# The action of tertiary amines on fluorinated organic compounds related to Viton A

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Vince, Michael E. J. (1965) *The action of tertiary amines on fluorinated organic compounds related to Viton A*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/8723/

UNIVERSITY OF DURHAM

A THESIS

entitled

# "The Action of Tertiary Amines on Fluorinated Organic Compounds related to Viton A."

Submitted by

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A candidate for the degree of Doctor of Philosophy.

1965

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## Chapter 1. Introduction.

## Chapter 2. Discussion of Experimental Work.

# ACKNOWLEDGEMENTS

I should like to thank Professor W.K.R. Musgrave and Dr. R.D. Chambers for their continual help and encouragement in the supervision of this work.

I should also like to thank Dr. J. Hutchinson for many rewarding discussions, Drs. J.W. Emsley and L. Phillips for nuclear magnetic resonance measurements and the many laboratory technicians, especially Mr. L. Chadwick, for their considerable help.

Last, but by no means least, I should like to express my gratitude to the Ministry of Aviation and also to Yarsley Research Laboratories Limited for maintenance grants during the course of this work.

# MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1962 and August 1965. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

## SUMMARY

By the use of model compounds, investigations were carried out into the processes occurring during the cross-linking of Viton A. This fluorocarbon elastomer is a co-polymer of 1,1-difluoroethylene and hexafluoropropene, in which the predominating structure is $-CF_2CF(CF_3)CH_2CF_2CH_2CF_2-$. The model compounds used were 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane), $[(CF_3)_2CFCH_2CF_2\text{-}]_2$, and 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CFCH_2CF_3$. When the former compound was reacted with tri-n-butylamine a dehydrofluorination reaction predominated, giving the di-ene $(CF_3)_2C=CHCF_2CF=CHCF(CF_3)_2$. However, when the latter compound was reacted with tri-n-butylamine under identical conditions, an unexpected reaction occurred in which the tertiary fluorine was replaced by hydrogen, giving 2H,2H,3H-nonafluoro-(3-methylbutane), $(CF_3)_2CHCH_2CF_3$.

Tri-n-butylamine was reacted with other saturated fluorocarbon compounds which were not model compounds of the Viton A system. It was found that those compounds containing tertiary fluorine atoms were more reactive than those not containing the tertiary fluorine. A similar observation was made for compounds containing halogens other than fluorine; these were more reactive than compounds in which the only halogen was fluorine.

Reactions were also carried out between tertiary amines and fluorinated olefins. With tri-n-butylamine, the predominating reaction was one involving the addition of the elements of HF to the rearranged olefin. Thus, with decafluoro-(3-methylbut-1-ene), $(CF_3)_2CFCF=CF_2$,

the reaction product was 3H-undecafluoro-(3-methylbutane), $(CF_3)_2CHCF_2CF_3$. With trimethylamine, olefins containing allylic tertiary fluorine atoms underwent addition reactions to give fluorine containing tertiary amines, easily hydrolysed to amides. These reactions are of significance to the cross-linking of Viton A by tertiary amines, since allylic tertiary fluorine atoms can be formed in the elastomer by initial dehydrofluorination.

Preliminary attempts, largely unsuccessful, were made to prepare some fluorinated di-enes by dehalogenation and by dehydrofluorination of some mono-olefins. The most promising method of dehydrofluorination was the use of heated sodium fluoride.

## Fluorine Containing Organic Polymers.

Synthetic polymeric materials which are stable at high temperatures have, especially in the last few years, become very important. New technological demands from, for example, the aero-space industries, have lead to vigorous research directed to the synthesis and characterisation of high polymers capable of reliable performance under extreme conditions of use.

Some of the most valuable results have been obtained from work into fluorine containing polymers. Polymers containing fluorine show unusually high resistance to both chemical attack and thermal degradation. These properties are especially pronounced in the more highly fluorinated structures, polytetrafluoroethylene being the prime example. The stability of the fluorine containing polymers can be attributed to two factors:

(i) The high dissociation energy of the carbon-fluorine bond, 123 kcal./mole in $C_2F_6$, and

(ii) The relatively large size of the fluorine atom compared to the hydrogen atom giving rise to an increased shielding of the carbon-carbon bonds. [Covalent radii for fluorine and hydrogen are 0·72Å and 0·30Å respectively]. The size of the fluorine atom as compared to that of the hydrogen atom also leads to increased stiffness of the polymer chain, making for greater chemical stability.

Fluorine containing polymers can be very roughly divided into two groups, the homopolymers, which are polymers of one monomer molecule, and the co-polymers, which contain repeating units of two different monomer molecules, not necessarily present in the same concentrations. The physical properties of a homopolymer are determined largely by the structure of the monomer of which it is composed, although small modifications in properties can be brought about by varying polymerisation conditions. For example, during the polymerisation of hexafluoropropene, increase of pressure in the system favours the production of higher molecular weight polymers.[1] In the case of co-polymers, however, physical properties can be readily changed by altering the ratios of the two monomers in the reaction mixture. The products obtained from the co-polymerisation of varying ratios of vinylidene fluoride and 1,1,3,3,3-pentafluoropropene are thermoplastic when they contain 5 - 15% of the propene, and are elastomeric in the range 10 - 70% of the propene.[2]

It has been found that the monomers involved in a co-polymerisation reaction need not necessarily be homopolymerisable under the conditions of the reaction. The co-polymer derived from a non-homopolymerisable olefin and a homopolymerisable one can contain up to 50% of the former monomer. Consequently, co-polymers containing hexafluoropropene units can be produced by emulsion polymerisation techniques, even although $C_3F_6$ only homopolymerises at high pressures.[3]

Polytetrafluoroethylene, to be discussed more fully below, is an extremely useful polymer, but it has some serious limitations. Not least of these is that it is not thermoplastic, a point which makes for difficulties in fabrication. Also, P.T.F.E. is non-elastomeric in nature, which prohibits its use in some situations. To convert the highly crystalline polymer system that is P.T.F.E. to an elastomeric system, e.g. 'Viton A', there are basically three requirements.

[i] The rigid polymer backbone must be converted to a more mobile structure.

[ii] Heterogeneity must be incorporated into the polymer chain, i.e. bulky groups or atoms must be present.

[iii] Provision must be made for polymer chains to be cross-linked.

Thus, the crystalline polymer chain

$$-\!\!\left[ CF_2 \cdot CF_2 \right]\!\!-_n$$

has to be converted to a system of the type

$$-CF_2.CFX.[CF_2]_n.[Y-Z].CF_2-$$

where X is a bulky group or atom and [Y-Z] is some system capable of making a cross-link with a neighbouring polymer chain.

The following homo- and co-polymers illustrate how change in structure of monomer molecules affect physical properties of the polymer.

## HOMOPOLYMERS

### (a) POLYTETRAFLUOROETHYLENE. (P.T.F.E. or 'Teflon'*)

Polytetrafluoroethylene was discovered in 1941, by Plunket.[5] It

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*Registered trade name of E.I. du Pont Ltd.

is commercially by far the most important of the fluorine containing polymers, accounting for 90% of the estimated world consumption of 5,000 tons in 1964.

The literature on the industrial polymerisation of tetrafluoroethylene is vast,[6,7,8] however the usual technique is to use a peroxide initiator in either an inert fluorocarbon or in an aqueous medium.[9] Polymerisation, at -16° to 0°, can also be brought about by adding 0·5% of bis(trichloroacetyl)peroxide to a 10% solution of $C_2F_4$ in chloroform. Ziegler-Natta catalysts are claimed to bring about the slow polymerisation of $C_2F_4$ to a high polymer.[4] A low polymer version of P.T.F.E. can be obtained by carrying out the polymerisation in a mixture of carbon tetrachloride and chloroform, in the presence of relatively large amounts of dibenzoyl peroxide, giving products melting in the range 200° - 210°. The chloroform is an efficient chain transfer agent, thus leading to shorter polymer chains than is normally the case.

The fabrication of P.T.F.E. presents problems. Conventional moulding techniques cannot be employed with P.T.F.E. because of the viscosity of its melts. Instead, fabrication is accomplished by sintering, a technique more commonly employed in powder metallurgy. A method of moulding P.T.F.E. has been devised, however, in which finely divided P.T.F.E. is intimately mixed with a polychlorotrifluoroethylene oil to give a putty-like material containing up to 82% by weight of P.T.F.E.[10] The 'putty' is moulded to the desired shape and is then treated with a solvent for the polychlorotrifluoroethylene. Occasionally this process is followed by sintering, but this is not always necessary.

The structure of P.T.F.E. has been studied by both infrared[11] and electron microscope examination.[12] It has been shown to be an un-cross-linked polymer consisting of co-linear difluoromethylene chains, each one spiralling slightly to relieve overcrowding.

Massive polytetrafluoroethylene is a white, opaque solid with a waxy surface. The waxy surface can be modified by reaction with solutions of alkali or alkaline earth metals, or by graft polymerisation of another monomer.[13] The extremely good self-lubricating properties of P.T.F.E. has been a major reason for its usefulness. It is tremendously resistant to chemical attack, being affected by molten sodium only above 200°, and by elemental fluorine at 1 atmosphere and 150°. P.T.F.E. is completely non-inflammable and no solvent is known for it, although it is swollen by some fluorocarbon oils, as witnessed by their use in the formation of the moulding 'putty' previously mentioned. That P.T.F.E. is the best known solid dielectric material, apart from its high electrical resistivity, provides another reason for its commercial success.

### (b) <u>POLYCHLOROTRIFLUOROETHYLENE.</u> ('Kel-F'*)

'Kel-F' is a polymer which, unlike polytetrafluoroethylene, is a true thermoplastic, and can be extruded and moulded. The structure of polychlorotrifluoroethylene differs from that of P.T.F.E. in that the

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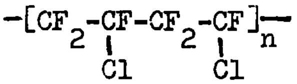
*Registered trade name of the Kellogg Co.

regularity of the backbone of P.T.F.E. is much diminished by the substitution of a fluorine in each monomer unit by a chlorine. The structure of 'Kel-F' has been shown to be:[14]



$$-[CF_2-\underset{Cl}{CF}-CF_2-\underset{Cl}{CF}]_n-$$

The bulky 'pendant' chlorine atoms introduce heterogeneity into the system and prevent the polymer from being highly crystalline.

The patent literature gives many details for the preparation of 'Kel-F'.[15-21] Polymerisation of chlorotrifluoroethylene can be made to give either high polymeric solids or low polymers (telomers), which are oils. Telomers are obtained by carrying out polymerisations in chloroform solution (c.f. low molecular weight polytetrafluoroethylene), using large amounts of benzoyl peroxide - up to 5%. The polychlorotrifluoroethylene telomers are high boiling liquids, which have found use as heat transfer agents. Often, in order to improve thermal stability, the chlorine in the oils is replaced, at least partially, by fluorine by treatment with cobalt trifluoride.[22] High polymers of chlorotrifluoroethylene are usually prepared by suspension polymerisation in an aqueous medium using a persulphate/bisulphite catalyst.

Although 'Kel-F' can be fabricated from the melt, thermal decomposition at the working temperature is quite significant.[23] To alleviate this problem of thermal decomposition, the use of metal salts as stabilisers has been suggested.[24]

Though polychlorotrifluoroethylene is less thermally stable than P.T.F.E., it still finds considerable use. It has some better mechanical properties than P.T.F.E. and may be plasticised. It is swollen by some solvents, but retains a high resistance, generally, to chemical attack. At elevated temperatures, and especially in basic solvents, chlorine tends to split off. Amines react especially readily with chlorotrifluoroethylene polymers, a fact to be discussed more fully at a later stage.

(c) <u>POLYHEXAFLUOROPROPENE</u>. (P.H.F.P.)

The chlorine atoms in polychlorotrifluoroethylene are the source of its low thermal and chemical stability compared to P.T.F.E. In polyhexafluoropropene, the chlorine of 'Kel-F' is effectively replaced by $CF_3$ groups. Hexafluoropropene proved, in fact, to be rather difficult to homopolymerise - all attempts up to 1952 had failed to produce a homopolymer. In 1953, Manowitz[25] claimed to have made a homopolymer of $C_3F_6$ by γ-ray irradiation, getting a 14% conversion per megaroentgen. Previous to 1960, other attempts at homopolymerisation had yielded only dimers, trimers and tetramers of $C_3F_6$.[26-28] Finally, in 1960, Eleuterio[3] succeeded in preparing polyhexafluoropropene. Drastic conditions of temperature and pressure were needed, with the presence of a hydrogen-free radical initiator.

$$nCF_3.CF{=}CF_2 \xrightarrow[225^{\circ}/3,000\text{ atms.}]{(CF_3S)_2Hg} [-CF_2.CF(CF_3)-]_n$$

The polymer obtained had a molecular weight dependant on polymerisation pressure:-

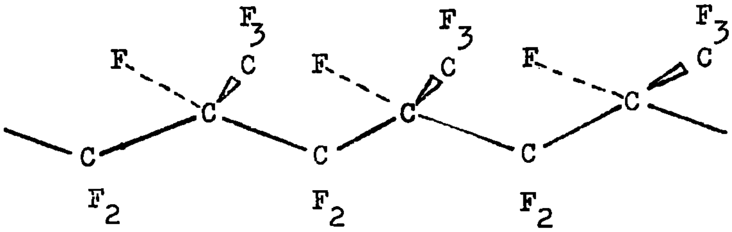
Table 1

| Pressure (atms.) | Viscosity ($\eta$ inh.) |
|---|---|
| 2,500 | 0·2 |
| 3,500 | 0·5 |
| 4,400 | 0·6 |
| 4,600 | 0·7 |
| 4,800 | 0·8 |
| 5,000 | 1·0 |

The table[29] indicates the effect of variations of pressure on the molecular weight, measured as a function of the inherent viscosities of polymer solutions. The polymerisations were all carried out at 225° with equal volumes of perfluoro-1,3-dimethylcyclobutane as solvent.

It has been claimed[4] that $C_3F_6$ will undergo a slow polymerisation in the presence of Ziegler catalysts to give high molecular weight crystalline products, melting at 110-120°. It was suggested that the polymers thus formed would probably have an isotactic structure:

$$CF_3\cdot CF{=}CF_2 \xrightarrow[CH_2Cl_2;\ 30^{\circ}/15\ \text{days}]{[(CH_3)_2CHO]_4Ti/[(CH_3)_2CHCH_2]_3Al}$$



However, subsequent work[29(a)] has shown that the product from these reactions is not a homopolymer of hexafluoropropene. It is, in fact, a co-polymer derived from hexafluoropropene and the solvent.

The X-ray diffraction pattern[29] of the 'Eleuterio' P.H.F.P. indicates that it has an essentially amorphous structure. N.M.R. studies[29] indicate that some head-to-head structure is present, possibly suggesting that some chain termination occurs by coupling.

Polyhexafluoropropene softens in the range 210-250°, and has a rather disappointing thermal stability. However, P.H.F.P. retains a number of the desirable properties of P.T.F.E., i.e. high density, resistance to chemical attack and excellent electrical characteristics. Moreover, polyhexafluoropropene is thermoplastic as a consequence of the 'pendant' $CF_3$ groups; the melt viscosity is such that it is suited to compression or injection moulding.

## (d) POLYTRIFLUOROETHYLENE.

If one fluorine atom on each alternate carbon atom in P.T.F.E. is substituted by a hydrogen atom, a polymer with a very different thermal stability results. That the presence of one hydrogen atom per monomer unit should make the polymer less thermally stable than, as is the case, polyvinylidene fluoride which contains twice as much hydrogen, is at first sight a little surprising. The lower thermal stability of polytrifluoroethylene than that of polyvinylidene fluoride is a direct consequence of the fact that trifluoroethylene itself will undergo radical attack at either end of the double bond.[30-33] Thus the polymer will contain sequences such as

$-CHF-CF_2-CHF-CF_2-$ (i)

$-CHF-CF_2-CF_2-CHF-$ (ii)

$-CF_2-CHF-CHF-CF_2-$ (iii)

Haszeldine[30] attributes the low thermal stability of polytrifluoroethylene to the presence of sequences of the third type. He states that hydrogen fluoride is more readily eliminated from structure (iii) than from the $-CH_2-CF_2-$ structure of polyvinylidene fluoride. HF elimination from structure (iii) would give groups such as $-CF_2-CF=CH-CF_2-$ which could then break down further, presumably by an oxidative process.

Should such a mode of polymerisation ever become feasible, it would be very useful to compare the thermal stability of a polytrifluoroethylene produced by a Ziegler polymerisation, where practically all head-to-tail polymerisation would be expected, with that of polytrifluoroethylene produced by the conventional radical techniques.[34]

## (e) POLYVINYLIDENE FLUORIDE.

In his work on radical addition to vinylidene fluoride, Haszeldine[35] indicates that the structure of polyvinylidene fluoride consists entirely of alternating methylene and difluoromethylene groups:

$$-(CH_2-CF_2-CH_2-CF_2)_n-$$

More recently however, $F^{19}$ N.M.R. studies on the polymer[36,37] have shown that a substantial amount, between ten and twelve per cent, of head-to-head structure exists in polyvinylidene fluoride.

The usual free radical techniques[38,39] are employed to produce polyvinylidene fluoride. Polymerisations have also been effected by gamma-irradiation[21] and in the presence of a boron catalyst, $R_3B$ or $R_2BX$ (R = alkyl, X = halogen).[40] The polymer formed by the usual procedures is a tough transparent, or translucent thermoplastic material which softens between 145° and 160°.[41] It can be cold-drawn to a permanent increase in length of at least 100%, the X-ray diagram changing from the highly crystalline type to the fibre type. The crystallinity of polyvinylidene fluoride, even at low 'n' values, is thought to be due to an orientation of chains brought about by a type of hydrogen bonding.

The methylene groups in the polymer diminish the rigidity of the carbon backbone and also provide sites for cross-linkages to be made. These same methylene groups, however, also confer poor thermal stability on the polymer.

Polyvinylidene fluoride dissolves in cyclohexanone and dimethylformamide, fibres having been spun from this latter solution. By pressing polyvinylidene fluoride at 200°, tough films can be made, having tensile strengths as high as 4,500 p.s.i.[41]

## (f) POLYVINYLFLUORIDE

The homopolymer of the remaining fluorinated ethylene, vinyl fluoride, is the least stable of all the polymers so far mentioned. Haszeldine[42] says that radical attack on vinyl fluoride occurs solely at the methylene end of the molecule, thus indicating that polyvinylfluoride consists entirely of repeating head-to-tail units

$$-[CFH\cdot CH_2\cdot CFH\cdot CH_2]-$$

His theory of thermal instability[30] suggests that this is an intrinsically unstable structure which readily loses HF. It is probable, however, that the structure of polyvinylfluoride is not entirely head-to-tail. The N.M.R. work of Wilson III and Santee Jr.[37] has indicated that 26-32% of head-to-head structure exists in the polymer. The percentage of head-to-head structure in the polymer increases with increasing polymerisation temperature.

Polymerisation of vinyl fluoride has been effected by peroxide initiation,[43,44,45] γ-ray initiation[46] and by the use of trialkyl boron catalysts in aqueous suspension.[47] The polymer produced by peroxide induced polymerisations is in the form of soft, white chunks, which crush readily to a powder. The powder softens between 170° and 190°;

a slightly higher melting point is claimed for the polymer produced by use of boron catalysts. For peroxide initiated material, the melt viscosity decreases with increase in polymerisation temperature;[47] this is almost certainly due, at least partially, to the increasing amount of head-to-head structure.[37]

## (g) OTHER HOMOPOLYMERS.

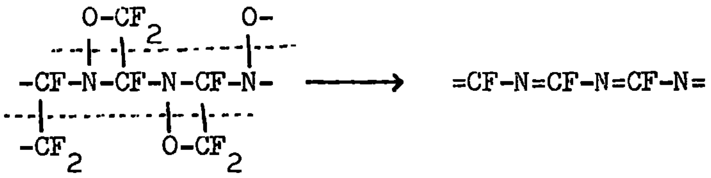
Various homopolymers of fluorinated butadienes have been described in the literature.[48-53] Hexafluoro-1,3-butadiene has been said[48] to be even more difficult to homopolymerise than hexafluoropropene, but a rubbery solid has been obtained under high pressure conditions.[49] Russian workers[50] have obtained up to 90% of solid polymer by carrying out reactions in lead ampoules at 90-130° under 6,000 atmospheres of nitrogen, with a catalyst of diethylperoxydicarbonate. They also mentioned that catalysts such as $Et_3Al$, $Bu_3B$ and potassium persulphate were ineffective. The reluctance of H.F.B. to homopolymerise, and, for that matter, to co-polymerise, is probably not solely because of steric reasons. The electron clouds in the molecule lack mobility, due to the influence of the highly polar fluorine atoms. The π-electrons are localized near each bond, giving rise to a system with, in effect, two isolated double bonds.[51]

A patent[52] claims that, among other olefins, 1,1,2,4,4-pentafluoro-1,3-butadiene has been homopolymerised using a persulphate catalyst. However, no details of the polymer were mentioned. Persulphate catalysis has also been used to polymerise 1,1,2,3-tetrafluoro-1,3-butadiene.[53] $CF_2:CF\cdot CF:CH_2$ was said to polymerise quite easily to high molecular weight polymers which were elastomeric down to quite low temperatures. The polymers melted in the range 225-300° and had good chemical resistance. Moreover, they were insoluble in common organic solvents. Infra-red spectroscopy indicated that the mode of polymerisation was primarily by 1,4-addition. The main objection to the wide use of this material is, of course, the difficulty in obtaining the monomer at a reasonable cost.

Quite an interesting polymer is obtained from 1,1-difluoro-2-methylene-3-(difluoromethylene)cyclobutane.[54] Spontaneous polymerisation is claimed, even at low temperatures, giving a hard, white solid. On heating to 165°, the polymer is converted to a rubbery form, which, however, reverts to a crystalline modification on being worked at room temperature.

Several other fluorinated homopolymers have been made, among them are included fluorinated polystyrenes. Polypentafluorostyrene,[55] $-[C_6F_5CH\cdot CH_2]_n-$, has a similar softening point to polystyrene, but has greater thermal and chemical stabilities. So far, homopolymers of octafluorostyrene have not been reported.

One final homopolymer worth of mention is that which is the result of polymerising trifluoronitrosoethylene.[56] The monomer homopolymerises at 80° and 40 atm., giving a translucent, elastomeric material which, on heating to 400°, evolves carbonyl fluoride. The residue is a pale yellow solid which exhibits absorption at 5·65μ, a wavelength associated with the -CF=N·CF- entity. Haszeldine postulates the following reaction:



$$-CF-N-CF-N-CF-N- \longrightarrow =CF-N=CF-N=CF-N=$$

The high thermal stability of the initial homopolymer is probably due to the presence of the oxazetidine ring.

Although some of the homopolymers described have been elastomeric or thermoplastic materials, various reasons mitigate against their use as such, with the notable exception of polychlorotrifluoroethylene. Polyhexafluoropropene, one of the most stable thermoplastics, both thermally and chemically, is not easily produced, and the monomers for the elastomeric materials described are expensive to produce. However, by co-polymerising two monomers, thermoplastic and elastomeric materials can be obtained comparatively readily. In some systems, one of the monomers will homopolymerise much more readily than the other, e.g. in the system $C_2F_4$ and $C_3F_6$, consequently care has to be taken to ensure that reaction conditions are such that the product is in fact a homogeneous co-polymer and not largely a homopolymer mixed with a small amount of co-polymer.

The discussion of co-polymers will be divided very roughly into two parts; those polymers derived from the polymerisation of tetrafluoroethylene with another monomer, and those resulting from the copolymerisation of vinylidene fluoride with a second olefin.

## CO-POLYMERS DERIVED FROM TETRAFLUOROETHYLENE.[57-72]

The co-polymer derived from the polymerisation of tetrafluoroethylene with chlorotrifluoroethylene can be made with properties varying between those of polychlorotrifluoroethylene and polytetrafluoroethylene since both monomers readily homopolymerise. The patent literature indicates that peroxide initiation is usually employed to effect the co-polymerisation.[57,58] Thus, the patent by Miller[58] describes the co-polymerisation of $C_2F_4$ and $CF_2CFCl$ in a Pyrex tube. The initiator used is trichloroacetyl peroxide, $(CCl_3CO_2)_2$, and a small amount of a 'Freon' solvent is used. The polymerisation took place at $-17^{\circ}$ for 185 hours, giving a product which could be moulded at $300^{\circ}$. As stated above, the properties of the co-polymer can be varied quite easily, but in the polymers which are reasonably thermoplastic, i.e. those which contain more than trace amounts of $CF_2CFCl$, the chlorine atoms are a source of thermal and chemical instability. As is the case with 'Kel-F' and 'Kel-F elastomer', organic bases and metal oxides split off chlorine. One can eliminate this source of instability by replacing the chlorine by a more stable group - the trifluoromethyl group.

The co-polymer of hexafluoropropene and tetrafluoroethylene is by far the most important of the $C_2F_4$ co-polymers. Unlike polytetrafluoroethylene, it is a true thermoplastic, a factor which quite often outweighs its extra cost. The co-polymerisation is initiated usually by peroxides[59,60] although a patent[61] describes the use of hexafluoroazomethane as the radical source. The resulting polymer, usually known as 'Teflon 100-X'*, has a melting point of 290°, which is higher than most other thermoplastics. The structure of 'Teflon 100-X' resembles that of 'Kel-F' in that the main polymer chain has bulky groups (or atoms, in the case of the 'Kel-F') attached to it, which make what would otherwise be the resinous P.T.F.E. chain more mobile. In contrast to the $C_2F_4$-$CF_2CFCl$ co-polymer, which can contain any proportion of chlorotrifluoroethylene, 'Teflon 100-X' can contain a maximum of 50% of hexafluoropropene, i.e. a 'pendant' $CF_3$ group can be attached to every fourth carbon atom at the most. In fact, a $F^{19}$ N.M.R. study[62] on 'Teflon 100-X' at 215° and 310° (i.e. below and above its melting point) has estimated that in fact the co-polymer contains approximately 9 mole % of hexafluoropropene. Because the $CF_3$ group is not as labile as the Cl atom, 'Teflon 100-X' has a higher thermal stability than chlorotrifluoroethylene polymers. Also, its resistance to chemical attack is greater, being similar to P.T.F.E. in this respect. For example, the following reagents produced no change in tensile strength after 120 hours at 205°; acetophenone, piperidine, 20% hydrochloric acid and 30% sulphuric acid.[63] Unlike 'Teflon', 'Teflon-100-X' has a true melting point, hence it can be fabricated by extrusion or injection moulding. The fact that P.T.F.E. must be fabricated by a sintering technique means that some minute pores

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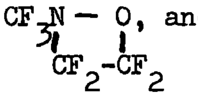
* Registered trade name of E.I. du Pont Ltd.

exist in the finished article, whereas with the co-polymer, the process of melting gives a product virtually free of all voids. Consequently, 'Teflon 100-X' is more impermeable to gases and more free from potential electrical faults than is 'Teflon'. Another advantage of the co-polymer is that insulation of wires can be carried out continuously, whereas the sintering technique necessary with 'Teflon' imposes a limit on the length of insulated wire produced.

The co-polymer between vinylidene fluoride and tetrafluoroethylene is readily made by emulsion polymerisation, using potassium[64] or ammonium[65] persulphate initiators. The product is obtained in the form of a powder at room temperature, which Russian workers[66] have shown to be crystalline, having a rhombic unit cell. This structure remains constant over quite widely varying ratios of $C_2F_4$ to $CH_2:CF_2$. When a powder which contained 34 mole % of $C_2F_4$ was heated to 100°, an extensible rubber resulted.[64] When a product containing largely $C_2F_4$ was subjected to 300° for 5 minutes, no discolouration was observed.[65] However, increasing the proportion of vinylidene fluoride in the co-polymer does, as might be expected, lead to a lower degree of stability.

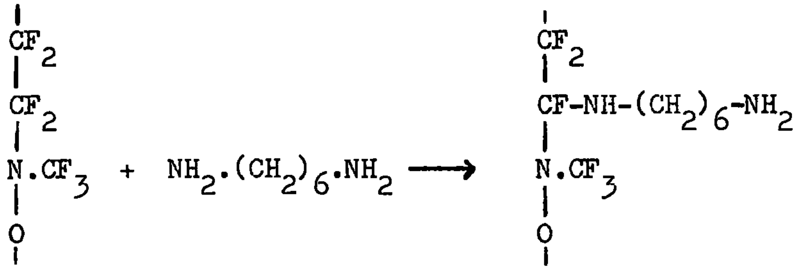
Judging by the lack of references to the tetrafluoroethylene-vinylidene fluoride co-polymer in the more recent literature, industry sees no great future for it.

Fluorocarbon polymers have generally been investigated for their solvent resistance and high thermal stability. However, the low temperature recovery from elastic deformation of these polymers is often rather tardy. The co-polymer between tetrafluoroethylene and trifluoronitrosomethane[67-71] is interesting in that it has very good low temperature flexibility (Tg = -51°C). Haszeldine[67] reported that $C_2F_4$ combined slowly and quantitatively with $CF_3NO$ in the dark at room temperature to give 30-65% of perfluoro-2-methyl-1,2-oxazetidine,

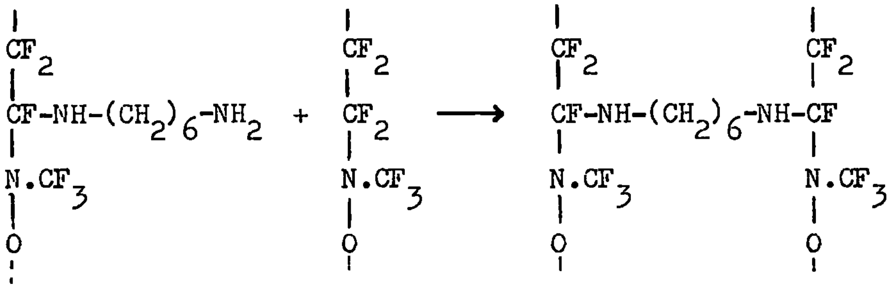


$\begin{array}{l} CF_3N - O \\ \quad\;\; | \quad\;\; | \\ \quad CF_2-CF_2 \end{array}$, and 35-70% of an almost colourless viscous oil containing a 1:1 ratio of the starting olefins. A lowering of the reaction temperature produced a greater percentage of polymeric material.

Solid polymers are obtained by the low temperature bulk co-polymerisation of the monomers (e.g. Ref. 68,69). The reaction mechanism has been shown to be free radical rather than ionic by the lack of effect of Lewis acids and the pronounced effect of radical transfer agents and inhibitors. The co-polymer is said to be colourless and transparent, with an amorphous structure.[70] It is insoluble in all hydrocarbon solvents, but dissolves in some fluorocarbon solvents. The physical properties of the polymer can be improved by vulcanisation. The vulcanisation can be brought about by treatment with primary or secondary diamines.[69,70] Thus, hexamethylene diamine quickly gels a solution of the co-polymer in the cyclic ether $C_8F_{16}O$. In view of the known lability of fluorines on carbon atoms $\alpha$ to nitrogen, the cross-linking mechanism can be visualised as follows:

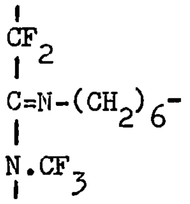


$$\begin{array}{l} | \\ \mathrm{CF_2} \\ | \\ \mathrm{CF_2} \\ | \\ \mathrm{N.CF_3} \\ | \\ \mathrm{O} \\ | \end{array} + \mathrm{NH_2.(CH_2)_6.NH_2} \longrightarrow \begin{array}{l} | \\ \mathrm{CF_2} \\ | \\ \mathrm{CF\text{-}NH\text{-}(CH_2)_6\text{-}NH_2} \\ | \\ \mathrm{N.CF_3} \\ | \\ \mathrm{O} \\ | \end{array}$$



$$\begin{array}{l} | \\ \mathrm{CF_2} \\ | \\ \mathrm{CF\text{-}NH\text{-}(CH_2)_6\text{-}NH_2} \\ | \\ \mathrm{N.CF_3} \\ | \\ \mathrm{O} \\ | \end{array} + \begin{array}{l} | \\ \mathrm{CF_2} \\ | \\ \mathrm{CF_2} \\ | \\ \mathrm{N.CF_3} \\ | \\ \mathrm{O} \\ | \end{array} \longrightarrow \begin{array}{llr} | & & | \\ \mathrm{CF_2} & & \mathrm{CF_2} \\ | & & | \\ \mathrm{CF\text{-}NH\text{-}(CH_2)_6\text{-}NH\text{-}} & & \mathrm{CF} \\ | & & | \\ \mathrm{N.CF_3} & & \mathrm{N.CF_3} \\ | & & | \\ \mathrm{O} & & \mathrm{O} \\ | & & | \end{array}$$

Possibly some further elimination of HF occurs, giving such unsaturated structures as



$$\begin{array}{l} | \\ \mathrm{CF_2} \\ | \\ \mathrm{C{=}N\text{-}(CH_2)_6\text{-}} \\ | \\ \mathrm{N.CF_3} \\ | \end{array}$$

Other co-polymers of tetrafluoroethylene have been described. For example, a patent[72] deals with the production of heat resistant, thermoplastics by the co-polymerisation of tetrafluoroethylene with 1,1-dihydroperfluoroalk-1-enes in an aqueous medium using free radical initiators.

The co-polymers of tetrafluoroethylene, though they may be thermoplastic materials, are not usually elastomeric in nature, with the notable exception of the $C_2F_4$-$CF_3NO$ co-polymer. Inclusion of methylene groups into the polymer chains tends to produce elastomeric materials, which, by virtue of these same methylene groups, can be cross-linked to give useful materials.

## VINYLIDENE FLUORIDE CO-POLYMERS

There are two important co-polymers of vinylidene fluoride, one being 'Kel-F elastomer' (co-polymer of vinylidene fluoride and chlorotrifluoroethylene) and the other 'Viton A' (the co-polymer of vinylidene fluoride and hexafluoropropene).

Chlorotrifluoroethylene and vinylidene fluoride have been co-polymerised in a number of ways.[73-80] Peroxide or redox catalysts are generally used in aqueous emulsion or suspension, or bulk polymerisations, giving polymers which can be made to contain various proportions of the two monomers. Products from polymerisations in aqueous media are in the form of an elastomeric sponge which can be cross-linked and moulded. The structure of the co-polymer is essentially of the type $-CH_2CF_2.CF_2CFClCH_2CF_2-$, but probably a small proportion of the type $-CF_2CFClCF_2CH_2-$ does occur. The good elastic and mechanical properties of the co-polymer are ascribed to the presence of the methylene groups in the polymer chains.[73] The low temperature properties of the elastomer are especially good; it is still flexible at $-57^{\circ}$. Before cross-linking, the elastomer is soluble in several organic compounds, esters, ether-alcohol mixtures and ketones. Thermal stability and resistance to chemical reagents generally is good, but basic compounds, especially amines, do tend to attack the co-polymer.

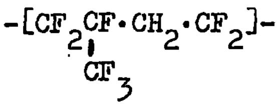
Table 2. The Effect of Fluids on a typical Kel-F elastomer.[77]

| Reagent and Conditions | Tensile Strength (P.S.I.) | Increase in Volume |
|---|---|---|
| Untreated Elastomer | 3750 | 0 |
| Silicon Fluid, 400°F/ 70 hrs. | 2475 | +6.9% |
| Diester Fluid, 350°F/ 70 hrs. | 554 | +105% |
| 70/30 iso-octane/toluene 70 hrs. at rm.tp. | 1610 | +24% |
| 'Red' $HNO_3$, 70 hrs/Rm.tp. | 580 | +22% |

Cross-linking of the elastomer can be carried out in a number of ways. Among the methods available are the use of organic peroxides,[73] polyamines,[73] isocyanates,[78] isothiocyanates,[78] basic metal oxides[76] and inorganic polysulphides.[76] A patent[81] describes a method of improving the scorch resistance of the vulcanisate by incorporating a compound which liberates carbon dioxide on heating to 100-300°F, for example, using hexamethylene diamine as cross-linking agent, a better product is obtained if a small proportion of ammonium oxalate or benzoyl peroxide is added. The actual cross-linking process probably occurs by a mechanism rather similar to that for 'Viton', which will shortly be described.

Although Kel-F elastomer is a step in the right direction towards the ideal elastomeric material, i.e. a Teflon-like material with some pendant bulky groups (or atoms) and just sufficient hydrogen to effect cross linking, the presence of chlorine in the polymer chain impairs really high temperature and chemical resistance. If the chlorine is replaced by a less labile entity, a more stable polymer should result. When the substituent is trifluoromethyl, the resulting product is known as 'Viton A'*.

As has been indicated, 'Viton A' is a co-polymer of vinylidene fluoride and hexafluoropropene. The composition of this co-polymer can be more readily controlled than that of the previous one simply by altering the amount of $C_3F_6$ in the system, since this monomer does not homopolymerise. The maximum possible amount of $C_3F_6$ in the polymer is 50 mole %, corresponding to a structure



$$-[CF_2\underset{\displaystyle CF_3}{\underset{|}{CF}}\cdot CH_2\cdot CF_2]-$$

In fact, the structure of Viton has been very thoroughly investigated by N.M.R.[82] Ferguson showed the dominant structure to be that indicated above, but with some short polyvinylidene fluoride chains incorporated.

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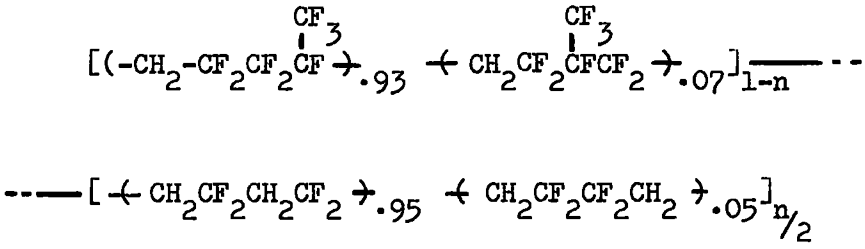
* Trade name of E.I. du Pont Ltd.

Little or no homopolymerisation of hexafluoropropene occurs, i.e. there are no adjacent $C_3F_6$ units. He deduced the structure of Viton to be



$$[(-CH_2-CF_2CF_2\overset{\overset{CF_3}{|}}{C}F-)_{.93}\;-(CH_2CF_2\overset{\overset{CF_3}{|}}{C}FCF_2-)_{.07}]_{\overline{1-n}}\text{-}\,\text{-}$$

$$\text{-}\,\text{-}\text{---}[-(CH_2CF_2CH_2CF_2-)_{.95}\;-(CH_2CF_2CF_2CH_2-)_{.05}]_{n/2}$$

where n is the mole fraction of vinylidene fluoride.

Viton was first described in 1957, when Dixon and his co-workers[83] at du Ponts reported the co-polymerisation of vinylidene fluoride and hexafluoropropene. An emulsion technique, with a persulphate/bisulphite catalyst, was employed to effect the polymerisation. Temperatures up to 100° were used; reaction was complete in about twenty minutes, giving a latex from which the solid polymer is coagulated by addition of an electrolyte. The polymer is then in the form of a white powder, but it becomes clear on drying and pressing. X-ray studies[83] have shown the co-polymer to be essentially amorphous, and there is little tendency to the formation of a crystalline structure on stretching. Co-polymers have been prepared up to the theoretical maximum of 50 mole % of hexafluoropropene. The ability of the co-polymer to recover from elastic deformation increases as the percentage of $C_3F_6$ increases, but tensile strength decreases.

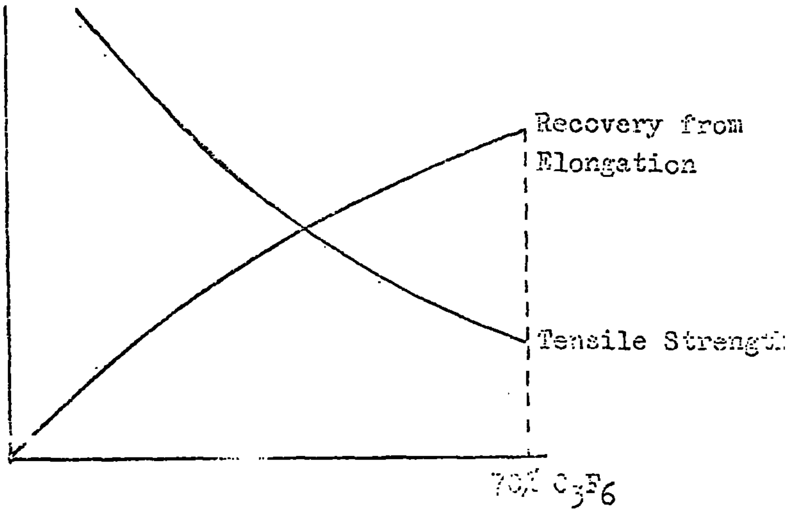


Fig. 1

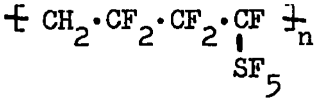
Physical properties vs. % composition by weight

Viton elastomers are resistant to most solvents, with the exceptions of esters and ketones. They retain their elasticity down to -20 to -25° and may be used up to 315° for short periods.[84]

Low molecular weight co-polymers have been made;[85,86] they usually exist as liquids, greases or waxes and are useful as plasticizers for fluorocarbon elastomers. The low molecular weight co-polymers may be vulcanized to give solid products.

Vulcanization of the raw Viton elastomers gives products with much improved mechanical properties. (A discussion of the vulcanization, or cross-linking, of Viton follows later in this section). Briefly, the cross-linking of Viton can be effected in any one of three ways; the most usual method is by the use of amines, peroxide and radiation cures are less frequently used. The vulcanized product resulting from a peroxide or radiation cure is only slightly coloured, amine vulcanizations usually produce a very dark material. The resistance of the vulcanized Viton to chemical attack in general is very good; it is extremely resistant to oxidative attack. However, ketones and esters do swell the vulcanizate, thus placing restrictions upon its use. A very important point is that it is not attacked by fuel oils and hydraulic fluids, even at quite high temperatures. Thus, Viton is finding increasing use in the aircraft and automotive industries. Peroxide or radiation cured elastomer is more resistant to corrosive chemicals than is the amine cured material, this fact suggests that degradation occurs at the site of the cross-link.

Other co-polymer incroporating vinylidene fluoride have been made; one quite interesting co-polymer is that derived from perfluorovinylsulphur pentafluoride and vinylidene fluoride.[87] An aqueous persulphate/bisulphite initiating system was used, giving a white rubbery solid containing 51•5 mole % $CF_2{:}CF{\cdot}SF_5$ and 48•5 mole % $CH_2{:}CF_2$. The co-polymer was stated to be stable to 250° in air. Its structure is postulated as



$$\left[ CH_2{\cdot}CF_2{\cdot}CF_2{\cdot}\underset{\displaystyle SF_5}{\underset{|}{CF}} \right]_n$$

analogous to Viton A.

Table 3.[84] Resistance of Viton A (vulcanized) to Chemical Reagents; 7 days immersion at 77°F

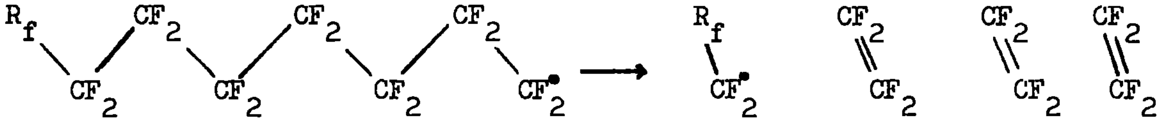
| Reagent | Volume Increase, % | Tensile Strength, P.S.I. | Max. Elongation |
|---|---|---|---|
| None | - | 2300 | 320 |
| Acetone | 374 | - | - |
| Aniline | 5 | 1725 | 280 |
| Benzene | 22 | 1980 | 300 |
| Carbon Disulphide | 3 | 2100 | 370 |
| Carbon Tetrachloride | 2 | 1940 | 315 |
| Cyclohexanone | 350 | - | - |
| D.M.F. | 375 | - | - |
| Dioxan | 205 | - | - |
| EtOAc | 375 | - | - |
| Ethanol | 2 | 1920 | 360 |
| Methylene Chloride | 30 | 775 | 240 |
| Pet. Ether | 3 | 2150 | 320 |
| Trichloroethylene | 6 | 1840 | 355 |
| Glacial Acetic Acid | 180 | - | - |
| 37% HCl | 32 | - | - |
| 48% HF | 12 | 2200 | 360 |
| 90% $HNO_3$ | 24 | 2000 | 340 |
| Fuming $H_2SO_4$ | 12 | 1780 | 290 |
| 50% NaOH | 0 | 2600 | 335 |

## Thermal stability of fluorine containing polymers.[88-91]

Thermal stability studies on polymers have been carried out primarily with the object of correlating chemical structure with the thermal stability. By far the most stable of the organo-fluorine polymers are the fully fluorinated polytetrafluoroethylene and the co-polymer of hexafluoropropene and tetrafluoroethylene. Replacing one of the fluorine atoms in each monomer unit of P.T.F.E. by a chlorine, i.e. 'Kel-F', causes the stability in vacuum to drop by approximately 150°. Substituting another fluorine by hydrogen causes a further drop in stability of 40°. These facts indicate that fully fluorinated structures are, on the whole, much more stable than the polymers containing other atoms. However, Wall[92] has reported very disappointing stabilities for perfluoro- polymers with side-chains.

Of the elastomeric materials previously discussed, the co-polymer of vinylidene fluoride and hexafluoropropene is the most stable. Replacing the pendant $CF_3$- group in Viton by Cl (giving Kel-F elastomer) decreases the thermal stability by about 60°. The vinylidene fluoride/ chlorotrifluoroethylene co-polymers show an increase in stability as the proportion of vinylidene fluoride increases.

Madorsky[88] and co-workers have studied the thermal stabilities of various homopolymers and have found their stabilities to increase in the order poly-$CH_2$:CHF $<$ poly-$C_2H_4$ $<$ poly-$CF_2$:CFH $<$ poly-$CF_2$:$CH_2$ $<$ poly-$C_2F_4$. Polytetrafluoroethylene can be pyrolysed to give practically 100% monomer; this occurs when the pyrolysis is carried out at low pressures (under 5 cms. of mercury). Higher pressures yield increasing amounts of hexafluoropropene, octafluoro-cyclobutane and other fluorocarbons. The mechanism of degradation of P.T.F.E. was assumed by Madorsky[88] to involve firstly chain scission, and then 'unzipping' of monomer units at free radical chain ends.



However, more recent work[93] has indicated that 'unzippering' occurs with the formation of difluoromethylene diradicals. Hydrofluoro-polymers tend to eliminate hydrogen fluoride, forming double bonds in the polymer chain. Further degradation occurs by the breaking of a C-C bond in the β position. Polytrifluoroethylene and polyvinyl fluoride degrade with complete volatilisation, but polyvinylidene fluoride stabilises to some extent at about 70% weight loss. W.W. Wright[90,91] has studied stabilities of fluorocarbon polymers quite thoroughly. His results, which are in substantial agreement with those of Madorsky, are summarised in Figures 2 and 3.

