Journal of Fluorine Chemistry, 18 (1981) 417–439

Received: April 27, 1981

REACTIONS OF TETRAFLUOROETHYLENE OLIGOMERS.

PART 1. SOME PYROLYTIC REACTIONS OF THE PENTAMER AND HEXAMER AND OF THE FLUORINE ADDUCTS OF THE TETRAMER AND PENTAMER

PAUL L. COE, SIMON F. SELLERS, JOHN COLIN TATLOW

Chemistry Department, The University of Birmingham, P.O. Box
363, Birmingham B15 2TT (Great Britain)

HAROLD C. FIELDING and GRAHAM WHITTAKER

I.C.I. Ltd., Mond Division, P.O. Box 8, The Heath, Runcorn,
Cheshire WA7 4QD (Great Britain)

SUMMARY

Pyrolyses of these highly branched fluorocarbons over glass beads caused the preferential thermolyses of C-C bonds where there is maximum carbon substitution. Fluorinations of perfluoro-3,4-dimethylhex-3-ene (tetramer) (I) and perfluoro-4-ethyl-3,4-dimethylhex-2-ene (pentamer) (II) over cobalt (III) fluoride at 230° and 145° respectively afforded the corresponding saturated fluorocarbons (III) and (IV), though II gave principally the saturated tetramer (III) at 250°. Pyrolysis of III alone at 500-520° gave perfluoro-2-methylbutane (V), whilst pyrolysis of III in the presence of bromine or toluene afforded 2-bromononafluorobutane (VI) and 2H-nonafluorobutane (VII) respectively. Pyrolysis of perfluoro-3-ethyl-3, 4-dimethylhexane (IV) alone gave a mixture of perfluoro-2-methylbutane (V), perfluoro-2-methylbut-1-ene (VIII), perfluoro-3-methylpentane (IX), perfluoro-3,3-dimethylpentane (X), and perfluoro-3,4- dimethylhexane (III). Pyrolysis of IV in the presence of bromine gave (VI) and 3-bromo-3-trifluoromethyl-decafluoropentane (XI): with toluene, pyrolysis gave VII and

3H-3-trifluoromethyldecafluoropentane (XII). Pyrolysis of II at 500° over glass gave perfluoro-1,2,3-trimethylcyclobutene (XIII) and perfluoro-2,3-dimethylpenta-1,3(E)- and (Z)-diene (XIV) and (XV) respectively. The diene mixture (XIV and XV) was fluorinated with CoF$_3$ to give perfluoro-2,3-dimethylpentane (XVI) and was cyclised thermally to give the cyclobutene (XIII). Pyrolysis of perfluoro-2-(1'-ethyl-1'-methylpropyl)-3-methylpent-1-ene (XVII) (TFE hexamer major isomer) at 500° gave perfluoro-1-methyl-2-(1'-methylpropyl)cyclobut-1-ene (XVIII) and perfluoro-2-methyl-3-(1'-methylpropyl)buta-1,3-diene (XIX). Fluorination of XVIII over CoF$_3$ gave perfluoro-1-methyl-2-(1'-methylpropyl)cyclobutane (XX), which on co-pyrolysis with bromine gave VI. XIX on heating gave XVIII. Reaction of XVIII with ammonia in ether gave a mixture of E and Z 1-trifluoromethyl-2-(1'-trifluoromethylpentafluoropropyliden-1'-yl)tetrafluorocyclobutylamine (XXI) which on diazotisation and hydrolysis afforded 2-(2'trifluoromethyltetrafluorocyclobut-1-en-1'-yl)-octafluorobutan-2-ol (XXII).

