirby (University of Cambridge), "Structure and Reactivity in Intramolecular and Enzymic Catalysis".

16th May Dr. J.F. Nixon (University of Sussex), "Spectroscopic Studies on Phosphines and their Coordination Complexes".

* 23rd May Dr. B. Wakefield (University of Salford), "Electron Transfer in Reactions Of Metals and Organometallic Compounds with Polychloropyridine Derivatives".

13th June Dr. G. Heath (University of Edinburgh), "Putting Electrochemistry in Mothballs".

* 14th June Professor I. Ugi (University of Munich) "Synthetic uses of Super Nucleophiles".

* 25th Sept. Professor R. Soulen (Southwestern University, Texas), "Applications of HSAB Theory to Vinylic Halogen Substitution and a few Copper Coupling Reactions".

2. Durham University Chemical Society.

1976-77

* 19th Oct. Dr. J.A. Salthouse (University of Manchester), "Chemistry and Energy".

* 26th Oct. Dr. R.E. Richards (University of Oxford), "Nmr Measurements on Intact Biological Tissue".

* 2nd Nov. Dr. B. Sutcliffe (University of York), "The Chemical Bond as a Figment of the Imagination".

16th Nov. Mr. R. Ficken (Rohm & Haas), "The Graduate in Industry".

* 30th Nov. Dr. R.J. Donovan (University of Edinburgh), "The Chemistry of the Atmosphere".

* 18th Jan. Professor I. Fells (University of Newcastle), "Energy Storage and the Chemist's Contribution to the Problem".

8th Feb. Dr, M.J. Cleare (Johnson Matthey Research Centre), "Platinum Group Metals as Anti-Cancer Agents".

1st Mar. Professor J.A.S. Smith (Q.E.C., London), "Double Resonce".

* 8th Mar. Professor C. Eaborn (University of Sussex), "Structure and Reactivity".

1977-78

* 13th Oct. Dr. J.C. Young & Mr. A.J.S. Williams (University of

Aberystwyth), "Experiments and Considerations Touching Colour".

* 20th Oct. Dr. R.L. Williams (Metropolitan Police Forensic Science Dept.), "Science and Crime".

* 3rd Nov. Dr. G.W. Gray (University of Hull), "Liquid Crystals - Their Origins and Applications".

* 24th Nov. Mr. G. Russel (Alcan), "Designing for Social Acceptibility".

* 1st Dec. Dr. B.F.G. Johnson (University of Cambridge), "Chemistry of Binary Metal Carbonyls".

2nd Feb. Professor R.A. Raphael (University of Cambridge), "Bizarre Reactions of Acetylenic Compounds".

16th Feb. Professor G.W.A. Fowles (University of Reading), "Home Winemaking".

* 2nd Mar. Professor M.W. Roberts (University of Bradford), "The Discovery of Molecular Events at Solid Surfaces".

* 9th Mar. Professor H. Suschitsky (University of Salford), "Fruitful Fissions of Benzofuroxans".

* 4th May Professor J. Chatt (University of Sussex), "Reactions of Coordinated Dinitrogen".

* 9th May Professor G.A. Olah (Case Western Reserve University, Cleveland, Ohio), "Electrophilic Reactions of Hydrocarbons".

1978-79

* 10th Oct. Professor H.C. Brown (Purdue University), "The Tool of Increasing Electron Demand in the Study of Cationic Processes".

* 19th Oct. Mr. F.C. Shenton (Public Analyst, Co. Durham), "There is Death in the Pot".

26th Oct. Professor W.J. Albery (I.C., London), "Photogalvanic Cells for Solar Conversion".

* 9th Nov. Professor A.R. Katritsky (University of East Anglia), "Some Adventures in Heterocyclics".

* 16th Nov. Dr. H.C. Fielding (I.C.I. Ltd.), "Fluorochemical

Surfactants & Textile Finishes".

* <u>23rd Nov.</u> Dr. C. White (University of Sheffield), "The Magic of Chemistry".

* <u>18th Jan.</u> Professor J.C. Robb (University of Birmingham), "The Plastics Revolution".

<u>8th Feb.</u> Mr. C.G. Dennis (Vaux Ltd.), "The Art and Science of Brewing".

<u>1st Mar.</u> Professor R. Mason (Govt. Scientific Advisor), "The Scientist in Defence Policy".

<u>10th May</u> Professor G. Allan (Chairman S.R.C.), "Neutron Scattering for Polymer Structures".

* Indicates events attended.

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