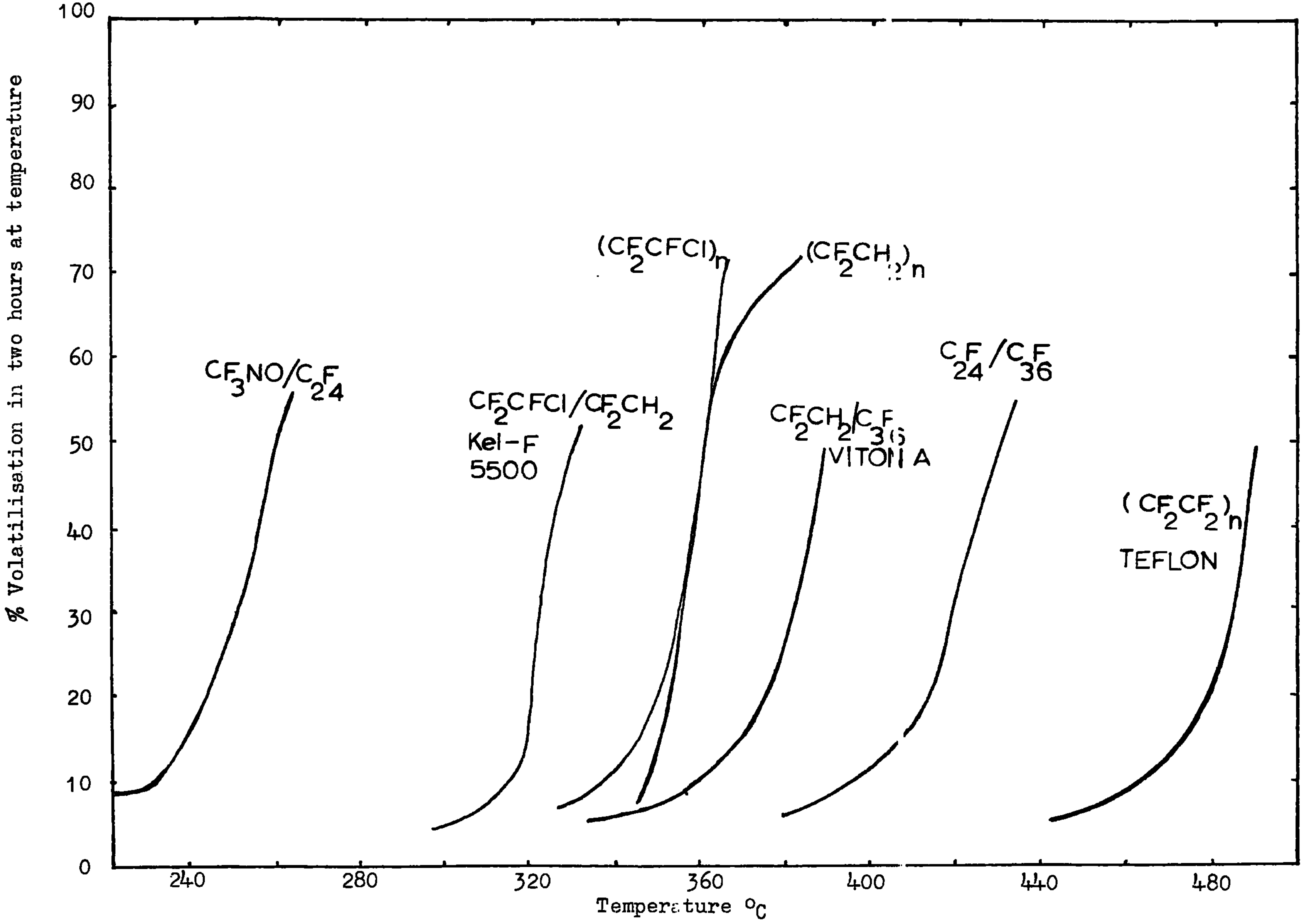
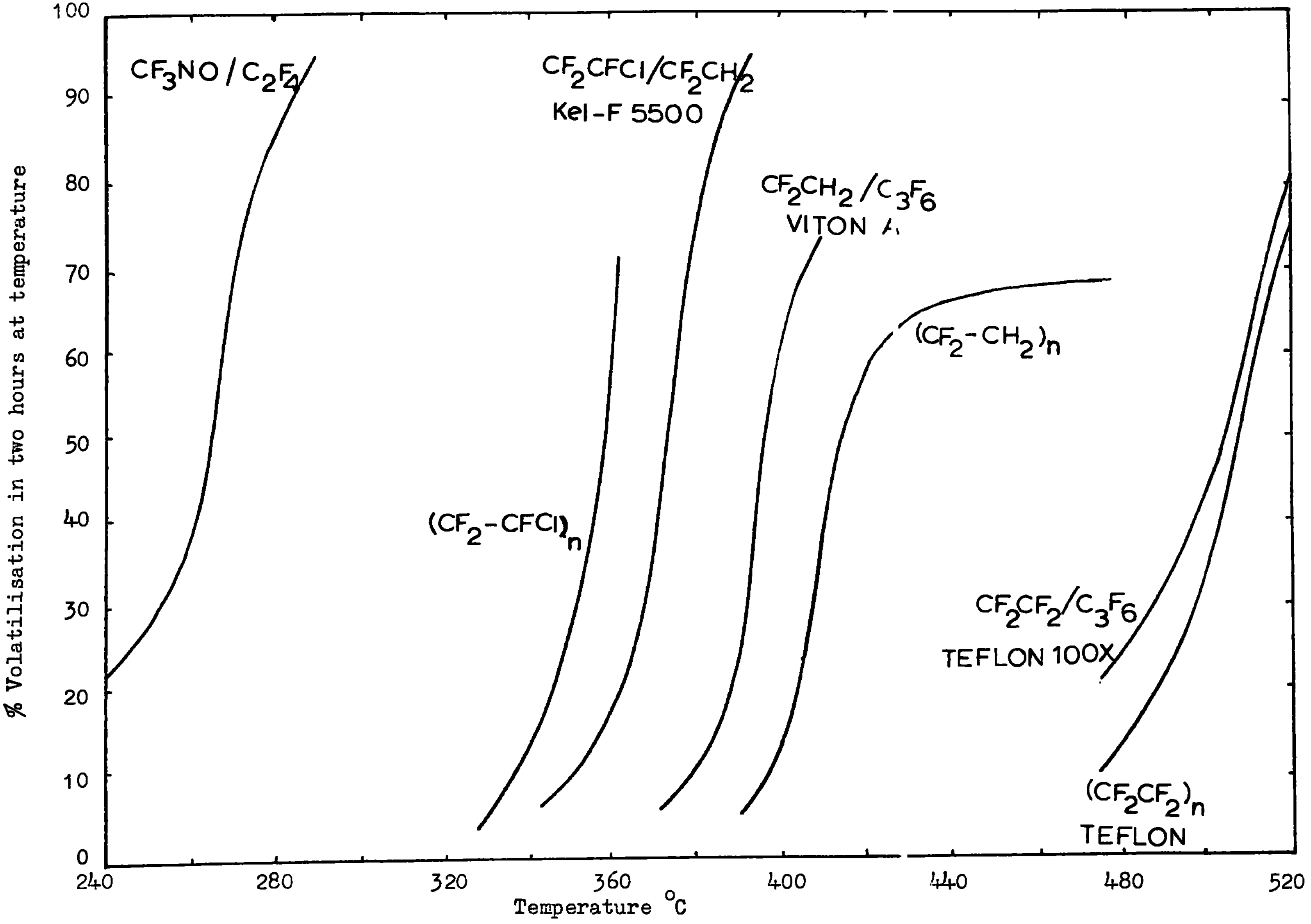


**Fig. 2** THERMAL STABILITIES OF VARIOUS FLUORINE - CONTAINING POLYMERS IN OXYGEN



<u>Fig. 3</u> THERMAL STABILITIES OF VARIOUS FLUORINE- CONTAINING POLYMERS IN VACUUM

## The Cross-linking of Viton A.

### (i) The purpose of Vulcanisation.

The product from the co-polymerisation of vinylidene fluoride with hexafluoropropene can not be utilised in the form in which it is first obtained. The raw elastomer can be compared to coagulated latex, which must be vulcanised before it can be used in the manufacture of, for example, motor vehicle tyres. Vulcanisation is the process whereby the high polymer chains are coupled by short cross-links to form a three dimensional network. These cross-links are usually only present in very small proportions, but their existence greatly improves the mechanical characteristics of the polymer. For polymers which are intended for service under high temperature and chemically degradative conditions, it is essential that the nature of the cross-link should be such that it is as least as stable as the polymer chain. The old adage 'A chain is only as strong as its weakest (cross-) link' is very true in these circumstances. Cases are known in which the vulcanisate is appreciably less stable (both thermally and chemically) than the raw polymer, Viton A being an important example. One must be mindful that during the vulcanisation process, the possibility exists that the main polymer chain may be modified in the region of the cross-link, giving a basically less stable system than that existing in the raw polymer. It has also been found that where a number of cross-linking systems are available, the thermal stability of the vulcanisate depends greatly upon the actual system used (see Table 4).

Table 4

Thermal stabilities of Butyl rubber vulcanisates

| Maximum temperature ($^{o}F$) for intermittent use. | Cross-linking system |
|---|---|
| 250 | Thiuram-thiazole |
| 275 | Sulphur-donor |
| 300 | Quinoid |
| 350 | Methylolphenol resins activated by metal halides |

## Methods of vulcanising Viton A.

Because of the high chemical stability of Viton A elastomer, the formation of cross-links is of necessity a very difficult process. However, in spite of the relative inertness of Viton A, various methods have been devised to effect the formation of cross-links. An ideal curing system is one which has no, or very little, curing activity at the compounding temperature, but which produces the maximum number of cross-links in the minimum of time at the curing temperature. Three main methods have been used to produce the cross-links, (i) the action of amines, (ii) the action of peroxides, and (iii) the action of ionizing radiations. None of these general methods can be said to be the ideal method, however, the amine cure affords the most convenient way of introducing cross-links into the system. Consequently, the radiation and peroxide curing systems are but infrequently used.

Aliphatic diamines were the first curing agents used for Viton A.[94] They were very difficult to use since they were extremely 'scorchy" i.e. they produced rather extensive degradation, although effective vulcanisates were obtained. To reduce the scorching tendency, derivatives of diamines are used.[95] The most commonly used examples are the carbamate

$$NH_3^+(CH_2)_6NHCO_2^-$$

and the bis-cinnamylidene derivatives of hexamethylenediamine. Hexamethylenediamine carbamate is quite unreactive at room temperature, but decomposes rapidly in the range 55° to 80°C. to produce the free diamine. Ethylenediamine carbamate has also been used; cures produced by ethylenediamine carbamate are less liable to scorch than those involving hexamethylenediamine. Physical measurements (stress-strain tests and compression set results) have shown that 0·85 moles of ethylenediamine carbamate produces a state of cure equal to that of 1 mole of hexamethylenediamine carbamate.

Not only diamines will effect a cure of raw Viton elastomer, monoamines also can be used. These latter compounds usually require rather higher processing temperatures than do the diamines, hence their use is somewhat restricted. It should be noted that primary, secondary and tertiary monoamines all form cross-links in Viton. A discussion of the mechanism whereby the cross-links are formed follows later.

Monoamines are used in conjunction with diamines to give vulcanisates which have greatly enhanced states of cure compared to the product obtained when the diamine alone is used.[96] Tertiary monoamines are particularly effective co-curing agents. Effective cross-links can also be formed when a tertiary amine - dithiol curing is employed.[97] Dithiols do not cross-link Viton when used alone, but used in combination with tertiary amines, vulcanisates are produced which exhibit good properties except with respect to high temperature ageing. Apart from this last factor, the vulcanisate is essentially the same in physical properties as that produced by the more firmly established diamine cure.

High energy radiation can be used to cure Viton A. During the curing process hydrogen fluoride is evolved. $\beta$-radiation from a Van der Graaff generator[96] or $\gamma$-irradiation by a cobalt-60 source[98] have both been used. Precautions must be taken to remove oxygen from the system as completely as possible in order to avoid the incorporation of functional groups into the polymer. The radiation cure suffers from all the disadvantages inherent in the use of high energy radiation; the vulcanisate in no way possesses properties which might compensate for the hazards involved with the use of radiation.

Peroxides, as has already been stated, will bring about cross-link formation in Viton. Benzoyl peroxide is the most widely used peroxide (e.g. Ref. 84), but others have been used. A patent[99] describes the use of up to 10% of cumyl peroxide as a curing agent. The disadvantages of the peroxide curing system are that the process is very scorchy and the degree of cross-linking is only moderate.

## The technology of the vulcanisation of Viton A.

Whatever the curing system employed for the raw elastomer, the procedure followed is always very much the same. In the first place, the elastomer is compounded on conventional rubber processing equipment with fillers, metal oxide acid acceptor and curing agent. The metal oxide is almost invariably magnesium oxide. The required article is then formed by moulding in a press for a period of 10 to 60 minutes at 130° to 150°. The suggested reason for this preliminary cure is to develop sufficient cross-links in the sample to prevent sponging by the release of trapped air and decomposition products during the following oven cure. The oven cure takes place during 15 to 24 hours at 200°. Optimum properties are only developed in an air circulating oven. This latter point is important - very poor degrees of vulcanisation are produced if a closed oven is used.

Viton cannot be cross-linked to an effective state of cure by any known curing agent, unless there is included in the curing formulation an acid acceptor such as magnesium or zinc oxide. This is true equally of radiation, peroxide and all known amine cures. The dithiol/amine curing system is especially specific in that magnesium oxide alone will act as an acid acceptor. Magnesium oxide alone has no curing effect on Viton.

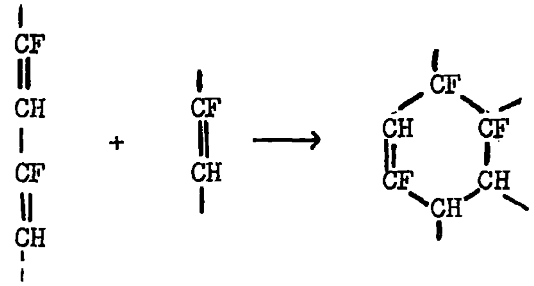
A typical[84] curing formulation for Viton is shown below:

Table 5

| | | | | |
|---|---|---|---|---|
| Viton A | 100 | parts | by | weight |
| Magnesium oxide | 15 | " | " | " |
| Carbon black | 20 | " | " | " |
| Hexamethylenediamine carbamate | 1 | " | " | " |

Situations arise where it is not always possible or desirable to employ an oven cure for Viton. A curing system which is effective at low temperatures is very desirable. Such a system is described in a patent.[100] Viton is compounded with carbon black, magnesium oxide and diallylamine and subjected to a temperature of about 130° for two hours. The 'activated' Viton is washed with water and then dissolved in an equal weight of ethyl methyl ketone to which is added about 1·5% hexamethylenedithiol and 0·5% tri-amyl amine. This mixture can be applied with a pressure gun or a trowel, hardening after seven days.

Obviously, to produce better curing systems for both room and high temperature cross-linking, an understanding of the actual cross-linking mechanism is required. In some cases, the cross-linking mechanism is fairly easily visualized. When Viton is irradiated with either $\beta$ particles or $\gamma$ rays, sufficient energy is available not only to break chemical bonds, but also to remove electrons from the main carbon-carbon polymer chain. Hydrogen fluoride is evolved, leaving olefinic double bonds. Smith[96] has suggested that cross-linking occurs by thermal elimination of hydrogen fluoride from neighbouring atoms, during the post curing stage, leading to conjugated double bonds. The conjugated system then reacts with a double bond in an adjacent chain by a Diels-Alder reaction leading to a fluorinated cyclohexene:



There is some slight evidence for this suggested mode of cross-linking, but it is by no means unambiguous. It is a feature of polymers that, upon irradiation, not all the radicals produced enter into reaction at once.[101] A number of radicals remain free to react with each other over a period of time. It is entirely possible that cross-links are formed by the reaction of radicals in neighbouring chains.

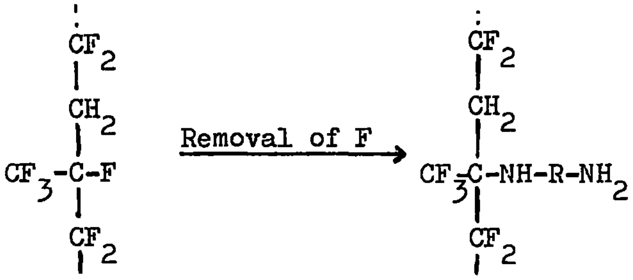
$$-CH_2\cdot CF_2\cdot CF(CF_3)\cdot CH_2CF_2- \xrightarrow{\alpha \text{ or } \beta} -CH_2\cdot CF_2\cdot CF(CF_3)\cdot \dot{C}H\cdot CF_2-$$

Linking of two chains

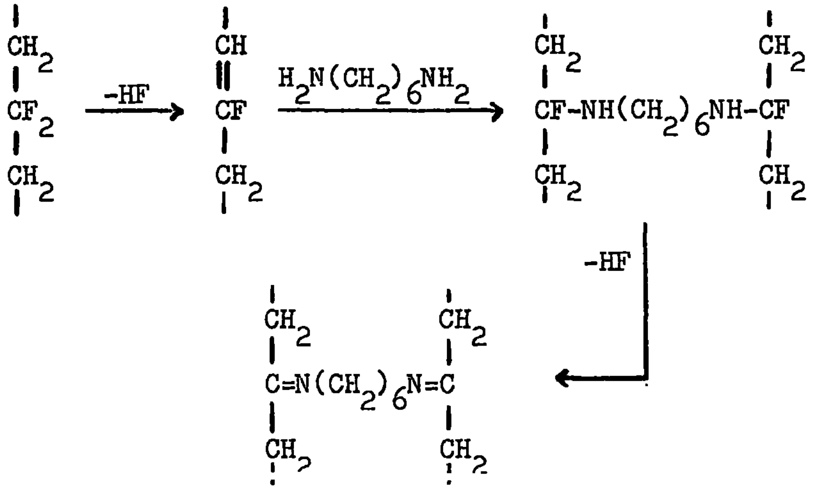
Although some degree of cross-linking is achieved during irradiation, optimum properties are not realised unless the polymer is subsequently subjected to the high temperature post curing cycle. The reaction of the free radicals remaining after the irradiation will be accelerated by heating. The formation of cross-links during the post curing cycle comes to a definite end after a few hours at 200°; this fact ties in rather better with the idea that cross-linking occurs by reaction of the residual free radicals than by heat induced dehydrofluorinations.

Cross-linking by peroxides probably follows a somewhat similar path to that of radiation induced cures. It is, of course, quite possible that cross-linking occurs by a combination of both processes, reaction at unsaturated sites and combination of radicals.

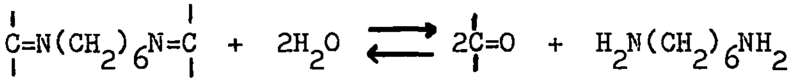
Where amines are used as curing agents, the mechanism of vulcanisation can be envisaged as either a simple alkylation involving removal of a fluorine atom although there is no evidence in the literature for this.



It is much more probable that a base catalysed elimination of hydrogen fluoride producing unsaturation in the polymer chain. The actual cross-linking step would be the addition of the amine across the double bond. A discussion of the reactions of amines with olefinic double bonds follows later. It has, in fact, been shown[102] that primary diamines react further than simply adding across the double bonds. Di-imine formation has been postulated by further elimination of HF; the existance of an imine structure was demonstrated by hydrolysis, when 70% of the amine originally present in the vulcanisate was recovered. In summary, the cross-linking of Viton by diamines is a three stage process:



The existance of the imine structure, with its relative susceptibility to hydrolysis, provides the reason for the necessity of using an air circulating oven during the post cure. Water, from the neutralisation of hydrogen fluoride by magnesium oxide, must be removed to prevent the equilibrium

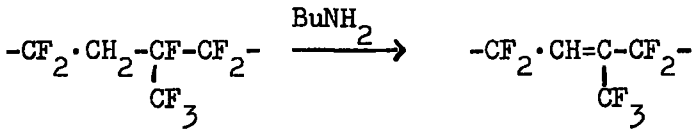


$$>C=N(CH_2)_6N=C< + 2H_2O \rightleftharpoons 2>C=O + H_2N(CH_2)_6NH_2$$

from occurring, so that a permanent cross-link is established.

A similar situation probably exists with the tertiary amine/dithiol curing system. The tertiary amine probably eliminates hydrogen fluoride from the polymer chain, leaving a double bond to which the thiol then adds.

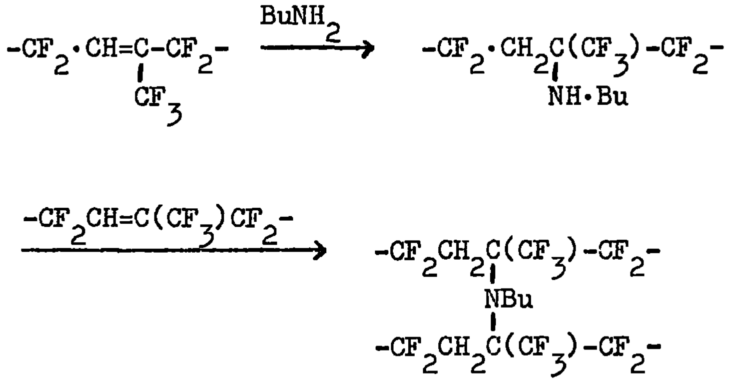
Monoamines, as has already been stated, will effect a cure of Viton. It is readily seen just how a primary monoamine can effect the cross-linking, but the mechanism whereby secondary and tertiary monoamines form cross-links is rather more obscure. Primary monoamines can be visualised as forming cross-links according to two schemes, (a) and (b). The first step in each case is the same.



$$-CF_2\cdot CH_2-\underset{CF_3}{\underset{|}{C}}F-CF_2- \xrightarrow{BuNH_2} -CF_2\cdot CH=\underset{CF_3}{\underset{|}{C}}-CF_2-$$

Then either

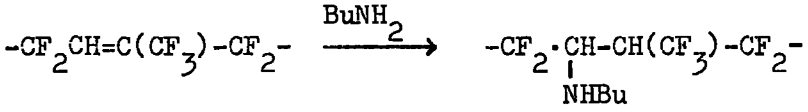
(a)



$$-CF_2\cdot CH=\underset{CF_3}{\underset{|}{C}}-CF_2- \xrightarrow{BuNH_2} -CF_2\cdot CH_2\underset{NH\cdot Bu}{\underset{|}{C}}(CF_3)-CF_2-$$

$$\xrightarrow{-CF_2CH=C(CF_3)CF_2-} \begin{array}{c} -CF_2CH_2C(CF_3)-CF_2- \\ | \\ NBu \\ | \\ -CF_2CH_2C(CF_3)-CF_2- \end{array}$$

Or (b)



$$-CF_2CH=C(CF_3)-CF_2- \xrightarrow{BuNH_2} -CF_2\cdot \underset{NHBu}{\underset{|}{C}}H-CH(CF_3)-CF_2-$$

etc.

Reaction (a) is in agreement with the mode of addition proposed by Pruett and co-workers[103] for butylamine to fluoro-olefins.

Secondary and tertiary monoamines cause cross-linking, according to Smith,[96] merely by producing unsaturated sites in neighbouring polymer chains, which then react without further involvement of the amine. A more complete discussion of cross-linking by tertiary amines follows in the second chapter.

The simple pictures of cross-linking outlined above can not be the only processes that occur when Viton is vulcanised. One objection to this simple view is that Viton is unusual among elastomers in that its resilience at room temperature decreases with increased state of cure. As the temperature is raised to 100°, this tendency is reversed to give the more usual increase in resilience with increased state of cure. This behaviour is not that of an elastomer which is cross-linked simply by a bifunctional reagent across adjacent chains. However, this anomalous behaviour might well be expected of a polymer network formed by simultaneous cross-linking and chain scission, especially if it assumed that the amount of chain scission increases with increase in the state of cure.

In view of the complex processes that obviously occur during the vulcanisation of Viton, and also since a more complete understanding of the vulcanisation process could possibly lead to a more efficient cross-linking agent, considerable effort has been devoted to studies of the cross-link process.

Most of the work has been carried out by either J.F. Smith and co-workers at du Ponts, or by K.L. Paciorek and co-workers of the Wyandotte Chemicals Corporation.

## Methods of study of the cross-linking processes in Viton A.

Studies aimed at elucidating the processes occurring in Viton during vulcanisation have been mainly carried out on the elastomer itself, either in solution or in the mass. Some work has also been carried out on model compounds.

Both Smith[96] and Paciorek[104] have carried out work on the reactions of solutions of raw Viton elastomer in either tetrahydrofuran or diglyme with various amines. Primary amines were shown to cause the elimination of hydrogen fluoride more quickly than did secondary amines, and much more quickly than tertiary amines.

By means of viscosity measurements, the chain scission caused by tertiary amines was followed during the course of reactions. The viscosity of solutions fell fairly quickly at first, then after about 25 hours at room temperature the fall became more gradual. After 200 hours, the intrinsic viscosity had fallen to approximately one half of its initial value.

It is probable that similar degradation occurs with primary and secondary amines, but Smith was unable to demonstrate this in his solution experiments because of the tendency towards gel formation. It can be seen from the figures that the fall in the rate of HF elimination very roughly occurs after the same time(25 hours) as the change in the rate of fall of intrinsic viscosity.

Paciorek's work on solutions of Viton in diglyme substantially confirmed the above work. She, too, found a marked difference in the rate of dehydrofluorination by primary amines as compared with the rate by secondary and tertiary amines. Her results are summarised in Table 6. All the amines resulted in strong discolouration of the solutions at room temperature. Of the amines investigated, only hexamethylenediamine

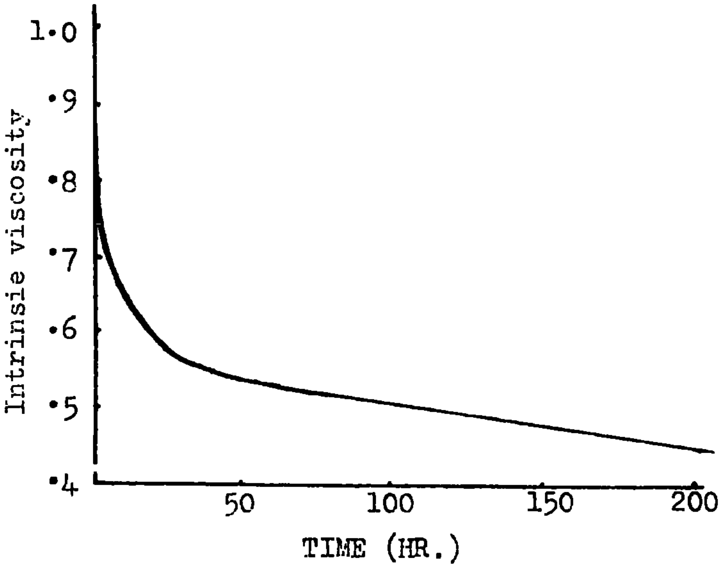


Fig. 4. Effect of treatment with trimethylamine on intrinsic viscosity of Viton A.

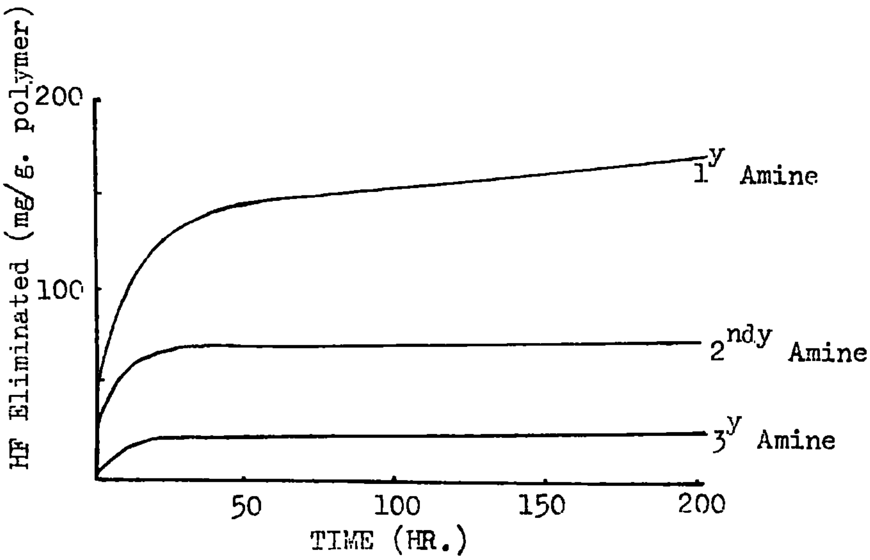


Fig. 5. Rate of elimination of HF from Viton A by action of amines.

| Amine | Amine, %[a] | Temp. °C | Crystalline Precipitate | Gel | Conversion to hydro-fluoride, % | Reaction time, days |
|---|---|---|---|---|---|---|
| Butylamine | 18 | 25 | Slight | No | 57[b] | 6 |
| Butylamine | 89 | 25 | Yes | No | 28[b] | 18 |
| Dibutylamine | 89 | 25 | Yes | No | 45[c] | 20 |
| Dibutylamine | 18 | 190 | No | Little | - | 1 |
| Piperidine | 89 | 25 | No | No | 47[b] | 8 |
| Piperidine | 18 | 190 | No | Yes | - | 1 |
| Triethylamine | 88 | 25 | No | No | 7[c] | 17 |
| Triethylamine | 19 | 190 | No | No | - | 1 |
| Diethylcyclohexylamine | 88 | 25 | No | No | 5[c] | 20 |
| Diethylcyclohexylamine | 18 | 190 | No | Little | - | 1 |
| Hexamethylenediamine | 18 | 25 | No | Yes | 72[b] | 1 |
| $(CH_3)_2NCH_2CH_2N(CH_3)_2$ | 88 | 25 | Trace | No | 7[b] | 12 |
| $(CH_3)_2NCH_2CH_2N(CH_3)_2$ | 18 | 190 | Trace | No | - | 1 |

[a] Based on tertiary fluorine content of the polymer and equivalent weight of amine.

[b] Based on the formation of amine dihydrofluoride.

[c] Based on the formation of amine monohydrofluoride.

TABLE 6

resulting in gel formation at low temperatures, although piperidine at 190° produced gelation.

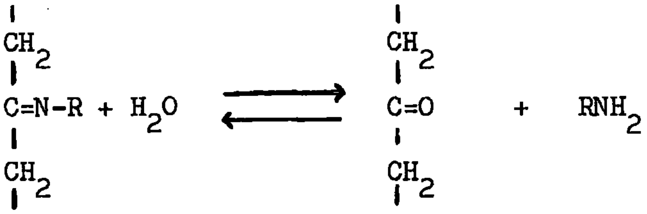
Attempts by Smith to establish the existence of double bonds in amine-treated Viton by chemical means failed. Conventional reagents diagnostic of double bonds, such as permanganate, chlorine or bromine, could not be used since untreated Viton in solution was attacked by them. Ozonolysis of the amine-treated polymer with 6% ozone in oxygen caused no reduction in molecular weight. Infra-red absorption spectroscopy proved to be more useful, in that bands attributable to olefinic double bonds appeared after amine treatment. Chemical studies on vulcanisates are probably only of limited use, since the proportion of chemical change required to produce a significant change in mechanical properties is extremely small. There is no certainty that the reactions observed by prolonged application of amines are those reactions which cause vulcanisation. Physical methods are more useful in that small amounts of chemical change can be detected.

Russian workers[105] studied the infra-red absorption spectra of polyamine vulcanisates of Viton elastomers. During the preliminary milling at 120°, it was suggested that the hydrofluoride salt of the diamine used was formed. Additional diamine reacted with the unsaturated sites to form cross-links containing the C-N and C=N entities. At the post-curing temperature of 200°, the HF salt decomposes, and, in the absence of magnesium oxide, destroys the imine link. The same workers[106] have also carried out infra-red studies on the structural transformations occurring in Viton elastomers during heating. When the raw elastomer was heated between 150° and 200°, various double bonds were formed. Heating to 150° in an airflow leads to the formation of an increased number of double bonds. Raising the temperature to 220°, i.e. the temperature of the post cure, caused the disappearance of these olefinic absorption bands. This last treatment is accompanied by a decrease in solubility, which serves as an indication of a cross-linked structure. This work supports Smith's ideas of cross-link formation by interaction of double bonds in neighbouring polymer chains,[102] although, of course, not ruling out the possibility that other mechanisms occur simultaneously.

The role of the acid acceptor in curing formulations has been examined in some detail.[102] It is suggested that magnesium oxide - the usual acid acceptor - actively contributes to the elimination of HF from the polymer chain. The evidence for this supposition is mainly based on infra-red spectroscopy; studies on the effect of concentration of magnesium oxide on cross-link density have also been carried out. The necessity of the post curing process arises, at least in part, from the neutralisation of magnesium oxide with HF, according to the simple equation

$$MgO + 2HF \longrightarrow MgF_2 + H_2O$$

As has been previously indicated, it is necessary to eliminate water from the curing system to prevent the equilibrium from producing an appreciable



$$-CH_2-\underset{\underset{CH_2}{|}}{C}{=}N-R + H_2O \rightleftharpoons -CH_2-\underset{\underset{CH_2}{|}}{C}{=}O + RNH_2$$

proportion of carbonyl structure, which would reduce the degree of cure.

The suggestion that magnesium oxide acts as a catalyst for hydrogen fluoride elimination during the cross-linking reaction is considered more fully in the discussion.

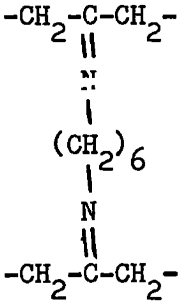
Investigations of Viton systems by physical methods have either been by means of Differential Thermal Analysis (D.T.A.) or by Stress-Relaxation studies. Paciorek,[107] in her paper on the differential thermal analysis of fluoroelastomer systems, makes the very valid point that studies on solutions of the raw elastomer represent idealised cases. This criticism applies with even more force to studies on model compounds. The D.T.A. results indicate that magnesium oxide does induce some small degree of cross-linking at temperatures from 150° to ca. 250° (c.f. Ref. 106). Also, it was indicated fairly clearly that amines modified the elastomer for more than other curing agents, for example, benzoyl peroxide. Whatever the vulcanising agent, the thermal stability of the raw elastomer was always greater than the vulcanisate. Moreover, the amine produced vulcanisate was less stable than the benzoyl peroxide vulcanisate, a fact obviously related to the unsaturation produced by amines.

Stress-relaxation techniques utilise a form of Hooke's Law,

$$f = nkTA_o ( \lambda - \lambda^{-2})$$

where f is the force required to extend a rubber strip, original cross-sectional area $A_o$ to an extension ratio $\lambda$ at constant temperature T. n Is the number of network chains per unit volume of vulcanisate. There are two types of stress-relaxation measurement, continuous and intermittent. In the continuous technique the rubber is held in continuous extension and the decay in tension noted. Information on scission processes only is obtained by this method, since any cross-links formed during the extension do not contribute to the tension. The intermittent technique involves the occasional stretching of the rubber to a constant $\lambda$, and the measurement of the force so required. This latter measurement shows the net effect of scission and cross-linking processes on the network.

Using the above techniques, workers at the Royal Aircraft Establishment, Farborough,[108] have shown that the initial network formed between the raw Viton elastomer and hexamethylene diamine breaks down rapidly in air at 250°C., half of the network being destroyed in 90 minutes. The network was found to be completely stable in vacuum over the time scale of the experiments, hence it was concluded that breakdown was an oxidative process. Moreover, the way in which the rate of continuous stress-relaxation varied with cross-link density suggested that network scission occurred in the cross-links or in the main polymer chain at the sites of the cross-links. Concurrent with the breakdown of the initial network, appreciable numbers of new cross-links are formed, giving a second network much more thermally stable than the first. Results also indicate that when scission does occur in the second network, it occurs in the main polymer chains. Now it has been shown[102] that the structure at the cross-links of a hexamethylene diamine cured Viton is:

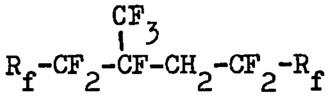


$$\begin{array}{c} -CH_2-\overset{}{C}-CH_2- \\ \| \\ N \\ | \\ (CH_2)_6 \\ | \\ N \\ \| \\ -CH_2-C-CH_2- \end{array}$$

Therefore, to produce a vulcanisate with an initial network which is more thermally stable than that incorporating hexamethylene diamine, an oxidatively stable cross-linking agent is required. The benzene ring in p-phenylenediamine fulfils this condition. In fact, the use of p-phenylenediamine as a cross-linking reagent leads to a reduction in the rate of network breakdown at all temperatures up to 250°.

The use of model compounds to elucidate the cross-linking mechanism of Viton A has the considerable advantage that the chemistry involved with model compounds should be relatively straightforward as compared to studies on the elastomer itself. However, against this advantage, it must be remembered that the environment at a reactive site (whatever this may be) in a polymer chain bears little or no resemblance to the environment of a model compound; in the former case one has a rigidly held chain with possible steric hindrance from other chains, and in the latter case one has a discrete, relatively simple molecule. A further fact to be borne in mind is that it is seldom possible to prepare a polymer as a pure compound in the strict chemical sense, hence one is not wholly justified in extrapolating results obtained from model compounds to the polymer system.

In the case of Viton A, the model compound should contain the following structure if it is to be a reasonable representation of the polymer:

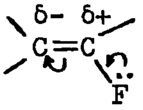


$$R_f\text{-}CF_2\text{-}\overset{\overset{\displaystyle CF_3}{|}}{C}F\text{-}CH_2\text{-}CF_2\text{-}R_f$$

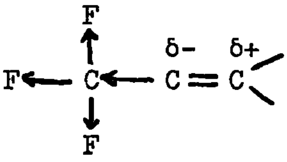
Paciorek[109,110] and Hutchinson[111] have prepared model compounds of Viton, and have carried out some reactions; discussion of their work is deferred until later pages.

## The reactions of amines with polyfluoro-olefins and some other organo-fluorine derivatives.

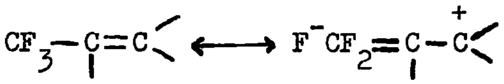
As might be expected, amines readily take part in nucleophilic additions to highly fluorinated olefins. The direction of nucleophilic attack can usually be predicted by considering the polarisation of the olefin, which arises from a combination of the mesomeric effect of vinylic fluorine, the inductive effect and the hyperconjugative effect. Thus,



(Mesomeric effect)



(Inductive effect)



$$CF_3-\underset{|}{C}=C{<} \longleftrightarrow F^-\,CF_2=\underset{|}{C}-\overset{+}{C}{<}$$

(Hyperconjugative effect)

The overall polarisation of a fluoro-olefin with a terminal difluoromethylene group is $R_f\overset{\delta-}{C}F=\overset{\delta+}{C}F_2$. Hence addition will be largely by nucleophilic attack on the terminal carbon atom.

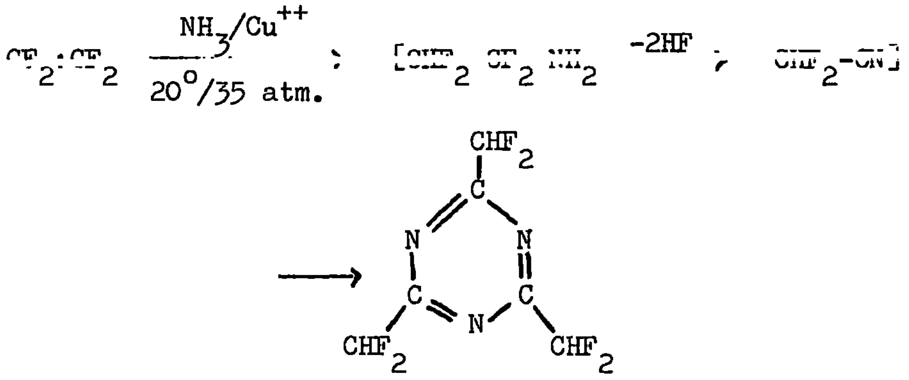
### Reactions of ammonia and primary amines

Nucleophilic reactions of amines to olefins quite often involve first the addition of the amine (or ammonia) to the olefin, and then the elimination of hydrogen fluoride. Thus, in the reaction of perfluorobut-1-ene with ammonia,[112] the following occurs:

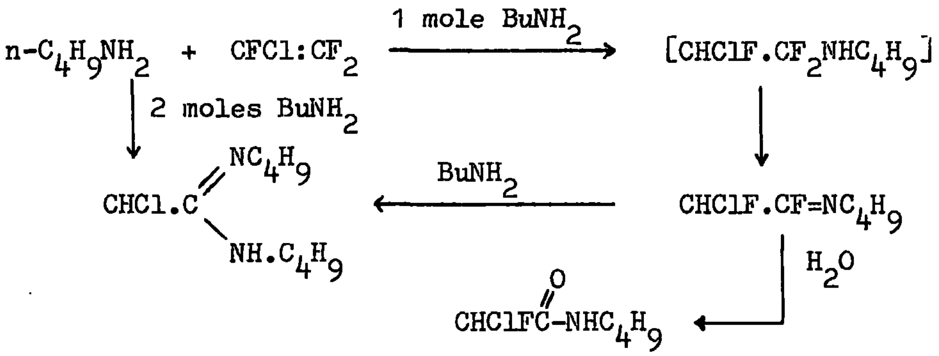
$$CF_3{\cdot}CF_2{\cdot}CF{=}CF_2 \xrightarrow{NH_3} [CF_3{\cdot}CF_2{\cdot}CFH{\cdot}CF_2NH_2]$$

$$\xrightarrow{-2HF} CF_3{\cdot}CF_2{\cdot}CFH{\cdot}CN \qquad (20\%)$$

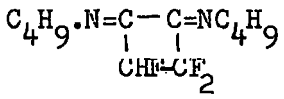
With tetrafluoroethylene, ammonia reacts exothermically, in fact, explosively if precautions are not taken, to give a triazine.[113,114] The postulated mechanism is that the nitrile first formed immediately trimerizes:



Amides can be prepared in good yields by the addition of primary amines to fluoro-olefins under hydrolytic conditions. On heating tetrafluoroethylene or chlorotrifluoroethylene with butylamine and borax, the source of water, at 100° for 8 hours, good yields of $CF_2HCONHC_4H_9$[115] and $CHClF.CONHC_4H_9$[116] respectively were obtained. Pruett et al.[6] reacted butylamine with chlorotrifluoroethylene under anhydrous conditions and isolated the imine formed by elimination of HF from the initial 1:1 addition product. The imine was readily hydrolysed to the amide, or with excess of butylamine, further addition and elimination occurred.

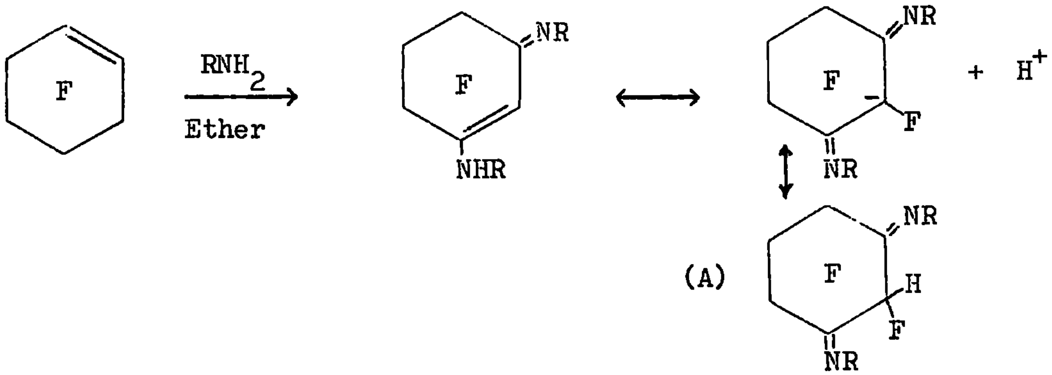


Pruett also reacted perfluorocyclobutene with butylamine[117] to produce the di-imine



$$\begin{array}{c} C_4H_9.N=\underset{|}{C}-\underset{|}{C}=NC_4H_9 \\ CHF-CF_2 \end{array}$$

Perfluorocyclohexene reacts with either ammonia or iso-propylamine in ether to give good yields of the amino-imines:[118]



Ultra-violet spectroscopy indicates that the formation of tautomer (A) is especially favoured. Undecafluorocyclohexane reacts to give excellent yields of identical products by first eliminating HF.

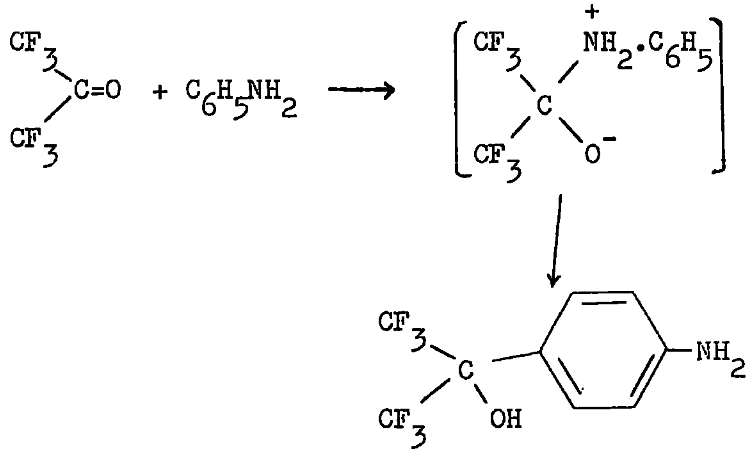
Of the reactions of primary amines with compounds not containing an olefinic double bond, that of methylamine with trifluoronitrosomethane is interesting.[119]

$$\begin{tikzcd} CH_3NH_2 + CF_3.N{:}O \arrow[r] & CF_3.N(O^-).N^+H_2CH_3 \arrow[d, "\begin{array}{l}(i)\ H^+\ \text{transfer}\\ (ii)\ -H_2O\end{array}"] \\ & CF_3.N{:}N.CH_3 \end{tikzcd}$$

Further reaction of methylamine with the azo-compound gives a solid of as yet unknown structure, melting point 273°.

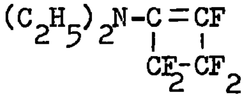
Hexafluoroacetone reacts with primary aromatic amines to give ultimately carbinols.[120,121] Initially, an unstable salt-like addition compound is formed, which slowly rearranges to the final product.

e.g.



## Reactions of secondary amines

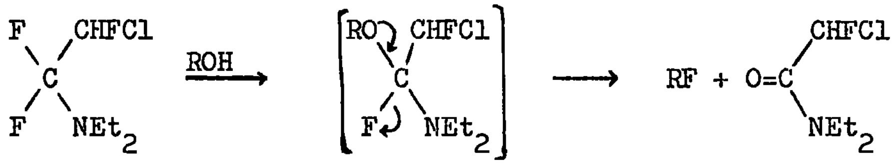
Reactions of secondary amines parallel the reactions of primary amines to quite a degree. Thus, addition to olefins occurs under moderate conditions, giving initially saturated products. However, as is the case with primary amines, the initial saturated product readily eliminates hydrogen halide. The tendency of the addition products of secondary amines with perfluorocyclobutene to lose hydrogen fluoride is greater than the tendency of secondary amine - chlorotrifluoroethylene adducts to eliminate HF.[117] For example, the addition of diethylamine to perfluorocyclobutene yields N,N-diethylpentafluoro-1-cyclobutenylamine



$$\begin{array}{l}(C_2H_5)_2N-\underset{|}{C}=\underset{|}{CF}\\ \qquad\quad\; CF_2-CF_2\end{array}$$

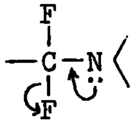
whereas addition to chlorotrifluoroethylene yields only N-(2-chloro-1.1.2-trifluoroethyl)-diethylamine; in the former case no N,N-diethyl-(1,2,3,3,-4,4-hexafluorocyclobutyl)amine was isolated. The tertiary amines formed from the reactions of olefins with secondary amines react very readily with water and hydroxylic compounds to yield substituted amides.

e.g.