INTRODUCTION

The paper [1] by Miller and co-workers, that first pointed the way to the vast potential of fluoride ion as a nucleophilic reagent in fluoro-alkene chemistry, was the forerunner of many advances of importance and interest. One of great significance has been the anionic polymerisation of tetrafluoroethylene, promoted by fluoride ion, which gives rise [2] to short chain oligomers. These perfluoroalkenes have highly branched carbon skeletons, in complete contrast to the products of free radical polymerisations or telomerisations of tetrafluoroethylene, which have structures of the type $(-CF_2-CF_2-)_n$. The products of oligomerisation induced by fluoride ion are now readily available and have stimulated much current interest [2,3] both fundamental and technical. Major products are the tetramer (I) and particularly the pentamer (II), in which appears the unusual perfluoro-3-methyl-3-pentyl group ('trident' ) having a quaternary carbon atom.

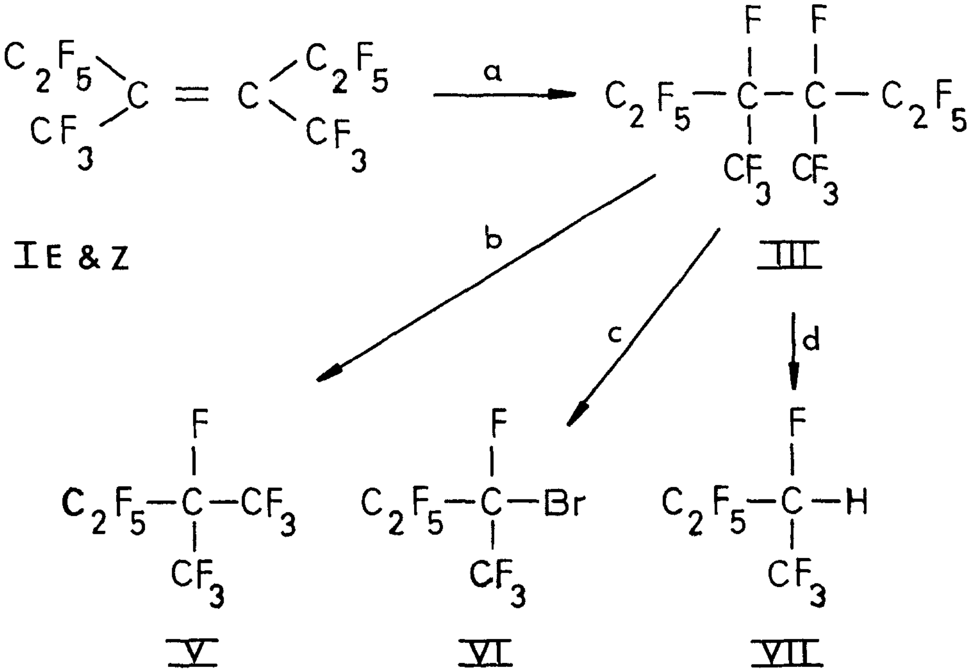
Work of ours, carried out long ago, established [4] that in saturated fluorocarbons, bonds between tertiary carbon atoms (e.g. as in $[CF_2]_5 >CF-CF< [CF_2]_5$) were less stable thermally than those involving secondary or primary carbon atoms, and could be cleaved selectively under free radical conditions. This was one of the first reactions of any type, of possible synthetic use,to be found for saturated fluorocarbons. Thermolytic reactions have found many applications in organofluorine chemistry generally [5]. It was of interest therefore to apply this sort of reaction to the highly branched oligomers of tetrafluoroethylene, and also to the fluoroalkanes made from them by saturation of the residual double bonds with fluorine. Did C-C bonds in these fluorocarbons become progressively weaker towards heat as the carbon atoms involved became more highly substituted with perfluoroalkyl groups?

RESULTS

Tetramer series

Our early work [4] on thermolytic fluorocarbon bond cleavage was done over Pyrex glass at 500 - 550^0. The pyrolysis of perfluoro-3,4-dimethylhex-3-ene (I) (tetrafluoroethylene tetramer) over platinum at 670^0 has already been reported [6] to give a mixture of perfluoro-2,3-dimethylbuta-1,3-diene and thence perfluoro-1,2-dimethylcyclobutene: perfluoro-3,4-dimethylhexa-2,4-diene by defluorination, and thence perfluoro-1,2,3,4-tetramethylcyclobutene, were obtained over iron [6]. We found that tetramer (I) was thermally stable over glass at up to 550^0, but above this, profound decomposition occurred, only low molecular weight products being obtained. Clearly therefore, the nature of the surface over which the reaction occurs plays a considerable part in determining the end products.