(122)

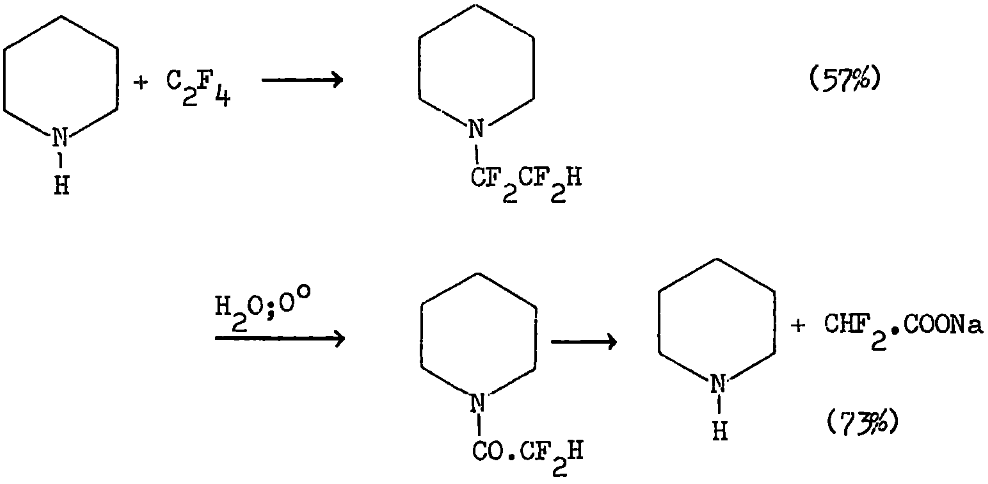
In fact, this method provides a route to alkyl fluorides (using alcohols) and acid fluorides (using carboxylic acids). The considerable lability of fluorine atoms α- to nitrogen was explained by a p-σ conjugative effect:[122]



With a large excess of secondary amine, chlorotrifluoroethylene will react to give ultimately tetrakis-(dialkylamino)ethylene. It is probable that the reaction occurs in several steps, the first step being a rapid addition of amine; subsequent steps were much slower, involving alternate loss of HX and addition of dialkyl amine to the resulting olefin.

The presence of two aryl groups in an amine (e.g. diphenylamine) renders the amine inactive toward addition to olefins. This can almost certainly be ascribed to the decrease in electron density on the nitrogen atom, due to the electron-withdrawing properties of the phenyl groups.

Russian workers[123] have shown that piperidine will add across tetrafluoroethylene under moderate conditions and in quite good yields to give N-(1,1,2,2-tetrafluoroethyl)piperidine. Treating this compound with ice gives N-difluoroacetylpiperidine, which will react further with dilute alkali to give difluoroacetic acid.



The rate of reaction[124] of various fluoro-olefins with diethylamine has been shown to increase in the order

$$CF_2{:}CF_2 < CF_2{:}CFCl < CF_2{:}CFBr.$$

This order is the order of increasing dipole moments of the olefins. Hurwitz and Miller[125] reported that secondary amines react with polyfluoro-olefins to give saturated products having exclusively α, α - difluoro- structures. Knunyants[126] has shown that the ratio between the primary addition product and the enamine resulting from HX elimination depends largely on the structure of the fluorinated olefin.

| Olefin $RR'C=CF_2$ | Product | |
|---|---|---|
| | $RR'CHCF_2NR''_2$ | $RR'C=CFNR''_2$ |
| $R = R' = F$ | 100% | 0% |
| $R = F, R' = CF_3$ | 70% | 30% |
| $R = R' = CF_3$ | 0% | 100% |

## Reactions of tertiary amines

Tertiary amines have, so far, shown little indication of reaction with olefinic double bonds,* except in those cases where a mono-olefin can react to form a conjugated di-ene.[127,128,129]

Most of the precursors of the di-enes were not very highly fluorinated compounds, and HBr or HCl was eliminated rather than HF. It seems quite possible that the reaction occurs through the formation and decomposition of a quaternary salt, a temperature of 180° being commonly employed. If the temperature was raised above 200°, the already very moderate yields

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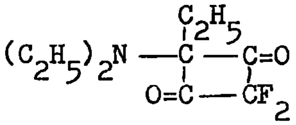
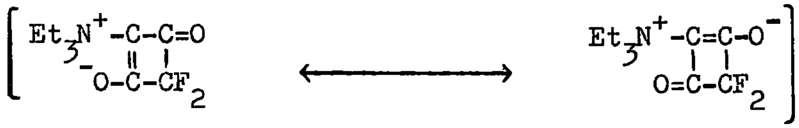
* But with one exception - see references 132 and 133.

of di-enes were reduced still further by the formation of 1-butene when tri-butylamine was used, and methyl halide when N,N-dimethyl aniline was used. Quaternary ammonium salts containing a fluorocarbon group have been prepared, for example

$$(CH_3)_3N + BrCH_2CH_2F \xrightarrow{\text{Room temperature}} [(CH_3)_3NCH_2CH_2F]^+Br^- \quad {}^{130}$$

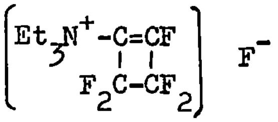
but no mention is made of their thermal stability. However, Collie[131] thermally decomposed tetramethylammonium fluoride to yield methyl fluoride.

There is one case in the literature which describes the reaction of a tertiary amine with an olefinic double bond. This is the reaction between hexafluorocyclobutene and triethylamine.[132,133] Rapp[132] found that reaction occurred between triethylamine and hexafluorocyclobutene at the temperature of solid carbon dioxide, giving a yellow crystalline solid, analysing as a 1:1 adduct. Pruett et al.[133] repeated and enlarged upon this work, using also other tertiary amines. The solid initially formed was found to be extremely susceptible to hydrolysis. Upon hydrolysing the solid, a stable crystalline material was obtained, analysing to $C_{10}H_{15}NO_2F_2$. Rapp assigned the structure  $(C_2H_5)_2N-\overset{C_2H_5}{\underset{O=C}{C}}-\underset{CF_2}{C}=O$ to the compound, whereas Pruett suggested a betaine structure:



$$\left[\begin{array}{l} Et_3N^+-C-C=O \\ \quad\;\; {}^-O-C-CF_2 \end{array}\right. \longleftrightarrow \left.\begin{array}{l} Et_3N^+-C=C-O^- \\ \qquad\;\; O=C-CF_2 \end{array}\right]$$

It was suggested that the structure of the solid first formed in the triethylamine/hexafluorocyclobutene reaction was

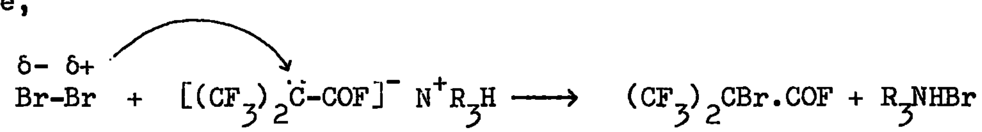


Reaction of triethylamine with α-hydrohexafluoroisobutyrylfluoride yielded a stable complex,[134,135] to which Knunyants assigned the structure (i) rather than (ii)

$$[(CF_3)_2C\text{-}CO.F]^-\overset{+}{N}R_3H \qquad [(CF_3)_2CH.CO\text{-}\overset{+}{N}R_3]F^-$$

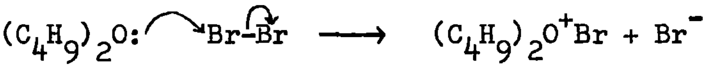
(i) (ii)

Bromination of the complex produces α-bromohexafluoroisobutyryl-fluoride,



$$\overset{\delta-}{Br}\text{-}\overset{\delta+}{Br} + [(CF_3)_2\dot{\ddot{C}}\text{-}COF]^- N^+R_3H \longrightarrow (CF_3)_2CBr.COF + R_3NHBr$$

When the bromination is carried out in butyl ether, the yield of bromo compound goes down.



$$(C_4H_9)_2O\!:\; Br\text{-}Br \longrightarrow (C_4H_9)_2O^+Br + Br^-$$

This suggests an electrophilic attack, a process occurring much more readily with structure (i) than structure (ii).

The reaction of trimethylamine with trifluoromethyl iodide, giving fluoroform in about 70% yield, has been carried out by Haszeldine and West.[136] Apart from fluoroform, a solid material, claimed to be a mixture of tetramethylammonium iodide and possibly $[NMe_3I]^+CF_3^-$, was isolated. In view of the work on complex formation between polyfluoro-iodoalkanes and Lewis bases,[137] it is quite possible that the first step in the reaction involves a complex of the type $CF_3\text{-}I \longleftarrow NMe_3$.

Homolytic fission of the carbon-iodine bond in polyfluoroiodoalkanes occurs readily; donation of electrons should make the fission of the bond more facile. A process such as

$$\mathrm{Me_3N{:}}\curvearrowright\mathrm{I}\overset{\curvearrowright}{-}\mathrm{CF_3} \longrightarrow \mathrm{Me_3N^{+\bullet}}\ \mathrm{I^-} + {}^{\bullet}\mathrm{CF_3}$$

could conceivably occur, the trifluoromethyl radical then abstracting a proton. This reaction is investigated in more detail in later pages.

## Addition of the elements of hydrogen fluoride to fluorinated olefins.

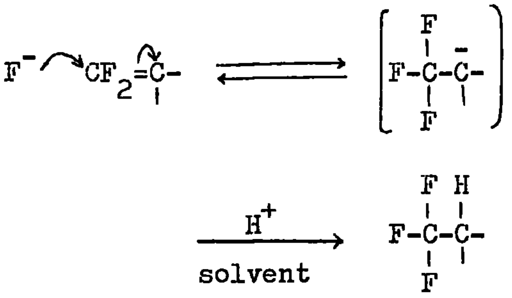
Addition of hydrogen fluoride to hydrocarbon olefins occurs with considerable ease when anhydrous hydrogen fluoride alone is used. For example, treatment of propylene with anhydrous HF at 0° results in a 61% yield of 2-fluoropropane.[138] However, with highly fluorinated olefins, electrophilic attack occurs with difficulty, owing to the inductive electron withdrawal from the double bond by fluorine and fluoroalkyl groups. Thus hexafluoropropene does not react with anhydrous hydrogen fluoride at 200°. Hydrogen fluoride will add to vinylidene fluoride[139] and tetrafluoroethylene[140] with relative ease; this fact is explained by the mesomeric electron release of the fluorine atoms partially compensating for their inductive effect. Replacement of a fluorine or a hydrogen atom by the trifluoromethyl group, which exhibits no mesomeric effect, renders the resulting propenes much more resistant to attack.

Although fluorocarbon olefins are very resistant to electrophilic addition of hydrogen fluoride, nucleophilic addition occurs very readily.

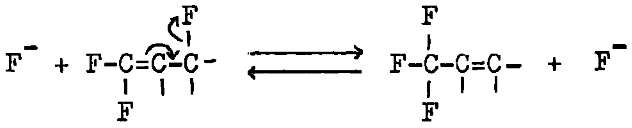
As has already been stated, anhydrous hydrogen fluoride does not react with hexafluoropropene at temperatures up to 200°; however, the use of potassium fluoride in a protogenic solvent, e.g. dimethylformamide, where attack is by fluoride ion, readily gives 2H-heptafluoropropane. Similarly, addition of the elements of hydrogen fluoride to chlorotrifluoroethylene readily occurs when potassium fluoride in formamide is used.[141]

$$CClF{=}CF_2 \xrightarrow[55^{\circ},\ 30\ \text{hrs.}]{KF,\ HCONH_2} CHClF{-}CF_3 \qquad 72\%$$

Miller and co-workers[142] have shown that olefins containing a terminal difluoromethylene group are especially reactive toward nucleophilic attack. The intermediate carbanion first formed by fluoride ion attack on the terminal difluoromethylene group can either abstract a proton from the solvent, as indicated above,



or a rearrangement may occur:



The internal olefins formed by rearrangement add hydrogen fluoride much more slowly than do the terminal olefins. The yields of a desired

HF addition product may be reduced by rearrangement, also abstraction of a proton produces a solvent anion, which can then react with the fluoro-olefin in competition with fluoride ion.

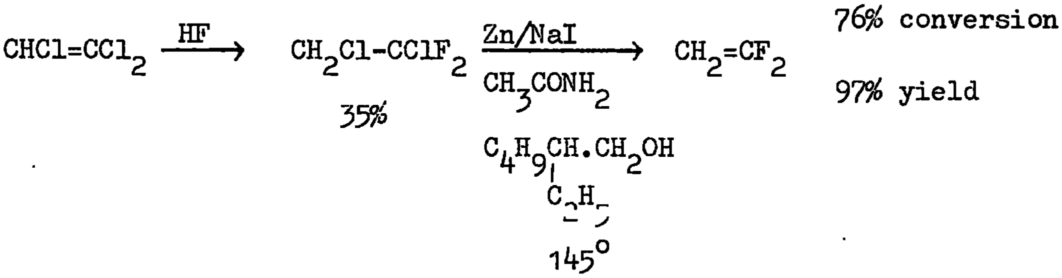
Miller and co-workers[143] have, in fact, shown that electrophilic addition to fluorinated olefins will occur. 2H-Heptafluoropropane was prepared in 47 percent yield by treating hexafluoropropene with anhydrous hydrogen fluoride and argentous fluoride at 125°. It was postulated that addition of the metal cation occurred,with subsequent reaction with $H_nF_{n+1}^-$.

## The preparation of fluoro-olefins.

The methods used for the preparation of fluoro-olefins are many. The four most important methods employed are (i) the dehalogenation of vicinal halogenoparaffins, (ii) the dehydrohalogenation of fluorinated halogeno-compounds, (iii) the pyrolysis of fluorinated compounds and (iv) the fluorination of a halogeno-olefin by halogen exchange. Other methods also are used, e.g. the addition of hydrogen halides to alkynes, the free radical addition of, usually, fluoro-alkyl bromides or iodides to olefins or acetylenes, and the reaction of organometallic compounds with olefins.

### (i) Dehalogenation.

The usual agent employed for the dehalogenation of vicinal halogenoparaffins is zinc. The solvent used is usually an alcohol, often ethyl alcohol. The very important chlorotrifluoroethylene is but one example of an olefin produced by dehalogenation using zinc in either methyl alcohol[144] or ethyl alcohol.[145] Vinylidene fluoride has been prepared in good yield by dehalogenation of 1,1-difluoro-1,2-dichloroethane.[146]



$$\mathrm{CHCl{=}CCl_2} \xrightarrow{\mathrm{HF}} \underset{35\%}{\mathrm{CH_2Cl{-}CClF_2}} \xrightarrow[\substack{\mathrm{CH_3CONH_2}\\ \mathrm{C_4H_9}\underset{\substack{|\\ \mathrm{C_2H_5}}}{\mathrm{CH}}\mathrm{.CH_2OH}\\ 145^{\circ}}]{\mathrm{Zn/NaI}} \mathrm{CH_2{=}CF_2} \quad \begin{array}{l}76\%\ \text{conversion}\\ 97\%\ \text{yield}\end{array}$$

Reactions are generally carried out at the reflux temperature of the solvent, except in a few cases where autoclaves must be used in order to allow a temperature greater than reflux temperature. For example, the dehalogenation of 1,2-dichlorotetrafluoroethane requires a reaction temperature of 110° for 5 hours when zinc in methanol is employed.[147] The choice of a solvent depends largely on the relative boiling points of the solvent and the desired product; however, this is not the sole consideration. Using zinc and alcohol, it proved impossible to prepare pure $\mathrm{CF_2{=}CFCONH_2}$ from $\mathrm{CF_2BrCFBrCONH_2}$, presumably because of the addition of the alcohol to the resulting acrylamide. If acetone was employed as solvent, good yields of the acrylamide were obtained.[148] The halogens removed are usually chlorine, bromine or iodine, but in situations where the grouping $\mathrm{-CF_2CH_2I}$ exists, it is possible to remove 'IF'.[149,150] Gilman[149] employed the reaction of magnesium with 2,2,2-trifluoroethyliodide to produce vinylidene fluoride, whereas McBee[150] used zinc in acetic acid to remove 'iodine fluoride' from $\mathrm{n\text{-}C_3F_7CH_2I}$.

(ii) Dehydrohalogenation.

The base catalysed elimination of hydrogen halide is probably the most used laboratory method for producing fluoro-olefins. Usually, the base is an alkali metal hydroxide, but it may also be an alkoxide or a tertiary amine. The elimination proceeds by the mechanism

$$B:^{-} + H\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}X \rightleftarrows BH + {}^{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}X \longrightarrow \overset{|}{\underset{|}{C}}=\overset{|}{\underset{|}{C}} + X^{-}$$

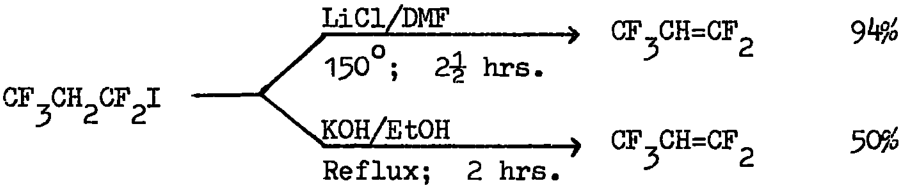
Elimination occurs most readily when X = I; bromine is eliminated more readily than chlorine, and fluorine is by far the least readily eliminated. However, Knunyants[151] has eliminated hydrogen fluoride from 1,1,2,3,3,3-hexafluoropropane under very mild conditions, and in good yield, by using potassium hydroxide in di-n-butyl ether.

$$CF_3CHF.CHF_2 \xrightarrow[0^{o}]{n\text{-}Bu_2O;\ KOH} CF_3\text{-}CF{=}CHF \qquad 97\%$$

Many examples of the elimination of hydrogen iodide have been reported, just one example is the dehydroiodination of 2H,2H-1-iodononafluoro(3-methylbutane).[152]

$$(CF_3)_2CF.CH_2CF_2I \xrightarrow[2\ hrs.]{KOH;\ 90^{o}} (CF_3)_2CF.CH{=}CF_2 \quad 85\%$$

Tertiary amines can be used in some cases to prepare conjugated dienes[127] where alkali metal hydroxides will only remove one mole of hydrogen halide. Potassium hydroxide may be used with an alcohol as solvent, but, as can also happen when alkoxides are used, ether formation may reduce yields. When alkali metal hydroxides are used as dehydrohalogenating agents, it is possible that, apart from the desired elimination of HX where X is Cl, Br or I, elimination of HF may occur.[153] If lithium chloride in dimethylformamide is used, elimination from iodides of hydrogen iodide occurs exclusively.[153] Improvement in yields may also result from using lithium chloride rather than (e.g.) potassium hydroxide:[153]



Tatlow et al.[154] have described the dehydrofluorination of 1-methylnonafluorocyclohexene to 3-methyleneoctafluorocyclohexene by the use of sodium fluoride at high temperatures. The temperatures used were in the range 380° to 490°, but yields of the di-ene were not at all good.

(iii) Pyrolysis.

The preparation of fluorine containing olefins by pyrolysing fluorocarbon compounds is commercially very important. The most used of all fluoro-olefins, tetrafluoroethylene, is prepared in this way.[155] Chlorodifluoromethane, produced by the fluorination of chloroform by HF, is passed through a graphite, silver or platinum furnace at 650-750°C and at about 0·5 atmospheres pressure. Under these conditions, hydrogen chloride splits off, producing the diradical $-CF_2-$, which then dimerizes to tetrafluoroethylene. Compounds containing skeletons with three, four or more carbon atoms are also produced, but to a much smaller extent. When tetrafluoroethylene itself is pyrolysed, the nature of the products depends upon the conditions employed. Perfluorocyclobutane formation is at a maximum at about 550°, whereas at 750° no perfluorocyclobutane is formed, instead, perfluorobut-1-ene predominates. At 650°, about 40% of hexafluoropropene is produced - this is a commercial preparation of hexafluoropropene. The composition of the products from the pyrolysis of polytetrafluoroethylene between 500 and 700° depends mainly on the pressure at which the pyrolysis is carried out, being largely independent of the actual temperature of the pyrolysis.[156] At low pressures, the formation of tetrafluoroethylene is encouraged. At 41 mm. pressure, 14·5% of hexafluoropropene is obtained, while at atmospheric pressure, only a very small amount of tetrafluoroethylene is produced. When the polytetrafluoroethylene chain 'unzips', the difluoromethylene diradical formed reacts with another $CF_2$ to give $C_2F_4$; in a low pressure system, it is unlikely that a collision between a further '$CF_2$' and a tetrafluoroethylene molecule will occur. Increasing the pressure in the system increases the probability of such collisions occurring.

### (iv) Halogen Exchange.

The preparation of fluoro-olefins by means of halogen exchange is a method which is quite widely used. Under mild reaction conditions, halogen atoms in allylic positions are preferentially replaced by fluorine. More vigorous conditions give products with more complete substitution of halogen atoms, but double bonds are sometimes saturated, resulting in the formation of alkanes.

The reagents usually employed are either hydrogen fluoride (quite often with a catalyst) or antimony fluorides. Hydrogen fluoride has been used[157] to prepare vinyl fluoride by passing it together with vinyl chloride over a catalyst of mercuric and barium chlorides on active carbon. However, the preferred way of preparing vinyl fluoride is to add HF to acetylene. Hexachloropropene will undergo exchange when passed with HF over a zirconium tetrafluoride catalyst on activated carbon. The resulting products depend rather upon the temperature at which the reaction is carried out, however, fluorination ceases when all the allylic chlorines have been replaced. If aluminium fluoride is used as catalyst, $CF_3CCl=CCl_2$ and HF react further at 400° to give $CF_3CCl=CF_2$.[158]

Antimony trifluoride reacts rapidly with hexachloropropene to give a mixture of products, consisting mainly of $CF_3CCl=CCl_2$ with a small amount of $CClF_2CCl=CCl_2$.[159] A more reactive fluorinating agent is obtained if some antimony is in the penta-valent state; $SbF_3Cl_2$, or a mixture of this with the trifluoride is commonly used. Thus, $CCl_3CH=CH_2$ cannot be fluorinated by $SbF_3$ alone, but using $SbF_3/SbF_3Cl_2$ Haszeldine prepared $CF_3CH=CH_2$.[160] Rearrangement may sometimes lead to unexpected products; Henne[161] found that allylic fluorination of $CClF_2CF:CF_2$ with $SbF_3/Cl_2$ did not give $CF_3CF:CF_2$ because rearrangement to $CF_3CF:CClF$ occurred.

Maynard[162] has used potassium fluoride in polar solvents, N-methyl-2-pyrrolidone was preferred, to replace chlorine in hexachlorobutadiene to give 2H-heptafluorobut-2-ene in 65% yield. Using chloroethanes and ethylenes, however, fluorine was introduced only to a very limited extent. Dechlorination or dehydrochlorination more commonly occurred.

# Chapter 2

# DISCUSSION OF EXPERIMENTAL WORK

## Introduction

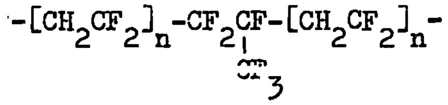
The work described in this thesis follows on from the investigations started by Hutchinson[111] into the reactions between model compounds of Viton A and tertiary amines. The work originated because it was felt that the ideas expressed by Smith[96] at du Pont's as to the nature of the cross-linking mechanism of Viton by tertiary amines were not wholly correct. Also, it is quite possible that a more thorough knowledge of the actual processes occurring during cross-linking might lead eventually to a better curing formulation.

Apart from these factors, very little work has been carried out on the reactions of fluorocarbon compounds in general with tertiary amines.

As has already been indicated in the first chapter (Page 50) the use of model compounds, i.e. compounds which contain the basic elements of the Viton structure, has the advantage that actual chemical reactions should be comparatively easy to study as compared to those reactions which occur when the co-polymer itself is used. There are, of course, objections to the use of a simple compound to follow reactions which occur in a polymer. Briefly the two main objections are that the reactive sites in a polymer are not strictly comparable to the reactive sites in a simple molecule, and that a polymer is hardly ever a pure compound - reaction could conceivably occur solely at sites present in (say) 1% of the material.

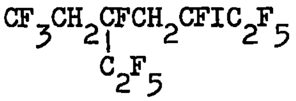
Notwithstanding these objections, other workers, notably Paciorek,[110] have used the model compound approach. However, it was felt that the systems used by Paciorek did not accurately reflect the true situation existing in Viton A.

As has previously been stated (Page 23), the structure of Viton A is predominantly of the type



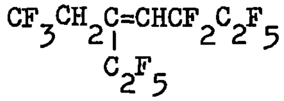
$$-[CH_2CF_2]_n-CF_2\underset{CF_3}{\underset{|}{CF}}-[CH_2CF_2]_n-$$

hence any system chosen as a model for Viton should, of course, bear some relation to this above structure. Paciorek used iodides, for example the compound



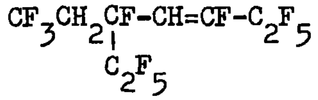
$$CF_3CH_2\underset{C_2F_5}{\underset{|}{CF}}CH_2CFIC_2F_5$$

While this compound is not a true representation of the Viton system, the olefin produced by elimination of the elements of hydrogen iodide could well represent a step in the cross-linking mechanism. It was probably quite reasonable to use the above compound since work on the polymer itself has suggested that olefin formation is a primary step. However, one should bear in mind that in the polymer hydrogen fluoride elimination would be expected to occur in such a way as to involve the 'tertiary' fluorine atoms, rather than the $CF_2$ fluorines. Thus one would expect the olefin



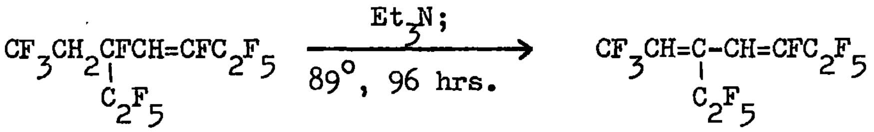
$$CF_3CH_2\underset{\displaystyle C_2F_5}{\underset{|}{C}}{=}CHCF_2C_2F_5 \qquad \text{(i)}$$

rather than



$$CF_3CH_2\underset{\displaystyle C_2F_5}{\underset{|}{CF}}{-}CH{=}CF{-}C_2F_5 \qquad \text{(ii)}$$

to be formed initially. Should the olefin (i) represent the first step in cross-linking process, the remainder of Paciorek's work would be invalid. Paciorek in fact used the olefin (ii) and reacted it with triethylamine. She found that after prolonged refluxing, hydrogen fluoride was eliminated to give a conjugated di-ene.



$$CF_3CH_2\underset{\displaystyle C_2F_5}{\underset{|}{CF}}CH{=}CFC_2F_5 \xrightarrow[89^{\circ},\ 96\ \text{hrs.}]{Et_3N;} CF_3CH{=}\underset{\displaystyle C_2F_5}{\underset{|}{C}}{-}CH{=}CFC_2F_5$$

So far, no further work has been published concerning the reactions of this di-ene with tertiary amines, or concerning the effect of heating it to high (ca. 200°) temperatures for extended periods of time.

Hutchinson[111] prepared saturated model compounds which were quite good representations of the Viton system. The most used of the model compounds was 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane), $[(CF_3)_2CFCH_2CF_2]_2$. When this compound was treated with tertiary amines, a product was obtained which was unsaturated, but which was, however, not fully characterised. $F^{19}$ nuclear magnetic resonance measurements indicated that at least one of the tertiary fluorine atoms had been eliminated, but the structure of the remaining part of the molecule was not elucidated.

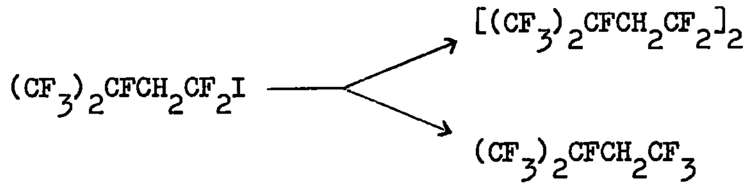
$$[CF_3]_2CF\text{-}CH_2CF_2CF_2CH_2\text{-}CF[CF_3]_2 \xrightarrow[130^{\circ},\ 5\ \text{hrs.}]{nBu_3N} (CF_3)_2C{=}CH\text{-}R_f$$

In this present work, the above reaction was more fully investigated, as was the reaction between the rather more simple model compound 2H,2H-decafluoro-(3-methylbutane) and tri-n-butylamine.

Preparation of Model Compounds.

The route used to prepare the two model compounds mentioned above was essentially that shown in the scheme below:

$$(CF_3)_2CFI \ + \ CH_2{=}CF_2 \longrightarrow (CF_3)_2CFCH_2CF_2I$$



$$(CF_3)_2CFCH_2CF_2I \longrightarrow [(CF_3)_2CFCH_2CF_2]_2$$

$$(CF_3)_2CFCH_2CF_2I \longrightarrow (CF_3)_2CFCH_2CF_3$$

The initial heptafluoro-2-iodopropane was prepared by adding the elements of iodine fluoride 'IF' to hexafluoropropene.[163] It is worth mentioning that the addition of the heptafluoro-2-iodopropane to vinylidene fluoride can be made to occur rather more quickly than is indicated in the relevant paper.[152] At 185°, a reaction time of 36 hours was required to obtain optimum results. However, it was found that on one occasion when a related reaction was being attempted, that between heptafluoro-2-iodopropane and trifluoroethylene, the pressure gauge on the autoclave showed quite a surprisingly rapid decrease in pressure. It was thought that it was probable that a leak existed in the autoclave head, hence the autoclave was rapidly cooled in the hope of saving some of the starting material. However, on opening the autoclave, a good yield of the addition compound was obtained. For this particular reaction it is necessary to use the free radical initiator azo-bis-butyronitrile. Traces of mercury, presumably originating from the vacuum system used to fill the autoclave, were found in the autoclave. It is probable that the mercury removes traces of iodine present which would otherwise inhibit the action of the azo-bis-butyronitrile.[164] Since this inadvertent addition of mercury had such a pronounced effect on reaction times, it was decided to attempt to speed up the reaction between heptafluoro-2-iodopropane and vinylidene fluoride in a similar way. Addition of half of one percent of azo initiator and a few drops of mercury did in fact allow the reaction time to be cut from 36 hours to 5 hours without a significant change in the yield.

### Coupling reactions of 2H,2H-1-iodononafluoro-(3-methylbutane), $(CF_3)_2CF.CH_2CF_2I$.

It has been shown[165] that polyfluoroalkyl iodides with the end grouping $-CH_2CF_2I$ will undergo a coupling reaction under the influence of ultra-violet radiation and in the presence of mercury. Using this technique, the model compound 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane),

$$(CF_3)_2CF-CH_2CF_2CF_2CH_2-CF(CF_3)_2$$

was produced from 2H,2H-1-iodononafluoro-(3-methylbutane).

Although good yields of coupled compound can be formed by this method, up to 75%, the reaction time is somewhat long, being of the order of three to four days for optimum results. Also, the mercuric iodide formed has quite often adhered to the wall of the reaction tube, preventing the transmission of the u.v. light. Consequently it was decided to attempt to carry out the coupling reaction by an alternative method.

Henne[166] has shown that for molecules with a terminal $-CF_2X$ group or a $-CFClX$ group ($X = Br$ or $I$), a doubling of the chain length can be obtained by the action of zinc in acetic anhydride. For optimum results, the temperature has to be maintained as low as possible. The addition of methylene chloride performs this function of maintaining a reasonably low temperature. When the zinc/acetic anhydride method of coupling was applied to the iodide $(CF_3)_2CFCH_2CF_2I$, a fairly vigorous reaction set in after an initial short induction period, thus one was sure that some reaction was occurring. In fact, quite good yields of the coupled compound were obtained in a much shorter time than was necessary for the mercury/u.v. method of coupling. Unlike the mercury/u.v. method of coupling, no side reactions seemed to occur, certainly no reduction of the iodide or elimination of hydrogen iodide was observed. There was only one significant difficulty inherent in the zinc/acetic anhydride method of coupling and this was that considerable care had to be taken to ensure that all the acetic anhydride was completely hydrolysed before separation, by distillation, of the coupled compound from the methylene chloride. Failure to ensure the complete hydrolysis of the anhydride resulted in the formation of tarry material. It is quite surprising just how difficult it proved to achieve complete hydrolysis of the anhydride.

## Reaction of Model compounds of Viton A with tertiary amines.

Hutchinson[111] reacted the model compound $[(CF_3)_2CF.CH_2CF_2]_2$ with a variety of potential dehydralogenation reagents, including an anion exchange resin, alkali metal hydroxides, potassium fluoride and amines. Of these various methods, the use of amines was the only really fruitful method, and of the amines used tri-n-butylamine was the most successful. However, the one compound isolated proved difficult to identify. It was only during the course of the work for this thesis that it was isolated in a pure state and identified.

The reaction of tri-n-butylamine with the above model compound has been carried out in an absence of any solvent, since it was desired to reproduce as faithfully as possible the conditions used during the curing processes of Viton. Some reactions were attempted using diethyl ether as solvent, but no significant reaction was observed, even over a period of two months.

3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) was heated usually with an equi-molar amount of tri-n-butylamine in a well stirred reaction vessel for periods of from five to seven hours at temperatures ranging from 110° to 135°.

Under the optimum conditions (5 hrs., 130°), a very dark, almost black, reaction product resulted. All volatile material was vacuum distilled from this. Of this volatile material, V.P.C. showed one component to be present to the extent of about 70-75% of the whole. This component was eventually isolated in a pure state by means of preparative scale gas chromatography.

The infra-red spectrum of this material showed it to be unsaturated, with a single peak at 1709 cm.$^{-1}$ The molecular weight, initially determined by the Victor Meyer method, showed fairly satisfactorily that two moles of HF had been eliminated. The ultra-violet spectrum of the material showed two bands occurring at 198 mμ ( $\epsilon$ = 200) and 223 mμ ( $\epsilon$ = 64), indicating the absence of a conjugated system. Assuming that two moles of hydrogen fluoride were in fact eliminated, three possible structures can be suggested:

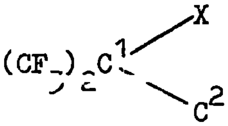
$(CF_3)_2C{=}CH{-}CF_2{-}CF_2{-}CH{=}C(CF_3)_2$ (i)

$(CF_3)_2C{=}CH{-}CF_2{-}CF{=}CH{-}CF(CF_3)_2$ (ii)

$(CF_3)_2CF{-}CH{=}CF{-}CF{=}CH{-}CF(CF_3)_2$ (iii)

Since the U.V. spectrum indicates a lack of conjugation, structure (iii) probably is not present. $F^{19}$ nuclear magnetic resonance favours structure (ii) rather than (i). The N.M.R. results, however, were not entirely conclusive. The spectrum shows that there is present four different groups of fluorine in the intensity ratio of

12:2:1:1. (Full N.M.R. data is included in the appendix). The fluorines which give rise to the largest group are in fact four trifluoromethyl groups. This largest group splits into three chemically shifted sub-groups in the intensity ratio of 3:3:6. This indicates two equivalent $CF_3$ groups and two non-equivalent. The former could well arise from a system of the type



where there is free rotation about $C^1$-$C^2$ (hence a single bond), and X could be fluorine, although not necessarily so. The two non-equivalent $CF_3$ groups arise from a structure

$$(CF_3)_2C{=}CRR'$$

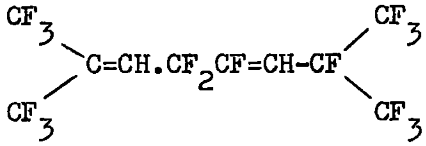
in which the trifluoromethyl groups are cis and trans to the substituents R and R'.

From the chemical shifts, there is clearly a $-CF_2-$ group, giving rise to an AB quartet. There is another mid-field peak of overall intensity one; this band is partially obscured by the $CF_2$ quartet. The band is a multiplet of at least seven peaks. The complexity of the band taken in conjunction with its chemical shift indicates a structural element $-CF{=}C-$.

The remaining band of overall intensity one occurred at high applied fields, but the value for the chemical shift (130 p.p.m.) was rather higher than is normally the case for tertiary fluorine in $(CF_3)_2CF-$

compounds (ca. 108 p.p.m.). The value is more nearly that of a -CFH- fluorine, but the proton magnetic resonance spectrum will not allow such a structure. The P.M.R. indicates the presence of two hydrogens in different environments.

Thus it would seem that the best possibility for the structure of the compound resulting from the reaction of 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) with tri-n-butylamine is



although the shifts of the fluorines in the heptafluoroiso-propyl grouping are not the same as those observed for $(CF_3)_2CF\text{-}CH{=}CF_2$.

It was to confirm the above di-ene structure that oxidative studies were carried out. The oxidizing agent used was that introduced by Burdon and Tatlow,[167] potassium permanganate in dry acetone. The oxidation reactions required slight warming to make them proceed, but it was found that reaction was complete in approximately half an hour. Volatile material was evolved during the course of the reaction; this was later shown to be a mixture of carbon dioxide and 2H-heptafluoropropane.

Both the $CO_2$ and the $i\text{-}C_3F_7H$ were initially identified by their very characteristic infra-red spectra; the propane was then fully characterized. At first, it was rather difficult to explain away the formation of the 2H-heptafluoropropane, but when the same compound was produced by the oxidation of $(CF_3)_2CF{\cdot}CH{=}CF_2$

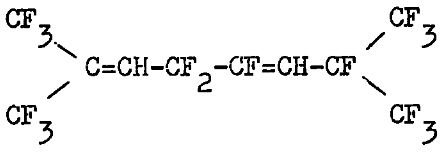
under identical conditions, it was thought that the $(CF_3)_2CF\text{-}COOH$ first produced could well have decarboxylated. A search of the literature showed that this was in fact the case.[168] In the presence of Lewis bases, acids having a tertiary fluorine atom readily decarboxylate.

Trifluoroacetic acid was also isolated from the reaction mixture. During the work-up stages, the mixture was at one point made alkaline. $F^{19}$ N.M.R. showed the presence of two components, each having but one kind of fluorine. After standing the alkaline solution for several hours, $F^{19}$ N.M.R. indicated the presence of only one of the previous compounds. Bigelow[169] has shown that hexafluoroacetone in alkaline solution is cleaved to give trifluoroacetic acid. The information obtained by N.M.R. is entirely consistent with a scheme such as

$$(CF_3)_2C{=}O \quad + \quad H_2O \xrightarrow{-OH} CF_3H \quad + \quad CF_3COOH$$

The extremely volatile gas trifluoromethane would escape from solution. The hexafluoroacetone was derived from the $(CF_3)_2C{=}C$ entity in the original molecule.

Thus, the oxidation evidence confirmed that the structure of the compound resulting from the reaction of 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) with tri-n-butylamine was indeed



An accurate value for the molecular weight of this compound was eventually obtained by mass spectrometry; the value found was precisely that required (426). Mass spectrographic facilities only became available during the course of the last year.

An attempted hydrogenation of the material was unsuccessful under the conditions employed, consequently it was not possible to obtain a quantitative idea of unsaturation by this method.

An interesting point arose from the fact that the yield of olefinic material in the reactions was over fifty per cent; since only an equimolar amount of amine was used, this at first raised a problem because it was assumed that one mole of amine could only eliminate one mole of hydrogen fluoride. However, a stable white crystalline material was eventually isolated from the involatile portion of the reaction mixture. Analysis of this material indicated that it was not tri-n-butyl ammonium fluoride, but rather a material of composition $(n\text{-}C_4H_9)_3N.3HF$. An identical compound was synthesized from tri-n-butylamine and hydrogen fluoride. A survey of the literature showed that amine polyhydrofluorides are not in fact unknown.[170,171] Berliner and Hann[170] isolated compounds stated to be (e.g.) $C_6H_5NH_2(HF)_4$. This present work indicates that the amine mono- or di-hydrofluorides must be quite effective dehydrofluorinating agents; this seems quite reasonable since alkali metal fluorides have been shown to effect dehydrofluorinations.

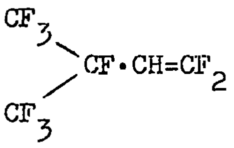
However, it did not prove possible to prepare the monohydrofluorides in order to see if they would react with mono-enes from which HF could possibly be eliminated.

The synthesis of the amine tri-hydrofluoride was carried out by bubbling HF much diluted with nitrogen into the neat liquid amine. This procedure was found to be more successful than attempted preparations using a solution of the amine in ether. When an ether solvent was used, a white precipitate was formed. but this was found to be extremely difficult to obtain in a dry state. Possibly this was the mono-hydrofluoride which one could well expect to be hygroscopic; the tri-hydrofluoride is certainly not hygroscopic, samples having been exposed to the atmosphere for up to six months with no visible deterioration. The stability of the tri-hydrofluoride is presumably because no fluoride ion as such exists, the anion is $(H_2F_3)^-$ which will have no tendency to be solvated by water.

Since magnesium oxide appears to play a vital part in the cross-linking processes occurring in Viton A,[97] reactions between 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane), $[(CF_3)_2CFCH_2CF_2]_2$, and MgO were carried out, both in the absence of and also in the presence of tri-n-butylamine. When magnesium oxide alone was used, no reaction occurred at the reflux temperature of the model compound (140°) even after a period of two days. However, when the reaction was carried out with the tri-n-butylamine also present, a very complex product was obtained from which it proved impossible to isolate any pure compounds. A considerable amount of tarry material was also formed, accounting for over 90% of the weight of the starting materials. This particular piece of work was useful in that it indicated that magnesium oxide alone does not affect a cure of Viton A, at least at temperatures up to 140°, but that the function of the magnesium oxide is to react with some intermediate produced by the amine, apart from its function as an acid acceptor. Certainly the work on the reactions of tertiary amines with olefins (to be discussed in later pages) would suggest the role as an acid acceptor is rather important.

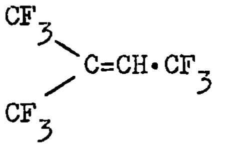
### Reaction of the model compound 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CF.CH_2CF_3$, with tri-n-butylamine.

In view of the difficulty experienced in determining the structure of the compound arising from the reaction of $[(CF_3)_2CFCH_2CF_2]_2$ with tri-n-butylamine, it was decided to carry out a reaction using the chemically similar but rather more simple compound, 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CF.CH_2CF_3$. It was thought that the most probable reaction that would occur would be the elimination of a mole of hydrogen fluoride to give an olefin. The most probable olefins to be expected would be either



(i)

or



(ii)

The terminal olefin (i) is readily prepared by the dehydroiodination of $(CF_3)_2CF.CH_2CF_2I$,[152] thus if (i) should be the product from the amine reaction it could readily be identified. One would also expect the internal olefin (ii) to be easily identified by infra-red and $F^{19}$ nuclear magnetic resonance spectroscopy.

### The preparation of 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CFCH_2CF_3$

A convenient method of preparation of the above compound is that used by Hutchinson.[152] However, the reaction to replace iodine by fluorine was modified slightly in that it was carried out in an autoclave. The main reason for this procedure was that the method employed by Hutchinson to make the fluorinating agent, $SbF_3Cl_2$, was not terribly convenient.

Finally, an even more convenient method of replacing the iodine in 2H,2H,1-iodononafluoro-(3-methylbutane), $(CF_3)_2CF.CH_2CF_2I$, by fluorine was evolved. It was found that it was not necessary to use antimony trifluoride dichloride. Instead, a mixture of antimony trifluoride and antimony pentachloride was used, with no significant reduction in yields.

### Reaction of $(CF_3)_2CF.CH_2CF_3$ with tri-n-butylamine.

Reactions of tri-n-butylamine with half and equi-molar proportions of 2H,2H-decafluoro-(3-methylbutane) were carried out in sealed tubes, either under the influence of heat or ultra-violet radiation. In both cases, one main product was formed which was eventually shown to be

2H,2H,3H-nonafluoro-(3-methylbutane), $(CF_3)_2CH.CH_2CF_3$, in approximately 40% yield. The tertiary amine had effectively replaced the 'tertiary' fluorine atom by hydrogen rather than producing an olefin, as might have been expected. Infra-red spectroscopy of the product in the region 5•5µ to 6•5µ showed a complete absence of any absorption, indicating a saturated structure.* This lack of absorption in the unsaturated region of the infra-red posed a problem, especially since a molecular weight determination (Regnault) indicated that a loss of one fluorine atom had occurred. However, the accuracy of Regnault's method is not sufficiently great to choose between the olefinic structure $C_5HF_9$ (M.W. 232) and a saturated structure $C_5H_3F_9$ (M.W. 234) in which one of the original fluorines had been replaced by a hydrogen atom. $F^{19}$ nuclear magnetic resonance suggested that a saturated structure was much more probable than an olefinic structure, in that the N.M.R. spectrum showed the presence of three $CF_3$ groups, two of these being equivalent. Also very significant was the absence of a high field peak due to tertiary fluorine. Proton magnetic resonance did not prove to be of great value, although the very broad spectrum was not inconsistent with the structure $(CF_3)_2CH.CH_2CF_3$.

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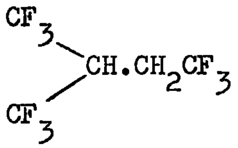
* Work on the reaction between $(CH_3)_3N$ and $(CF_3)_2CF{\cdot}CH{=}CF_2$ has shown that the olefin $(CF_3)_2C{=}CH{\cdot}CF_3$ does not show any signs of unsaturation in its infra-red spectrum - see Page 112 and I.R.No. 11.

Mass spectrometry proved extremely helpful in confirming the compound to be



rather than an olefinic molecule $C_5HF_9$. It is quite well known (e.g. ref. 175) that saturated fluorocarbons show very little sign of a molecular-ion peak in their mass spectra, whereas unsaturated fluorocarbons do exhibit a molecular-ion peak. Results obtained from several compounds during the course of this work have shown that saturated fluorocarbons invariably produce a fragment with a highest mass number of (M-19), where M is the molecular weight of the compound under investigation. Again, with unsaturated compounds, the highest mass number observed proved to be the molecular weight. One is therefore justified in using mass spectrometry to confirm the presence or absence of an olefinic double bond in an aliphatic fluorocarbon compound.*

In the case of the reaction product from tri-n-butylamine and 2H,2H-decafluoro-(3-methylbutane), mass spectrometry showed a highest mass number of 215. This fact, in combination with the Regnault molecular weight determination of 230, was indicative of a saturated compound of molecular weight 234. This value is exactly that required for the formula $C_5H_3F_9$. Additional evidence for this structure was obtained

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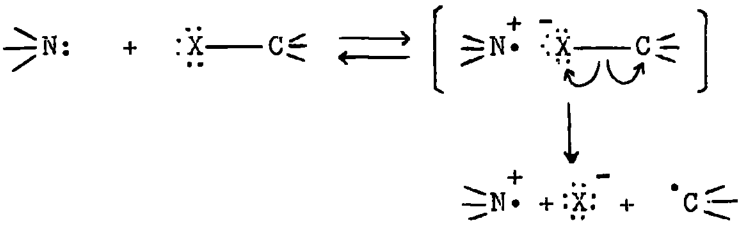
* See also Ref. 175, p.55.

from the observation that the most abundant fragment occurred at a mass number of 77. This mass number can only be accounted for by a fragment with an empirical formula $C_3H_3F_2$. It is of course just conceivable that recombination of smaller fragments could give rise to a fragment of mass number 77, but the abundance of such a fragment would be extremely small.