We investigated next the pyrolysis of the saturated fluorocarbon perfluoro-3,4-dimethylhexane (III). This was prepared in good yield by fluorination of tetramer (I) over cobalt (III) fluoride at 230-240^0. The structure of III was clear from its ^{19}F nmr spectrum, which showed that no skeletal rearrangement had occurred. Pyrolysis of III alone over glass beads (Scheme I) at 500-520^0 gave a major isolable product (V) in good yield (volatile fragmented material was also formed). Mass spectrometry of V indicated the formula C_5F_{12}; ^{19}F nmr data suggested the presence of three trifluoromethyl groups, two coincident and one with septet splitting. A signal due to a CF_2 group was split into a doublet of septets, and there was a complex signal for a tertiary fluorine atom. These data are consistent with the product's being perfluoro-2-methylbutane (V). This presumably arises by abstraction of a



REAGENTS:

(a) CoF_3

(b) PYROLYSIS AT 500 - 520 °C OVER GLASS BEADS.

(c) AS (b) IN THE PRESENCE OF Br_2

(d) AS (b) IN THE PRESENCE OF TOLUENE.

Scheme 1

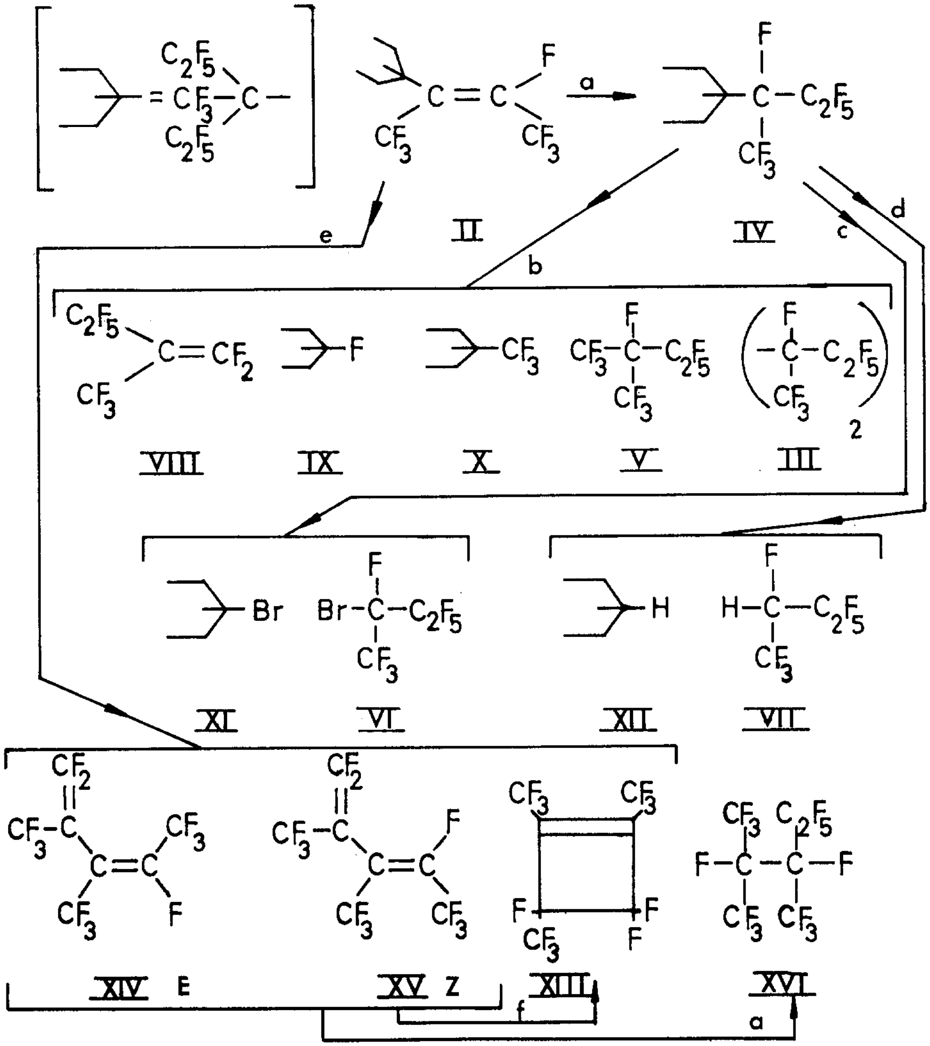
trifluoromethyl group by the first formed radical, which arises from cleavage of the central C-C bond linking the two tertiary carbons, the yield on this pyrolysis suggesting that this bond is much weaker than the others. Pyrolysis of perfluoro-dicyclohexyl or -isopropylcyclohexane in the presence of bromine or toluene yielded [4] fluorocarbon bromides or hydrides by saturation of the radicals formed by tertiary C-C bond cleavage. In analogous reactions, fluorocarbon III yielded 2-bromononafluorobutane (VI) and 2-H-nonafluorobutane (VII), characterised by their ^{1}H, ^{19}F nmr spectra, mass spectra and elemental analyses. Compounds V [7], VI [8], and VII [9] had all been made previously in other ways.

Pentamer series

It was immediately clear from fluorinations that the pentamer (II) was much less stable thermally than the tetramer (I). Passage over CoF_3 at 250° or above led to the formation in good yield of the fluorinated tetramer (III) as the only isolable product, and at 200° the tetramer (I) itself was formed. The initial step in the reaction is presumed to be de-oligomerisation of pentamer to tetramer initiated by fluoride ion, a process known to occur readily in solution [10]. Fluorination of pentamer (II) over CoF_3 at 145-150° in a stream of nitrogen gave two products in addition to unreacted starting material. The first was a mixture of the tetramer isomers (I) and the second a new saturated fluorocarbon (IV) of formula $C_{10}F_{22}$. ^{19}F nmr spectroscopy indicated the presence of three perfluoroethyl groups, two other trifluoromethyl groups, and a tertiary fluorine atom. The product was therefore perfluoro-3-ethyl-3,4-dimethylhexane (IV) i.e. arising simply from saturation of the pentamer double bond.

Thermal reactions (Scheme 2) were carried out over glass beads with IV alone and in the presence of bromine and toluene. It was obvious immediately that the quaternary - tertiary C-C bond was even less stable than the tertiary - tertiary, breaking at just over 300°.

The pyrolysis of IV alone at 300 - 320° produced a much more complex mixture than that obtained from III at 500°. Five components in addition to some unreacted starting material were isolated by glc separations. The first component isolated was shown by comparison of ir and nmr spectra to be perfluoro-2-methylbutane (V). The second product had a mass number corresponding to C_5F_{10} and its ir spectrum showed the presence of a strong double bond absorption at 1730cm^{-1}.



REAGENTS:

(a) CoF_3.

(b) PYROLYSIS AT 300-320° OVER GLASS BEADS.

(c) AS (b) IN THE PRESENCE OF Br_2.

(d) AS (b) IN THE PRESENCE OF TOLUENE.

(e) AS (b) BUT AT 500°.

(f) HEAT UNDER PRESSURE AT 300°.

Scheme 2

^{19}F nmr spectroscopy confirmed the structure as perfluoro-2-methylbut-1-ene (VIII). The third component was shown by ^{19}F nmr to contain the characteristic $CF_3(C_2F_5)_2C$-(trident) residue and a single tertiary fluorine atom: mass spectrometry confirmed the structure as the known [11] perfluoro-3-methylpentane (IX). The fourth component was shown by mass spectrometry to be a C_6F_{14} isomer; ^{19}F nmr confirmed the structure as the known [11] perfluoro-3,3-dimethylpentane (X). The fifth component was perfluoro-3,4-dimethyl hexane (III). Possible routes to these compounds are discussed below.