The mechanism of the reaction whereby the 2H,2H,3H-nonafluoro-(3-methylbutane) is produced is not very clear. However, one can postulate two fairly feasible mechanisms. The first of these is that the reaction proceeds via an intermediate charge-transfer complex, similar to those which have been shown to be formed when tri-ethylamine reacts with carbon tetrachloride.[176] The formation of a charge-transfer complex is also postulated by Reinecke[177] to account for the catalytic effect of tertiary amines in the dehalogenation of aliphatic halides, Stevenson and Coppinger[176] have suggested that the charge-transfer complex leads to the homolytic cleavage of the carbon-halogen bond:

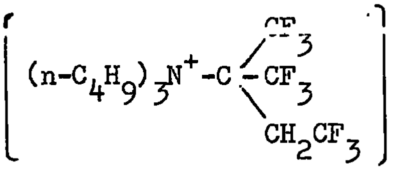


The resulting radicals could then abstract protons from the solvent. American workers[178] have proposed that the reaction between several organic halides and amines, in the presence of ultra-violet light, proceeds as a non-chain photo-decomposition process via the formation of an intermediate complex. If the reaction were to be a simple photolysis of the carbon-halogen bond, one might expect it to proceed in, for example, a paraffin solvent. When carbon tetrachloride is irradiated by ultra-violet light in a hydrocarbon solvent, no such reaction occurs.

Charge-transfer complexes quite often show an ultra-violet absorption shifted to the red from the absorption of the donor molecule. The charge-transfer band is usually rather more intense and diffuse than the band due to the donor in a non-complexing solvent. However, the absence of a red-shifted band does not necessarily mean that a charge transfer complex does not exist. The band could be superimposed on the existing absorption bands,[179] especially in the case of an acceptor of low electron affinity and a donor with a high ionization potential.

A series of investigations on the ultra-violet spectra of mixtures of tri-n-butylamine and 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CF.CH_2CF_3$, were carried out with the aim of establishing the existence of a charge-transfer complex. Measurements carried out on dilute solutions in cyclohexane did not produce any satisfactory results. However, by using a short-path-length cell (path-length of the order of $7 \times 10^{-4}$ cm.), it was shown that solutions of the amine in the fluorocarbon did show a band shifted approximately 100 Å to the red of the amine absorption band. This would indicate that a charge-transfer complex can occur between $(CF_3)_2CF.CH_2CF_3$ and $(n\text{-}C_4H_9)_3N$. Actually demonstrating that the reaction does proceed via this complex is rather difficult.

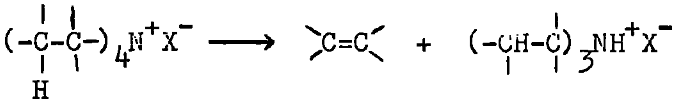
The alternative postulate for the reaction mechanism is one which proceeds through the formation of an unstable quaternary ammonium salt. This would involve direct nucleophilic displacement of fluoride from a polyfluoroalkyl group, which is not known to occur. In the present reaction, the postulated quaternary salt would be



$$\left[(n\text{-}C_4H_9)_3N^+\text{-}C(CF_3)(CF_3)(CH_2CF_3)\right]F^-$$

Homolytic fission of the carbon-nitrogen bond could then occur, by supplying ultra-violet light or thermal energy. The resulting radicals could then abstract protons in a similar manner to those produced via a charge-transfer intermediate. The proposed mode of decomposition of the quaternary ammonium salt is, however, not the normal process. So far, two modes of thermal decomposition are known: the reverse Menschutkin (i) and the Hofmann types (ii).[180]

$$R_4N^+X^- \longrightarrow RX + R_3N \qquad (i)$$



$$(\text{-}\underset{H}{C}\text{-}C\text{-})_4N^+X^- \longrightarrow {>}C{=}C{<} + (\text{-}CH\text{-}C)_3NH^+X^-$$

The actual mechanism of the reaction between tri-n-butylamine and 2H,2H-decafluoro-(3-methylbutane) could even be a combination of the two suggested mechanisms, the charge-transfer complex merely serving to bring the reactants into close proximity, facilitating the formation of the quaternary ammonium salt.

Although the mechanism is not clear, it seems probable that at some stage free radicals are present. Should this be so, it would indicate that free radical intermediates could well be formed in the cross-linking of Viton A. This type of process need not be very common to form the cross-linking network in Viton A. The more common reaction is one of dehydrofluorination.

Gladstone[181] has shown the polychlorotrifluoroethylene reacts with amines to give products from which the amine hydrochloride could be isolated. He suggests that the reaction in which the hydrogen chloride is produced must involve the free pair of electrons on the nitrogen of the amine. This result could be explained in a similar way to the reaction between $(CF_3)_2CF.CH_2CF_3$ and tri-n-butylamine.

## Reaction of 2H,2H-decafluoro-(3-methylbutane) with some nucleophiles.

In view of the rather unexpected reaction discussed above, it was decided to attempt to replace the tertiary fluorine by hydrogen using lithium aluminium hydride, and by a methyl group using methyl lithium. In each case, the temperature at which the reaction could be carried out was limited by the low boiling point ($45^{\circ}$/770 mm.) of the fluorocarbon. With the lithium aluminium hydride, no reaction was observed even after prolonged refluxing. It was not thought wise to increase the reaction temperature by sealing the reactants in a tube. When methyl lithium was added to a solution of the fluorocarbon in ether, no reaction was apparent, but after two hours gentle refluxing a brown colouration had developed. Unfortunately, the only volatile material isolated from the reaction mixture - apart from ether - was practically pure starting compound. Repeated experiments afforded no better results, hence it would seem unlikely that the reaction of tri-n-butylamine with 2H,2H-nonafluoro-(3-methylbutane) proceeds via a direct nucleophilic attack.

## Reactions of tri-n-butylamine with other saturated fluorocarbon compounds.

### (i) With 2H-undecafluoro-(3-methylbutane), $(CF_3)_2CF.CFHCF_3$.

By analogy with the reaction between $(CF_3)_2CF.CH_2CF_3$ and $(n\text{-}C_4H_9)_3N$, it was expected that one could obtain 2H,3H-decafluoro-(3-methylbutane), $(CF_3)_2CHCFHCF_3$, by the reaction of tri-n-butylamine with $(CF_3)_2CF.CFHCF_3$. Should it then prove possible to eliminate two moles of hydrogen fluoride from the product, the interesting compound perfluoroisoprene, $CF_2{=}C(CF_3).CF{=}CF_2$, would result.

The fluorinated methylbutane was prepared according to the following scheme:

$$(CF_3)_2CFI + CHF{:}CF_2 \longrightarrow (CF_3)_2CF(CFHCF_2)_nI \qquad \text{(i)}$$

$$(CF_3)_2CFCFHCF_2I \xrightarrow[80^{\circ}]{SbF_3Cl_2} (CF_3)_2CFCFHCF_3 \qquad \text{(ii)}$$

Reaction (i) could only be carried out in the presence of azobisisobutyronitrile. However, the reaction between the amine and the fluorocarbon did not go as expected. It proved extremely difficult to find reaction conditions at which any new products resulted. The use of heat and ultra-violet irradiation both produced either extensive decomposition or else very little reaction at all. What little volatile material was isolated (less than 5% of the weight of the starting materials) turned out to be a mixture of two olefins in a 1:1 ratio. It proved impossible to separate these, because of the similarity of their retention times on the V.P.C. coupled with the small quantity available. Infra-red spectroscopy showed the presence of two absorption bands in the C=C stretching region, one occurring at 5•78µ and the other at 5•93µ. The band at 5•93µ can be ascribed to the olefin $(CF_3)_2C=CFCF_3$; the band at 5•78µ does not arise from the olefin $(CF_3)_2CF\cdot CF=CF_2$ since this gives rise to a band at 5•6µ.

One suggestion as to why only very small amounts of volatile products result from this reaction is that it is possible that the compound $(CF_3)_2CH.CFHCF_3$ is formed, but that, under the conditions necessary for its formation, it then eliminates HF to give perfluoroisoprene, which might be expected to polymerise fairly readily.

(ii) <u>With 2H,2H-octafluorobutane.</u>

In order to ascertain whether the replacement of fluorine by hydrogen takes place only in a compound which contains tertiary fluorine, a reaction between 2H,2H-octafluorobutane and tri-n-butylamine was carried out.

Haszeldine[182] prepared 2H,2H-octafluorobutane by heating 2H,2H-1-iodo-octafluorobutane with mercurous fluoride. The author found the reaction to be more easily accomplished, also affording a higher yield (82% as compared to 48%), when antimony trifluoride dichloride was employed as the fluorinating agent.

The fluorocarbon $C_2F_5CH_2CF_3$ was found, as was expected, to be less reactive than $(CF_3)_2CFCH_2CF_3$. After heating for 40 hours at 120° with a two molar proportion of tri-n-butylamine, very little reaction seemed to have taken place. Infra-red spectroscopy showed that most of the volatile reaction product was the original butane, but the presence of some olefinic material was indicated by an absorption band in the region 5·7 - 5·8μ. Increasing the reaction time to approximately 100 hours lead to the formation of appreciable amounts (~15% yield) of this olefin compound. The olefin was eventually separated by gas chromatography, using a perfluorotributylamine column cooled to ca. 10°. Infra-red spectroscopic measurements identified the compound as trans-2H-heptafluorobut-2-ene.

Maynard[162] has reported the synthesis of this compound by the reaction of hexachlorobutadiene with potassium fluoride in N-methylpyrollidone. An attempt to repeat Maynard's work in order to obtain a small quantity of the 2H-heptafluorobut-2-ene was only partially successful. Only a very small yield ($< 5\%$) of olefinic material was obtained. This was possibly due to the fact that tetramethylene sulphone was used as solvent, because of the non-availability (at the time) of N-methyl pyrrolidone. The infra-red spectrum of this olefinic product was very similar to that of the compound resulting from the reaction of $(n\text{-}C_4H_9)_3N$ with $C_2F_5CH_2CF_3$.

It seems that for a fluorine atom to be replaced by hydrogen, that fluorine atom must be attached to a tertiary carbon atom. In other cases, the reaction of the fluorocarbon with a tertiary amine is one of hydrogen fluoride elimination. Even in some cases where a tertiary carbon-fluorine bond does exist, HF elimination still occurs, although probably not to the exclusion of the substitution reaction. What determines the type of reaction is probably the existance or non-existance of a charge-transfer complex. Where a complex is formed, the strength of the bonding determines whether substitution or elimination occurs. For either reaction, the activation energy would be lowered by the formation of the complex.

One of Smith's[97] postulates for the actual cross-linking step occurring in Viton A when a tertiary amine was used as the cross-linking agent, was that unsaturated sites (formed by elimination of HF) in neighbouring chains reacted to form either cyclobutane or cyclohexane structures. Consequently an experiment was carried out in which 2H-nonafluoro-(3-methylbut-1-ene) was heated in a sealed tube to a temperature (200°) greater than that commonly employed in the post-curing cycle of Viton A. Even after extended periods of time, quantitative recovery of the $(CF_3)_2CF{\cdot}CH{=}CF_2$ was realised. This would seem to rule out the possibility of the cross-link formation taking place via a cyclobutane ring, although the possibility of cyclohexane formation in Viton A is not ruled out, since Smith postulated that this occurred by reaction of an isolated double bond in one chain with a conjugated dienic system in a neighbouring chain. Paciorek[109] conducted a similar experiment to that just described, arriving at a similar conclusion. The olefin used was 4-hydroperfluorohept-3-ene, $C_2F_5CF{=}CH.C_3F_7$.

These results agree with the work of Park et al.,[183] who showed that olefins of the type $CF_2{:}CHX$ (X = H, F, Cl or Br) would not homocyclize.

## Reaction of Perfluoro-alkyl iodides with tertiary amines.

Haszeldine[136] has reacted trifluoroiodomethane with trimethylamine. He found that high yields of fluoroform were produced on allowing the solid that was initially formed to stand for extended periods of time. The reaction was suggested to occur via the formation of $[N(CH_3)_3I]^+\ CF_3^-$ by nucleophilic attack on iodine, the trifluoromethyl anion then abstracting hydrogen from neighbouring molecules. More recent work[184] has shown that the initial reaction between trimethylamine and trifluoroiodomethane is the formation of an electron donor-acceptor complex similar to those between iodine and tertiary amines. Haszeldine's work was repeated and extended at Durham. In contrast to his finding that tetramethylammonium iodide was ultimately produced in the reaction, we have shown that in fact the main solid product is trimethylammonium iodide. Reactions were carried out in which the effect of heat and ultra-violet light on the rate of fluoroform formation were determined. Raising the reaction temperature from room to 55° increased the rate of formation of $CF_3H$ but slightly. However, by irradiating the solid initially formed with ultra-violet light, the rate of reaction increased greatly, resulting in a 90% conversion to fluoroform in 24 hours as compared to a 5·1% conversion after heating the solid to 55° for a similar period. If the formation of fluoroform occurs by the mechanism postulated by Haszeldine, i.e. formation of $[N(CH_3)_3I]^+ CF_3^-$ and then abstraction of a proton by $CF_3^-$, one would not have expected that ultra-violet light would accelerate the reaction to any great degree. If, however, the reaction proceeds via the donor-acceptor complex, $Me_3N \rightarrow I\text{-}CF_3$, ultra-violet light would be expected to speed up the reaction - as is the case. Of course, should the donor-acceptor complex break down to the 'Haszeldine' type of complex, the above argument would not be applicable.

A similar experiment was carried out between 2-iodoheptafluoropropane and tri-n-butylamine. On mixing the reactants, immediate formation of a solid occurred which on irradiation by U.V. for a day, or on standing at room temperature for an extended period (30 days), produced 2H-heptafluoropropane in yields up to 46%. That the initial reaction product in this case is better represented as a 1:1 donor-acceptor complex than a compound

$$[(C_4H_9)_3N\ I]^+\ \ FC^-(CF_3)_2$$

was demonstrated by infra-red spectroscopy. The infra-red spectrum of the complex could almost be regarded as the spectrum of tri-n-butylamine superimposed on that of 2-iodoheptafluoropropane. The frequencies of some bands were slightly reduced, but no new bands were present in the spectrum.

<u>Reaction of 1,1,2-trichloro-trifluoroethane with trimethylamine.</u>

During preliminary attempts to synthesize $(n-C_4H_9)_3N.3HF$, it was noticed that a precipitate was formed on allowing a solution of tri-n-butylamine in Isceon 113* (1,1,2-trichloro-trifluoroethane) to stand overnight. This reaction between the Isceon and the amine was investigated fairly fully. It was shown that trimethylamine was more reactive than was tri-butylamine, and that ultra-violet light produced a greater increase in reaction rate than did increase in temperature.

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*Registered trade mark of Imperial Smelting Corp.

The main product isolated from the reaction was $CF_2Cl.CFClH$ in yields varying (according to reaction conditions) from 5 to 60%. Trialkylamine hydrochlorides were also produced, but the solids resulting from the reactions were not wholly the simple hydrochlorides. However, no trace of any anion other than chloride was found in this solid. The dichloro-trifluoroethane produced could be dechlorinated to give trifluoroethylene.[185]

The results of the reactions of various tertiary amines with Isceon 113 are summarised in the following table:

TABLE 7. Reactions of Tertiary amines with Isceon 113

| Amine | Method | Reaction time (hrs.) | % conversion to $CF_2Cl.CFClH$ |
|---|---|---|---|
| $(CH_3)_3N$ | U.V. | 5 | 16 |
| " | U.V. | 96 | 60 |
| " | Thermal(150°) | 72 | Negligible |
| $(C_2H_5)_3N$ | U.V. | 96 | 5 |
| " | Thermal(120°) | 84 | 5 |
| $(C_4H_9)_3N$ | U.V. | 120 | Trace |
| " | Thermal(120°) | 84 | Trace |

TABLE 8. Summary of reactions of tertiary amines with saturated fluorocarbon compounds.

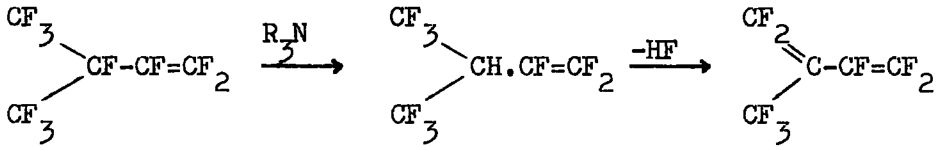
| Amine | Starting material | Reaction Conditions | Products | Yields, % |
|---|---|---|---|---|
| $(n\text{-}C_4H_9)_3N$ | $[(CF_3)_2CFCH_2CF_2]_2$ | 120°; 7 hrs. | $(CF_3)_2C{=}CHCF_2CF{=}CHCF(CF_3)_2$ | 50 |
| $(n\text{-}C_4H_9)_3N$ | $(CF_3)_2CFCH_2CF_3$ | 125°; 24 hrs. | $(CF_3)_2CHCH_2CF_3$ | 38 |
| $(n\text{-}C_4H_9)_3N$ | $(CF_3)_2CFCH_2CF_3$ | u.v.; 90 hrs. | $(CF_3)_2CHCH_2CF_3$ | 47 |
| $(n\text{-}C_4H_9)_3N$ | $(CF_3)_2CFCFHCF_3$ | 140°; 24 hrs. | Decomposition | - |
| $(n\text{-}C_4H_9)_3N$ | $C_2F_5CH_2CF_3$ | 120°; 100 hrs. | trans-$CF_3CF{=}CHCF_3$ | 15 |
| $(CH_3)_3N$ | $CF_3I$ | u.v.; 24 hrs. | $CF_3H$ | 60 |
| $(n\text{-}C_4H_9)_3N$ | $(CF_3)_2CFI$ | u.v.; 24 hrs. | $(CF_3)_2CFH$ | 46 |
| $(CH_3)_3N$ | $CF_2ClCFCl_2$ | u.v.; 24 hrs. | $CF_2ClCFClH$ | 60 |

## The Reaction of Tertiary Amines with Fluorinated Olefins.

Up to the present time, comparatively little work has been carried out into the reactions of tertiary amines with fluorinated olefins. The work of Rapp[132] and Pruett[133] previously referred to (page 59) describes the reactions of tri-alkylamines with perfluorocyclobutene.

Apart from the reason that little work has been conducted in this field, it was decided to investigate the tertiary amine-polyfluoro-olefin system because of its possible bearing on the cross-linking processes occurring in Viton A. Also, should a process occur similar to that observed for the reaction between tri-n-butylamine and 2H,2H-decafluoro-(3-methylbutane), i.e. replacement of tertiary fluorine by hydrogen, it was thought possible that conjugated dienes might be prepared in this way.

e.g.



However, as will be seen, this type of reaction did not occur, at least it did not occur to any great extent.

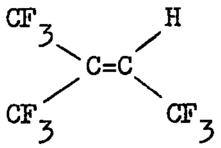
Initial reactions were carried out using tri-n-butylamine, but, hoping to simplify the system, trimethylamine was later used.

### Reactions of tri-n-butylamine with fluorinated olefins

(i) With 2H-nonafluoro-(3-methylbut-1-ene), $(CF_3)_2CF.CH{=}CF_2$.

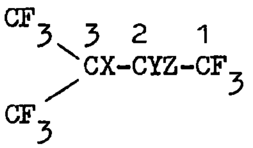
Reactions were usually carried out by irradiating with U.V. a mixture of the olefin and an equi-molar amount of $(C_4H_9)_3N$ in either glass or silica sealed tubes. Reaction mixtures which were heated lead to similar products being formed but not in as good yields or as cleanly.

Vapour phase chromatography showed that two products resulted from the reaction, with similar retention times to the starting olefin. However, when the reactions were allowed to proceed to the stage where no $(CF_3)_2CF{\cdot}CH{=}CF_2$ remained, infra-red spectroscopic examination of the two volatile components indicated that both were saturated. The products were characterised as $(CF_3)_2CHCH_2CF_3$, which had previously been produced from the reaction of $(CF_3)_2CF.CH_2CF_3$ with $(n\text{-}C_4H_9)_3N$, and the olefin $(CF_3)_2C{=}CH.CF_3$. This internal olefin was unusual in that it exhibited no absorption in the C=C stretching frequency region of the infra-red spectrum. Coupled with this, was the anomalous $F^{19}$ N.M.R. spectrum. This too indicated that the molecule was saturated, with free rotation about all carbon-carbon bonds. Two groups of fluorine atoms exist in the intensity ratio of 2:1 having chemical shifts of -20·0 and -14·2 p.p.m. respectively, measured from trifluoroacetic acid. One would expect that the olefin

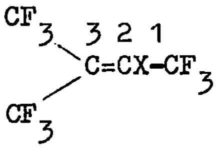


would show three chemically shifted groups of fluorines in the intensity ratios of 1:1:1 instead of the two chemically shifted groups that do occur.

Molecular weight measurement by Regnault's method gave a value in the region of 230; this information coupled with the fact that the mass spectrum of the compound gave a fragment at mass 232 indicated that this largest fragment shown on the mass spectrum was in fact the molecular ion. This in itself indicates the presence of an olefinic structure, since saturated polyfluorocarbon compounds do not give molecular ions.[175] Additional evidence for the olefinic structure is the presence of a large fragment at mass 75. It has been the experience of the author that compounds containing the structural entities



or



invariably first lose a fluorine atom from $C^1$ and then both trifluoromethyl groups from $C^3$, leaving fragments

$$CX\text{-}CYZ\text{-}CF_2 \quad \text{and} \quad C{=}CX\text{-}CF_2$$

respectively. Thus, $(CF_3)_2CH.CH_2CF_3$ gives a fragment of relative high intensity at mass number 77, corresponding to a fragment $C_3H_3F_2$, and $(CF_3)_2C{=}CF.CF_3$ (discussed in later pages) gives a high intensity fragment at mass number 87, corresponding to a fragment $C_3F_3$.

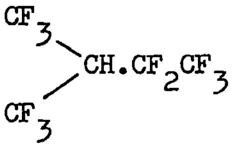
Ultra-violet spectroscopy was also indicative of an unsaturated compound, showing an absorption band in the correct region for fluoro-olefins ($\lambda_{max}$ = 207 mμ, $\epsilon$ = 101·5).

Haszeldine[186] has prepared 2H-nonafluoro-(3-methylbut-2-ene) by another route, but unfortunately gives no data for the compound, other than its boiling point. The measured boiling point (33°) of the compound described above agrees with that recorded by Haszeldine.

(ii) <u>Reaction of tri-n-butylamine with decafluoro-(3-methylbut-1-ene).</u>

The above olefin, $(CF_3)_2CF.CF{=}CF_2$, was prepared by the dehydro-iodination of 2H,1-iododecafluoro-(3-methylbutane), $(CF_3)_2CF.CFH.CF_2I$.[187]

Irradiation of $(CF_3)_2CF.CF{=}CF_2$ with equi-molar quantities of tri-n-butylamine by ultra-violet light proceeded smoothly giving mainly one product in yields up to 52% (measured by V.P.C.). The compound was shown to be saturated, and molecular weight determinations by Regnault's method and by mass spectrometry gave a value of 270. Coupled with (i) infra-red spectroscopic and (ii) $F^{19}$ N.M.R. evidence, indicating (i) no unsaturation and (ii) two equivalent $CF_3$ groups, one non-equivalent $CF_3$ group, one difluoromethylene group and <u>no</u> tertiary fluorine, the structure of the product was thus shown to be



$$(CF_3)_2CH.CF_2CF_3$$

Heating tri-n-butylamine with decafluoro-(3-methylbut-1-ene) gave a complex mixture of products in low yields, one of which was 3H-undecafluoro-(3-methylbutane), $(CF_3)_2CHCF_2CF_3$. Because of the complexity of the product, no serious attempt was made to investigate the thermal reaction.

A reaction in which sodium carbonate was added to the amine and terminal olefin mixture in order to try to prevent HF addition to the but-2-ene first formed was not very successful, only a very small recovery of volatile material was obtained.

(iii) Reaction of tri-n-butylamine with hexafluoropropene.

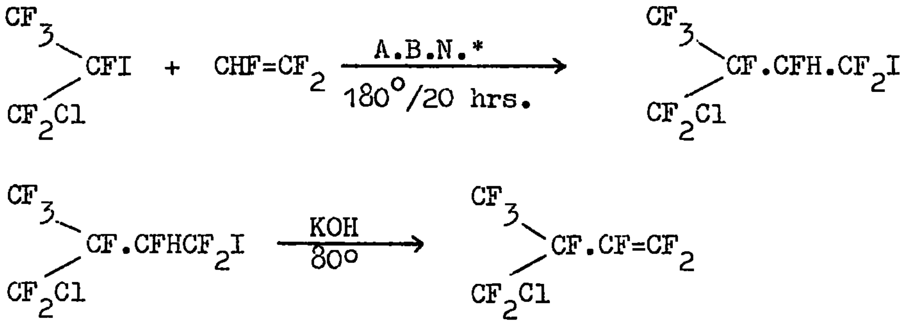
In view of the results obtained in the previous reaction, it was decided to use an olefin which could not undergo rearrangement, and also, one which would react to give a known product having a very characteristic infra-red spectrum. Hexafluoropropene obviously cannot rearrange, except possibly to perfluorocyclopropane, and the expected product, 2H-heptafluoropropane, does have a very characteristic infra-red spectrum.

It was found that heating hexafluoropropene with tri-n-butylamine to temperatures of up to 120° for 24 hours produced very little reaction. The effect of ultra-violet light, on the other hand, was most marked. After being irradiated for 24 hours, a product was obtained in good yield (74% of the weight of the $C_3F_6$) which comprised more than 80% 2H-heptafluoropropane with very little unreacted hexafluoropropene. Obviously extensive degradation of some $C_3F_6$ molecules must have occurred to produce the additional fluorine atom required to convert $C_3F_6$ to $C_3HF_7$. Since at least 55% of the hexafluoropropene was converted to 2H-heptafluoropropane, some of the $C_3F_6$ molecules not converted to $C_3F_7H$ must necessarily have been decomposed to give more than one fluoride ion per molecule.

### (iv) Reaction of tri-n-butylamine with 4-chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CF{\cdot}CF{=}CF_2$.

The above olefin was prepared by the following route:

$$C_3F_6 + ICl \longrightarrow CF_3CFI.CF_2Cl$$



$$\begin{matrix}CF_3 \\ CF_2Cl\end{matrix}\!\!>CFI + CHF{=}CF_2 \xrightarrow[180^{\circ}/20\ \mathrm{hrs.}]{\mathrm{A.B.N.}^*} \begin{matrix}CF_3 \\ CF_2Cl\end{matrix}\!\!>CF.CFH.CF_2I$$

$$\begin{matrix}CF_3 \\ CF_2Cl\end{matrix}\!\!>CF.CFHCF_2I \xrightarrow[80^{\circ}]{\mathrm{KOH}} \begin{matrix}CF_3 \\ CF_2Cl\end{matrix}\!\!>CF.CF{=}CF_2$$

Whereas the previous olefin and tri-n-butylamine mixtures were not miscible at room temperature, the above olefin was. This in itself indicates some degree of interaction between the two reactants, and consequently an enhanced reactivity was expected. On first mixing the reactants, a slight white precipitate was seen which, however, soon disappeared. Ultra-violet irradiation of the mixture gave a product which was shown by analytical V.P.C. to be mainly one compound. This was separated and shown to be 3H,1-chlorodecafluoro-(3-methylbutane), $(CF_3)_2CH.CF_2CF_2Cl$. That the compound was this and not $(CF_3)(CF_2Cl)CH.CF_2CF_3$ was clearly shown by $F^{19}$ N.M.R. measurements (see Appendix). Two equivalent $CF_3$ groups were shown to be present in the molecule whereas the latter formulation would show two non-equivalent $CF_3$ groups.

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* A.B.N. - azobisbutyronitrile.

### (iv) The reaction of tri-n-butylamine with 2H-heptafluorobut-1-ene, $C_2F_5CH=CF_2$

This reaction was carried out in order to investigate whether rearrangement occurred in an unbranched olefin containing hydrogen on the double bond. In fact, this olefin proved much less reactive than those containing a branched chain, i.e. those olefins which possessed a tertiary fluorine atom. The conditions necessary to induce reaction resulted in the formation of substantial amounts of tarry material from which could be isolated the amine tri-hydrofluoride already mentioned. The volatile materials that could be recovered from the reactions consisted largely of the 2H-heptafluorobut-1-ene with a small amount ($< 10\%$) of saturated material, identified as 2H,2H-octafluorobutane.

Again, this reaction proceeded much more readily by ultra-violet irradiation than it did by heating. Certainly heating to above $160^{\circ}$ did cause reaction, but in this case no volatile materials could be isolated.

In all of the reactions carried out between tri-n-butylamine and fluorinated olefins, appreciable quantities of tri-n-butylamine tri-hydrofluoride were isolated. This lead to the idea that reactions might have occurred through initial formation of the amine hydrofluoride which then added the elements of HF to the rearranged olefin. However, attempts to add HF to olefins by using the amine tri-hydrofluoride under a variety of conditions were usually without much success. Only in the case of hexafluoropropene were amounts of the HF adduct obtained in yields similar to those obtained by the use of tri-n-butylamine. Among the fluorinated olefins which were almost completely unreactive toward $(n\text{-}C_4H_9)_3N.3HF$ were

(i) $(CF_3)_2CF\cdot CH=CF_2$
(ii) $(CF_3)_2CF\cdot CF=CF_2$
(iii) $(CF_3)_2C=CF.CF_3$
(iv) $(CF_2Cl)(CF_3)CF\cdot CF=CF_2$
(v) $CF_3CF=CFCF_3$
(vi) cyclic-$C_6F_{10}$
and (vii) $CF_3C\ CCF_3$

Olefins (i), (iii) and (iv) did show some signs of reactivity to the hydrofluoride, but only small traces of new compounds were observed. Solvents used included chloroform, ethyl acetate and iso-propanol.

This lack of reactivity is almost certainly accounted for by the low nucleophilic strength of the $[H_2F_3]^-$ species. Presumably, in the reactions between fluoro-olefins and tri-n-butylamine, the addition of HF takes place via nucleophilic attack by $F^-$ before it is complexed to the $[H_2F_3]^-$ anion.

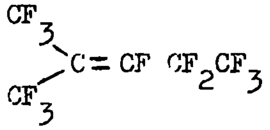
Not only did the tri-hydrofluoride fail to add HF across the double bonds of the olefins, but it also failed to rearrange the terminal olefins to the internal isomers, even after a period of eight weeks in chloroform solution (c.f. Miller's work,[142] when a solution of tetraethylammonium fluoride in chloroform effected complete rearrangement in 24 hours). This also strongly suggests that it is the initial formation of uncomplexed fluoride ion that effects the reactions, both rearrangements and HF additions.

The Reactions of Trimethylamine with fluorinated olefins.

Reactions were carried out with trimethylamine and fluorinated olefins in the hope that the fate of the amine could be more easily determined, since trimethylamine is a less complex compound than tri-n-butylamine. Also, it was hoped that the reactivity of the amine-olefin system would be greater than was the case with tri-n-butylamine because of the greater nucleophilic strength of trimethylamine.

(i) Reaction of trimethylamine with hexafluoropropene.

After heating equi-molar amounts of trimethylamine and hexafluoropropene to approximately $120^{o}$ for 40 hours, a product was obtained which was shown to be a mixture of a dimer and a trimer of $C_3F_6$ (46% yield of dimer and 21% of trimer). Also obtained in rather smaller yields (ca. 16%) than the dimer and trimer was a molecule which gave a molecular weight (mass spec.) which corresponded to the dimer with one mole of HF added. All three compounds were isolated by a combination of fractional distillation and gas chromatography. The infra-red spectra of the dimer and trimer showed absorptions at 5•90μ and 5•98μ respectively, indicating the presence of $R_fCF_2(CF_3)C{=}C$ entities ($R_f$ = F or perfluoroalkyl). $F^{19}$ N.M.R. measurements* clearly showed that the dimer had the structure



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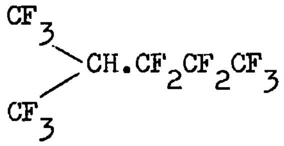
* Full $F^{19}$ N.M.R. data is included in the appendix.

The $F^{19}$ N.M.R. spectrum* of the $C_6HF_{13}$ molecule also was very helpful. This indicated the following structure:



The compound shown, by molecular weight measurements, to be a trimer of $C_3F_6$ proved to be a mixture of at least two components. The N.M.R. spectrum was quite complex, although analytical scale V.P.C. only indicated the presence of one compound. Consequently no definite structure can be assigned to the trimer of $C_3F_6$.

Eleuterio[188] has prepared unsaturated oligomers of hexafluoropropene by heating the $C_3F_6$ with alkali metal or ammonium halides. He obtained good yields of dimers and trimers, although only 2% of the dimer mixture was the compound described above. Unfortunately no infrared or $F^{19}$ N.M.R. data is included in the patent.

### (ii) Reaction of trimethylamine with decafluoro-(3-methylbut-1-ene), $(CF_3)_2CF.CF=CF_2$

Trimethylamine reacts exothermally with an equi-molar proportion of $(CF_3)_2CF.CF=CF_2$ at low temperatures to give a white, solid product which on standing for 24 hours becomes completely liquid. Three components can be separated from this liquid. The most volatile component (b.p. 27°) was shown to be decafluoro-(3-methylbut-2-ene),

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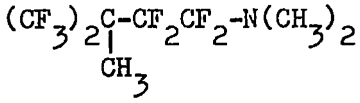
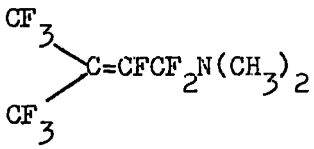
* Full $F^{19}$ N.M.R. data is included in the appendix.

$(CF_3)_2C{=}CFCF_3$, by infra-red spectroscopy, $F^{19}$ N.M.R. and molecular weight measurements. The remaining two components, accounting for approximately half the weight of the starting materials, were very moisture sensitive, fuming in air. Fractional distillation under reduced pressure afforded a method of separation, although the boiling points were not very different. The higher boiling material analysed to a 1:1 adduct of trimethylamine and $C_5F_{10}$. $F^{19}$ N.M.R. spectroscopy indicated a molecule containing two equivalent $CF_3$ groups and two $CF_2$ groups. Also, the proton N.M.R. spectrum indicated two different groups of hydrogen atoms in the ratio 2:1. Thus the structure of this compound is almost certainly



$$(CF_3)_2\underset{\displaystyle CH_3}{\overset{}{C}}-CF_2CF_2-N(CH_3)_2$$

Infra-red spectroscopic examination of the lower boiling of the two moisture sensitive compounds showed a band at 5·9µ, indicating the $(CF_3)_2C{=}CF-$ entity. Also, analysis figures suggested a molecule $C_7H_6F_9N$. $F^{19}$ N.M.R. examination supported a structure



Hydrolysis of the latter of these two compounds occurred very readily, distilled water at room temperature for two hours giving the compound $(CF_3)_2C{=}CFCO.N(CH_3)_2$. The formula was assigned on the evidence obtained from mass spectroscopic and $F^{19}$ N.M.R. measurements. The hydrolysis reaction proved very useful in that the resulting compound could easily be handled in air, and could also be safely purified by preparative scale gas chromatography.

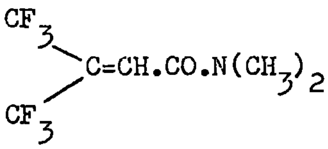
The mechanism for the production of $(CF_3)_2C=CFCF_3$ would at first sight seem to be the fluoride ion catalysed rearrangement[142] of the terminal olefin. However, in the initial reaction of trimethylamine with the terminal olefin no trace of liquid is apparent in the reaction tube, hence it does not seem likely that the rearrangement is straightforward.

### (iii) Reaction of Trimethylamine with 4-chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CFCF=CF_2$

The reaction between trimethylamine and the above olefin was rather more exothermic than the corresponding reaction with decafluoro-(3-methylbut-1-ene). The reaction appeared to follow much the same course, i.e. immediate formation of a white solid, even at very low temperatures, which decomposed on standing to a liquid. However, the liquid product was rather more unstable than the corresponding one in the decafluoro-(3-methylbut-1-ene reaction. It proved impossible to isolate a pure sample of this material, decomposition occurring even under high vacuum distillation. The unstable product was hydrolysed under mild conditions and a compound, formed in yields better than 80%, was isolated. This was shown to be $(CF_3)_2C=CFCO.N(CH_3)_2$, identical to one of the hydrolysis products prepared in the preceding reaction. No other compound was isolated, and it appears that none was formed, certainly not to any great extent. In contrast to the previous reaction, no rearranged olefin was formed.

### (iv) Reaction of Trimethylamine with 2H-nonafluoro-(3-methylbut-1-ene), $(CF_3)_2CFCH{=}CF_2$

In sharp contrast to the two previous reactions, the above reaction was not exothermic. On allowing the reaction tube to warm to room temperature only a slight precipitate was apparent, whereas in the two previous cases the contents of the reaction tubes became completely solid. The greater part of the product obtained was a very volatile compound, boiling at 33°. Infra-red spectroscopy indicated that it was identical to the compound obtained from the reaction of tri-n-butylamine with 2H-nonafluoro-(3-methylbut-1-ene), fairly conclusively shown to be 2H-nonafluoro-(3-methylbut-2-ene). The high yield (ca. 80%) of this compound supports the idea that it is simply the rearranged terminal olefin, $(CF_3)_2C{=}CHCF_3$. A small amount of relatively involatile material was obtained, and this was hydrolysed to give a compound thought to be



$$(CF_3)_2C{=}CH.CO.N(CH_3)_2$$

### (v) Reaction of Trimethylamine with 2H-heptafluorobut-1-ene, $C_2F_5CH{=}CF_2$.

The above reaction was attempted in order to investigate the effect of not having an allylic tertiary fluorine in the system. In fact, no reaction at all occurred under conditions comparable with those employed for all three previous reactions.

TABLE 9. Reaction of fluorinated olefins with equi-molar quantities of tri-n-butylamine.

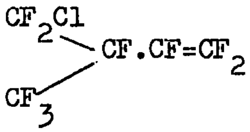
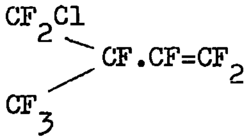
| Olefin | Reaction Conditions | Products | Yields, % |
|---|---|---|---|
| $(CF_3)_2CFCH=CF_2$ | U.V. irradiation, 96 hrs. | $(CF_3)_2CHCH_2CF_3$<br>$(CF_3)_2C=CHCF_3$ | 5<br>71 |
| $(CF_3)_2CFCF=CF_2$ | U.V. irradiation, 16 hrs. | $(CF_3)_2CHCF_2CF_3$<br>$(CF_3)_2C=CFCF_3$ | 52<br>Trace |
| $C_3F_6$ | Heat; 120°, 24 hrs. | Starting material | - |
| $C_3F_6$ | U.V. irradiation, 24 hrs. | $(CF_3)_2CFH$ | 59 |
|  $(CF_2Cl)(CF_3)CF.CF=CF_2$ | U.V. irradiation, 24 hrs. | $(CF_3)_2CHCF_2CF_2Cl$ | 51 |
| $C_2F_5CH=CF_2$ | U.V. irradiation, 48 hrs. | Starting material<br>$C_2F_5CH_2CF_3$ | 55<br>10 |

TABLE 10. Reaction of fluorinated olefins with equi-molar quantities of trimethylamine

| Olefin | Reaction Conditions | Products | Yields, % |
|---|---|---|---|
| $C_3F_6$ | 120°, 40 hrs. | $(CF_3)_2C{=}CFCF_2CF_3$<br>$(CF_3)_2CHCF_2CF_2CF_3$<br>$C_9F_{18}$ | 46<br>16<br>21 |
| $(CF_3)_2CFCF{=}CF_2$ | 20°, 12 hrs. | $(CF_3)_2C{=}CFCF_3$<br>$(CF_3)_2C{=}CFCF_2N(CH_3)_2$<br>$(CF_3)_2C(CH_3)CF_2CF_2N(CH_3)_2$ | 46<br>24<br>19 |
|  $(CF_2Cl)(CF_3)CF.CF{=}CF_2$ | 20°, 12 hrs. | $(CF_3)_2C{=}CFCF_2N(CH_3)_2$ | 40 |
| $(CF_3)_2CFCH{=}CF_2$ | 50°, 48 hrs. | $(CF_3)_2C{=}CFCF_3$<br>$(CF_3)_2C{=}CHCF_2N(CH_3)_2$* | 77<br>10 |
| $C_2F_5CH{=}CF_2$ | 130°, 24 hrs. | No reaction save decomposition | |

* Not fully characterised.

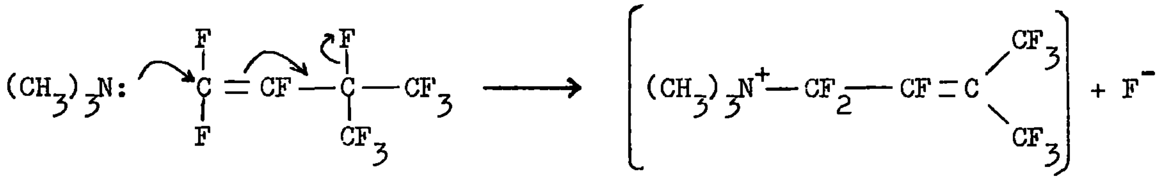
## The mechanisms of the reactions between fluorinated olefins and tertiary amines.

The mechanisms for the reactions between trimethylamine and fluorinated olefins will be discussed first and then the reactions between tri-n-butylamine and fluorinated olefins will be discussed in the light of the results obtained in the trimethylamine reactions.

Addition compounds between tertiary amines and fluoro-olefins are unknown, except for those between (e.g.) triethylamine and hexafluorocyclobutene.[132,133] The reactions that have been described in the preceding pages show that the following requirement must be fulfilled before addition reactions occur between trimethylamine and aliphatic fluoro-olefins, i.e. an allylic tertiary fluorine atom must be present. It is unlikely that reaction occurs between trimethylamine and olefins containing a tertiary fluorine atom that is not allylic, nor does reaction occur with olefins containing allylic fluorine atoms which are not 'tertiary'.

In addition, the compound is more reactive if the double bond is fully fluorinated. When even one vinyl hydrogen is present, the reactivity of the system is greatly reduced.

The formation of the compounds described probably occurs via the initial solid compound formed between the trimethylamine and the olefin. The exact nature of the compound is not at all clear, although it seems very possible that it is a quaternary ammonium salt. The ease of formation of the supposed quaternary salt can be accounted for by the susceptibility of the terminal difluoromethylene group to nucleophilic attack. An SN2' substitution occurs, giving, in the case of decafluoro-(3-methylbut-1-ene), the following reaction:

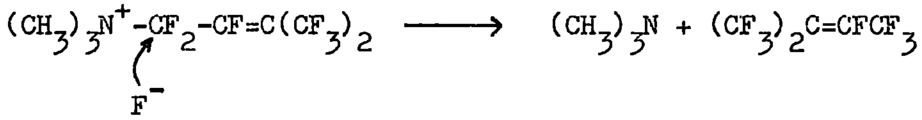


The inductive effects of the two trifluoromethyl groups would aid the elimination of fluoride ion.

The quaternary salt could react in three ways:

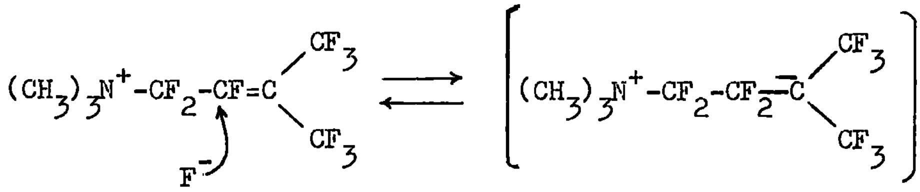
(i) Decomposition to give methyl fluoride and the dimethylperfluoroalkenylamine.

(ii) An SN2 reaction could occur, involving attack on the carbon of the difluoromethylene group by fluoride ion, with subsequent elimination of trimethylamine, the final fluorine containing product being $(CF_3)_2C{=}CFCF_3$;

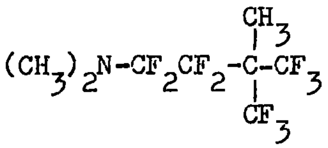


$$(CH_3)_3N^+\text{-}\underset{F^-}{CF_2}\text{-}CF{=}C(CF_3)_2 \longrightarrow (CH_3)_3N + (CF_3)_2C{=}CFCF_3$$

(iii) Carbanion formation by fluoride ion attack as follows:

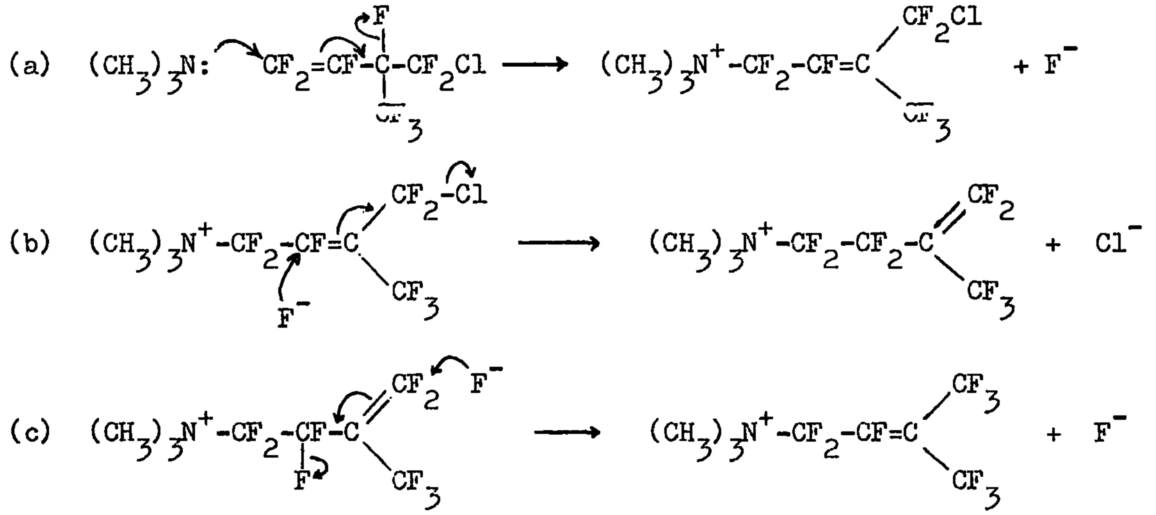


Then migration of a $(CH_3)^+$ group could well occur giving the final product



$$(CH_3)_2N-CF_2CF_2-C(CH_3)(CF_3)-CF_3$$

In the reaction of trimethylamine with 4-chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CF-CF=CF_2$, the probable sequence of events is as follows:



Reactions (b) and (c) occur concurrently, the ultimate product being the quaternary ammonium chloride

$$[(CH_3)_3N^+-CF_2-CF=C(CF_3)_2]Cl^-$$

The quaternary salt decomposes exclusively to methyl chloride and the tertiary amine

$$(CH_3)_2N-CF_2-CF=C(CF_3)_2$$

Presumably the reactions (ii) and (iii) described for the reaction of trimethylamine with decafluoro-(3-methylbut-1-ene) do not occur because of the weaker nucleophilic strength of chloride ion compared to fluoride ion. Certainly no internal olefin, $(CF_3)_2C=CF.CF_2Cl$, arising from reaction (ii) is formed, and, as far as can be ascertained, no product from reaction (iii) is obtained either [this would be $(CF_3)_2(CH_3)C-CFCl-CF_2-N(CH_3)_2$].