Pyrolysis of IV in the presence of bromine gave VI and a compound (XI) shown by elemental analysis and mass spectrometry to have the formula C_6BrF_{13}. The ^{19}F nmr spectrum was consistent with the retention of the trident group. Thus, XI was 3-bromo-3-trifluoromethyldecafluoropentane. In a similar way, co-pyrolysis of IV with toluene yielded VII and 3H-3-trifluoromethyldecafluoropentane (XII).

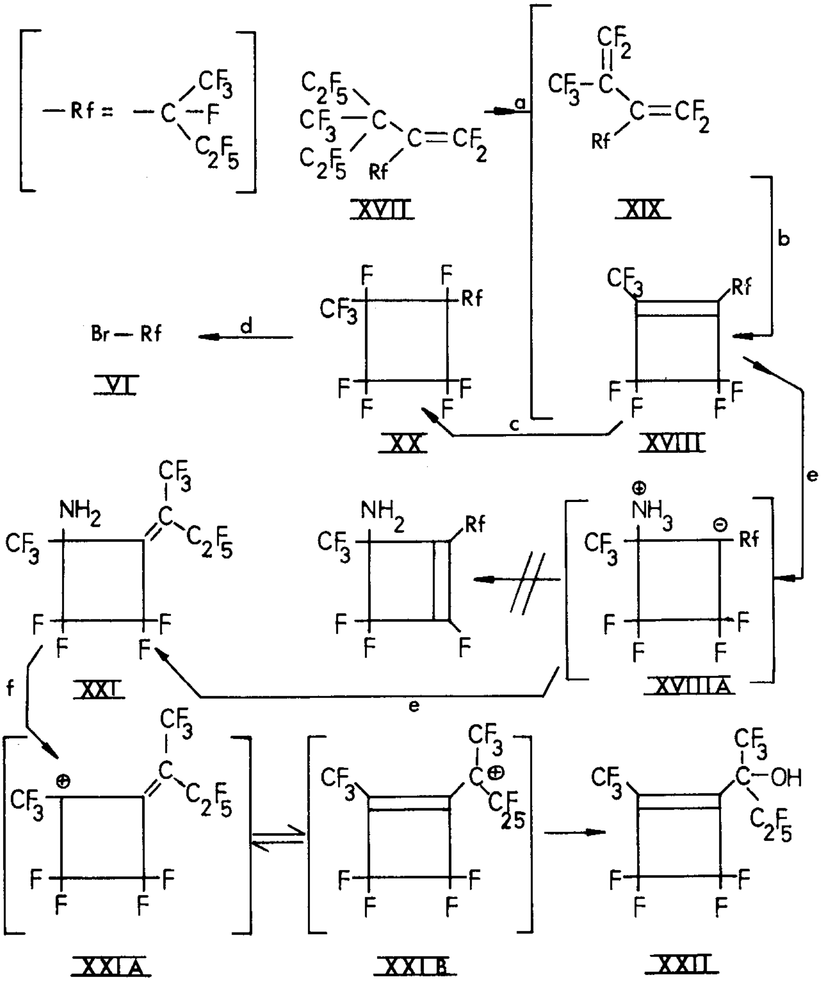
As indicated above, the pentamer (II) decomposed much more readily on fluorination than did the tetramer (I). There was less difference on pyrolysis over glass but by 500^{o}, II had decomposed to give a mixture of three isolable components. Separation by glc gave first the minor product as a liquid (XIII) with formula C_7F_{12} (elemental analysis and mass spectrometry), a weak C = C absorption at 1710 cm^{-1} in the ir, but with no selective uv absorption. ^{19}F nmr spectroscopy indicated three trifluoromethyl groups, a CF_2 group as an AB system, and a tertiary fluorine atom, but no vinylic fluorine atoms. These data correspond to the structure perfluoro-1,2,3-tris(trifluoromethyl)cyclobutene for XIII. The second product had a strong uv absorption and peaks in its ir spectrum at 1750 and 1700cm^{-1} characteristic of a perfluoro-1,3-diene structure [12]. The ^{19}F nmr spectrum showed peaks corresponding to three different CF_3 - groups, a single vinylic fluorine atom and a vinylic CF_2 group showing an AB pattern. The compound was thus perfluoro-2,3-dimethylpenta-1,3-diene (XIV) and from the magnitude of the coupling constants had the 3(E) configuration. The third component (XV) was assigned as the stereoisomer of XIV , namely perfluoro-2,3-dimethylpenta-1,3(Z)-diene.
Since our work was completed, XIV and XV have been described, one in a mixture, from the fluoride ion isomerisation of perfluoro-3,4-dimethylpenta-1,2-diene [13], our nmr data being in good agreement with the published values, though we believe the stereochemical designations

(cis and trans) should be reversed. The dienes (XIV and XV) were further characterised as a mixture by fluorination with CoF_3, to give the known [11] perfluoro-2,3-dimethylpentane (XVI), and by conversion in poor yield to the cyclobutene (XIII) on heating in a Carius tube at 300°. It seems that XIV and XV are the primary products of pyrolysis, and, once formed, slowly cyclise to XIII.

Hexamer series

Attempts at fluorination of the major hexamer oligomer, perfluoro-2-(1'ethyl-1'-methylpropyl)-3-methylpent-1-ene (XVII) resulted in complete fragmentation of the molecule which could be due either to thermal breakdown or to de-oligomerisation induced by fluoride ion (from CoF_3). We therefore investigated XVII itself, the thermal decomposition of which, like that of the pentamer (II), occurred at about 500° over glass (Scheme 3). A liquid product was obtained in good yield which was shown by glc to contain two major components, one predominating. Separation (glc) afforded the major component (XVIII) and careful fractionation of the products from several pyrolyses yielded a pure sample of the minor product (XIX). Each had a molecular formula C_9F_{16}. For XVIII, ir spectroscopy showed a weak band at $1690cm^{-1}$ (C = C), but there was no selective uv absorption in the region 200-350nm. The ^{19}F nmr spectrum was complex, but could be analysed as showing 3 CF_3 groups, 3 CF_2 groups, and a tertiary fluorine. It was consistent with the proposed structure, perfluoro-1-methyl-2-(1'-methylpropyl)cyclobut-1-ene (XVIII). This structure was further substantiated by fluorination over CoF_3 to yield a mixture of the geometrical isomers of perfluoro-1-methyl-2-(1'methylpropy cyclobutane (XX), confirmed as C_9F_{18} by mass spectrometry and elemental analysis. The retention of the cyclobutane skeleton in this high-temperature fluorination is surprising. Although XX gave a complex ^{19}F nmr spectrum, this was consistent, three tertiary fluorines being distinguishable. Pyrolysis of XX in the presence of bromine yielded the known 2-bromononafluorobutane (VI), thus confirming the side chain structure. Unfortunately, no bromotrifluoromethylhexafluorocyclobutane could be detected.

The minor product (XIX) from the original pyrolysis of XVII had strong bands at 1720 and $1745cm^{-1}$ in its ir spectrum and showed a strong uv absorption. The ^{19}F nmr spectrum showed bands corresponding to three different CF_3 groups, a saturated CF_2 group, two vinylic CF_2 groups and a



REAGENTS:

(a) PYROLYSIS AT 500° OVER GLASS BEADS.

(b) HEAT UNDER PRESSURE AT 230°.

(c) CoF_3

(d) AS (a) IN THE PRESENCE OF Br_2.

(e) LIQUID NH_3 IN DIETHYL ETHER.

(f) $NaNO_2/H_2O/H_2SO_4$.

Scheme 3

The pathway from XXI to XXII need not involve a discrete carbonium ion. An alternative would be attack by hydroxylic species on the non-ring end of the double bond of the diazonium salt derived from XXI, with loss of nitrogen in an allylic displacement. This route is favoured by Professor R.D. Chambers (personal communication).

single tertiary fluorine atom. These data suggested that the compound was perfluoro-2-methyl-3-(1'-methylpropyl)buta-1,3-diene (XIX). The diene structure was further confirmed by heating XIX at 230° for 150h in a sealed tube, when the product was the cyclobutene (XVIII). Again, the diene XIX seems to be the primary product of pyrolysis, but in this case is converted more readily to the corresponding cyclobutene (XVIII) (two terminal $=CF_2$ groups instead of one).