The products from the reaction of trimethylamine with $(CF_3)_2CF.CH=CF_2$ are $(CF_3)_2C=CH.CF_3$ and a small percentage of $(CF_3)_2C=CH-CF_2-N(CH_3)_2$. Since none of the compound $(CF_3)_2(CH_3)C-CFHCF_2N(CH_3)_2$ is formed, carbon 3 in the quaternary salt

$$[(CF_3)_2C={}^3CH-{}^4CF_2-N^+(CH_3)_3]\ F^-$$

must be much less susceptible to nucleophilic attack by $F^-$ than carbon 4, as might be expected.

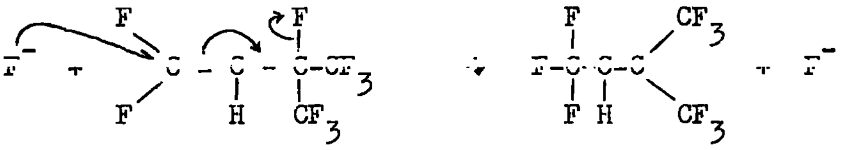
Infra-red spectroscopy gives support to the idea that the solid first formed in the olefin - trimethylamine reactions is a quaternary salt of the type

$$[(CF_3)_2C=CF\cdot CF_2-\overset{+}{N}(CH_3)_3]\ F^-$$

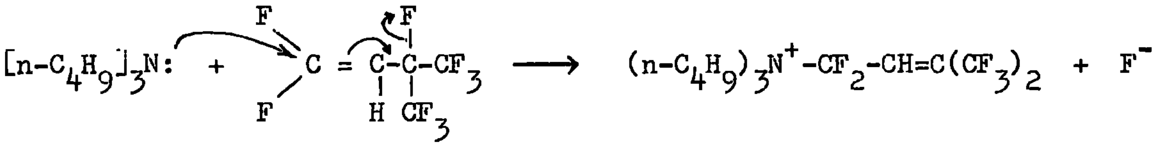
rather than a complex between the nitrogen lone pair and the terminal olefin π electron system. The carbon-carbon double bond absorption occurs at 6·1μ in the solid (c.f. 5·9μ for $(CF_3)_2C=CFCF_3$ and 5·6μ for $(CF_3)_2CF\cdot CF=CF_2$).

These reactions, especially the reaction with 2H-nonafluoro-(3-methylbut-1-ene), $(CF_3)_2CF.CH=CF_2$, are of some significance to the cross-linking of Viton A, where some tertiary allylic fluorine atoms can be formed by initial dehydrofluorination.

The reaction of tri-n-butylamine with 2H-nonafluoro-(3-methylbut-1-ene), $(CF_3)_2CFCH=CF_2$, to give mainly the internal olefin $(CF_3)_2C=CHCF_3$, with small amounts of the saturated compound $(CF_3)_2CHCH_2CF_3$ is fairly readily explained. The formation of the internal olefin is the result of the SN2' reaction known to occur with fluoro-olefins.[142]

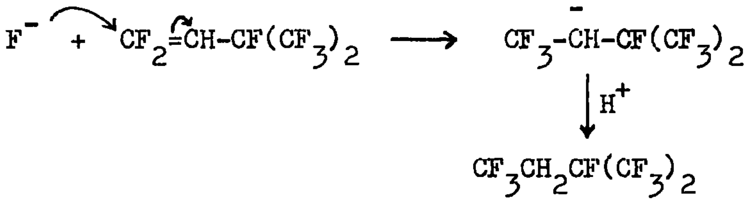


The catalytic amount of fluoride ion necessary for the reaction to occur probably originates from a similar reaction involving tri-n-butylamine as the nucleophile:



$$[n\text{-}C_4H_9]_3N: + CF_2=CH\text{-}CF(CF_3)\text{-}CF_3 \longrightarrow (n\text{-}C_4H_9)_3N^+\text{-}CF_2\text{-}CH=C(CF_3)_2 + F^-$$

The mechanism for the formation of 2H,2H,3H-nonafluoro-(3-methylbutane), $(CF_3)_2CHCH_2CF_3$, is rather more obscure. However, it is quite conceivable that carbanion formation occurs concurrently with the SN2' reaction, resulting in the addition of HF:



$$\begin{tikzcd} F^- + CF_2=CH\text{-}CF(CF_3)_2 \arrow[r] & CF_3\text{-}\overset{-}{C}H\text{-}CF(CF_3)_2 \arrow[d, "H^+"] \\ & CF_3CH_2CF(CF_3)_2 \end{tikzcd}$$

As has already been shown, the compound $(CF_3)_2CFCH_2CF_3$ does react with tri-n-butylamine to give $(CF_3)_2CHCH_2CF_3$. Another possible mechanism, though much less probable than the above mechanism, is one which involves the addition of HF to the internal olefin $(CF_3)_2C{=}CHCF_3$ to produce either $(CF_3)_2CHCFHCF_3$ or $(CF_3)_2CFCH_2CF_3$. The tertiary fluorine atom of these compounds would have to be replaced by hydrogen. Certainly the formation of $(CF_3)_2CHCFHCF_3$ is not favoured because of the relatively low susceptibility towards nucleophilic attack of carbon '2' in the internal olefin $(CF_3)_2\overset{'2'}{C}{=}CHCF_3$.

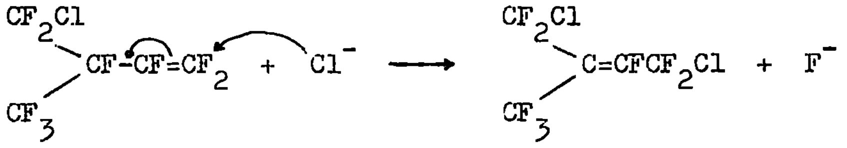
The mechanism whereby 3H-undecafluoro-(3-methylbutane), $(CF_3)_2CHCF_2CF_3$, is formed in the reaction between tri-n-butylamine and decafluoro-(3-methylbut-1-ene), $(CF_3)_2CFCF{=}CF_2$, is quite straightforward. It involves an SN2' attack on the terminal difluoromethylene group to give the rearranged olefin $(CF_3)_2C{=}CFCF_3$ which then undergoes nucleophilic addition of HF. Nucleophilic addition of HF would be expected to occur more easily with the olefin $(CF_3)_2C{=}CFCF_3$ than with $(CF_3)_2C{=}CHCF_3$, as indeed seems to be the case. The initial fluoride ion required for the SN2' reaction and for the addition of HF to the internal olefin almost certainly comes from a nucleophilic attack of the tri-n-butylamine on the terminal difluoromethylene group of the original olefin (c.f. the reaction of trimethylamine with olefins).

That the above mechanism is the true one is supported by two facts:

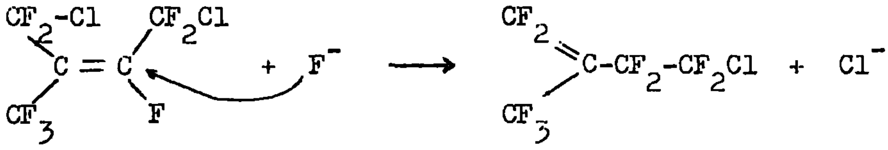
(i) The crude reaction product exhibits absorption in the infra-red at 5·85μ, which was shown to be due to the double bond in $(CF_3)_2C{=}CFCF_3$, and (ii) that no $(CF_3)_2CFCFHCF_3$ is formed, some of which might have been expected had the mechanism involved the initial formation of a secondary carbanion, afterwards rearranging to the more stable tertiary carbanion. The lifetime of the secondary carbanion might reasonably be assumed to have been long enough for at least some hydrogen abstraction to occur.

The U.V. irradiation of a mixture of $C_3F_6$ and tri-n-butylamine produces $(CF_3)_2CFH$ in good yields whereas heating the mixture to 120° produces only small amounts of the propane. This suggests that the reaction producing the fluoride ion needed for HF addition to $C_3F_6$ occurs via a charge-transfer reaction involving a n ⟶ π* transition between the lone pair of electrons on the nitrogen and the π electron system of the olefin.

Although the mechanism for the formation of $(CF_3)_2CHCF_2CF_2Cl$ from the reaction between tri-n-butylamine and $(CF_2Cl)(CF_3)CFCF{=}CF_2$ is not firmly established, it is possible to make feasible suggestions on the basis of Miller's work[142] and the results described in the preceding pages. One possibility is the sequence of reactions as follows:

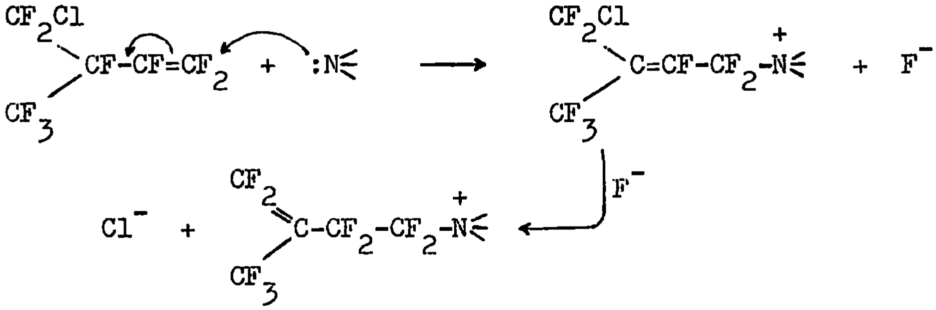


$$(CF_2Cl)(CF_3)CF{-}CF{=}CF_2 + Cl^- \longrightarrow (CF_2Cl)(CF_3)C{=}CFCF_2Cl + F^- \qquad (i)$$


(ii)

The last olefin above could either undergo nucleophilic addition of HF or else rearrange (by $F^-$ attack) to the internal olefin $(CF_3)_2C=CF-CF_2Cl$. The latter course is favoured because it is known[142] that terminal olefins readily undergo fluoride ion catalysed rearrangements to the internal olefin. Miller[143] has also shown that $S_N2'$ substitution of chlorine readily occurs (reaction (ii) above).

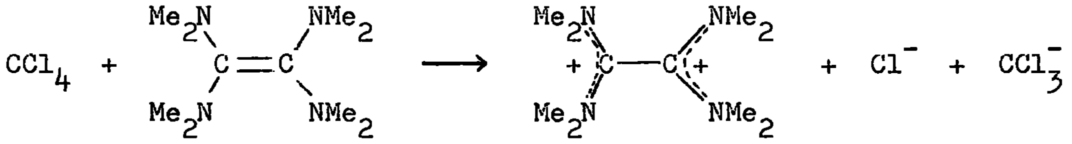
The initial formation of chloride ion would be facilitated by complex formation of the type suggested in a recent paper.[184] Alternatively, chloride ion could be produced by the sequence:



That preferential attack by chloride ion should occur in reaction (i) above can be explained by the fact that fluoride ion tends to be removed as the complex anion $[H_2F_3]^-$. Reaction (ii) probably proceeds very rapidly, the fluoride ion required being in the immediate vicinity having been produced in reaction (i). The probable rate determining step in the formation of $(CF_3)_2CHCF_2CF_2Cl$ is the initial production of chloride ion. The fact that the reaction proceeds by U.V. irradiation and not thermally suggests that in fact the chloride ion is initially produced by complex formation between the chlorine of the $CF_2Cl$ group and the amine.

## Addendum

A recent paper (J. Org. Chem., 1965, 30, 3082) describes the reactions between polyhalogenated compounds and tetrakis(dimethylamino)ethylene. Effectively, one halogen atom is substituted by hydrogen, thus when carbon tetrachloride was treated with the amine, chloroform was isolated in 54% yield. The postulated reaction mechanism was as follows:



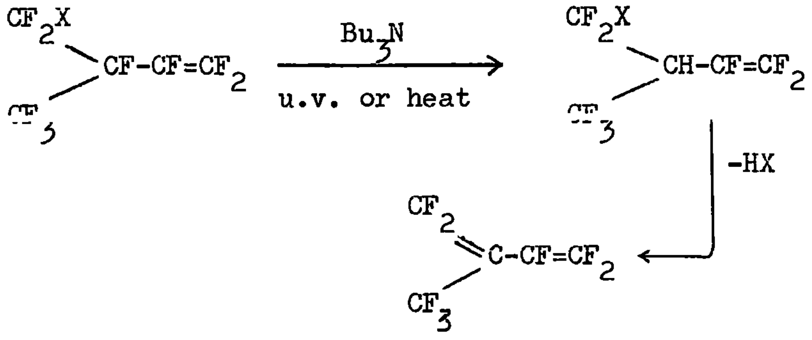
The trichloromethyl carbanion presumably abstracting a proton to give chloroform.

However, it is difficult to apply this mechanism to the reaction of tri-n-butylamine with (e.g.) 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CFCH_2CF_3$, where the tertiary fluorine atom is replaced by hydrogen. The above mechanism involves the simultaneous transfer of two electrons; this is quite feasible with even a di-functional amine but would not be expected to occur with a mono-functional amine such as $(n\text{-}C_4H_9)_3N$.

With a mono-functional tertiary amine the donation of one electron would lead to the formation of an anion and a radical, as has already been postulated for the reaction between tri-n-butylamine and 2H,2H-decafluoro-(3-methylbutane).

## The preparation of some fluorine containing olefins.

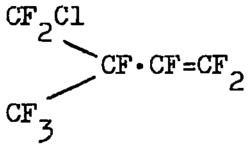
During the course of the previous work it appeared that it might be possible to prepare some fluorinated conjugated di-enes by the reaction of tertiary amines with fluorinated mono-olefins. Thus it was hoped to prepare perfluoro-isoprene, $CF_2=C(CF_3)CF=CF_2$, by the following route:



X = F or Cl

However, the step involving reaction with the tertiary amine does not proceed in the desired manner. Instead, the compounds which result are either a rearranged olefin or else this olefin to which the elements of hydrogen fluoride has been added. Similar attempts to prepare 2H-heptafluoro-(3-methylbuta-1,3-diene), $CF_2=C(CF_3)CH=CF_2$, also failed.

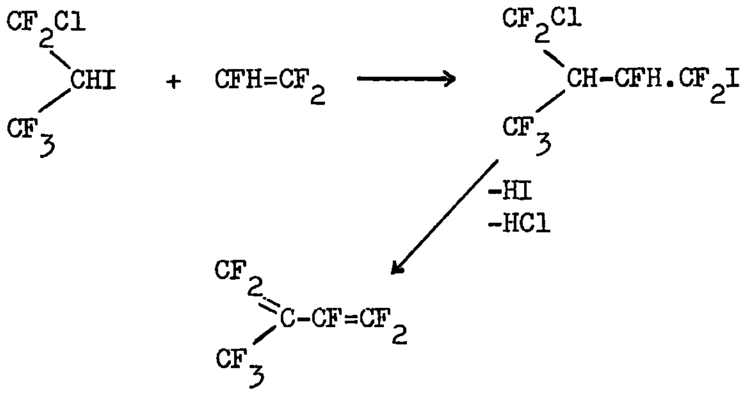
An alternative route was devised which involved the removal of ClF from the olefin



Unfortunately the removal of the elements of ClF proved unexpectedly difficult and in fact has not yet been accomplished. Several different methods were used for the attempted removal of 'chlorine fluoride', including the use of zinc alone or together with ethanol, acetic acid, acetic anhydride and dioxan. In all these cases there was no reaction and the starting material was recovered.

Other dehalogenating agents which were tried were steel wool, ferric oxide, and magnetite ($Fe_3O_4$). In all cases they were packed into a heated glass tube and the olefin was passed through in a stream of nitrogen, temperatures employed ranged from 300° to 500° in 50° intervals. In the case of $(CF_3)(CF_2Cl)CF{\cdot}CH{=}CF_2$ there was considerable decomposition, some hydrogen fluoride was formed and the very small amount of organic material recovered was a complex mixture. With $(CF_3)(CF_2Cl)CF{\cdot}CF{=}CF_2$ results were much the same with steel wool and ferric oxide, but a 40% recovery of organic material was obtained when magnetite was used under its optimum conditions (400°). Lower temperatures gave only starting material and higher temperatures produced much decomposition. Examination by V.P.C. revealed a mixture of eight components, none in high concentration.

One other method has been attempted for the preparation of perfluoroisoprene. 2H-pentafluoropropene was reacted with iodine chloride to give 2H-1-chloro-2-iodopentafluoropropane,[189] $CF_3CHICF_2Cl$, and then an addition of this iodide to trifluoroethylene was attempted. The desired sequence of reactions was



In spite of considerable effort, the addition of the iodide to trifluoroethylene has still to be achieved. Methods tried include the use of heat alone, heat with azobisbutyronitrile, and ultra-violet light. With free radical initiators either no reaction occurs or, on raising the reaction temperature, extensive decomposition results.

Another idea contemplated for the preparation of perfluoroisoprene is the addition of trifluorovinyl iodide or bromide to 2H-pentafluoropropene, although this has as yet not been attempted.

As part of a general plan to prepare conjugated di-enes, work has been carried out to eliminate HF from mono-olefins of the type

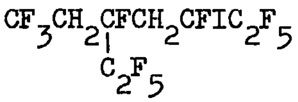
$$(CF_3)_2CFCHXCF_2CX{=}CF_2,$$

with X = H or F. The mono-olefins can be prepared by the addition of 2-iodoheptafluoropropane to two moles of olefin $CHX{=}CF_2$ and the subsequent elimination of hydrogen iodide. When X = H, i.e. the starting olefin is vinylidene fluoride, the reactions to produce the mono-olefin are straightforward. When $(CF_3)_2CFI$ is added to two moles of trifluoroethylene, gas chromatography shows three components, in the ratio 2:2:1, in the fraction analysing to $(CF_3)_2CF(CFHCF_2)_2I$. These components were isolated by preparative scale V.P.C. The two components in highest abundance were shown to be diastereo-isomers of $(CF_3)_2CF{\cdot}(CFHCF_2)_2I$. Dehydro-iodination of each gave the same olefin. Attempts to dehydroiodinate the third component failed, it was concluded that this was the compound $(CF_3)_2CF.CFHCF_2CF_2CFHI$. Ultra-violet spectroscopy supported these ideas. In Table 7 below, the absorption maxima are presented together with those of some other fluoro-alkyl iodides.

TABLE 7

| | $\lambda_{max.}$ (mμ) |
|---|---|
| $(CF_3)_2CF.CFHCF_2CFHCF_2I$ $\{$ | 272·2<br>272 |
| $(CF_3)_2CF.CFHCF_2CF_2CFHI$ | 268 |
| $CF_3CF_2CF_2I$ | 271 |
| $CF_3CH_2CF_2I$ | 271 |
| $CF_3CH_2I$ | 262 |
| $CF_2BrCH_2I$ | 266 |

Paciorek[110] in her work on model compounds of Viton A, also prepared diastereo-isomers which she separated by gas chromatography. The diastereo-isomers of the iodide



$$CF_3CH_2\underset{\displaystyle C_2F_5}{\underset{|}{C}}FCH_2CFIC_2F_5$$

were said to have almost identical refractive indices although their infra-red spectra were surprisingly different. A similar observation has been made for the diastereo-isomers of $(CF_3)_2CF.CFHCF_2CFHCF_2I$. Refractive indices are $n_D^{20} = 1{\cdot}348$ and $1{\cdot}346$ respectively. (The refractive index for $(CF_3)_2CF.CFHCF_2CF_2CFHI$ is $n_D^{20} = 1{\cdot}350$). The infra-red spectra of the diastereo-isomers in this case are also dissimilar.

The elimination of hydrogen fluoride from the mono-olefins has not proved easy. The standard methods of eliminating hydrogen halide did not prove successful. Knunyants[151] has used potassium hydroxide in di-butyl ether to remove HF from 1H,2H-hexafluoropropane in good yields at low temperatures. This reagent did not prove effective up to 120°. The same paper also describes the use of molten KOH at temperatures up to 170°. This method proved altogether too vigorous for the elimination of hydrogen fluoride from the mono-olefins used. Either conditions were such that hardly any reaction at all occurred, or else practically no recovery of organic material was obtained. One new product was isolated by combining the material recovered from several experiments. The infra-red and mass spectra of the compound were consistent with the structure $(CF_3)_2CF.CH_2CF{=}CH.CF_3$.

The most successful method for HF elimination proved to be the use of sodium fluoride at temperatures from 350° to 550°. A 1:1 mixture of sodium fluoride and asbestos wool was used, the asbestos acting as a carrier for the NaF powder. Tatlow[154] has described a similar method of dehydrofluorination. In a series of experiments using $(CF_3)_2CFCH_2CF_2CH{=}CF_2$

only low yields of di-olefinic material were obtained. Under optimum conditions (450°, 3 litres $N_2$/hr.) a 90% recovery of organic material was obtained, analytical scale V.P.C. indicated this to be 55% starting olefin, 30% $(CF_3)_2CF.CH_2CF{=}CH.CF_3$ and 15% of di-olefin. The di-olefin was separated and shown to be

$$(CF_3)_2C{=}CH.CF{=}CH.CF_3$$

rather than the desired $(CF_3)_2CF.CH{=}CF.CH{=}CF_2$. The 2H,4H-decafluoro-(5-methylhexa-2,4-diene) was characterised by infra-red, ultra-violet and mass spectroscopy. The ultra-violet maximum occurred at 229mμ ($\epsilon = 1{\cdot}386 \times 10^4$).

No success has yet been obtained in eliminating HF from the mono-olefin $(CF_3)_2CFCFH.CF_2CF{=}CF_2$.

# Chapter 3

# EXPERIMENTAL WORK

## Infra-red Spectroscopy

Infra-red spectroscopy proved to be a valuable analytical tool. Three instruments were used for recording spectra. They were

(i) The Grubb-Parsons G.S.-2A double beam grating spectrometer,

(ii) The Grubb-Parsons "Spectromaster",

and (iii) The Perkin-Elmer "Infracord 137E" sodium chloride spectrophotometer. This last instrument was mainly used for following the courses of reactions, the Grubb-Parsons instruments being used for recording reference spectra.

Samples were in the form of a thin liquid film between potassium bromide discs, or, in the case of gases and volatiles liquids, in a cylindrical cell with potassium bromide end windows. The cell could be attached to a vacuum-line by means of a ball-joint. The occasional solid sample was pressed into a thin disc with potassium bromide.

## Ultra-violet Spectroscopy

Ultra-violet spectroscopy was used for three main purposes, the determination of the structures of some polyfluoroalkyl iodides, the determination of the possible existance (or otherwise) of charge-transfer complexes between tertiary amines and fluorocarbon compounds and also as a qualitative test for conjugation.

The sample was usually dissolved in cyclohexane and the solution placed in a 1 cm. path-length quartz cell, but in the search for absorption due to charge-transfer complexes, a mixture of amine and fluorocarbon compound was used without a solvent. In this latter case, short path-length cells (path-lengths from 1 to 7 x $10^{-3}$ mm.) were used.

In most cases, the instrument used was the Optica C.F.4.DR double beam spectrophotometer, but in the later stages of the work a Unicam S.P.600 was also used.

## Nuclear Magnetic Resonance Spectroscopy

$F^{19}$ resonance data was obtained using an A.E.I. R.S.2. spectrometer operating at 60 Mc/s. Proton resonance data was obtained by using either the same A.E.I. machine, or by the use of a Perkin-Elmer R10 spectrometer. Internal references were used, being either fluoro-trichloromethane or hexafluorobenzene for $F^{19}$ studies, and tetramethylsilane for proton resonance measurements.

Except for the more simple cases, spectra were interpreted by Drs. L. Phillips and J.W. Emsley.

Data for decafluoro-(2-methylbut-2-ene) was initially obtained by Dr. L.H. Sutcliffe of Liverpool University, using a Varian V-4300B spectrometer operating at 56·4 Mc/s. The results were later confirmed on the Durham instrument.

## Molecular Weight Measurements.

Several of the compounds prepared in this work have appreciable vapour pressures at room temperature, consequently Regnault's method proved to be a very convenient way of determining molecular weights.

A glass bulb, of volume 145 mls., fitted with a high vacuum tap and B10 cone was used. The bulb could be attached to a vacuum system and filled with a vapour to an accurately measured pressure. The weight of the vapour could be found by weighing the bulb before and after filling. Hence, knowing the volume, weight and temperature of the vapour occupying the bulb, the molecular weight was readily calculated.

The molecular weights of less volatile liquids were found by using a Victor Meyer type apparatus, which was usually calibrated with a known compound of similar structure to the material under investigation.

Extremely accurate molecular weights were obtained by the use of a mass spectrometer.

## Mass Spectroscopy

Initially, mass spectra were obtained by Mr. P. Kelly of the University of Newcastle-on-Tyne using a Metropolitan-Vickers M.S.2. instrument. More recently, an A.E.I. M.S.9 has become available at Durham University. This latter machine is capable of measuring the masses of ions to an accuracy of 5 parts per million, thus considerable reliance can be placed on values obtained for molecular weights, especially when taken in conjunction with values obtained by (e.g.) Regnault's method.

Occasionally, and especially when the M.S.2 machine was used, a 'mass-marking' technique was employed. The marker employed was invariably perfluoro-tri-n-butylamine.

## Vapour-Phase Chromatography

### Analytical Scale V.P.C.

Two instruments were used, the Griffin and George Mark IIB model and the Perkin-Elmer 'Fractometer' Model 451. Of the two machines, the Perkin-Elmer was by far the more used, giving far superior resolution of samples. However, the Griffin and George machine does have the advantage that columns can be easily prepared with any required stationary phase. Whichever of the two machines was used, the column employed was usually one which contained a polar stationary phase; in the case of the Griffin and George it was tricresylphosphate (T.C.P.) on kieselguhr and with the Perkin-Elmer it was di-nonylphthalate on celite. For gases, an acetonylacetone column four metres long was used. This could be cooled to about -15°.

### Preparative Scale V.P.C.

Most of the separations carried out by vapour phase chromatography were effected by means of the 'home-made' apparatus of the 'suck-through' type described by Hutchinson.[111] Basically this consisted of a glass U-tube, one inch in diameter and about six feet long, contained in a lagged oven. The column lead on to a separately heated thermistor detection system[172] and then to the trapping system. For gases or very volatile liquid mixtures, a separate apparatus was used with provision for a refrigerated column having a stationary phase of perfluoro-tri-butylamine, leading to a thermistor detector operating at room temperature.

A commercial preparative scale chromatography unit, the Aerograph 'Autoprep' A-700, has been increasingly used over recent months. Although the resolution obtainable with this machine is quite outstanding, recovery of materials is quite often very poor and is never better than 60%. When only small quantities of materials were available, it was sometimes impossible to recover more than enough of the pure material than that quantity needed for, e.g., an infra-red spectrum. In spite of this objection, the 'Autoprep' has proved to be of great value.

## High Pressure Reactions

A number of autoclaves were used in this work, primarily for the preparation of polyfluoroalkyliodides. Internal volumes ranged from 50 mls. to 1000 ml. The 50 ml., 100 ml. and 150 ml. autoclaves were a commercial type, manufactured by Baskerville and Lindsay Ltd. These autoclaves were electrically heated in an apparatus which slowly rocked them. They were fitted with pressure gauges, making it possible to follow the courses of reactions being carried out. An autoclave of approximately 500 ml. internal volume was frequently used for the preparation of fairly large quantities of starting materials. This autoclave was not fitted with a pressure gauge, but since most reactions carried out therein were reactions which had been previously carried out in one of the smaller autoclaves which were fitted with pressure gauges, the lack of a pressure gauge did not prove an obstacle. The 500 ml. autoclave was rotated in either an oil bath (for temperatures up to 140°)

or in an electrical heater. Mixing of the contents of the autoclave was improved by having in the vessel one or two short lengths of stainless steel rod.

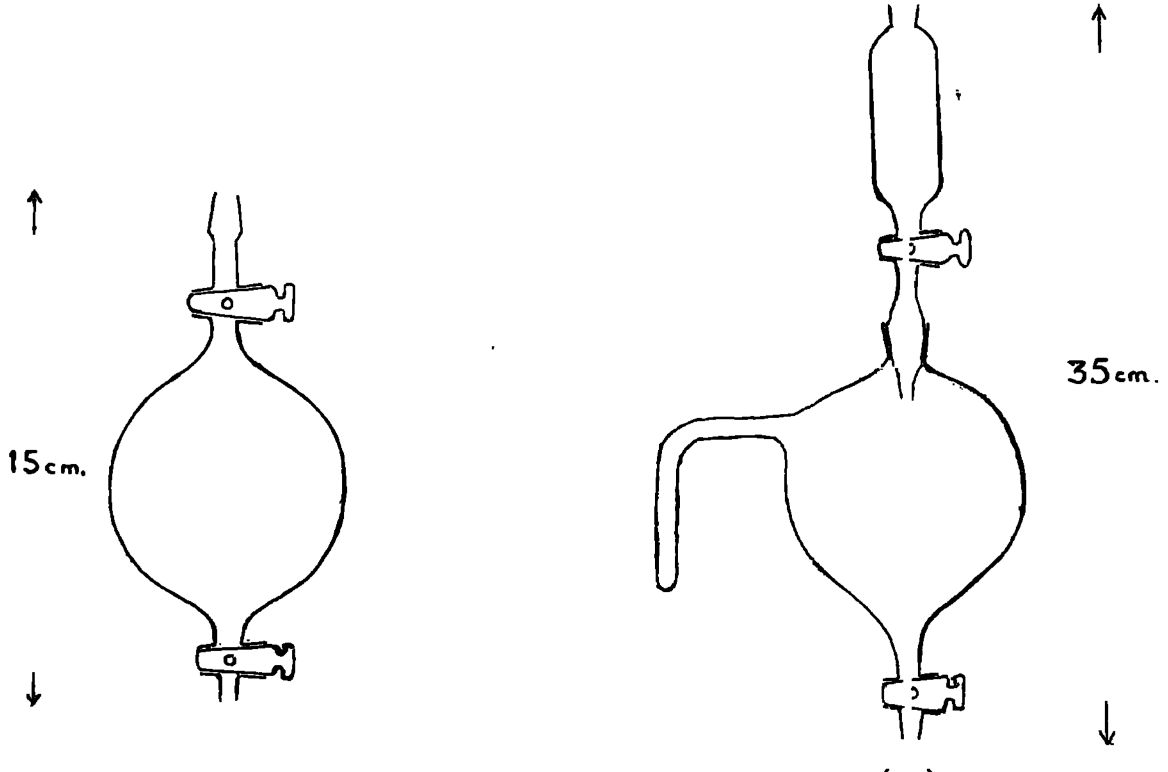
The largest autoclave used was of 1000 ml. capacity which could be rotated at an angle of 45° over two gas burners. To maintain an even temperature in the autoclave, the gas flames had to be continuously checked since the pressure in the gas main could vary considerably. However, the temperature of the contents of the 'bomb' was known fairly accurately since a thermometer well was provided.

With the exception of the largest autoclave, the vessels could all be conveniently filled with gases by cooling them in liquid air or nitrogen, evacuating them by attaching them to a simple vacuum system and then condensing, through the vacuum system, the previously weighed gas. Involatile liquids and solids were placed in the autoclaves before screwing down the heads of the vessels. The one litre autoclave was filled with gases by first condensing the gas required into one of the smaller autoclaves and then connecting the two by steel pressure pipe. The valves of both autoclaves were opened, with the one litre autoclave cooled as much as was practicable by standing it in a bucket containing solid $CO_2$.

## Fluorine Analyses.

Halogen analyses were carried out by the method described by Johncock,[173] or, in the case of a gas or a volatile liquid, by a modification of the method described by Savory.[174] The method described by Savory involved weighing the sample in a 100 ml. bulb, and then quantitatively transferring, by means of a vacuum system, the known weight of gas into a bulb fitted with a side-arm. This bulb was also fitted with a dropping funnel into which was placed the diphenylsodium-dimethoxyethane complex used to decompose the halogen containing compound. The present method obviates the need for a quantitative transference of material through the vacuum system, since the sample is weighed in the bulb in which it is ultimately decomposed. The bulb is shown in Fig. 6 with, for the purpose of comparison, the system employed by Savory. The simplicity of the bulb enables it to be constructed such that its weight will allow the accurate measurement of about 60-100 mgm. of sample into it. The rather bulky system of Savory could not be made sufficiently light in order to allow direct weighing.

Where samples were not soluble in di-iso-propyl ether, the method of Johncock could not be used, instead, a sodium fusion in a small steel 'bomb' was used. Occasionally samples were found which, although being soluble in di-iso-propyl ether, gave inconsistent values for the percentage of fluorine. In these cases too, sodium fusion was employed. Apparently, the biphenyl sodium reagent does not fully decompose all fluorine containing compounds in the usual time allowed (some 10-15 minutes) for this reagent.



(i) (ii)

Fig. 6. Apparatus for fluorine analyses of gases and volatile liquids; (i), as currently used and (ii), as described by Savory.[174]

## Preparation of Model Compounds

### 1. Preparation of 2H,2H-1-iodononafluoro-(3-methylbutane).

An autoclave (150 mls.) into which had been sealed azo-bis-butyronitrile (0·5 g.) and mercury (0·5 ml.), was charged with heptafluoro-2-iodopropane (74 g., 0·25 moles) and 1,1-difluoroethylene (19·5 g., 0·304 moles). The whole was quickly heated to 185°C and rocked for 5 hours. After allowing to cool, a gas (1 g.) was vented, later shown by its infra-red spectrum to be 1,1-difluoroethylene. A liquid (91 g.) coloured by iodine was poured from the autoclave. This liquid was fractionally distilled through a 25 cm. heated Vigreux column. Three main fractions were obtained:

Fraction 1. Boiling range 39° - 45°C; 7 g.
Fraction 2. Boiling range 101° - 105°; 76 g.
Fraction 3. Boiling above 105°; 8 g.

Fraction 1 was shown by analytical V.P.C. (Tri-cresylphosphate, 100°) and infra-red spectroscopy to be essentially pure heptafluoro-2-iodopropane.

Fraction 2 was shown by analytical V.P.C. (tri-cresylphosphate, 150°) to consist of 90% one component. Careful refractionation yielded a material more than 95% pure, which was shown by infra-red spectroscopy and analytical V.P.C. to be identical to authentic 2H,2H-1-iodononafluoro-(3-methylbutane) 2H,2H-1-iodononafluoro-(3-methylbutane). (Found: F, 48·0; I, 34·8. Calculated for $C_5H_2F_7I$: F, 47·5; I, 35·3%. B.p. 103°/755 mm.; lit.,[152] 103°/750 mm.).

Fraction 3 was assumed to be mainly higher telomers of general formula $(CF_3)_2CF.[CH_2CF_2]_nI$, where n is largely equal to two.

The composition of the crude reaction product was calculated from chromatogram areas as being $(CF_3)_2CFI$, 10%; $(CF_3)_2CFCH_2CF_2I$, 80%; and higher telomers, 10% by weight. This represents an 80% conversion of heptafluoro-2-iodopropane into 2H,2H-1-iodononafluoro-(3-methylbutane).

### 2. Coupling of 2H,2H-1-iodononafluoro-(3-methylbutane).

#### (a) With mercury and ultraviolet light.[152]

The iodide (50 g., 0·139 moles) was sealed under vacuum in a thin walled Pyrex tube (ca. 150 ml.) with just sufficient mercury to form a continuous pool when horizontal. The tube was then rotated in a horizontal plane at 15 cm. from a 1 kw. Hanovia U.V. lamp. After three days, the contents of the tube were very dark. The temperature in the region of the tube was approximately 65°. The tube was opened into a vacuum system and a colourless liquid (20·5 g.) was distilled from the tube. Analytical scale V.P.C. (tricresylphosphate, 80°) showed this to consist largely of one component with two minor components ($< 5\%$) and approximately 10% of starting iodide. Distillation of this mixture through a short Vigreux column gave one main fraction b.p. 139-140° (17 g., 52·5%), this fraction was $[(CF_3)_2CF{\cdot}CH_2CF_2]_2$. (Found: F, 73·2; C, 25·8. $C_{10}H_4F_{18}$ calculated: F, 73·5; C, 25·7%).

#### (b) With zinc and acetic anhydride.[166]

The iodide (20 g., 0·0555 moles) in methylene chloride (30 ml.) was contained in a flask (200 ml.) fitted with reflux condenser and mercury-seal stirrer. Granulated zinc (12 g., 0·184 moles, freshly washed with dilute sulphuric acid and then dried) and acetic anhydride (12 g.) were added. After 10 min. the methylene chloride began to reflux and a white precipitate was formed. After a further 15 min. heat was applied to maintain reflux; this was continued for a further 4 hr. The mixture was then filtered to remove zinc iodide and excess zinc. The methylene chloride solution was refluxed with dilute sulphuric acid to hydrolyse the acetic anhydride. The organic layer was separated, washed with bicarbonate solution and dried over $P_2O_5$. Fractional distillation through a short helices packed column yielded 10 g. material, b.p. 135-140°. Analytical V.P.C.(T.C.P., 80°) showed this to be at least 90% one component, identical retention time to the 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) prepared above. Estimated yield (from V.P.C.) 69·5%. From this, 5·3 g. (41%) of $[(CF_3)_2CFCH_2CF_2]_2$ was isolated by preparative scale V.P.C. (T.C.P., 60°), and was shown to be identical to the coupled compound prepared above by its infra-red spectrum.

## The reaction of 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) with tri-n-butylamine.

### Reaction in the absence of solvent.

A flask fitted with a reflux condenser and mercury-seal stirrer was charged with 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) (30 g., 0·0644 moles). To this was added tri-n-butylamine (11·9 g., 0·0644 moles) dropwise and with constant stirring. The mixture was heated to 130° at which temperature it was maintained for five hours. At the end of this time, the reaction vessel was cooled. The contents of the vessel were extremely dark, but traces of crystalline material could be seen. A sample of this material was washed several times with dry ether and was later identified as tri-n-butylamine trihydrofluoride, $(n\text{-}C_4H_9)_3N.3HF$. The bulk of the reaction product was washed with dilute hydrochloric acid to remove excess amine, and then the organic layer was separated. From this, 21 g. of material were distilled at room temperature and 0·001 mm. Hg. This material was dried over $P_2O_5$ and distilled through a short Vigreux column. 19·1 g. of material, b.p. 130°/765 mm. was obtained. Analytical V.P.C. (T.C.P., 65°) showed that this was largely one component, estimated at 85% of the total. The compound was separated by preparative scale V.P.C. (T.C.P., 60°). To obtain material of purity greater than 99%, it was necessary to repeat the chromatography process at least three times, consequently the amount of pure material available was very little since recoveries from the chromatography apparatus were never better than 60%. Also, other compounds were present which had extremely similar retention times, thus necessitating very drastic 'cutting' of the chromatograph peaks. The use of a silicone elastomer column only agravated this last mentioned problem. The use of the Aerograph 'Autoprep' certainly lead to better resolution of the mixture, but the recovery from this instrument was very poor (less than 40%).

The infra-red spectrum of the material showed a single peak at 1709 cm.$^{-1}$ in the carbon-carbon unsaturation region. (I.R. No.2).

The $F^{19}$ magnetic resonance spectrum showed four groups of fluorine in the intensity ratio 12:2:1:1. The $H^1$ magnetic resonance spectrum showed two groups of hydrogen in the intensity ratio of 1:1. Detailed N.M.R. data is included in the appendix.

The material from the original reaction mixture which was not volatile under high vacuum at room temperature was heated to 50° at 0•001 mm. pressure. 2•2 g. of a yellow oil distilled which solidified on standing. The infra-red spectrum of this material showed the presence of a considerable proportion of C-H and C-F bonds.

## Oxidation of the material from the above reaction.

Analar potassium permanganate (7•9 g., 0•05 moles) was dissolved in dry acetone (200 ml.)[167] and contained in a flask fitted with a reflux condenser leading to a trap cooled in liquid air. To the oxidizing mixture was added the unknown compound (8 g.). After ensuring that no spontaneous reaction had set in, the vessel was heated to reflux for two hours. At the end of this time, a volatile liquid (2•2 g.) was observed in the cold trap. Infra-red spectroscopy clearly showed this to be a mixture of carbon dioxide and 2H-heptafluoropropane. The carbon dioxide was removed by passage through sodium hydroxide pellets, leaving 2H-heptafluoropropane (1·8 g.) shown to be pure by infra-red spectroscopy. (Found: M, 168; i-$C_3F_7H$ requires M, 170).

Assuming one mole of 2H-heptafluoropropane is produced by one mole of unknown material, a yield of 56·8% was realised.

Water (200 ml.) was added to the original acetone solution, and the acetone removed on the water pump. The aqueous solution was acidified and then continuously ether extracted for 50 hrs. After removing the ether, 2 ml. of an acid liquid remained. This was taken up in dilute NaOH solution; from this solution the s-benzylthiouroneum derivative was prepared. An infra-red spectrum of this material was compared with that of an authentic s-benzylthiouroneum derivative of trifluoroacetic acid; they were in fact identical.

A mixed melting point (168·5°) also indicated that the compound was the s-benzylthiouroneum derivative of trifluoroacetic acid.

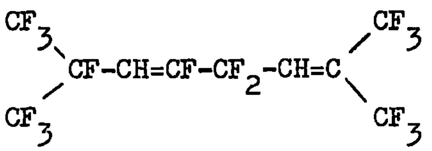
### Attempted hydrogenation of the product from the reaction of tri-n-butylamine with 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane).

The unsaturated compound (1·75 g.) was dissolved in ethanol (40 ml.) in the flask of an atmospheric hydrogenation apparatus. Palladized carbon (20 mg.) was added to the flask and the mixture shaken under hydrogen. After three hours, only 20 ml. of hydrogen appeared to have been absorbed. This was the calculated amount that the catalyst itself would absorb.

Continued shaking of the reaction flask for an additional 12 hrs. resulted in no further uptake of hydrogen. By adding an excess of water to the ethanol solution, the starting material was recovered unchanged.

The molecular weight of the unsaturated compound was first determined by Victor Meyer's method. This gave a value of 430. An accurate value for the molecular weight of the compound was found by the use of the mass spectrometer. A mass-marking technique was used; the mass-marker gave fragments at a mass number of 414 with another at 426. When the unsaturated compound was run through the spectrometer with the mass-marker, the height of the peak at 426 relative to that at 414 was greater than when the mass-marker alone was used, thus indicating the presence of an ion from the unsaturated compound of mass 426. Coupled with the fact that there was no fragment with a mass number greater than 426 not due to the mass marker, it was apparent that the ion at 426 was the molecular ion. This measurement was confirmed by the use of the A.E.I. M.S.9 instrument.

Taking all the evidence into consideration, the structure of the compound from the reaction of tri-n-butylamine with 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) at 130° in the absence of any solvent is



$$(CF_3)_2CF\text{-}CH{=}CF\text{-}CF_2\text{-}CH{=}C(CF_3)_2$$

(Found: M, 426; C, 27·9; F, 70·8%. $C_{10}H_2F_{16}$ requires: M, 426; C, 28·2; F, 71·4%).

## Oxidation of 2H-nonafluoro-(3-methylbut-1-ene)

For this reaction, the olefin 2H-nonafluoro-(3-methylbut-1-ene) was prepared by the dehydroiodination of 2H,2H-1-iodononafluoro-(3-methylbutane) by solid potassium hydroxide.[111]

2H-nonafluoro-(3-methylbut-1-ene) (5 g., 0·0215 moles) dissolved in dry acetone (10 ml.) was added slowly to potassium permanganate (3·58 g., 0·0226 mole) in dry acetone (150 ml.) contained in a flask fitted with a reflux condenser leading to a trap cooled in liquid air. After quite a short time, and without application of external heat, the solution began to gently reflux. The solution was heated gently in order to maintain the reflux for a total time of one hour. During this time, material could be seen to have collected in the cold trap. At the end of one hour, the solution was allowed to cool, and then water (200 ml.) was added. During the addition of the water the acetone solution effervesced, and more volatile material condensed in the cold trap. Infra-red spectroscopy showed the contents of the cold trap to be a mixture of carbon dioxide and 2H-heptafluoropropane. The carbon dioxide was removed by passing the mixture of gases through a potassium hydroxide tube attached to a vacuum system. The volatile material remaining was shown by infra-red spectroscopy to be pure 2H-heptafluoropropane (1·5 g., 0·0088 moles, 41·1%). (Found: F, 77·7%; M, 168. $C_3F_7H$ requires: F, 78·2%; M, 170).

## Reaction of 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) with magnesium oxide

$[(CF_3)_2CFCH_2CF_2]_2$ (1·3 g., 0·00279 moles) was heated at 140° for

48 hrs. with magnesium oxide (0·5 g., 0·0124 moles). From time to time, samples were taken and subjected to analysis by gas chromatography (T.C.P., 60°). No sign of any material other than 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) was observed. At the end of the 48 hrs., only a very slight colouration of the reaction mixture was apparent.

### Reaction of 3H,3H,6H,6H-octadecafluoro-(2,7-dimethyloctane) with tri-n-butylamine in the presence of magnesium oxide.

The fluorocarbon (2 g., 0·00428 moles) was sealed into a heavy walled tube with tri-n-butylamine (1·59 g., 0·00856 moles) and magnesium oxide (0·8 g., 0·02 moles). The tube was heated to 125° for 17 hrs. At the end of this time, the tube was opened and the volatile components pumped, under high vacuum, into a trap cooled in liquid air. The weight of volatile material was 0·4 g. Analytical scale V.P.C. (D.N.P., 87°) revealed the presence of thirteen components of which only the starting material and 3H,6H-hexadecafluoro-(2,7-dimethyloctadiene-2,5) could be recognised (by coincident retention times). These two components accounted for approximately 40% of the volatile material (measured from the area under the chromatograph).

The involatile material remaining in the reaction tube was a thick black intractable tar.

### Preparation of tri-n-butylamine tri-hydrofluoride, $(n\text{-}C_4H_9)_3N.3HF$

(i) Using di-ethyl solvent.

Tri-n-butylamine (2 g., 0·0108 moles) in dry ether (40 ml.) was contained in a two necked flask fitted with a 'Teflon' covered magnetic stirrer and a gas inlet, the bottom of which was below the surface of the ether. Gaseous hydrogen fluoride diluted with an equal volume of nitrogen was gently bubbled into the solution. A white precipitate immediately formed. However, attempts to isolate this precipitate resulted in the formation of a "slush".

(ii) Using no solvent.

Tri-n-butylamine (20 g., 0·108 moles) was contained in a two necked flask fitted with a magnetic stirrer and a gas inlet designed so as to protrude below the surface of the liquid. An exhaust lead to the top of the fumes cupboard. Anhydrous HF, much diluted with nitrogen, was bubbled into the amine. External cooling was employed so as to maintain the temperature of the reaction mixture between 5° and 10°. When no more HF was being absorbed, the mixture was allowed to stand. After ten hours a gel was observed which was dissolved in chloroform. The chloroform solution was poured into ether, resulting in the formation of a white solid which was filtered off. 17·1 g. (0·0697 moles) of this material were obtained. A sample was recrystallized from ethyl acetate giving tri-n-butylaminetrihydrofluoride, m.p. 142°. (Found: F, 23·2%; H, 11·7%. $C_{12}H_{30}F_3N$ requires F, 23·2%; H, 12·2%). (I.R. No. 3).

## Reaction of supposed tri-n-butylamine tri-hydrofluoride with aqueous sodium hydroxide.

The supposed tri-n-butylamine tri-hydrofluoride (2 g., 0·0816 mole) was dissolved in water (15 ml.) to which two drops of phenolphthalein solution had been added. Dilute sodium hydroxide solution was run in until the solution was just alkaline. The mixture was boiled for 15 mins. After cooling, the solution was ether extracted, the ether extract dried and the ether distilled off, leaving a material which was shown by infra-red spectroscopy and by boiling point measurement to be identical to a sample of authentic tri-n-butylamine. Yield 0·96 g., 0·055 mole, 65%.

## The preparation of 2H,2H-decafluoro-(3-methylbutane).

### (i) By reaction of 2H,2H-1-iodononafluoro-(3-methylbutane) with Antimony Trifluorodichloride.

Commercial antimony trifluoride was purified by placing it in a sintered disc extractor and extracting with dry methanol. After distilling off most of the methanol, pure antimony trifluoride precipitated on cooling. The solid was filtered on a Buchner funnel.

The pure antimony trifluoride (40 g., 0·224 moles) was sealed in a stainless steel autoclave (500 ml.) which was then cooled in liquid air and evacuated. Chlorine (15·9 g., 0·224 moles) was condensed onto the $SbF_3$. The autoclave was rotated for 3 hr. at 50°. At the end of this time the autoclave was opened; a grey liquid was apparent in the bottom of the autoclave. $(CF_3)_2CF.CH_2CF_2I$ (40 g., 0·111 moles), previously sealed in a thin-walled glass ampoule, was placed in the autoclave. After sealing the autoclave it was quickly evacuated and then shaken vigorously to break the ampoule. After heating the autoclave to 120° for 4 hr., a volatile liquid was obtained which boiled in the range 43° to 52°. Analytical scale V.P.C. (T.C.P., 60°) indicated the presence of two components in the ratio 10:1. The main component was separated by preparative scale V.P.C. (T.C.P., 60°) and was identified as 2H,2H-decafluoro-(3-methylbutane) by comparing its infra-red spectrum with that of an authentic sample.[111] Yield: 18 g., 64%; b.p. 44°/755 mm. (I.R. No. 4).

(ii) Using Antimony trifluoride/Antimony pentachloride.

Antimony trifluoride (15 g., 0·0838 moles), purified as in the previous experiment, and antimony pentachloride (10 g., 0·0335 moles) were placed in a three necked flask fitted with a dropping funnel, mercury seal stirrer and condenser leading to a trap cooled in solid carbon dioxide. The flask was heated to 100° and $(CF_3)_2CFCH_2CF_2I$ (25 g., 0·0694 moles) was slowly dropped in. Immediate reaction occurred and much iodine was liberated. After all the iodide had been added, a slow stream of nitrogen was blown through the flask. 12 g. of volatile material were recovered from the cold trap; fractionation of this through a 20 cm. Vigreux column produced 10·1 g., 57·7% yield, of 2H,2H-decafluoro-(3-methylbutane).

## The reaction of 2H,2H-decafluoro-(3-methylbutane) with tri-n-butylamine.

### 1. Thermal reactions:

### (i) Reaction at 180°.

$(CF_3)_2CFCH_2CF_3$ (10 g., 0·0397 moles) was sealed in a thick-walled glass tube with tri-n-butylamine (14·7 g., 0·0794 moles) which had been dried by distillation from sodium. The tube was heated for 22 hr. at 180°. At the end of this time, all volatile material was transferred to a vacuum system; very little volatile material was apparent ( $< 1$ g.). A thick black tar remained in the reaction tube. The volatile material was vacuum fractionated through a train of traps at different low temperatures. Two components were separated. The principal component (0·6 g.) boiled below room temperature. A molecular weight determination gave a value of 72·6 [$CF_3H$ requires M = 70]. The infra-red spectrum was very similar to that of fluoroform. The higher boiling fraction gave a molecular weight of 224. The infra-red spectrum indicated a saturated compound and was identical to that of a material later shown to be 2H,2H,3H-nonafluoro-(3-methylbutane), $(CF_3)CH.CH_2CF_3$.

### (ii) Reaction at 125°

$(CF_3)_2CF.CH_2CF_3$ (3·6 g., 0·0143 moles) was condensed into a thick-walled glass tube previously charged with tri-n-butylamine (5·3 g., 0·0286 moles). The tube was sealed under vacuum and allowed to warm to room temperature. The components were not miscible at this temperature. On warming the tube to 125°, one phase only was apparent. The tube was maintained at this temperature for 24 hrs. After opening the tube, all volatile material was vacuum transferred to a small flask. 1·4 g. of product, boiling $<50°/760$ mm. was obtained. Analytical scale V.P.C. (Di-nonylphthalate, 50°) revealed that the liquid was substantially ( $>90\%$) one component. Only one other component was present which was shown by coincident retention times to be the starting material, 2H,2H-decafluoro-(3-methylbutane). The principal component was isolated by preparative scale V.P.C. (tri-cresylphosphate, room temperature) and was shown to be <u>2H,2H,3H-nonafluoro-(3-methylbutane)</u>, $(CF_3)_2CHCH_2CF_3$. (Found: F, 72·3%; M, 234 by mass spectrometry and 230 by Regnault. $C_5H_3F_9$ requires: F, 73·1%; M, 234); b.p. 47°/755 mm.; $n_D^{20} < 1{\cdot}3$; I.R. No. 5.

The thick black tar remaining the reaction tube was extracted with boiling ethyl acetate. After filtering, the ethyl acetate solution deposited a crystalline material. Recrystallization from ethyl acetate produced a compound shown by infra-red spectroscopy and mixed melting point determination to be tri-n-butylamine tri-hydrofluoride, $(n\text{-}C_4H_9)_3N.3HF$.

2. <u>Ultra-violet reaction</u>:

$(CF_3)_2CF.CH_2CF_3$ (2·5 g., 0·00993 mole) was condensed onto dry tri-n-butylamine (3·68 g., 0·0198 mole) contained in a silica tube. The tube was sealed under vacuum. (For the purpose of easy sealing, a graded glass to silica tube had been pre-sealed to the silica reaction tube; the glass of the tube could then be attached to the vacuum line in the normal way). After having been sealed, the tube was rotated for 90 hr. at a distance of 20 cm. from a 500 watt Hanovia ultra-violet lamp. The temperature in the immediate vicinity of the lamp was 45° to 50°. At the end of 90 hr. the volatile components were removed by vacuum distillation. 1·6 g. of this crude material were obtained. Infra-red spectroscopy indicated that it was largely the compound $(CF_3)_2CH.CH_2CF_3$, although the presence of a weak band at 5·69μ indicated the presence of some, although not very much, olefin, probably $(CF_3)_2CF\text{-}CH{=}CF_2$. Analytical chromatography (di-nonyl-phthalate, 50°) showed very little olefin to be present ($< 5\%$); of the remainder, approximately 30% was the starting material, $(CF_3)_2CF.CH_2CF_3$, and 70% was the compound $(CF_3)_2CH.CH_2CF_3$, identical to that prepared in the thermal reaction. Estimated yield: 47%.

After the volatile material had been pumped out from the reaction tube, the dark residue was extracted with chloroform. Pouring the chloroform solution into a large volume of ether produced a white precipitate. After recrystallization from ethyl acetate, infra-red spectroscopy and fluorine analysis identified this compound as $(n\text{-}C_4H_9)_3N.3HF$.

## Proof of the structure of 2H,2H,3H-nonafluoro-(3-methylbutane), $(CF_3)_2CHCH_2CF_3$.

Details of both the $F^{19}$ N.M.R. and mass spectral results for compound $(CF_3)_2CHCH_2CF_3$ are included in the appendix (N.M.R. spectrum No.2 and mass spectrum No.2). Briefly, the $F^{19}$ spectrum indicated the presence of three trifluoromethyl groups, two of which were equivalent. The mass spectrum is entirely consistent with the molecule $(CF_3)_2CHCH_2CF_3$. Also, the fragment formed in the highest proportion was one which occurred at a mass to charge ratio of 77. The only possibility for such a mass to charge ratio is the fragment $C_3H_3F_2$ (assuming, of course, the presence of only carbon, hydrogen and fluorine).

## Reaction of 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CFCH_2CF_3$, with methyl-lithium.

$(CF_3)_2CFCH_2CF_3$ (2 g., 0·00794 mole) in 10 ml. diethyl ether was contained in a flask fitted with a stirrer, dropping funnel, and reflux condenser leading to a trap cooled to -78°. 44 ml. of an ethereal solution of methyl-lithium (0·1844 moles/litre) were slowly added to the fluorocarbon solution. No immediate reaction was apparent, therefore the solution was gently refluxed. After two hours, a brown colouration had appeared. The solution was allowed to cool and water (25 ml.) was added. The ether layer was separated and dried. Fractional distillation through a short Vigreux column left an oily brown residue (1·5 g.) which did not distil at temperatures up to 150° at atmospheric pressure. Analytical scale V.P.C. of the low boiling fraction (b.p. $< 40^{\circ}$) revealed the presence of only two components, the larger component being ether and the other the starting material, 2H,2H-decafluoro-(3-methylbutane).

## Reaction of 2H,2H-decafluoro-(3-methylbutane), $(CF_3)_2CFCH_2CF_3$, with lithium aluminium hydride.

$(CF_3)_2CFCH_2CF_3$ (5 g., 0·01985 mole) in dry di-ethyl ether was slowly added to lithium aluminium hydride (0·755 g., 0·01985 mole) also in dry di-ethyl ether. No visible reaction occurred at room temperature, therefore the mixture was refluxed for six hours. At the end of this time the excess $LiAlH_4$ was hydrolysed by the careful addition of water (20 ml.). After separating the organic layer, the volatile materials were distilled off. No residue remained, and analytical scale V.P.C. (T.C.P., 50°) revealed only the presence of ether and 2H,2H-decafluoro-(3-methylbutane).

## The reaction of tri-n-butylamine with 2H-undecafluoro-(3-methylbutane), $(CF_3)_2CFCFHCF_3$, and 2H,2H-octafluorobutane, $C_2F_5CH_2CF_3$.

### (i) Preparation of 2H-undecafluoro-(3-methylbutane).

An autoclave (internal volume 1 litre) was charged with 2-iodoheptafluoropropane (430 g., 1·452 mole), azobisbutyronitrile (4 g.) and mercury (5 g.). After cooling the autoclave to -78°, it was connected to a smaller autoclave (150 ml.) by steel pressure tubing. The smaller autoclave had been previously charged with trifluoroethylene (100 g.). The valves on both autoclaves were opened and the system allowed to equilibrate. After disconnecting the autoclaves and weighing the gas remaining in the smaller one, it was found that 92 g. (1·12 mole) of trifluoroethylene had been transferred to the large autoclave. This large autoclave was then heated to 180° as quickly as possible. The maximum pressure developed was 35 atmos. after a period of 20 min. After 2 hrs. had elapsed the pressure gauge indicated very little pressure inside the autoclave. The autoclave was cooled and vented through a trap cooled in liquid air. 28 g. of material boiling below room temperature was collected. A liquid (484 g.), only slightly coloured with iodine but containing obvious traces of red mercuric iodide, was removed from the autoclave. This material was fractionated through a 20 cm. Vigreux column. Two main fractions were collected:

Fraction (1). b.p. 98 - 102°C./762 mm.; 206 g.

Fraction (2). b.p. 139 - 145°C./762 mm.; 77 g.

Analytical scale V.P.C. (Si-Elastomer, 100°) indicated that fraction (1) was better than 95% pure. Further purification was effected by preparative V.P.C. (T.C.P., 120°), and the compound was identified as 2H-1-iododecafluoro-(3-methylbutane). (Found: F, 49·7; I, 33·7; C, 15·8. $C_5HF_{10}I$ requires: F, 50·2; I, 33·6; C, 15·86%). I.R. No.6, b.p. 102°/ 751 mm.

Fraction (2) was shown, by analytical V.P.C., to be a mixture of three components. These are examined in more detail in later pages.

The iodide $(CF_3)_2CF.CFHCF_2I$ was fluorinated using antimony trifluoride dichloride in a similar manner to that already described for the fluorination of 2H,2H-1-iodononafluoro-(3-methylbutane) (page 149). Yields of up to 68% of 2H-undecafluoro-(3-methylbutane) were obtained. (Found: F, 76·7%; M (by Regnault), 268. $C_5HF_{11}$ requires: F, 77·4%; M, 270). B.p. 42°/760 mm.; I.R. No.7; N.M.R. spectrum No. 3.

## Reaction of $(CF_3)_2CF.CFHCF_3$ with $(n\text{-}C_4H_9)_3N$

$(CF_3)_2CFCFHCF_3$ (15 g., 0·0556 mole) was condensed into a Carius tube containing $(n\text{-}C_4H_9)_3N$ (20·5 g., 0·112 mole). The tube was sealed and heated 140° for 24 hours. At the end of this time the tube was opened and all volatile material vacuum transferred to a flask. 2 g. of oily material were obtained. This was fractionated through a small Vigreux column to give 1•4 g. material boiling below 50°/760 mm. Analytical scale V.P.C. revealed the presence of two compounds of extremely similar retention times in a ratio of approximately 1:1. Infra-red spectroscopy showed absorption bands at 5•78 and 5•93µ, the latter being ascribed to the presence of $(CF_3)_2C=CFCF_3$.

The involatile residue in the reaction tube was extracted with chloroform; excess ether was added to the chloroform solution resulting in the formation of a white precipitate (6•5 g.). This was shown by infra-red spectroscopy to be $(n\text{-}C_4H_9)_3N.3HF$. The removal of ether and chloroform from the residual solution left a black oil.

(ii) Preparation of 2H,2H-octafluorobutane.

2H,2H-1-iodoheptafluorobutane was prepared in a similar manner to that used by Hutchinson.[111] From this, 2H,2H-octafluorobutane was prepared in 82% yield by the antimony trifluoride dichloride method already described. (Found: F, 74•8%; M, 200; Calculated for $C_4H_2F_8$; F, 75•3%; M, 202). B.p. 20°/765 mm.; lit.,[182] 18°.

## Reaction of $C_2F_5CH_2CF_3$ with $(n\text{-}C_4H_9)_3N$

2H,2H-octafluorobutane (5 g., 0•025 mole) was sealed into a Carius tube with tri-n-butylamine (9•25 g., 0•05 mole) and heated to 120-125° for 40 hours. At the end of this time, all volatile material was removed under vacuum, giving 3·5 g. of material boiling below room temperature. Analytical scale V.P.C. (perfluoro-tributylamine, 0°) showed this to be mainly (~80%) the starting material, but also containing approximately 20% of another compound. A sample of this latter compound was separated by preparative scale V.P.C. (perfluoro-tributylamine, 10°) and was identified as trans-2H-heptafluorobut-2-ene, $CF_3CF{=}CHCF_3$, by comparison of the infra-red spectrum with that given in the literature.[162] (Found: F, 72·9%; M, 180. Calculated for $C_4HF_7$: F, 73·1%; M, 182).

A considerable amount of tar-like material was recovered from the reaction tube, of which some was $(n\text{-}C_4H_9)_3N.3HF$.

## The Effect of heat on 2H-nonafluoro-(3-methylbut-1-ene).

$(CF_3)_2CFCH{=}CF_2$ (6·28 g., 0·02705 moles) was sealed in a heavy wall glass tube and then heated to 210° for 138 hours. At the end of this time, the contents of the tube were transferred to a vacuum line. Very little visible change was apparent, although there was a slight odour of hydrogen fluoride. Infra-red spectroscopy and analytical V.P.C. (D.N.P., 40°) revealed only unchanged starting material, recovery 6·27 g., > 99·5%.

## Reaction of trifluoromethyl iodide with trimethylamine.

### (i) Reaction at 55°.

Trifluoromethyl iodide (6·7 g., 0·034 moles) and trimethylamine (4·0 g., 0·067 moles) were condensed into a Carius tube. The tube was sealed under vacuum and allowed to warm to room temperature. As soon as both components melted, immediate reaction occurred with the formation of a white solid. The tube was heated to 55° for 18 hrs. at the end of which time all volatile material (9·0 g.) was transferred to a vacuum line. A solid (1·6 g.) remained in the reaction tube. The solid was recrystallised from iso-propanol. It was shown to be trimethylammonium iodide by comparison of its infra-red spectrum with that of an authentic sample of $(CH_3)_3\overset{+}{N}H\ I^-$. A test for fluoride ion (zirconium nitrate/ Alizarin S) on the original solid proved negative. Analytical scale V.P.C. (T.C.P., 0°) of the volatile material showed the presence of 5·1% fluoroform. The percentage of fluoroform in the volatile material should have been 5·7% calculated on the weight of trimethylammonium iodide formed.

(ii) Reaction at room temperature.

$CF_3I$ (6·7 g., 0·034 moles) and $(CH_3)_3N$ (4·0 g., 0·067 moles) were sealed in a Carius tube as before. The tube was allowed to stand at room temperature for 30 days. At the end of this time the tube was pumped out to give 2·5 g. solid (mostly $(CH_3)_3NHI$) and 8 g. of material boiling below room temperature. V.P.C. (T.C.P., 0°) indicated the presence of 9·6% fluoroform.

(iii) Reaction by ultra-violet irradiation.

$CF_3I$ (10 g., 0·051 moles) and trimethylamine (6 g., 0·103 moles) were sealed in a Carius tube as before. The tube was irradiated for 24 hrs. at 20 cm. from a 500 watt Hanovia U.V. lamp. The estimated temperature in the locality of the tube was 50°. After cooling the tube, all volatile material was removed (4·3 g.). The solid remaining in the tube was also removed (11·3 g.). Infra-red spectroscopic examination of the solid showed no C-F stretching bands. Recrystallisation from iso-propanol yielded 8·8 g. (0·047 moles) of trimethylammonium iodide. Analytical scale V.P.C. (T.C.P., 0°) of the volatile material showed only a small amount of $CF_3I$ (< 1%). Vacuum fractionation gave fluoroform (3·2 g., 89·6% based on $CF_3I$ used) identified by infra-red spectroscopy and molecular weight measurement. (Found: M, 68. Calculated for $CF_3H$: M, 70).

### Reaction of 2-iodoheptafluoropropane with tri-n-butylamine.

2-Iodoheptafluoropropane (5 g., 0·0169 moles) was condensed into a glass tube already charged with tri-n-butylamine (3·13 g., 0·0169 moles). The tube was sealed under vacuum. Immediately the contents of the tube became liquid an exothermic reaction ensued, the contents becoming solid. The tube was exposed to a 500 watt ultra-violet lamp for 63 hours and then opened into a vacuum system. A very volatile gas was obtained (0·45 g.) which was shown to be 2H-heptafluoropropane by its characteristic infra-red spectrum. (Found: F, 77·4%; M, 173. Calculated for $C_3HF_7$: F, 78·3%; M, 170). Yield 0·45 g., 15·6%.

### Reaction of 1,1,2-trichlorotrifluoroethane with tertiary amines.

#### (i) Reaction with trimethylamine at 150°.

1,1,2-trichlorotrifluoroethane (20 g., 0·1065 moles) was condensed into a heavy wall glass tube together with trimethylamine (7 g., 0·1185 moles). The tube was heated to 150° for 72 hrs.; very little change in the appearance of the contents of the tube occurred. Heating to 200° for a further 24 hrs. produced no change in appearance except for a slight darkening. After cooling, the tube was opened and all volatile material was pumped out. 26 g. of this material was obtain; infra-red spectroscopy indicated that this was a mixture of the two starting materials only. Analytical V.P.C. (D.N.P., 50°) also confirmed the absence of any new compound.

(ii) U.V. irradiation of $CF_2ClCFCl_2$ with $(CH_3)_3N$

A glass tube was charged with trimethylamine (28 g., 0·475 moles) and $CF_2ClCFCl_2$ (40 g., 0·213 moles). After evacuation the tube was sealed and then irradiated at 20 cm. from a 500 watt U.V. lamp. The temperature in the vicinity of the tube was approximately 50°. During the course of 96 hrs. the contents of the tube became completely solid. The tube was cooled in liquid air, opened, and all volatile material removed to a vacuum system. The weight of solid remaining in the tube was 19 g., infra-red spectroscopy indicating that this was largely, though not entirely, trimethylammonium chloride. The solid dissolved readily in distilled water, giving a positive test for chloride ion but negative for fluoride ion.

The volatile material (46 g.) pumped out of the tube was analysed by gas chromatography (D.N.P., 50°).

One new component was shown to be present to the extent of 47% of the mixture. The major part of the mixture was unchanged starting material. The new compound was isolated by preparative scale gas chromatography and identified as 1,2-dichloro-1,1,2-trifluoroethane, $CF_2Cl.CFHCl$. The infra-red spectrum was identical to that given in the literature.[190]

(Found: Cl, 46·2; F, 36·9%; M, 154. Calculated for $C_2HCl_2F_3$: Cl, 46·4; F, 37·2%; M, 153). B.p. 28°/757 mm., lit.,[190] 28·2°/760 mm.

(iii) Reaction of $CF_2ClCFCl_2$ with tri-n-butylamine at 120°.

The fluorocarbon (30 g., 0·16 moles) was sealed in a Carius tube with tri-n-butylamine (32 g., 0·173 moles) and heated to 120° for 84 hrs. At the end of this time 56·3 g. of liquid were recovered from the tube. 5·2 g. of a solid remained in the tube. The liquid was fractionated through a small Vigreux column giving 28·6 g. of liquid boiling below 50°. Analysis by gas chromatography (D.N.P., 50°) indicated that less than 5% of the liquid was $CF_2ClCFHCl$.

(iv) U.V. irradiation of $CF_2Cl.CFCl_2$ and tri-n-butylamine.

$CF_2ClCFCl_2$ (30 g., 0·16 moles) and $(n\text{-}C_4H_9)_3N$ (33 g., 0·1785 moles) were sealed in a glass tube as before. The tube was then irradiated for 96 hrs. at 20 cm. from a 500 watt U.V. lamp. At the end of this time 54·5 g. of liquid were recovered from the tube, 8·5 g. of solid remaining in the tube. The liquid was fractionated through a 20 cm. Vigreux column; 25 g. of material boiling lower than 50° was collected. Gas chromatography (D.N.P., 50°) indicated approximately 5% of $CF_2ClCFHCl$.

## Reactions of Tertiary Amines with Polyfluorinated Olefins.

### Preparation of Olefins.

Hexafluoropropene was obtained commercially. 2H-nonafluoro(3-methylbut-1-ene), $(CF_3)_2CF.CH{=}CF_2$ was prepared according to Hutchinson,[111] as was 2H-heptafluorobut-1-ene.

### (i) Preparation of decafluoro-(3-methylbut-1-ene), $(CF_3)_2CF.CF{=}CF_2$.

2H,1-iododecafluoro-(3-methylbutane) was prepared as previously described (page 156).

The iodide (37·8 g., 0·1 mole) was slowly added to a stirred solution of lithium chloride (6·37 g., 0·15 mole) in dry dimethylformamide. As soon as the iodide was added some slight effervescence was seen, the solution also becoming yellow. After all the iodide had been added the temperature was raised from 50° to 150° over 2 hrs. and maintained at this temperature for one hour. During the course of this time 22 g. of a volatile liquid had collected in a trap cooled in solid carbon dioxide. This material was fractionated through a 20 cm. Vigreux column, giving one main fraction, b.p. 26·5/747 mm. This was identified as decafluoro-(3-methylbut-1-ene). Yield 20·5 g., 82% (Found: F, 75·9%; M, 249. $C_5F_{10}$ requires: F, 76·1%; M, 250). I.R. No. 8. $n_D^{20} < 1{\cdot}3$.

### (ii) Preparation of 4-chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CF.CF{=}CF_2$

### (a) Addition of 1-chloro-2-iodohexafluoropropane to trifluoroethylene.

1-Chloro-2-iodohexafluoropropane was prepared by the addition of iodine monochloride to hexafluoropropene.[191]

Trifluoroethylene (81 g., 0·988 moles) was condensed into an autoclave (500 ml.) which had previously been charged with $CF_3CFICF_2Cl$ (430 g., 1·375 moles), azobisbutyronitrile (1 g.) and mercury (10 g.). The autoclave was sealed and heated to 180° for 21 hrs., with constant rotation. It was then cooled and vented; no gaseous material was obtained. On opening the autoclave, 517 g. of a dark liquid was obtained. This was fractionally distilled through a 20 cm. Vigreux column:

| | |
|---|---|
| Fraction 1: | 20° - 78°, 19 g. |
| Fraction 2: | 78° - 136°, 123 g. |
| Fraction 3: | 136° - 140°, 147 g. |
| Fraction 4: | >140°, 220 g. |

Fraction 2 was mainly the starting iodide, but contained also another material of longer retention time on the gas chromatograph. Fraction 3 was shown by V.P.C. (Si. El., 150°) to be > 95% one component. This was purified by preparative scale V.P.C. (Si. El., 150°) and identified as 2H-1-iodo-4-chlorononafluoro-(3-methylbutane), $(CF_3)(CF_2Cl)CFCFHCF_2I$. (Found: F, 43·9; Cl, 8·6; I, 29·5.

$C_5HClF_9I$ requires: F, 43·4; Cl, 8·95; I, 31·8%), b.p. 139°/765 mm. I.R. No. 9.

(b) Dehydroiodination of $(CF_3)(CF_2Cl)CFCFH.CF_2I$.

A three necked flask fitted with a mercury sealed stirrer, a dropping funnel, and a reflux condenser leading to a trap cooled to -78° was charged with powdered potassium hydroxide (107 g., 1·91 moles). The flask was heated to 80° in an oil bath, with continual stirring of the KOH. The iodide (150 g., 0·38 moles) was slowly added, immediate reaction occurring. After all the iodide had been added the temperature of the oil bath was slowly increased to 140°. A colourless liquid (76 g.) collected in the cold trap, but some water was obviously present. $P_2O_5$ was added to the liquid, which was subsequently fractionated through a 20 cm. Vigreux column. One main fraction was collected (71 g., b.p. 57°), analytical V.P.C. indicating at least 98% purity (crude yield 69%). A small sample was purified by preparative scale V.P.C. (T.C.P., 100°) and was identified as 4-chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CF.CF{=}CF_2$.

(Found: F, 64·3; Cl, 13·8. $C_5ClF_9$ requires: F, 64·2; Cl, 13·3%). B.p. 57·5°/769 mm; I.R. No. 10.

## Reactions with tri-n-butylamine

(i) 2H-nonafluoro-(3-methylbut-1-ene), $(CF_3)_2CFCH{=}CF_2$.

$(CF_3)_2CF.CH{=}CF_2$ (12·7 g., 0·0547 moles) was sealed into a silica tube with an equi-molar amount of tri-n-butylamine (10·1 g.). After irradiating at 20 cm. from a 500 watt Hanovia U.V. lamp for 4 days, the tube was opened and all volatile material (10·3 g.) pumped out. Infra-red spectroscopic examination of this crude material showed little sign of any carbon-carbon unsaturation.

Analytical V.P.C. (Autoprep; D.N.P.; 30°) investigation showed the presence of three components, one having the same retention time as the starting material. One of the other components was present in large excess. The estimated percentages (from chromatogram areas) were 88%, 5·6% ($(CF_3)_2CF.CH{=}CF_2$) and 6·5%. The two new components were separated by preparative scale V.P.C. (Autoprep; D.N.P.; 30°). The material of longest retention time was shown to be 2H,2H,3H-nonafluoro-(3-methylbutane) by comparison of infra-red and mass spectral data with that of $(CF_3)_2CHCH_2CF_3$ previously prepared.

The material comprising 88% of the crude reaction product was shown to be 2H-nonafluoro-(3-methylbut-2-ene) by mass spectroscopic evidence (see mass spectrum No. 3 in appendix). The largest ion occurred at mass 232, and was shown to be the molecular ion by a Regnault molecular weight measurement. The fragmentation pattern of the mass spectrum was entirely consistent with the structure $(CF_3)_2C{=}CH.CF_3$ (see discussion).

(Found: F, 72·9%; M, (Regnault) 230; M, (Mass Spec.) 232. Calculated for $C_5HF_9$: F, 73·6%; M, 232). B.p. 33°/760 mm., lit.[192*]: b.p. 33°.

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* No other data given.

I.R. No. 11; N.M.R. No. 4. Yield of $(CF_3)_2C{=}CHCF_3$, 9·1 g., 75·1% (based on gas chromatographic analysis of crude reaction product.

(ii) Decafluoro-(3-methylbut-1-ene), $(CF_3)_2CFCF{=}CF_2$.

A silica tube was charged with dry tri-n-butylamine (9·7 g., 0·0524 moles). Onto this was condensed decafluoro-(3-methylbut-1-ene), (13 g., 0·052 moles). After sealing the tube and allowing it to warm to room temperature, a slight white precipitate was apparent. Also, a trace of a yellow oil formed at the interface of the two immiscible liquids. The tube and contents was exposed to light from a 500 watt ultra-violet lamp for 16 hrs. At the end of this time the contents of the tube were dark in colour; a substantial amount of crystalline material was also apparent. The tube was frozen in liquid air, opened, and the volatile contents transferred to a vacuum line. The weight of volatile material recovered was 8·5 g., of which approximately 60% (by analytical V.P.C. - T.C.P., room temp.) was one new compound. Infra-red spectroscopic examination of the crude reaction product revealed an absorption at 5·88μ which was later shown to be due to decafluoro-(3-methylbut-2-ene), $(CF_3)_2C{=}CFCF_3$. The main component in the reaction product was separated by preparative scale V.P.C. (Autoprep, D.N.P., room temp.). The infra-red, $F^{19}$ N.M.R., and mass spectral evidence were all consistent with the compound $(CF_3)_2CHCF_2CF_3$, 3H-undecafluoro-(3-methylbutane).

(Found: C, 22·3; F, 76·8%; M, 267. $C_5HF_{11}$ requires: C, 22·2; F, 77·4%; M, 270). B.p. 38·7°/769 mm.; I.R. No. 12; N.M.R. No. 5.

The involatile material that remained in the reaction tube was dissolved in chloroform. On adding a large excess of ether a white crystalline material was thrown down. After filtering this off it was identified as tri-n-butylamine tri-hydrofluoride. Yield 2·12 g.

(iii) 4-Chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CFCF{=}CF_2$.

The olefin (14 g., 0·0525 moles) and tri-n-butylamine (10 g., 0·054 moles) were sealed under vacuum in a glass reaction tube. On shaking the tube at room temperature it was seen that the two components were miscible, also a white solid was precipitated. This, however, disappeared on standing. The tube was irradiated with ultra-violet light (20 cm. from 500 watt lamp) for 24 hours. After this it was frozen in liquid air and opened. The volatile contents (8·8 g.) were pumped into a cold trap. Analytical scale V.P.C. showed one major component to be present (ca. 60%) together with a smaller amount of starting material and several minor components. The major component was separated by preparative V.P.C. (D.N.P., 60°). Infra-red spectroscopy showed no unsaturation; $F^{19}$ N.M.R. indicated quite a simple molecule with no tertiary fluorine. There was present two equivalent trifluoromethyl groups and two non-equivalent $CF_2$ groups. Mass spectral data was consistent with the compound 3H-1-chlorodecafluoro-(3-methylbutane), $(CF_3)_2CHCF_2CF_2Cl$. Crude yield 5·2 g., 34·6%. (Found: C, 20·9; F, 67·2; Cl, 12·4%; M, 286. $C_5HClF_{10}$ requires: C, 20·9; F, 66·4; Cl, 12·38%; M, 286·5). B.p. 67°/769 mm.; I.R. No. 13; N.M.R. No.6.

(iv) Reaction of tri-n-butylamine with hexafluoropropene.

(a) Thermal reaction.

Hexafluoropropene (29 g., 0·1935 moles) was condensed into a Carius tube previously charged with tri-n-butylamine (17·3 g., 0·0935 moles). The tube was sealed under vacuum and then heated to 100° for 92 hrs. Little change in the appearance of the contents was apparent, except for a slight darkening of the colour. On emptying the tube 28 g. of a gas, boiling point < 0°, was obtained. This was identified by infra-red spectroscopy as the starting material, hexafluoropropene. V.P.C. (perfluoro-tributylamine, 0°) showed the presence of only hexafluoropropene in the volatile material.

(b) Ultra-violet reaction.

A Carius tube was charged with hexafluoropropene (11 g., 0·0734 moles) and tri-n-butylamine (13·5 g., 0·073 moles). After sealing under vacuum,the tube was irradiated for 24 hrs. at 20 cm. from a 500 watt U.V. lamp. The temperature of the tube was estimated as 50°. The volatile material in the tube was vacuum transferred to a flask, giving 8·6 g. of material boiling below 0°. Infra-red spectroscopic examination of this material indicated the presence of a large proportion of 2H-heptafluoropropane, but with some $C_3F_6$ still present. Analytical V.P.C. (Autoprep, D.N.P., room temp.) showed one main component (70% of the mixture) together with some starting material (ca. 25%) and three minor constituents (ca. 5%). The mixture was fractionated through a vacuum-jacketed column to give a product b.p. -18°, identified as 2H-heptafluoropropane. The crude yield of $C_3HF_7$, calculated from the chromatogram, was 48%.

The involatile material remaining in reaction tube was dissolved in $CHCl_3$. This solution was poured into excess ether. The solid precipitated (3·6 g.) was identified as $(n\text{-}C_4H_9)_3N.3HF$.

(v) Reaction of tri-n-butylamine with 2H-heptafluorobut-1-ene, $C_2F_5CH{=}CF_2$

2H-heptafluorobut-1-ene (16·2 g., 0·089 moles) and tri-n-butylamine (15 g., 0·0811 moles) were sealed in a Carius tube under vacuum. The tube was heated to 95° for 90 hrs. during which time no visible reaction occurred. On opening the tube there was obtained 14·6 g. of an unsaturated compound. Infra-red spectroscopy showed this to be unchanged starting material, with no other compounds present. The unchanged olefin was condensed into a silica reaction tube, again with 15 g. tri-n-butylamine. After irradiating with U.V. light for 48 hrs. a product was obtained (10·2 g.) which analytical V.P.C. (T.C.P., 30°) showed to be mainly unchanged starting material (75%) together with another compound (ca. 20%). The new compound was isolated by preparative scale V.P.C. (perfluoro-tributylamine, 10°) and identified as 2H,2Hoctafluorobutane by comparison of its infra-red spectrum with that of an authentic sample of $C_2F_5CH_2CF_3$ previously prepared (page 157).

## Attempted addition of HF to fluorinated olefins using tri-n-butylamine tri-hydrofluoride.

Tri-n-butylamine tri-hydrofluoride was prepared by passing anhydrous HF into cooled tri-n-butylamine. The crude product was recrystallised twice from ethyl acetate.

### HF Addition to Hexafluoropropene.

Seven Carius tubes (approximately 100 ml. internal volume) were each charged with hexafluoropropene (7·5 g., 0·05 moles) and $(n\text{-}C_4H_9)_3N.3HF$ (5 g., 0·024 moles). In addition, some of the tubes were also charged with a solvent for the amine tri-hydrofluoride. The tubes were then either heated or exposed to U.V. irradiation as summarised in the following table.

| Solvent (10 ml.) | Reaction conditions | Wt.material b.p. 20° in product | Mole % $(CF_3)_2CFH$ | % Yield $(CF_3)_2CFH$ |
|---|---|---|---|---|
| None | 75°/20 hrs. | 7·0 g. | 35 | 29 |
| None | U.V./24 hrs. | 7·2 g. | 5 | 4 |
| $CHCl_3$ | 100°/24 hrs. | 6·9 g. | 45 | 36 |
| $CHCl_3$ | U.V./24 hrs. | 6·7 g. | 50 | 39 |
| EtOAc | U.V./24 hrs. | 7·0 g. | 25 | 21 |
| $(CH_3)_2CHOH$ | U.V./24 hrs. | 6·5 g. | 55 | 42 |
| $(CH_3)_2CHOH$ | 100°/24 hrs. | 6·4 g. | 45 | 34 |

The 2H-heptafluoropropane produced in the reactions was identified by analytical scale V.P.C. (perfluorotributylamine, 0°). The mole percentage of $(CF_3)_2CFH$ in the product was calculated by measuring areas under the chromatograms.

Similar experiments were carried out using the following olefins:

(i) $(CF_3)_2CFCH=CF_2$,
(ii) $(CF_3)_2CFCF=CF_2$,
(iii) $(CF_3)_2C=CFCF_3$,
(iv) $(CF_2Cl)(CF_3)CFCF=CF_2$,
(v) $CF_3CF=CFCF_3$,
(vi) cyclic-$C_6F_{10}$
and (vii) $CF_3C\ CCF_3$

In none of these experiments was any success achieved in adding HF to the double bond.

The olefins $(CF_3)_2CFCH=CF_2$, $(CF_3)_2CFCF=CF_2$ and $(CF_2Cl)(CF_3)CFCF=CF_2$ were each allowed to stand in contact with a solution of $(n\text{-}C_4H_9)_3N.3HF$ (0·5 g., 0·0024 moles) in chloroform (10 ml.) at room temperature over a period of two months.

In all cases, no HF addition was observed neither was there any rearrangement of the olefins.

## Reactions of trimethylamine with polyfluorinated olefins.

### (i) Hexafluoropropene.

Hexafluoropropene (11·3 g., 0·0753 moles) and trimethylamine

(4·1 g., 0·0695 moles) were transferred from a vacuum line into a Carius tube. The tube was allowed to warm to room temperature. Below -60° the liquid in the tube was quite cloudy, probably due to the separation of solid trimethylamine. At room temperature both components were miscible. No obvious reaction occurred. The tube was heated to 100° for 84 hrs. at the end of which time a considerable amount of black material was present. After cooling, the tube was opened and all volatile compounds pumped out. An infra-red spectrum of the crude reaction product, of which there was 12·7 g., revealed the presence of an appreciable amount of trimethylamine (bands at 3·4µ and 3·6µ). The trimethylamine was removed by passing the crude reaction product several times through a tube packed with calcium chloride. The removal of the $(CH_3)_3N$ was followed by noting the decrease in intensity of the absorption bands at 3·4µ and 3·6µ. After all trimethylamine had been removed no compound boiling below room temperature remained. The remaining liquid (9·4 g.) was fractionated through a 15 cm. B10 Vigreux column.

Two fractions were collected, the first boiling in the range 53° to 55° (7·0 g.) and the second (2 g.) boiling from 56° to 110° (most of this boiled at 101°). Analytical scale V.P.C. (Autoprep, D.N.P., 50°) examination of the first fraction showed that it comprised two main compounds in the approximate ratio 3:1 with about 5% of a third component. The two main components were separated by preparative scale V.P.C.

(Autoprep, D.N.P., 50°) and identified as duodecafluoro-(4-methylpent-3-ene) and 4H-perfluoro-(4-methylpentane), $(CF_3)_2CH.CF_2CF_2CF_3$. Identification was by means of infra-red and $F^{19}$ N.M.R. spectroscopy. Molecular weights were accurately measured by mass spectrometry.

Duodecafluoro-(4-methylpent-3-ene):

(Found: C, 23·8; F, 76·1%; M, 300. Calculated for $C_6F_{12}$: C, 24·0; F, 76·0%; M, 300). B.p. 52°/769 mm.; lit.,[188] 50·5°. I.R. No. 14; N.M.R. No. 7.

4H-perfluoro-(4-methylpentane):

(Found: C, 22·2; F, 76·7%; M, 320. $C_6HF_{13}$ requires: C, 22·5; F, 77·2%; M, 320). B.p. 56°/769 mm.; I.R. No. 15; N.M.R. No. 8.

The higher boiling fraction from the original reaction product was examined by V.P.C. Although the V.P.C. indicated the presence of only one compound, the $F^{19}$ N.M.R. spectrum was complex and was not consistent with a single compound. However analysis figures and molecular weight determinations were consistent with the presence of isomers of $C_9F_{18}$.

(Found: C, 24·0; F, 75·2%; M, 450. Calculated for $C_9F_{18}$: C, 24·0; F, 76%; M, 450). A strong band occurred in the infra-red at 5·98μ, consistent with the structure $(CF_3)_2C=C(CF_3)R_f$.

### (ii) Reaction of trimethylamine with decafluoro-(3-methylbut-1-ene), $(CF_3)_2CF.CF=CF_2$.

### (a) 2:1 molar ratio of olefin to amine.

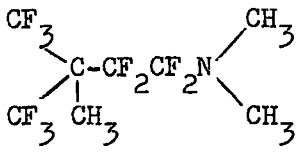
Decafluoro-(3-methylbut-1-ene) was distilled from silver powder and then from $P_2O_5$ to eliminate traces of halide ion and moisture.

The olefin (11•2 g., 0•0448 moles) was sealed in a Carius tube, together with trimethylamine (1•2 g., 0•0203 moles). Shortly after the tube was removed from a liquid air bath and the contents had become liquid, a vigorous reaction occurred, as evidenced by the formation of a white solid. The temperature of the tube was estimated to be below $-50^\circ$ during the formation of the solid. Complete reaction seemed to have occurred, the contents of the tube being completely dry. However, after allowing it to stand at room temperature for a few hours the solid began to show signs of liquefying. After 12 hrs. only a small amount of solid remained in an otherwise clear liquid. The liquid contents of the tube were transferred to a vacuum line. This material was readily separable into two fractions, one of which had a S.V.P. of 60 cm./$20^\circ$ (6•75 g.) and the other which had a S.V.P. of 0•5 cm./$20^\circ$ (4•14 g.).

The more volatile material contained some trimethylamine (shown by infra-red examination), therefore it was passed several times through $CaCl_2$. This procedure reduced the weight of volatile material to 6•0 g. Analytical V.P.C. (D.N.P., $30^\circ$) showed the volatile material to be largely one compound ($>98\%$). However, in view of the very similar retention times of this material and the starting olefin, the material was examined by infra-red spectroscopy. Again, only one compound was found to be present; no absorption band occurred at 5•6μ (due to the starting olefin). A strong absorption band did occur at approximately

5·9μ, indicative of the $(CF_3)_2C=C$ entity. A sample of the compound was purified by preparative scale V.P.C. (Autoprep, D.N.P., room temp.) and was identified as decafluoro-(3-methylbut-2-ene), $(CF_3)_2C=CF.CF_3$. $F^{19}$ N.M.R. measurements were entirely consistent with such a structure, showing three non-equivalent $CF_3$ groups and one =CF- group. (Found: F, 75·8%; M, 249 (Regnault), 250 (Mass Spec.). $C_5F_{10}$ requires: F, 76%; M, 250). B.p. 33°/769 mm.; I.R. No. 16; N.M.R. No. 9.

The less volatile fraction of the original reaction product was fractionated under reduced pressure. This material seemed to be very susceptible to hydrolysis by atmospheric moisture, fumes of HF being observed as soon as the material came into contact with air. Two main fractions were collected, the first boiling between 36° and 50° at 4 cm. pressure (2·9 g.) and the other boiling over the range 50° to 60° at 4 cm. pressure (0·4 g.). Both fractions were unstable, consequently pure samples of each were impossible to obtain. However, $F^{19}$ and proton N.M.R. studies gave results which were consistent with a 1:1 adduct of $(CH_3)_3N$ and $(CF_3)_2CF.CF=CF_2$ for the higher boiling fraction. The proton N.M.R. spectrum indicated the presence of two different groups of hydrogen atoms in the ratio of 2:1. The $F^{19}$ N.M.R. spectrum (No. 10) had no high field peaks, therefore the absence of tertiary fluorine could be assumed. There were three groups of fluorine atoms in the ratio of 3:1:1, occurring at -13·5 p.p.m., + 14·1 p.p.m., and +27·2 p.p.m. respectively (chemical shifts relative to $CF_3COOH$). These shifts are consistent with a compound



Analysis figures supported this formula.

(Found: C, 30·9; F, 61·3; Calculated for $C_8H_9F_{10}N$: C, 31·05; F, 61·4%).

The lower boiling fraction (36° - 50°/4 cm.) was more difficult to obtain in a pure state, consequently it was hydrolysed.

The compound (3 g.), thought to be $(CF_3)_2C{=}CFCF_2N(CH_3)_2$, was dropped into cold distilled water (15 ml.). After stirring the mixture for 4 hrs. the solution was neutralised and then ether extracted. After drying the ether extract and then distilling off the ether, a colourless liquid (2·5 g.) remained. This was purified by preparative scale V.P.C. (Autoprep, D.N.P., 120°) to give a compound identified as

$$\underline{(CF_3)_2C{=}CF.CO.N(CH_3)_2}$$

(Found: C, 33·5; H, 2·22; F, 53·1%; M, 253. $C_7H_6F_7NO$ requires: C, 33·2; H, 2·35; F, 52·6%; M, 253). B.p. 174·5°/766 mm.; I.R. No. 18, N.M.R. No. 11.

(b) <u>1:1 Molar ratio of olefin to amine.</u>

Trimethylamine (3 g., 0·0508 moles) and $(CF_3)_2CF.CF{=}CF_2$ (12·5 g., 0·05 moles) were sealed into a glass tube. A white solid formed on mixing the amine with the olefin. The tube was allowed to stand for 48 hrs. at room temperature. At the end of this time the contents of the tube had become almost completely liquid, with only a small amount of a white solid present.

The contents of the tube were separated into two main fractions on the vacuum line. The lowest boiling fraction (5·6 g.) was shown by infra-red spectroscopy to be largely ( > 80%) the internal olefin $(CF_3)_2C{=}CFCF_3$ together with some trimethylamine. The less volatile fraction (7·4 g.) was fractionated under reduced pressure to give three main fractions:

| | | | |
|---|---|---|---|
| Fraction 1: | b.p. | $< 20^{o}/5$ cm.; | 0·8 g. |
| Fraction 2: | b.p. | $50^{o}/5$ cm.; | 3·4 g. |
| Fraction 3: | b.p. | $69^{o}/5$ cm.; | 2·9 g. |

A viscous residue was left in the distillation flask. Fraction 1 consisted almost entirely of $(CF_3)_2C{=}CF.CF_3$. Fractions 2 and 3 were very unstable, fuming in air. The $F^{19}$ N.M.R. spectrum of Fraction 2 was consistent with the molecule $(CF_3)_2C{=}CF.CF_2N(CH_3)_2$ having bands attributable to $(CF_3)_2C{=}C$, $=CF-$, and $CF_2$, although spurious peaks were present in the spectrum, indicating the presence of impurities. Hydrolysis of this fraction yielded the compound previously identified as $(CF_3)_2C{=}CF.CO.N(CH_3)$. The $F^{19}$ N.M.R. spectrum of fraction 3 was identical to that of the compound already identified as

$$(CF_3)_2C(CH_3)-CF_2CF_2-N(CH_3).$$

### (iii) Reaction of trimethylamine with 4-chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CF.CF=CF_2$

The olefin (9·4 g., 0·0352 moles) was contained in a two necked flask fitted with a magnetic stirrer, a gas inlet tube, and a cold finger condenser at $-78^{\circ}$. The flask was cooled to $-60^{\circ}$ and trimethylamine (2·1 g., 0·0356 moles) was slowly passed in. Immediate exothermic reaction occurred, with the formation of a white precipitate. The flask was allowed to warm to room temperature over 8 hrs. and then held at that temperature for a further 72 hrs. All volatile material (8·8 g.) was removed under vacuum, leaving a 'mushy' solid in the flask. A sample of this was dissolved in distilled water and gave a positive test for chloride ion. Distillation of the material removed under vacuum gave two main fractions, the most volatile of which was the starting olefin (1·1 g.). The higher boiling fraction (7·0 g.) was unstable in air, giving off fumes of HF. The $F^{19}$ N.M.R. spectrum of this fraction was identical to that obtained in the previous reaction for the compound thought to be $(CF_3)_2C=CFCF_2N(CH_3)_2$. Attempts to obtain satisfactory analysis figures was not successful because of the difficulty in obtaining pure samples. However, qualitative tests for chlorine were negative.

Hydrolysis of the unstable compound (5 g.) was carried out by stirring it with water (15 ml.) for 1 hr. The resulting compound (3·6 g.) was identical to the compound already identified (page 177 ) as $(CF_3)_2C{=}CF.CO.N(CH_3)_2$.

(iv) Reaction of trimethylamine with 2H-nonafluoro-(3-methylbut-1-ene), $(CF_3)_2CF.CH{=}CF_2$

2H-nonafluoro-(3-methylbut-1-ene) (13·0 g., 0·056 moles) was condensed into a Carius tube together with trimethylamine (3·3 g., 0·056 moles). On allowing the tube to warm to room temperature some solid material was apparent in the tube. (The amount of solid was not nearly as great as that initially formed in the reactions of trimethylamine with $(CF_3)_2CFCF{=}CF_2$ and $(CF_2Cl)(CF_3)CF.CF{=}CF_2$). The tube was heated to 50° for 48 hrs., the contents then being pumped into a vacuum line. Very little solid (0·5 g.) was left in the reaction tube. The liquid in the vacuum line (15·8 g.) was transferred to a small fractionation apparatus. Two fractions were collected:

Fraction 1; b.p. $< 20^\circ$, 4·7 g.
Fraction 2; b.p. $24^\circ - 33^\circ$, 7·8 g.

A dark, moisture sensitive compound remained in the distillation pot, decomposing on standing to give some solid material.

The infra-red spectra of both Fraction 1 and 2 were very similar, each being a mixture of trimethylamine and the internal olefin, $(CF_3)_2C{=}CH.CF_3$. Therefore the two fractions were combined and stored in a vacuum line in contact with $H_2SO_4$. The material recovered after 30 hrs. (10 g.) was almost pure $(CF_3)_2C{=}CHCF_3$, as judged by analytical

V.P.C. (T.C.P., room temp.) and infra-red spectroscopy. Thus the weight of trimethylamine recovered from the reaction was 2·5 g. i.e. 12·5 g. - 10 g. Also, 3·0 g. of olefin must therefore have reacted with 0·8 g. of $(CH_3)_3N$ (approximately 1:1 molar ratio).

No attempt was made to purify the high boiling mixture in the distillation flask, instead it was hydrolysed with distilled water at 60°. The hydrolysis product [1·5 g.] was an impure liquid; attempts at purification by preparative scale V.P.C. (Autoprep, D.N.P., 120°) were only partially successful. 0·3 g. of a compound estimated to be 90% pure was obtained. The infra-red spectrum showed a broad absorption at 6·03µ, consistent with the C=CH-CO- structure. Mass spectroscopic examination of the impure material fully supported the structure $(CF_3)_2C=CH.CO.N(CH_3)_2$, except for some very minor peaks at mass numbers greater than 235, the molecular weight of the above compound. I.R. No.19.

### (v) Reaction of trimethylamine with 2H-heptafluorobut-1-ene, $C_2F_5CH=CF_2$.

No reaction occurred with 2H-heptafluorobut-1-ene under similar conditions to the trimethylamine reactions (i) - (iv). Heating $(CH_3)_3N$ with $C_2F_5CH=CF_2$ above 130° resulted in very extensive degradation, only tar-like products resulting.

## The attempted preparation of some fluorinated di-enes.

### Attempted de-chlorofluorination of 2H-4-chloro-octafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CFCH=CF_2$, and 4-chlorononafluoro-(3-methylbut-1-ene), $(CF_2Cl)(CF_3)CFCF=CF_2$.

### Preparation of $(CF_2Cl)(CF_3)CFCH=CF_2$.

An autoclave (150 ml.) was charged with 1-chloro-1-iodo-hexafluoropropane (110 g., 0·352 moles) and 1,1-difluoroethylene (15 g., 0·2345 moles). After rocking for 16½ hrs. at 200°, the autoclave was cooled and vented. No gaseous material was collected. A dark violet coloured liquid (107 g.) was poured from the autoclave. After washing with dilute thiosulphate solution and drying over $MgSO_4$, the liquid was fractionated.

| | | |
|---|---|---|
| Fraction 1: | Room temp. – 138°; | 23 g. |
| Fraction 2: | 138° - 141°; | 78 g. |
| Residue: | | 4 g. |

Analytical V.P.C. (Si. El., 150°) showed that fraction 2 was a mixture of two compounds in the ratio 9:1. The isomers were separated by preparative V.P.C. (Si. El., 130°); the compound in the larger proportion was identified as 2H,2H-1-iodo-4-chloro-octafluoro-(3-methylbutane), $(CF_2Cl)(CF_3)CFCH_2CF_2I$.

(Found: C, 15·6; Cl, 10·0; F, 54·1. $C_5H_2ClF_8I$ requires: C, 15·82; Cl, 9·36; F, 54·4%). B.p. 140°/761 mm., I.R. No. 20.

The iodide (50 g., 0·132 moles) was slowly dropped onto powdered KOH (38 g., 0·68 moles) at 90°, contained in a flask fitted with a stirrer, a dropping funnel, and a short Vigreux column leading to a trap cooled to -78°. After all the iodide had been added, the flask was purged with $N_2$. The liquid collected in the cold trap (25 g.) was stood over $P_2O_5$ overnight and then vacuum distilled from the $P_2O_5$. The colourless liquid was fractionated giving only one fraction, b.p. 63·5° - 65° (23 g.). Analytical scale V.P.C. [D.N.P., 60°] showed the purity of this fraction to be at least 98%. The compound was identified as <u>2H-4-chloro-octafluoro-(3-methylbut-1-ene)</u>, $(CF_2Cl)(CF_3)CFCH{=}CF_2$. Yield 67·8%.

(Found: C, 24·0; Cl, 14·5; F, 60·8. $C_5HClF_8$ requires: C, 24·1; Cl, 14·29; F, 61·15%). B.p. 64°/769 mm.; I.R. No. 21.

(i) <u>Attempted de-chlorofluorinations using zinc and polar solvents</u>.

(a) <u>Using ethyl alcohol as solvent</u>.

Zinc powder (2·7 g., 0·0415 moles) and $(CF_2Cl)(CF_3)CFCH{=}CF_2$ (2 g., 0·00805 moles) were sealed in a Carius tube with ethyl alcohol (10 ml.). The tube was heated for 24 hrs. to 50°. After this the liquid in the tube was completely distilled, all distilling below 80°. Vapour phase chromatography showed the presence of only ethyl alcohol and the olefin $(CF_2Cl)(CF_3)CF.CH{=}CF_2$. Addition of a large excess of water and separation of the organic layer gave a compound shown, by infra-red spectroscopy, to be almost pure starting olefin.

(b) Other attempted de-chlorofluorinations using zinc with a variety of other solvents, usually at their boiling points, were equally unsuccessful. Solvents used were acetic acid, acetic anhydride, a mixture of acetic acid and acetic anhydride, and dioxan.

Attempted de-chlorofluorinations of the fully halogenated olefin, $(CF_2Cl)(CF_3)CFCF=CF_2$, using the above techniques were also unsuccessful.

(ii) Attempted dechlorofluorinations by passage over heated steel wool.

The apparatus used was as shown in diagram 7 on the following page. The tube was heated to temperatures ranging from 300° to 500°, in 50° steps. The olefin was slowly vapourised into a stream of $N_2$ (30 ml./min.) which carried it into the reaction tube. The passage of nitrogen through the reaction tube was continued for a further hour after all the olefin had been added. The product in the liquid air trap was examined by vapour phase chromatography. At temperatures up to 400°, only starting material was recovered from the hydrogen containing olefin (up to 80% of original weight). Above 400° the recovery of organic material dropped. At 500° much decomposition occurred with some hydrogen fluoride formation. Less than 10% of the weight of the original organic material was recovered, and this was shown by V.P.C. to be a very complex mixture of compounds.

Similar results were obtained when the packing in the reaction tube was either ferric oxide or magnetite ($Fe_3O_4$).

Attempts to dechlorofluorinate the fully halogenated olefin,

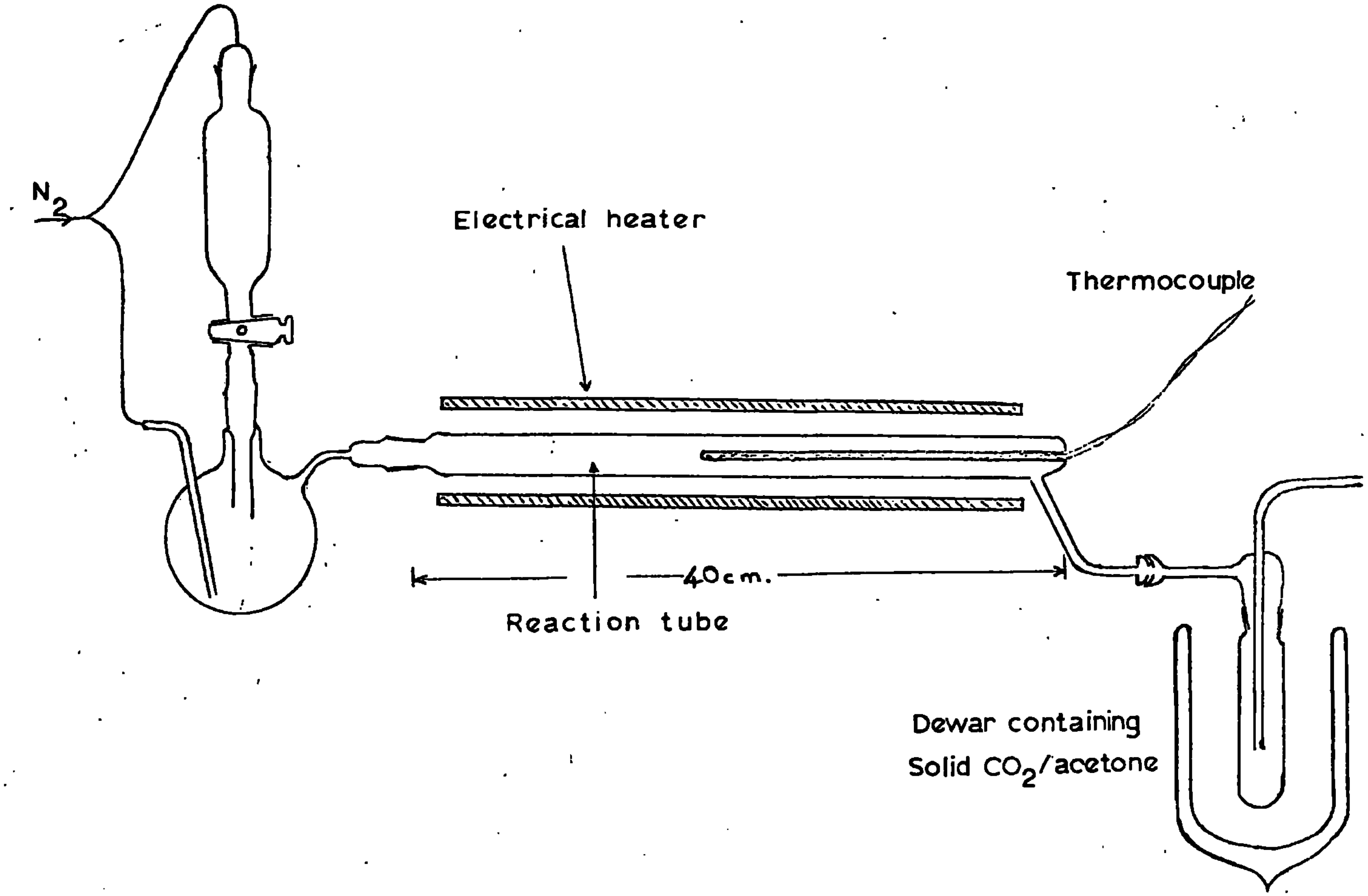


Fig. 7. Apparatus used for attempted dechlorofluorinations.

$(CF_2Cl)(CF_3)CFCF{=}CF_2$, gave similar results with the steel wool and ferric oxide packings, but the magnetite packing under its optimum conditions (400°) gave approximately 40% recovery of organic material. Examination by a Perkin-Elmer Fractometer (D.N.P., 60°) indicated mainly one product with three impurities, but on an Autoprep (Si. El., 40°) eight components were seen to be present, none in high yield.

### Attempted preparation of 2H,3H-1-iodo-4-chlorohexafluoro-(3-methylbutane), $(CF_2Cl)(CF_3)CH.CFH.CF_2I$

The above iodide would give an easy route to perfluoro-isoprene by first elimination of HI and then elimination of HCl.

(i) Addition of iodine chloride to 2H-pentafluoropropene.[189]

Iodine chloride (34·4 g., 0·212 moles) and $CF_3CH{=}CF_2$ (27·7 g., 0·21 moles) were sealed under vacuum in a Carius tube. The tube was heated to 150° for 16 hrs. At the end of this time it was cooled and opened. Some free iodine was apparent. A violet liquid (47 g.) was poured from the tube. Distillation through a 20 cm. Vigreux column gave three fractions:

| | | |
|---|---|---|
| Fraction 1: | b.p. < 40°; | 4·6 g. |
| Fraction 2: | b.p. 40° - 88°; | 2·7 g. |
| Fraction 3: | b.p. 88° - 96°; | 36·6 g. |

During the collection of fraction 1 a considerable amount of free chlorine was evolved. Fraction 3 was shaken with aqueous thiosulphate solution. After washing with water and drying over $MgSO_4$, a clear liquid was obtained (33·7 g.) which analytical V.P.C. (Si. El., 120°) indicated was 95% one compound. A sample purified by preparative V.P.C. (Si. El., 120°) was identified as 1-chloro-2-iodo-1,1,3,3,3-pentafluoropropane. (Found: Cl, 11·0; F, 29·9; I, 41·1. Calculated for $C_3HClF_5I$: Cl, 11·43; F, 30·4; I, 40·6%). B.p. 96°/763 mm.; lit.,[189] 94°. N.B. This compound is very noxious.

(ii) Attempted additions to trifluoroethylene.

(a) Using azobisbutyronitrile free radical initiator.

Reactions in which equi-molar amounts of iodide and olefin were used gave, at temperatures up to 150°, only starting materials. At temperatures above 150° decomposition occurred with the formation of carbon and other involatile materials. At 220°, a reaction in which 6·7 g. (0·0816 moles) of $C_2HF_3$ and 26 g. (0·0832 moles) of $CF_3CHICF_2Cl$ were used produced only 1·7 g. of dark liquid, which proved to be largely unchanged iodide.

(b) Using ultra-violet initiation.

Trifluoroethylene (2·1 g., 0·0256 moles) and $CF_3CHICF_2Cl$ (12 g., 0·0384 moles) were sealed in a glass tube. After irradiation for 120 hrs. at 20 cm. from a 500 watt ultra-violet lamp, a violet liquid (12·25 g.) was recovered. Distillation of this liquid indicated the presence of some very low boiling material, almost certainly trifluoroethylene. All the liquid distilled below 98°, infra-red spectroscopy and V.P.C. (Si. El., 120°) indicating it to be at least 95% unchanged starting material.

## The attempted dehydrofluorination of the olefins $(CF_3)_2CFCH_2CF_2CH=CF_2$ and $(CF_3)_2CFCFHCF_2CF=CF_2$

### (i) Preparation of the mono-olefins.

The olefin $(CF_3)_2CFCH_2CF_2CH=CF_2$ was prepared by the dehydroiodination of $(CF_3)_2CF(CH_2CF_2)_2I$.[111]

In the free radical addition of $(CF_3)_2CFI$ to trifluoroethylene (see page 155) a fraction boiling in the range 138° - 145° was obtained. This fraction analysed correctly for a 1:2 adduct of $(CF_3)_2CFI$ to $CFH=CF_2$. Analytical V.P.C. (D.N.P., 120°) showed this fraction to be a mixture of three components, in the ratio 2:2:1. Pure samples of each were prepared by preparative scale V.P.C. (Autoprep, D.N.P., 130°) and were designated C1, C2 and C3, in the order of their retention times on the D.N.P. column.

### Dehydroiodination of C1.

A three necked flask (250 ml.) fitted with a mercury sealed stirrer, dropping funnel and reflux condenser was charged with powdered potassium hydroxide (30 g., 0·54 moles). The flask was heated to 90° and the iodide (10 g., 0·0217 moles) was added dropwise. During the addition of the iodide a reaction commenced, with liquid refluxing in the condenser. After all the iodide had been added the reaction vessel was maintained at 90° for one hour. The product (5 g.) was distilled from the flask and found by analytical V.P.C. (D.N.P., 60°) to be largely ( > 95%) one compound. A pure sample was obtained by preparative V.P.C. (D.N.P., 60°)

and identified as $\underline{(CF_3)_2CFCFHCF_2CF{=}CF_2}$.

(Found: C, 25·1; F, 74·0%; M, 328. $C_7HF_{13}$ requires: C, 25·29; F, 74·4%; M, 332); b.p. 87°/770 mm.; I.R. No. 22. Crude yield 66%.

Dehydroiodination of C2

Dehydroiodination of the iodide C2 under identical conditions to those used above resulted in the formation of the identical olefin, $(CF_3)_2CFCFHCF_2CF{=}CF_2$ in similar yields.

Attempted dehydroiodination of C3

Using identical conditions to those described above, no reaction occurred between the iodide C3 and powdered KOH.

It was concluded that iodides C1 and C2 were diastereo-isomers of $\underline{(CF_3)_2CFCFHCF_2CFHCF_2I}$.

(C1 found: C, 18·3; H, 0·39; F, 54·4; I, 27·9. $C_7H_2F_{13}I$ requires: C, 18·25; H, 0·435; F, 53·7; I, 27·6%). $\lambda_{max.}$ 272·2mμ; I.R. No. 23; $n_D^{20}$ 1·348.

(C2 found: C, 18·4; F, 52·9; I, 27·5. $C_7H_2F_{13}I$ requires: C, 18·25; F, 53·7; I, 27·6%); $\lambda_{max.}$ 272mμ; I.R. No. 24; $n_D^{20}$ 1·346.

It was also concluded that iodide C3 was the compound $\underline{(CF_3)_2CFCFHCF_2CF_2CFHI}$.

(C3 found: C, 18·4; F, 53·4. $C_7H_2F_{13}I$ requires: C, 18·25; F, 53·7%); $\lambda_{max.}$ 268mμ; I.R. No. 25; $n_D^{20}$ 1·350.

(ii) Attempted dehydrofluorinations of mono-olefins.

(a) Using KOH in di-butyl ether.[151]

A three necked flask was fitted with a mercury sealed stirrer, a dropping funnel and a reflux condenser. The flask was charged with KOH (2•5 g., 0•0446 moles) and di-butyl ether (5 ml.) and heated to 70°. The olefin $(CF_3)_2CFCH_2CF_2CH{=}CF_2$ (5 g., 0•0169 moles) was slowly added. No apparent reaction occurred during a period of 2 hrs. At the end of this time the reflux condenser was replaced by a short fractionation column and the temperature slowly raised to 120°. A liquid (4•7 g., b.p. 92°) collected in a receiver. Analytical V.P.C. (D.N.P., 60°) showed this to be at least 95% one compound, identified by infra-red spectroscopy as the starting olefin.

A similar reaction using the olefin $(CF_3)_2CFCFHCF_2CF{=}CF_2$ gave a similar result. Again no reaction occurred.

(b) Using molten KOH

The apparatus used is shown in diagram 8 (following page).

$(CF_3)_2CFCH_2CF_2CH{=}CF_2$ (10 g., 0•0338 moles) was slowly distilled into a stream of nitrogen (3 l./hr.) and passed through a 95% KOH/water mixture at 210°. The KOH became very dark as the olefin was bubbled through. A clear liquid (3•1 g.) collected in a trap cooled to -78°. Analytical V.P.C. (D.N.P., 65°) showed this liquid to be a complex mixture containing no less than 12 components of which by far the biggest component was the starting material. Also present was one other main component to the extent of approximately 20%. A sample was separated by

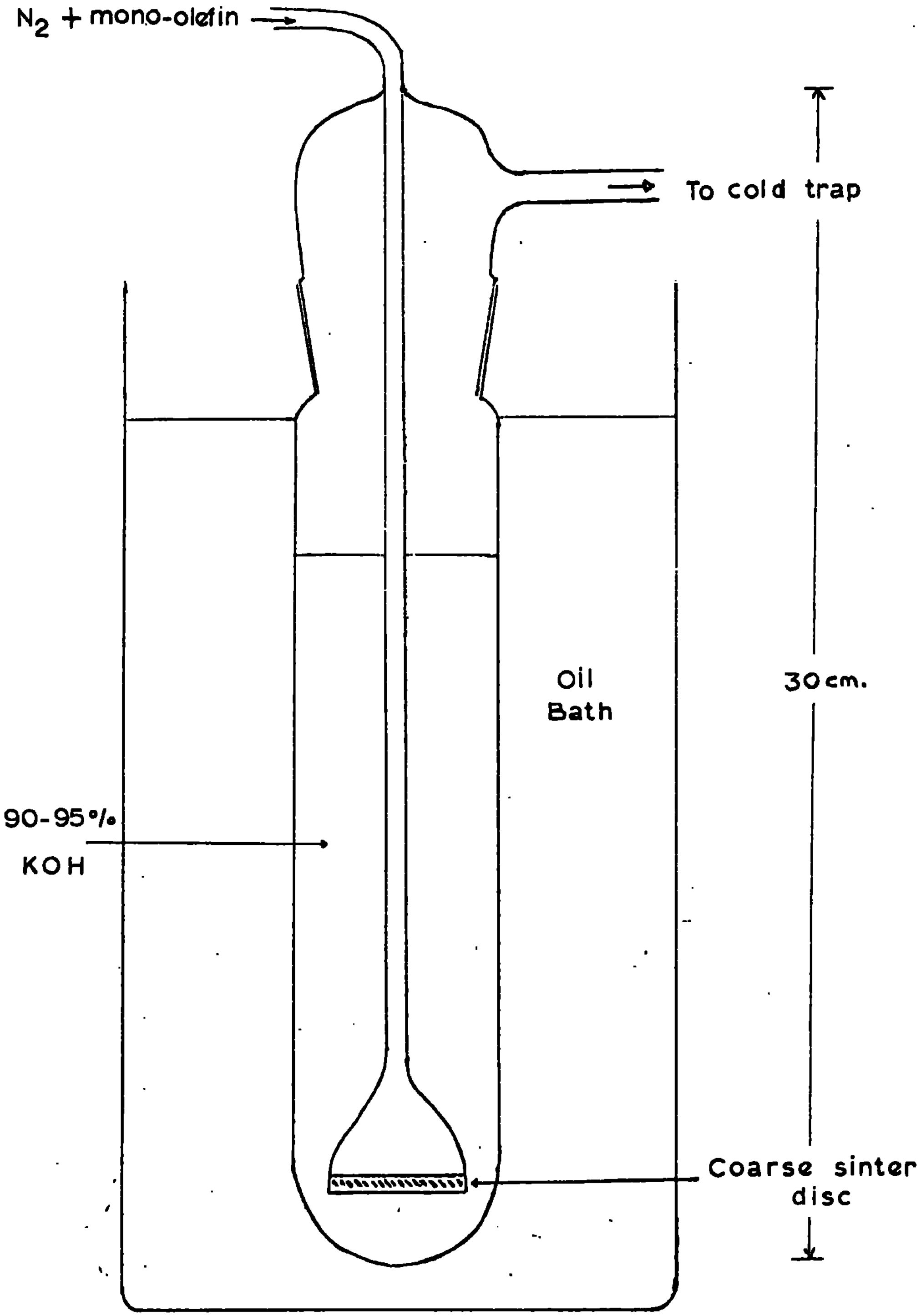


Fig. 8. Apparatus for molten KOH dehydrofluorinations.

preparative V.P.C. (D.N.P., 50°) and identified as $(CF_3)_2CFCH_2CF{=}CHCF_3$. (Found: C, 27·9; F, 70·3%; M (Mass Spec.), 296. $C_7H_3F_{13}$ requires: C, 28·4; F, 70·6%; M, 296); b.p. 108°/770 mm.; I.R. No. 26.

(iii) Using NaF/Asbestos.

The apparatus used in this experiment was similar to that shown in diagram 7 (page 185). The dehydrofluorinating agent was a mixture of equal volumes of sodium fluoride powder and asbestos wool.

The olefin $(CF_3)_2CFCH_2CF_2CH{=}CF_2$ (5 g., 0·0169 moles) was distilled into a stream of nitrogen (3 l./hr.) and passed through the reactor at 450°. After all the olefin had been added, nitrogen was passed for an additional hour. A clear liquid (4·5 g.) collected in a trap cooled to -78°. Analytical V.P.C. (D.N.P., 70°) showed this to consist of three main components: (a) the starting olefin (54·5%), (b) $(CF_3)_2CFCH_2CF{=}CHCF_3$ (30%) and (c) a new compound (15·5%). This last compound was purified by preparative V.P.C. (Autoprep, D.N.P., 50°) and identified as 2H,4H-decafluoro-(5-methylhexa-2,4-diene), $(CF_3)_2C{=}CHCF{=}CHCF_3$. (Found: C, 30·6; H, 0·92%; M (Mass Spec.) 276. $C_7H_2F_{10}$ requires: C, 30·4; H, 0·73%; M, 276); $\lambda_{max.}$ 229mμ ( $\epsilon = 1{\cdot}386 \times 10^4$); I.R. No. 27.

## Appendix 1: Infra-red Spectra.

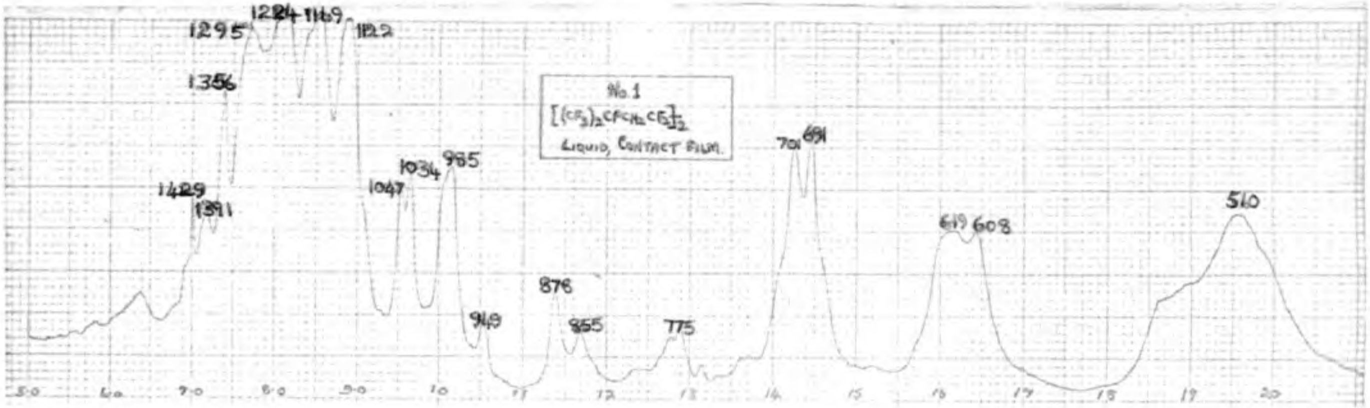
Some of the spectra shown in the following pages have been previously published (Nos. 1, 4, 8),[111] but are included for comparison purposes.

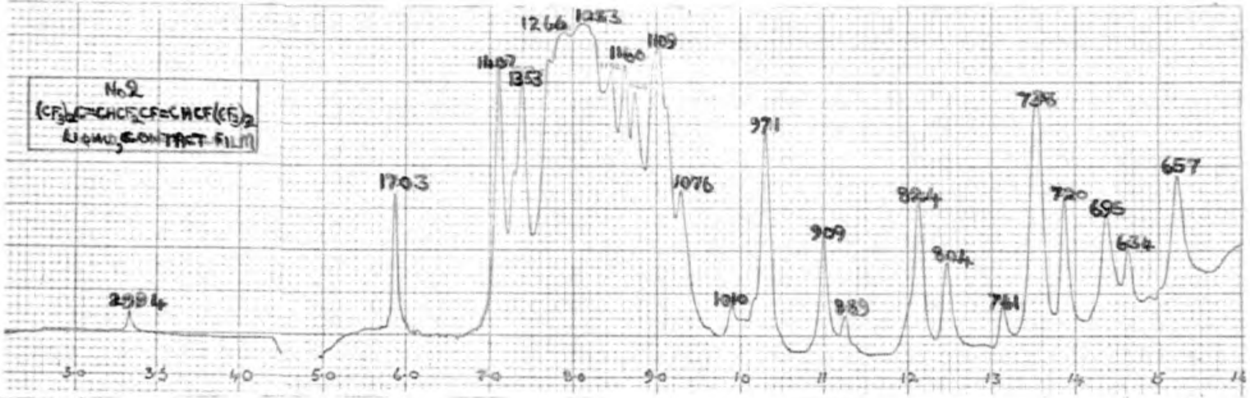
The spectra of some compounds not originally prepared by the author, namely $(CF_3)_2C{=}CHCF_3$ (No. 11),[192] $(CF_3)_2C{=}CFCF_2CF_3$ (No. 14),[188] and $(CF_3)_2CFCFHCF_2I$ (No. 6),[187] have been included because of their relevance to this work coupled with the fact that they have not been previously published.

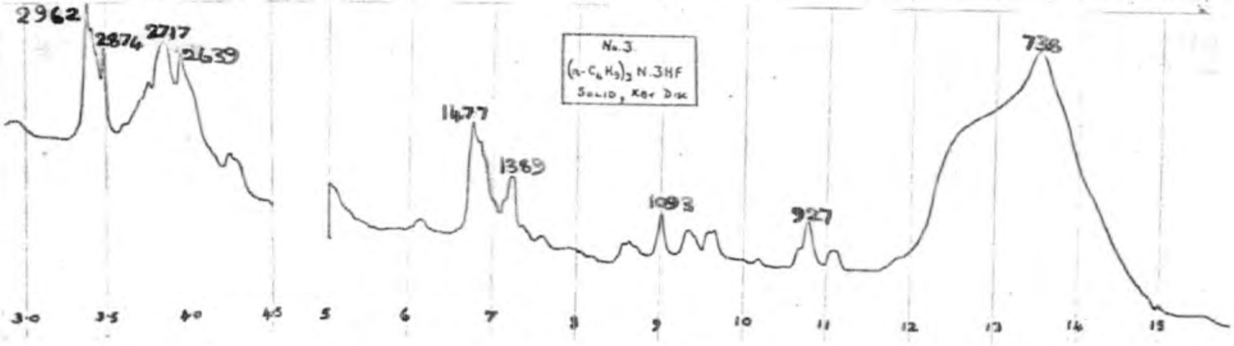
1. $(CF_3)_2CFCH_2CF_2CF_2CH_2CF(CF_3)_2$
2. $(CF_3)_2C{=}CHCF_2CF{=}CHCF(CF_3)_2$
3. $(n\text{-}C_4H_9)_3N.3HF$
4. $(CF_3)_2CFCH_2CF_3$
5. $(CF_3)_2CHCH_2CF_3$
6. $(CF_3)_2CFCFHCF_2I$
7. $(CF_3)_2CFCFHCF_3$
8. $(CF_3)_2CFCF{=}CF_2$
9. $(CF_2Cl)(CF_3)CFCFHCF_2I$
10. $(CF_2Cl)(CF_3)CFCF{=}CF_2$
11. $(CF_3)_2C{=}CHCF_3$
12. $(CF_3)_2CHCF_2CF_3$
13. $(CF_3)_2CHCF_2CF_2Cl$
14. $(CF_3)_2C{=}CFCF_2CF_3$
15. $(CF_3)_2CHCF_2CF_2CF_3$
16. $(CF_3)_2C{=}CFCF_3$
17. $(CF_3)_2C{=}CFCF_2N(CH_3)_2$
18. $(CF_3)_2C{=}CFCO.N(CH_3)_2$
19. Impure $(CF_3)_2C{=}CHCO.N(CH_3)_2$
20. $(CF_2Cl)(CF_3)CFCH_2CF_2I$
21. $(CF_2Cl)(CF_3)CFCH{=}CF_2$
22. $(CF_3)_2CFCFHCF_2CF{=}CF_2$

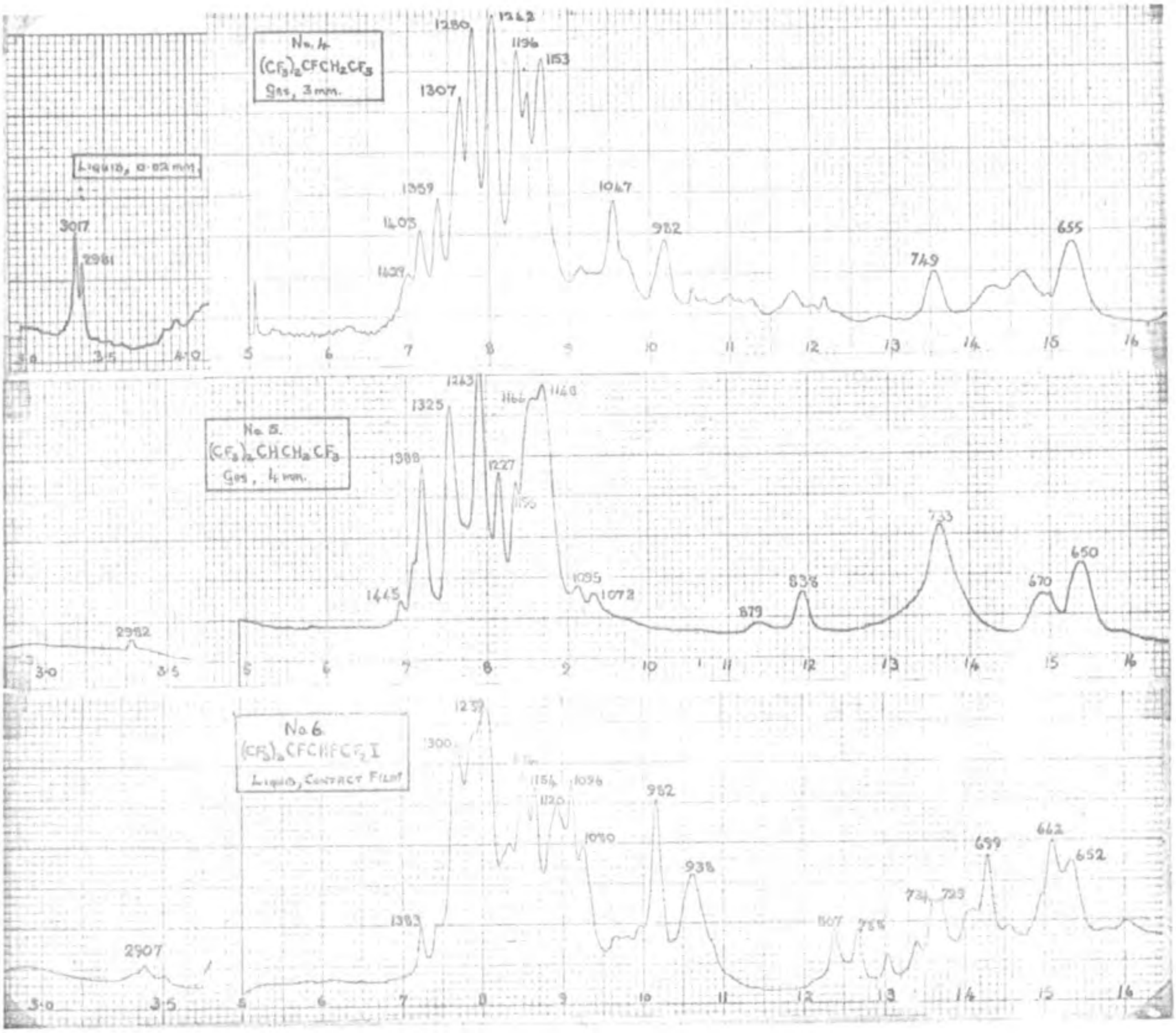
23 and 24. Diastereo-isomers of $(CF_3)_2CFCFHCF_2CFHCF_2I$

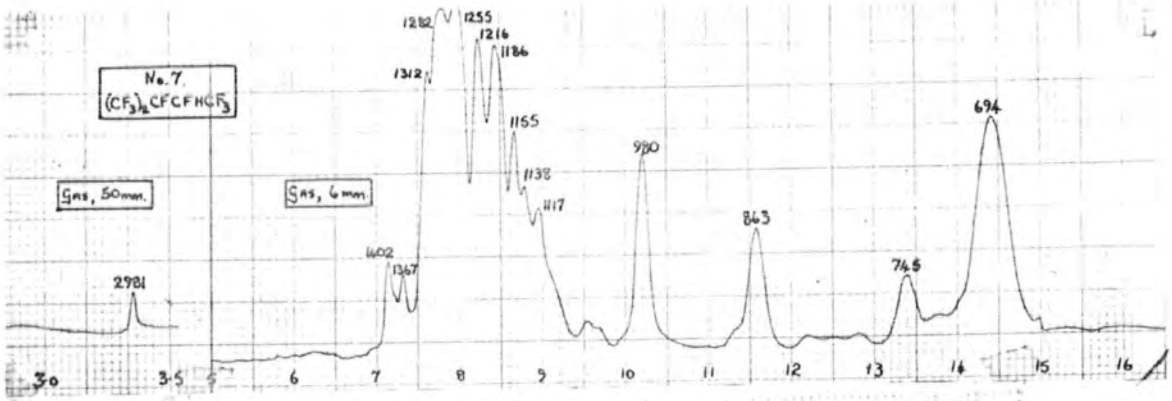
25. $(CF_3)_2CFCFHCF_2CF_2CFHI$
26. $(CF_3)_2CFCH_2CF{=}CHCF_3$
27. $(CF_3)_2C{=}CHCF{=}CHCF_3$

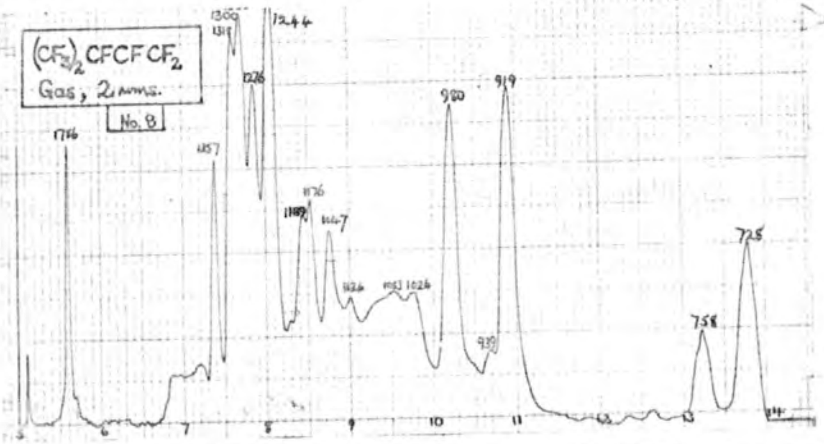

No. 1
[(CF$_3$)$_2$CFCH$_2$CF$_2$]$_2$
LIQUID, CONTACT FILM.
1295
1284
1169
1122
1356
1429
1391
1047
1034
985
949
876
855
775
701
691
619
608
510
5.0
6.0
7.0
8.0
9.0
10
11
12
13
14
15
16
17
18
19
20

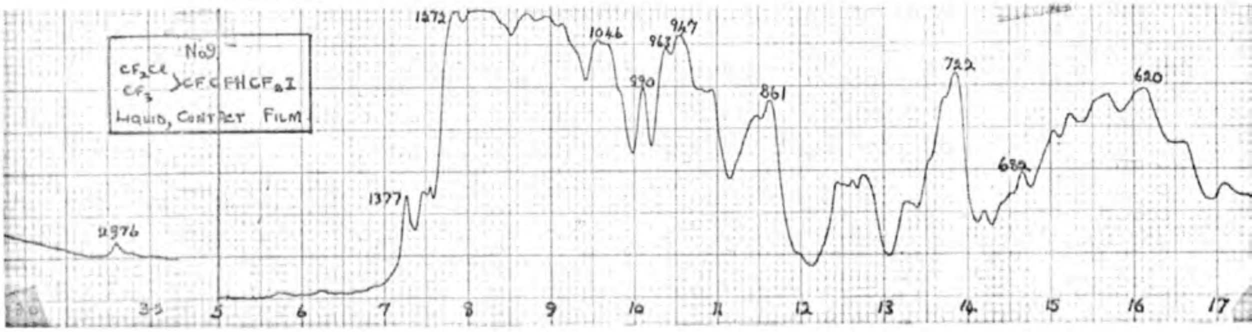

No 2
(CF$_3$)$_2$C=CHCF$_2$CF=CHCF(CF$_3$)$_2$
LIQUID, CONTACT FILM
2984
1703
1407
1353
1266
1253
1160
1109
1076
1010
971
909
889
824
804
761
738
720
695
684
657
3.0
3.5
4.0
5.0
6.0
7.0
8.0
9.0
10
11
12
13
14
15
16

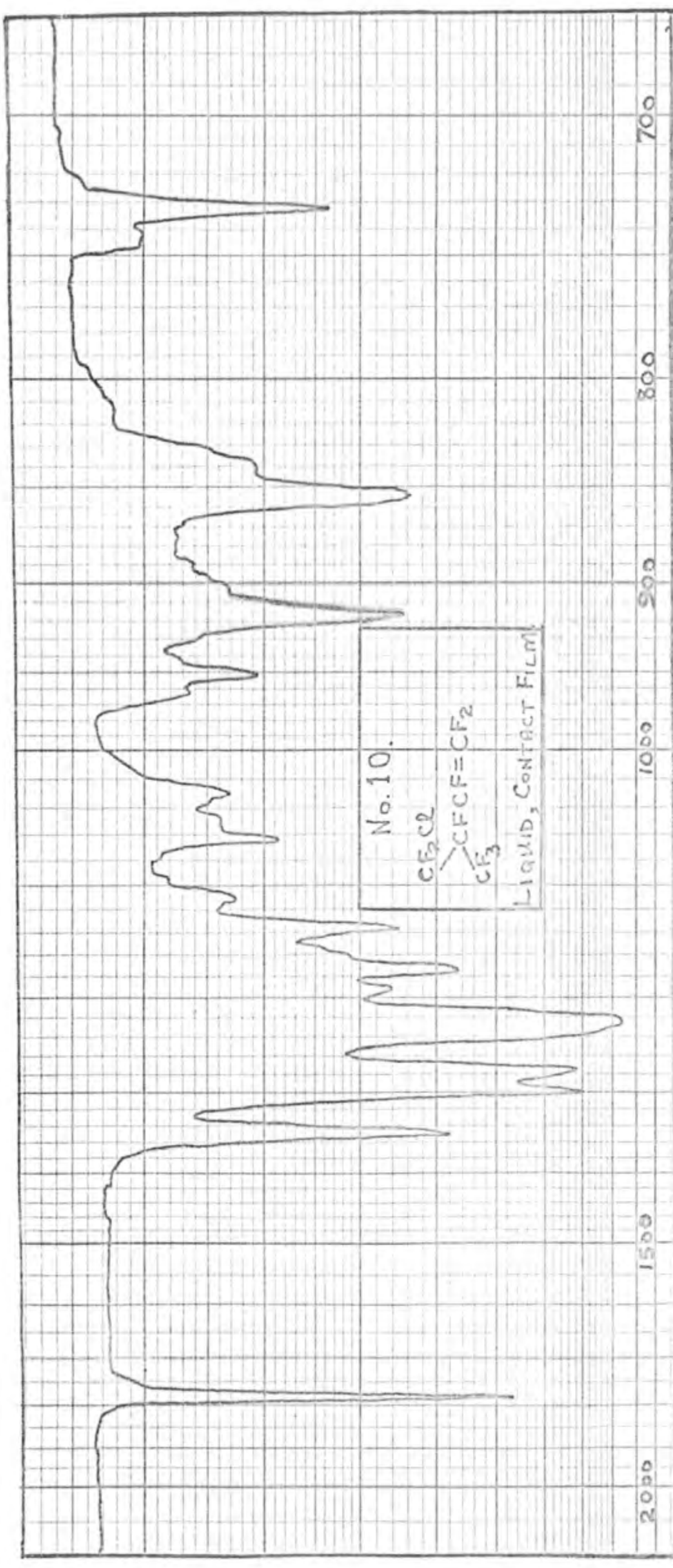

No. 3
(n-C$_4$H$_9$)$_3$ N.3HF
SOLID, KBr DISC
2962
2874
2717
2639
1477
1389
1093
927
738
3.0
3.5
4.0
4.5
5
6
7
8
9
10
11
12
13
14
15

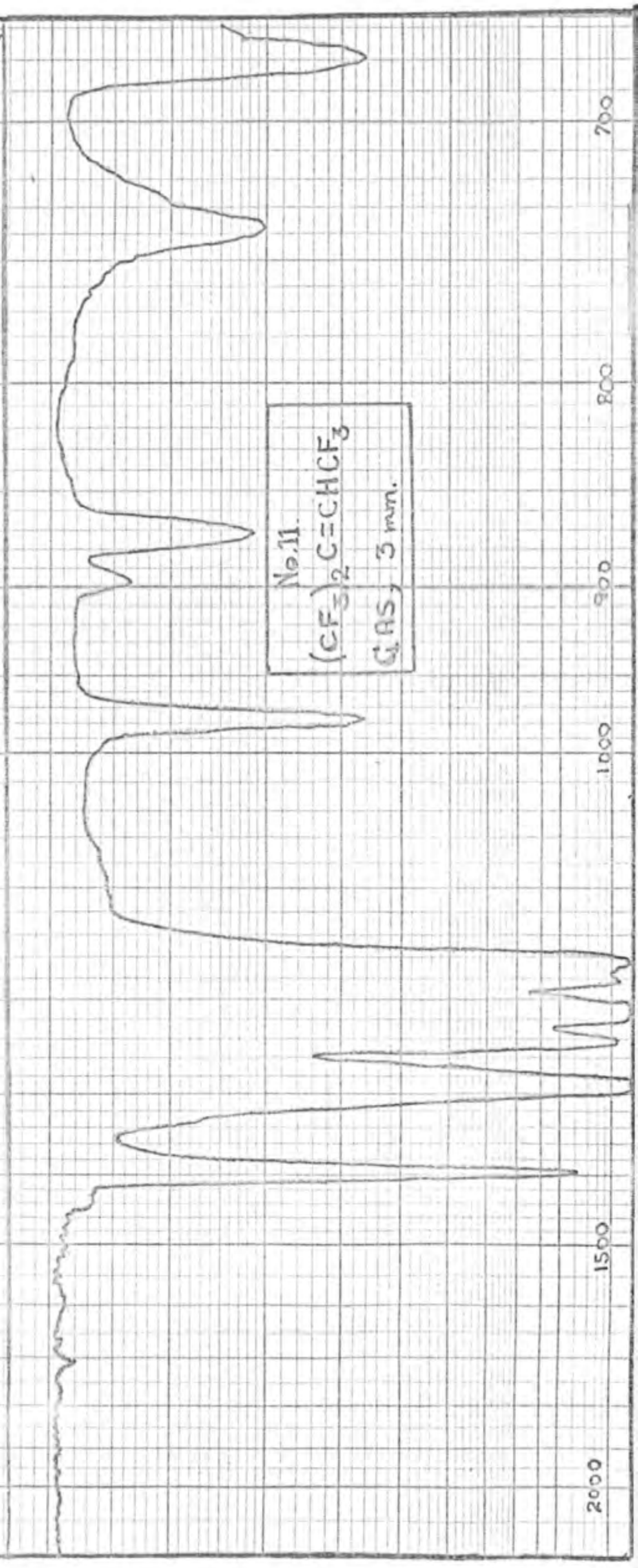

No. 4
$(CF_3)_2CFCH_2CF_3$
Gas, 3 mm.
Liquid, 0·02 mm.
3017
2981
1429
1403
1359
1307
1280
1262
1196
1153
1047
982
749
655
No. 5.
$(CF_3)_2CHCH_2CF_3$
Gas, 4 mm.
2962
1445
1388
1325
1263
1227
1195
1166
1148
1095
1072
879
836
733
670
650
No. 6
$(CF_3)_2CFCHFCF_2I$
Liquid, Contact Film
2907
1383
1300
1237
1154
1120
1096
1090
982
938
807
755
734
725
699
662
652
3·0
3·5
4·0
5
6
7
8
9
10
11
12
13
14
15
16

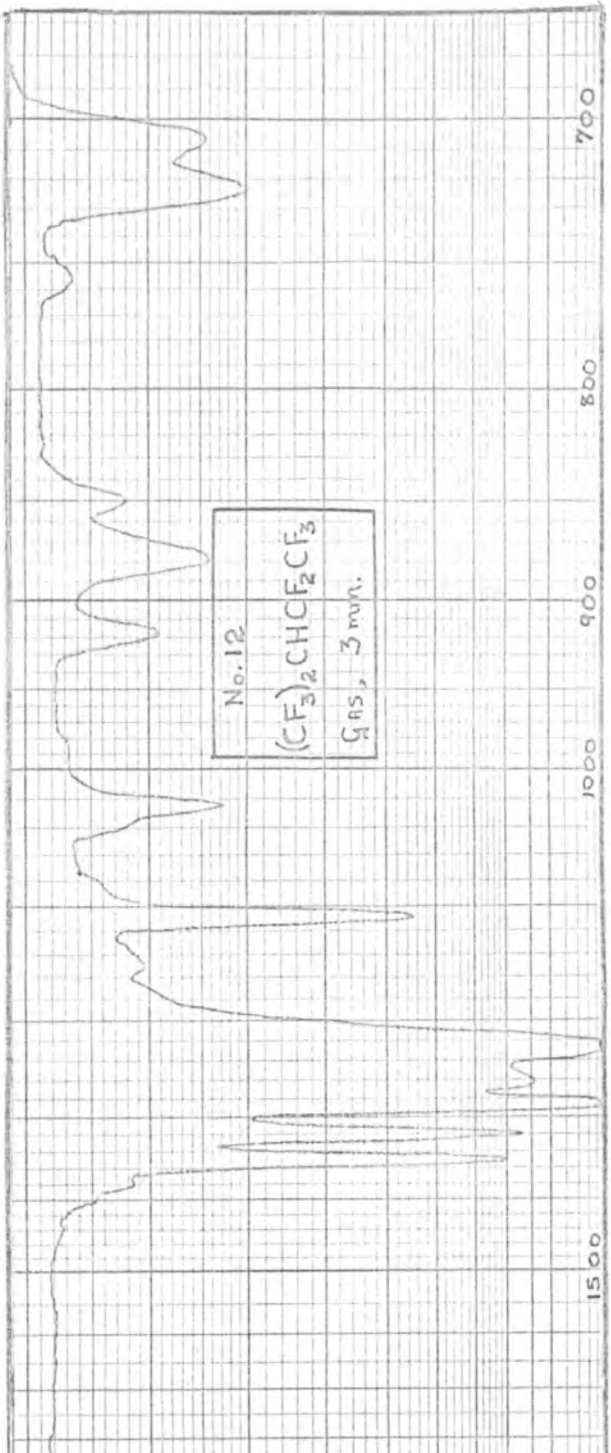

No. 7
$(CF_3)_2CFCFHCF_3$
Gas, 50mm.
Gas, 6mm
2981
1402
1367
1312
1282
1255
1216
1186
1165
1138
1117
980
843
745
694
3·0
3·5
5
6
7
8
9
10
11
12
13
14
15
16


$(CF_3)_2CFCFCF_2$
Gas, 2mms.
No. 8
1776
1357
1300
1311
1244
1226
1189
1176
1147
1126
1053 1024
980
939
919
758
725
5
6
7
8
9
10
11
12
13
14


No. 9
$CF_2Cl$ $CF_3$ >CFCFHCF$_2$I
Liquid, Contact Film
2976
1377
1272
1046
990
963
947
861
722
682
620
3·0
3·5
5
6
7
8
9
10
11
12
13
14
15
16
17


No. 10.
$CF_2Cl$
$CFCF=CF_2$
$CF_3$
Liquid, Contact Film
700
800
900
1000
1500
2000

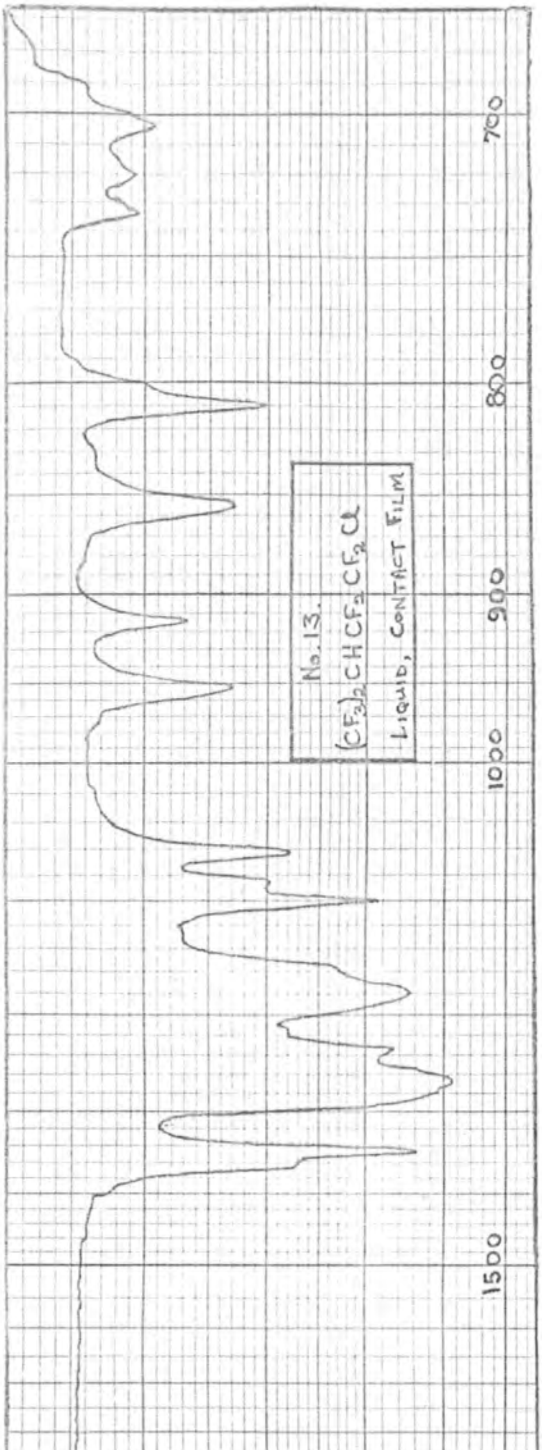

No. 11
$(CF_3)_2C=CHCF_3$
Gas, 3 mm.
700
800
900
1000
1500
2000



No. 12

$(CF_3)_2CHCF_2CF_3$

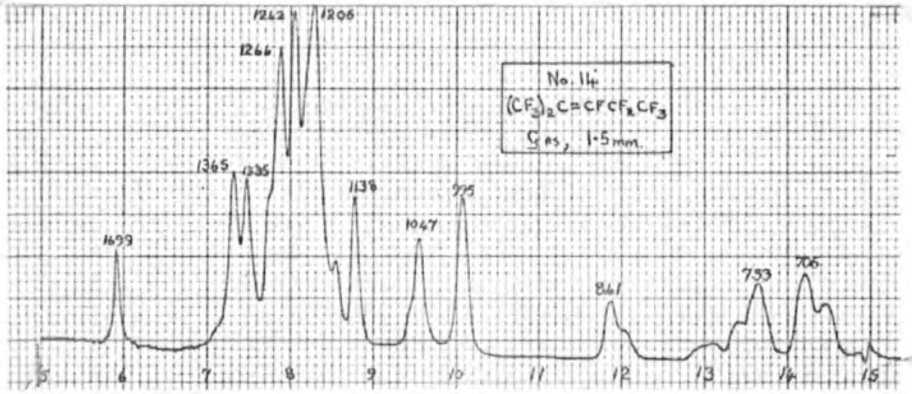
Gas, 3 mm.

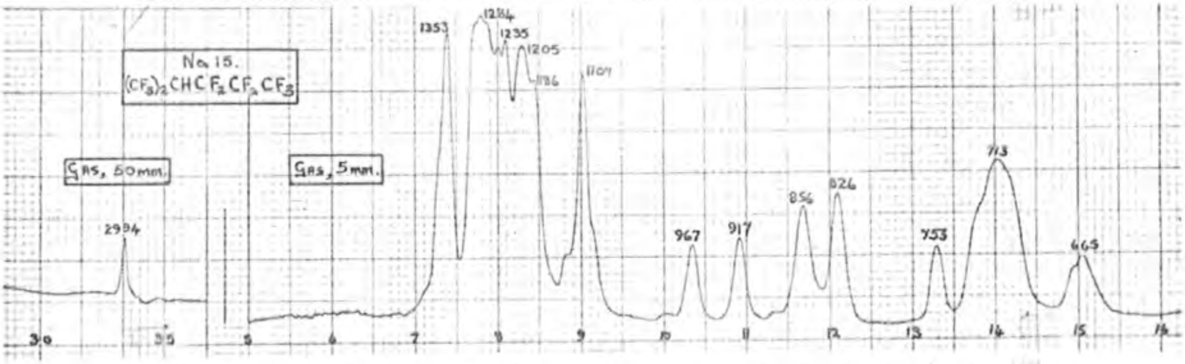


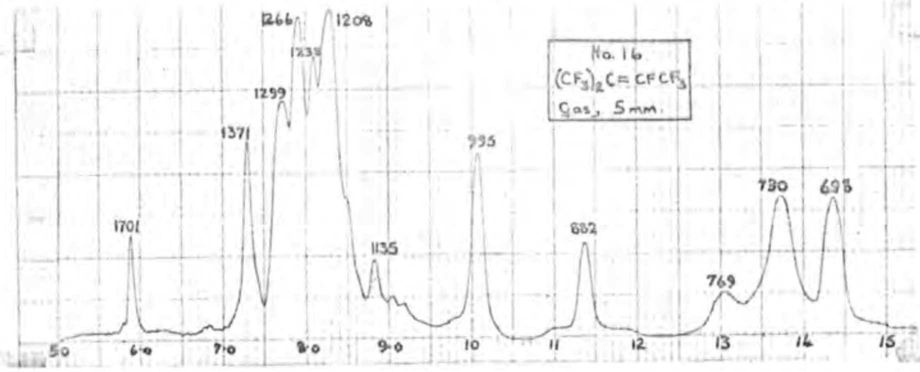
No. 13.

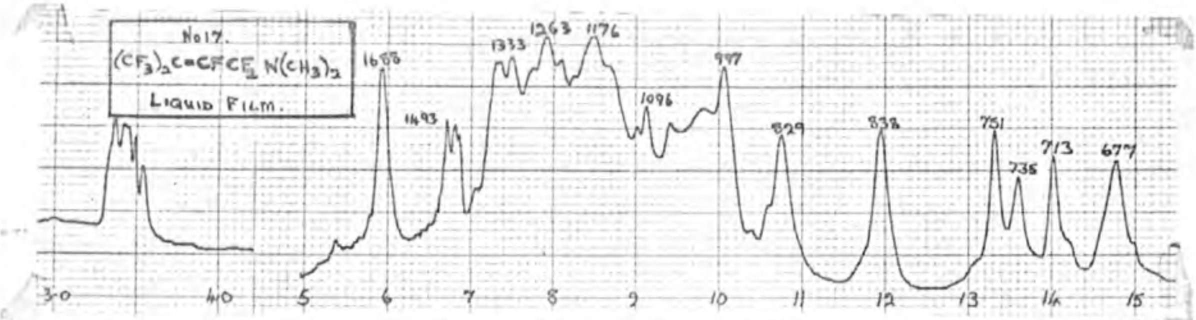
$(CF_3)_2CHCF_2CF_2Cl$

Liquid, contact film

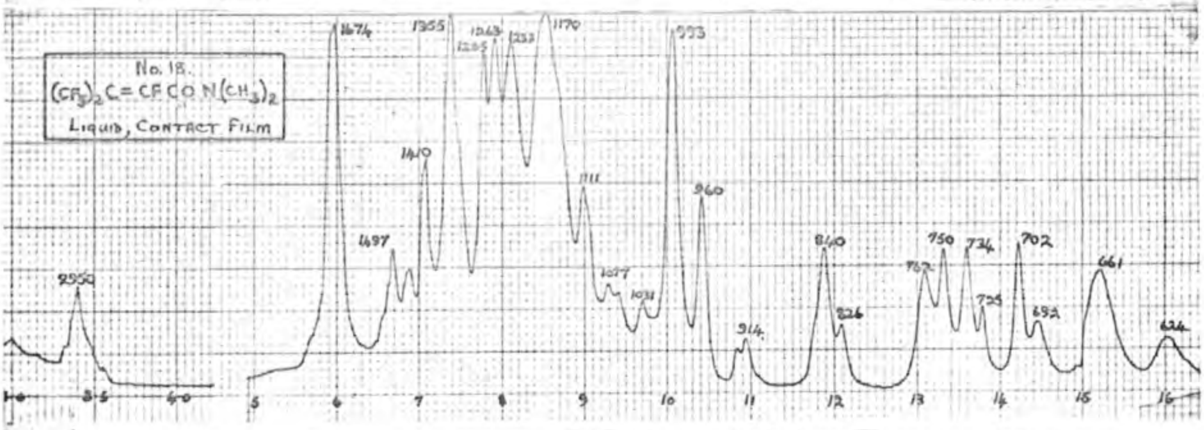

No. 14
$(CF_3)_2C=CFCF_2CF_3$
Gas, 1·5mm.
1699
1365
1335
1266
1242
1206
1138
1047
995
861
733
706
5
6
7
8
9
10
11
12
13
14
15


No. 15.
$(CF_3)_2CHCF_2CF_2CF_3$
Gas, 50mm.
Gas, 5mm.
2994
1353
1284
1235
1205
1136
1107
967
917
856
826
753
713
665
3·0
3·5
5
6
7
8
9
10
11
12
13
14
15
16

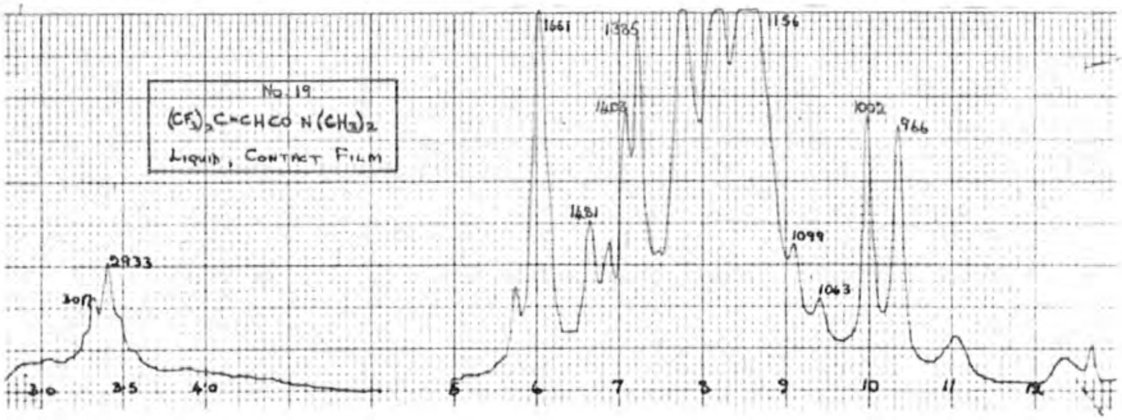

No. 16
$(CF_3)_2C=CFCF_3$
Gas, 5mm.
1701
1371
1299
1266
1233
1208
1135
995
882
769
730
695
5·0
6·0
7·0
8·0
9·0
10
11
12
13
14
15



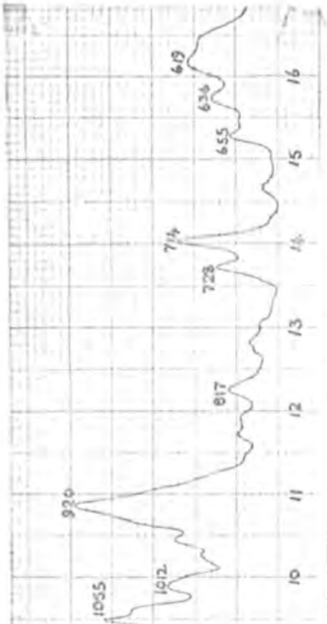
No 17.
$(CF_3)_2C=CFCF_2N(CH_3)_2$
Liquid Film.

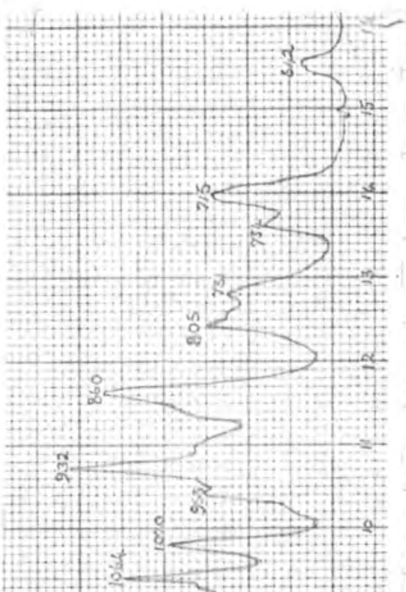


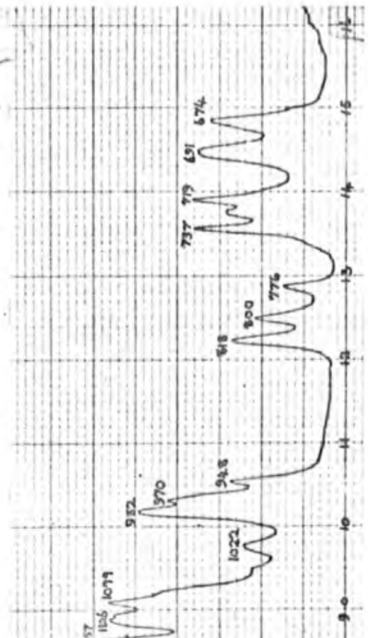
No. 18.
$(CF_3)_2C=CFCON(CH_3)_2$
Liquid, Contact Film

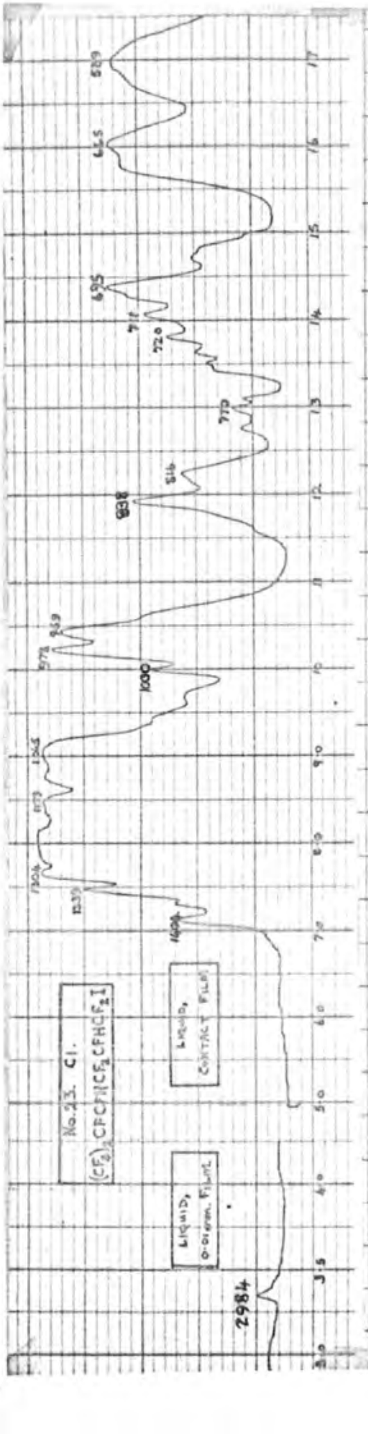


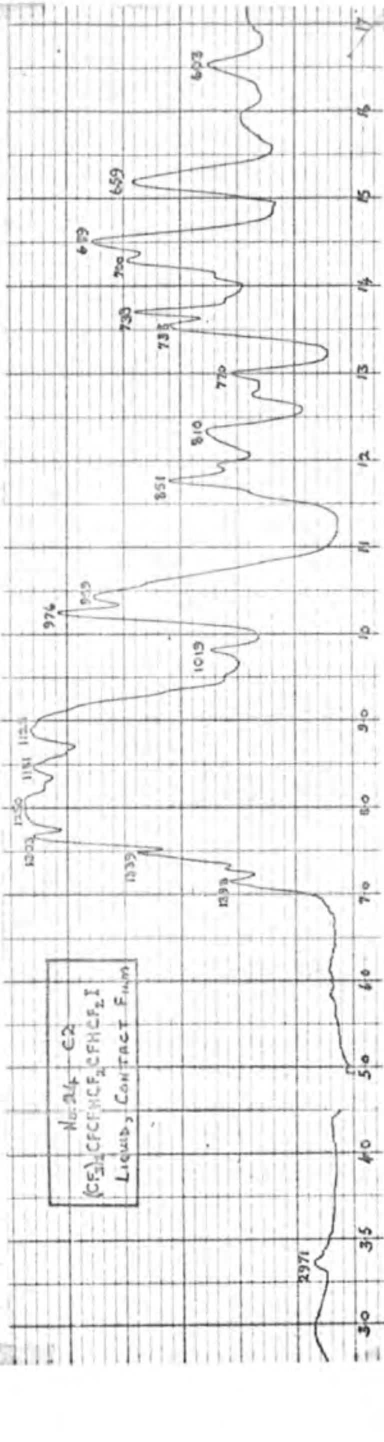
No. 19
$(CF_3)_2C=CHCON(CH_3)_2$
Liquid, Contact Film

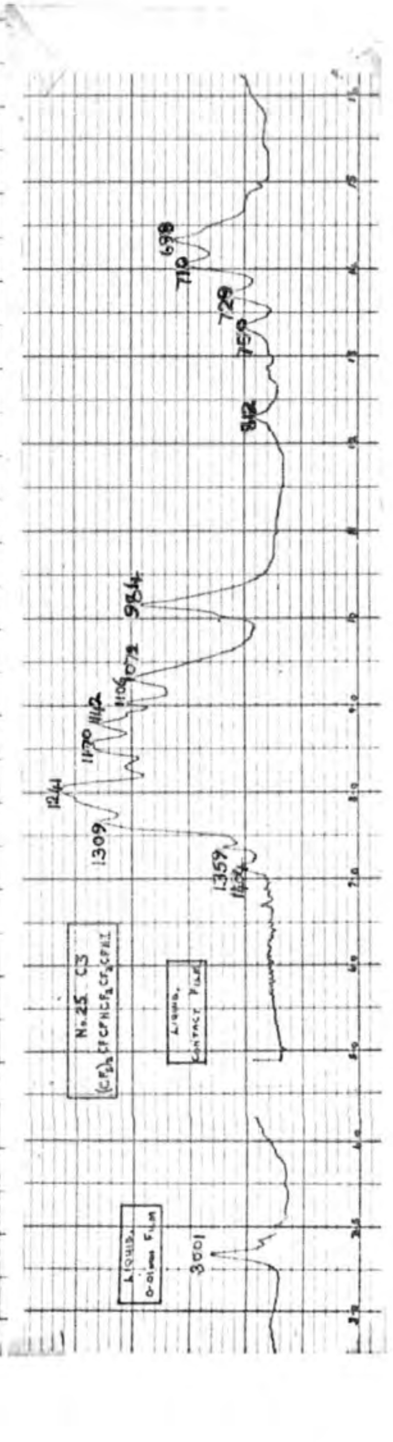

No. 20.
$CF_2Cl \rangle CFCH_2CF_2I$ / $CF_3$
Liquid, Contact Film
3008
2968
1428
1367
1336
1263
1229
1201
1112
1055
1012
920
817
728
714
655
636
619
3.5
5
6
7
8
9
10
11
12
13
14
15
16

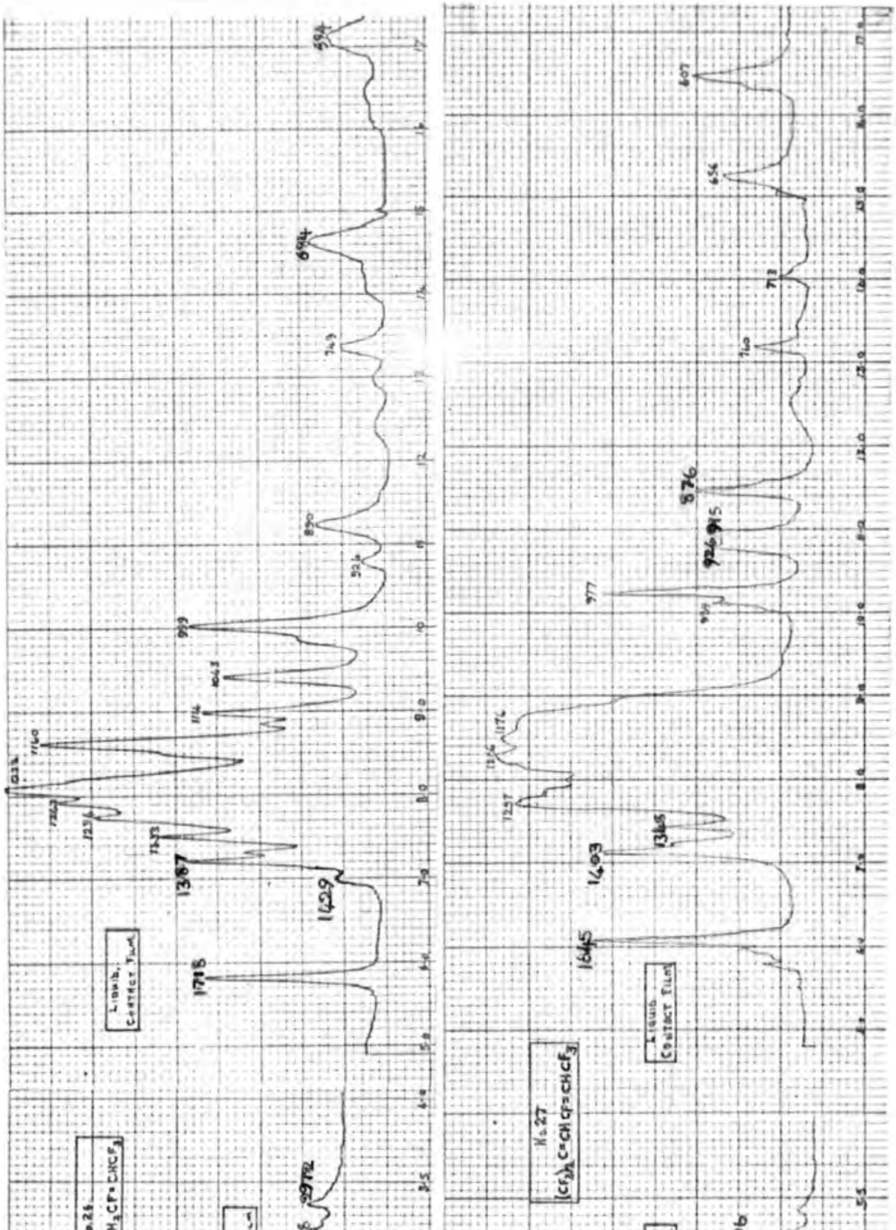

No. 21
$CF_2Cl \rangle CFCH{=}CF_2$ / $CF_3$
Liquid, Contact Film
2967
2924
1751
1335
1297
1205
1149
1064
1010
958
932
860
805
781
733
715
642
3.25
3.5
5
6
7
8
9
10
11
12
13
14
15
16


No. 22
$(CF_3)_2CFCFHCF_2CF{=}CF_2$
Liquid, Contact Film
2967
1787
1355
1302
1247
1179
1157
1126
1099
982
970
948
1022
818
800
776
737
719
691
674
3.0
3.5
4.0
5.0
6.0
7.0
8.0
9.0
10
11
12
13
14
15
16


No. 23. C1.
(CF3)2CFCFHCF2CFHCF2I
LIQUID, CONTACT FILM
LIQUID, FILM
2984
1404
1339
1304
1173
1145
1000
972
959
838
816
770
720
711
695
655
589
3.0
3.5
4.0
5.0
6.0
7.0
8.0
9.0
10
11
12
13
14
15
16
17

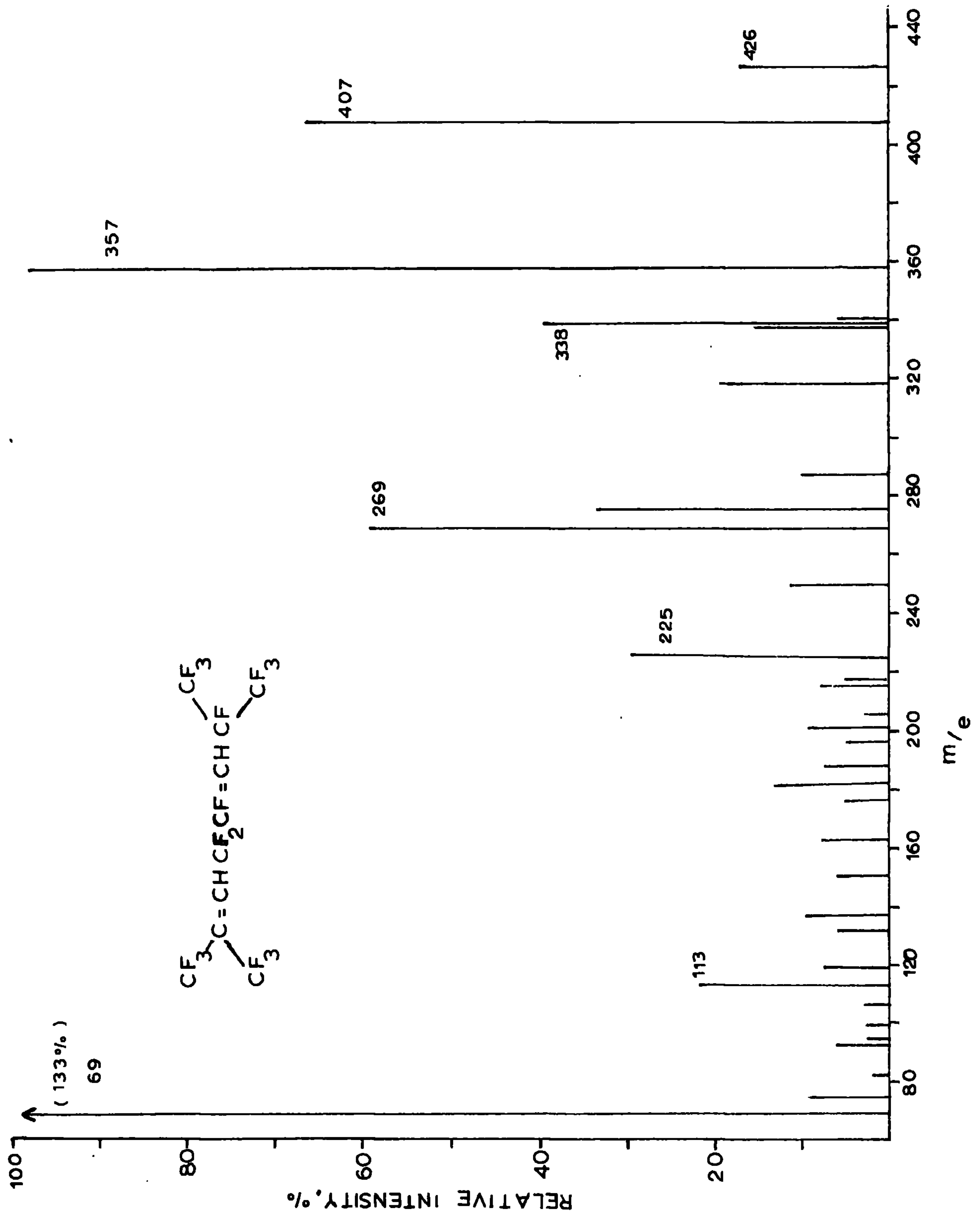

No. 24 C2
(CF3)2CFCFHCF2CFHCF2I
LIQUID, CONTACT FILM
2971
1398
1335
1302
1250
1181
1125
1019
976
959
851
810
770
735
730
700
689
659
603
3.0
3.5
4.0
5.0
6.0
7.0
8.0
9.0
10
11
12
13
14
15
16
17

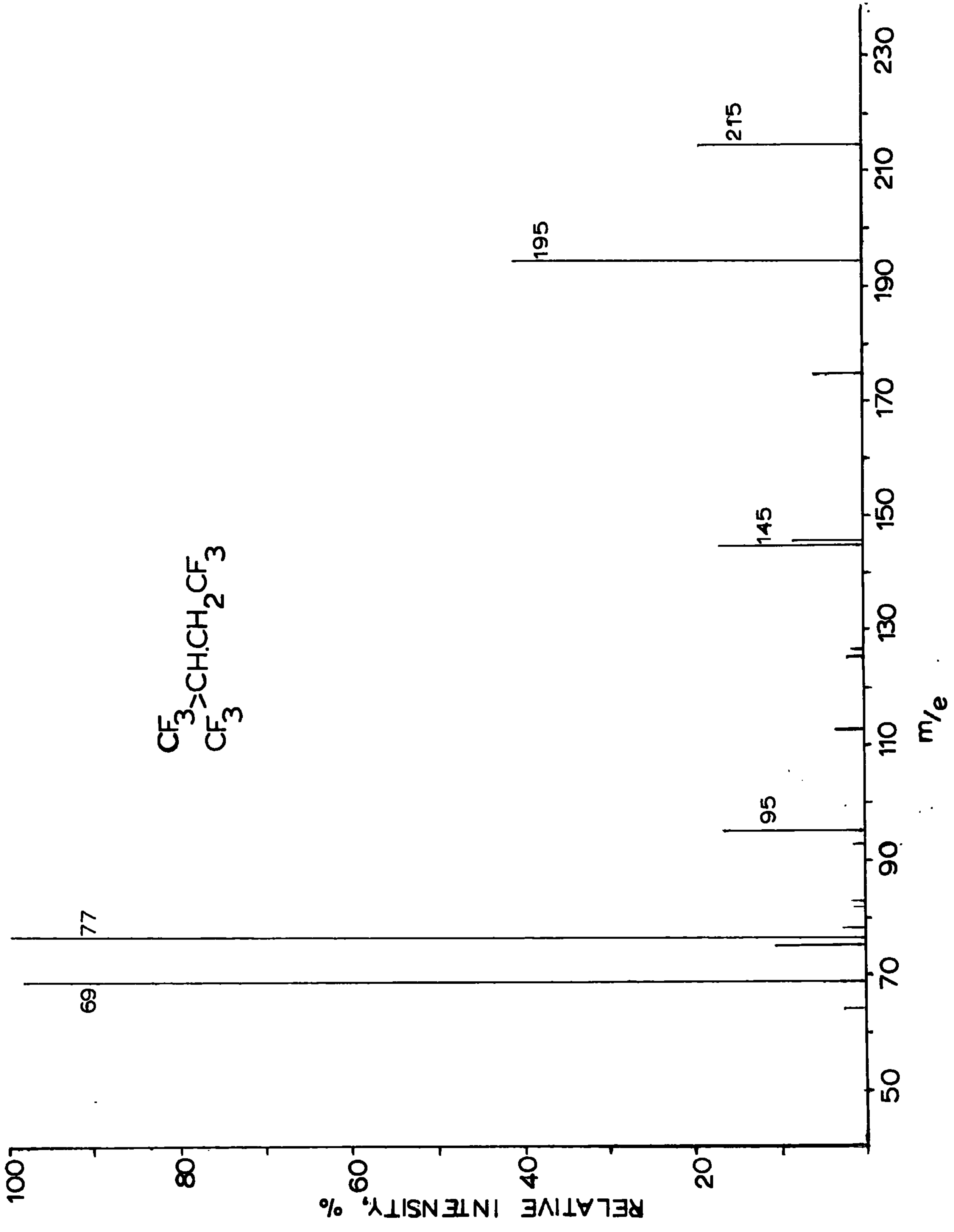

No. 25 C3
(CF3)2CFCFHCF2CF2CFHI
LIQUID, CONTACT FILM
LIQUID, FILM
3001
1359
1309
1241
1170
1142
1106
1072
984
842
750
729
710
698


No. 26
$(CF_3)_2CFCH_2CF=CHCF_3$
Liquid, 0.01 mm Film
Liquid, Contact Film
3115
2972
1718
1429
1387
1323
1236
1263
1232
1160
1114
1063
999
926
890
743
694
594
No. 27
$(CF_3)_2C=CHCF=CHCF_3$
Liquid, 0.01 mm Film
Liquid, Contact Film
3106
1645
1403
1365
1257
1216
1176
977
959
926
915
876
760
713
656
607

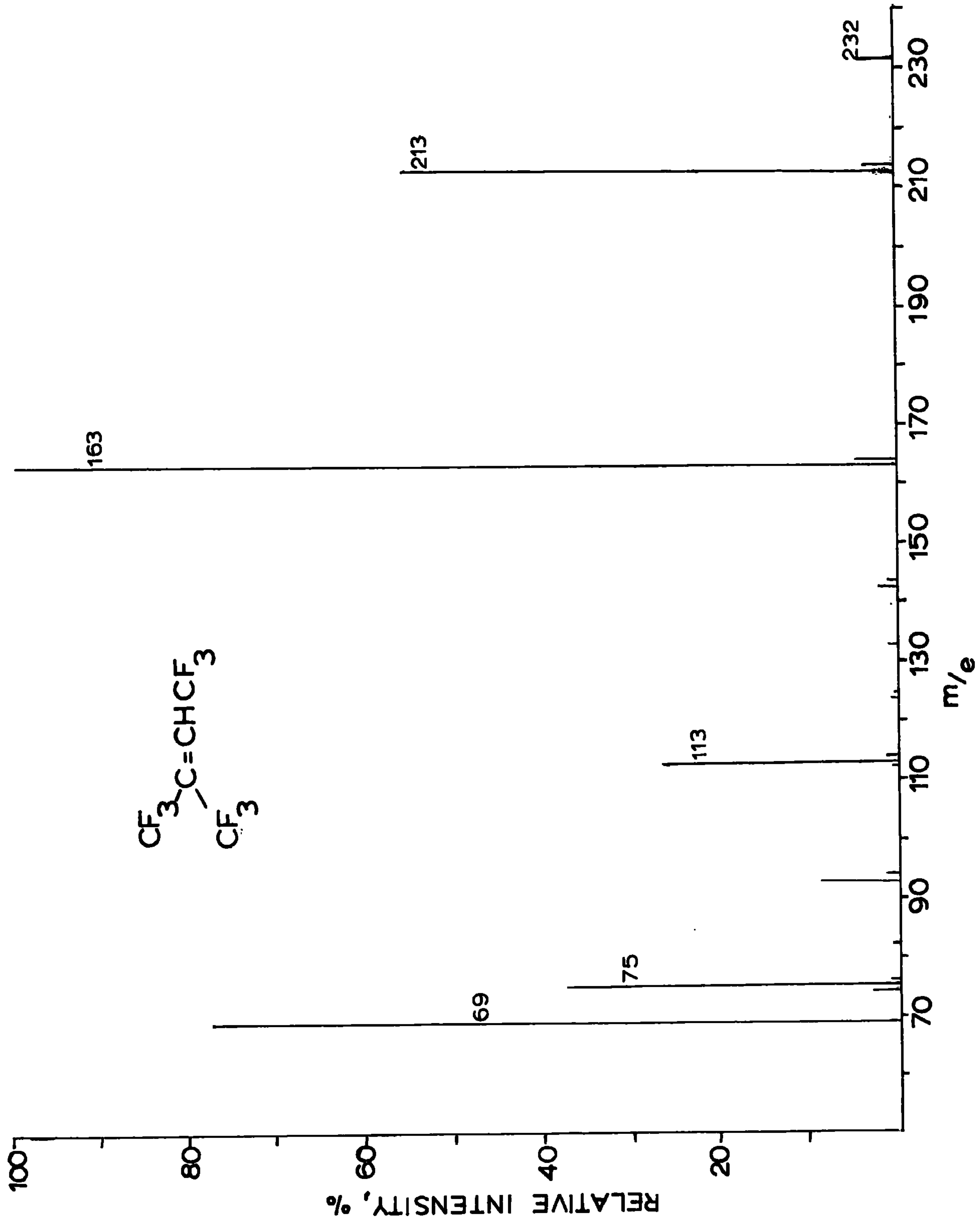
## Appendix 2: Mass Spectra

1. $(CF_3)_2C=CHCF_2CF=CHCF(CF_3)_2$
2. $(CF_3)_2CHCH_2CF_3$
3. $(CF_3)_2C=CHCF_3$


( 133% )
69
113
225
269
338
357
407
426
CF3
C = CH CF2CF = CH CF
CF3
CF3
CF3
RELATIVE INTENSITY, %
100
80
60
40
20
m/e
80
120
160
200
240
280
320
360
400
440



$CF_3 > CH.CH_2CF_3$
$CF_3$
69
77
95
145
195
215
RELATIVE INTENSITY, %
100
80
60
40
20
m/e
50
70
90
110
130
150
170
190
210
230


$CF_3$
$C=CHCF_3$
$CF_3$
69
75
113
163
213
232
70
90
110
130
150
170
190
210
230
m/e
100
80
60
40
20
RELATIVE INTENSITY, %

# Appendix 3

## Summary of N.M.R. Spectra.

| | Formula | Chemical Shifts, p.p.m.* | Relative Intensity | Assignation |
|---|---|---|---|---|
| 1. | $(CF_3)_2C{=}CHCF_2CF{=}CHCF(CF_3)_2$ | -12·9, -7·2 | 3,3 | $(CF_3)_2C{=}$ |
| | | -11·5 | 6 | $(CF_3)_2CX-$ |
| | | 35·0 | 2 | $-CF_2-$ |
| | | 34·17 | 1 | $=CF-$ |
| | | 132·9 | 1 | $CF-$ |
| 2. | $(CF_3)_2CHCH_2CF_3$ | -9·60 | 2 | $(CF_3)_2CH-$ |
| | | -11·95 | 1 | $CF_3CH_2-$ |
| 3. | $(CF_3)_2CFCFHCF_3$ | -4·5 | 6 | $(CF_3)_2CF-$ |
| | | -2·1 | 3 | $CF_3-$ |
| | | 119·2 | 1 | $CF-$ |
| | | 132·7 | 1 | $-CFH-$ |
| 4. | $(CF_3)_2C{=}CHCF_3$ | -20·0 | 2 | $(CF_3)_2C{=}$ |
| | | -14·2 | 1 | $CF_3-$ |
| | | -7·1 [from $(CH_3)_4Si$] | - | $=CH-$ |
| 5. | $(CF_3)_2CHCF_2CF_3$ | -18·69 | 6 | $(CF_3)_2CX-$ |
| | | 23·63 | 3 | $CF_3-$ |
| | | 33·96 | 2 | $-CF_2-$ |
| 6. | $(CF_3)_2CHCF_2CF_2Cl$ | -16·09 | 3 | $(CF_3)_2CX-$ |
| | | -6·86 | 1 | $-CF_2-Cl$ |
| | | 32·29 | 1 | $-CF_2-$ |

*$F^{19}$ shifts measured from $CF_3COOH$ as external reference - positive shifts are to high field of $CF_3COOH$.

| | Formula | Chemical Shifts, p.p.m. | Relative Intensity | Assignation |
|---|---|---|---|---|
| 7. | $(CF_3)_2C{=}CFCF_2CF_3$ | -23·5 | 3 | $(CF_3)_2C{=}C$ |
| | | -21·0 | 3 | $(CF_3)_2C{=}C$ |
| | | 2·1 | 3 | $CF_3$- |
| | | 16·5 | 1 | -CF= |
| | | 35·4 | 2 | $-CF_2-$ |
| 8. | $(CF_3)_2CHCF_2CF_2CF_3$ | -18·8 | 6 | $(CF_3)_2CX-$ |
| | | -0·5 | 3 | $CF_3$- |
| | | 30·9 | 2 | $-CF_2-$ |
| | | 44·6 | 2 | $-CF_2-$ |
| 9. | $(CF_3)_2C{=}CFCF_3$ | -23·3 | 3 | $(CF_3)_2C{=}C$ |
| | | -21·5 | 3 | $(CF_3)_2C{=}C$ |
| | | -13·7 | 3 | $CF_3$- |
| | | 18·0 | 1 | =CF- |
| 10. | $(CF_3)_2(CH_3)C{-}CF_2CF_2N(CH_3)_2$ | -13·5 | 6 | $(CF_3)_2CX-$ |
| | | 14·1 | 2 | $-CF_2-$ |
| | | 27·2 | 2 | $-CF_2-$ |
| | | -1·69 [from $(CH_3)_4Si$] | (1) | $-CH_3$ |
| | | -2·67 [ " ] | (2) | $-N(CH_3)_2$ |
| 11. | $(CF_3)_2C{=}CFCO.N(CH_3)_2$ | -21·2 | 3 | $(CF_3)_2C{=}C$ |
| | | -20·0 | 3 | $(CF_3)_2C{=}C$ |
| | | -7·86 | 1 | =CF- |
| | | -3·09[from $(CH_3)_4Si$] | | $N(CH_3)_2$ |

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