There has long been considerable interest in the reactions of perfluoroalkenes including perfluorocyclobutene derivatives with nucleophiles, especially in the mechanism of the reactions, now generally regarded as addition-elimination processes. In fact XVIII can only react at the double bond by addition-elimination, but elimination can occur from a ring CF_2 or involve the tertiary CF in the side chain to give an exocyclic double bond.

Many perfluoro-olefins have been treated with ammonia [14], those with vinylic fluorines giving nitriles [15] or imines [16] by HF loss from the incipient $-NH_2$ groups. With liquid ammonia in dry ether at -50°, XVIII gave one product (Scheme 3). Mass spectrometry and elemental analysis indicated the formula $C_9F_{15}NH_2$. 'H nmr spectroscopy showed a characteristic peak for NH_2 at 2.28, which collapsed on shaking the solution with D_2O. The ^{19}F nmr spectrum showed two sets of signals in approximately equal proportions, corresponding to geometrical isomers. There was complete absence of a signal due to a tertiary fluorine atom. Analysis of all the data indicated that the product was an E/Z mixture of 1-trifluoromethyl-2-(1'-trifluoromethylpentafluoropropyliden-1'-yl)-tetrafluorocyclobutylamine (XXI). We believe this to be one of the first examples of the formation of a perfluoro primary amine from a perfluoroalkene by direct amination.

Diazotisation of aliphatic primary amines often leads to complex products [17] due to formation of carbonium ions and their subsequent rearrangements. Fluoroamines of the type $R_fCH_2NH_2$ give diazoalkanes [18] whilst perfluoroamines of the type $(Rf)_3CNH_2$ with amino groups at a bridgehead position give alcohols under normal diazotisation conditions [19]. Diazotisation of XXI in aqueous solution at 0-5°, followed by refluxing the mixture until nitrogen evolution ceased, gave a single product (XXII). Its ir spectrum showed a strong band at $3600cm^{-1}$, indicative of an -OH group. The ^{19}F nmr spectrum indicated a single component, as distinct from the E/Z isomer mixture of the starting material. From the position of the signals for the three CF_3 groups in comparison with those for XVIII and XIII, it was evident that the double bond had moved back into the ring, giving the structure 2-(2'trifluoromethyltetrafluorocyclobut-1'-en-1'-yl)octafluorobutan-2-ol for XXII (Scheme 3).

DISCUSSION

Pyrolyses

Some interesting conclusions about stabilities of fluorocarbons can be drawn from this study. It is clear that in all these compounds certain C-C bonds are broken preferentially. Thermal decompositions of the saturated compounds (III and IV) follow a pattern which accords precisely with the early observations [4] of easy rupture of bonds between adjacent tertiary carbon atoms. In general, it seems that the bonds in fluorocarbons that break most easily in thermal reactions are those between carbon atoms having the maximum substitution by other carbons. The radicals formed then have the most branched structures at the radical centres, i.e. the stability order is tertiary > secondary > primary, and the main driving force is the production of two derived radicals with minimum energy input.

Thermolysis of III would result in the initial formation of radicals $CF_3\dot{C}F\ C_2F_5$ (IIIA). In the presence of bromine, or of toluene, these react to give products VI and VII, respectively, the latter accompanied by some bibenzyl. Without other reactants present, IIIA could decompose (a) by loss of $CF_3^{\bullet}$, (b) by loss of $F^{\bullet}$, (c) by capture of $F^{\bullet}$ or (d) by capture of $CF_3^{\bullet}$. The major product is perfluoro-2-methyl butane (V), explicable if one radical (IIIA) captures $CF_3^{\bullet}$ from the C_2F_5 group of another (though $CF_3CF = CF_2$ was not found).

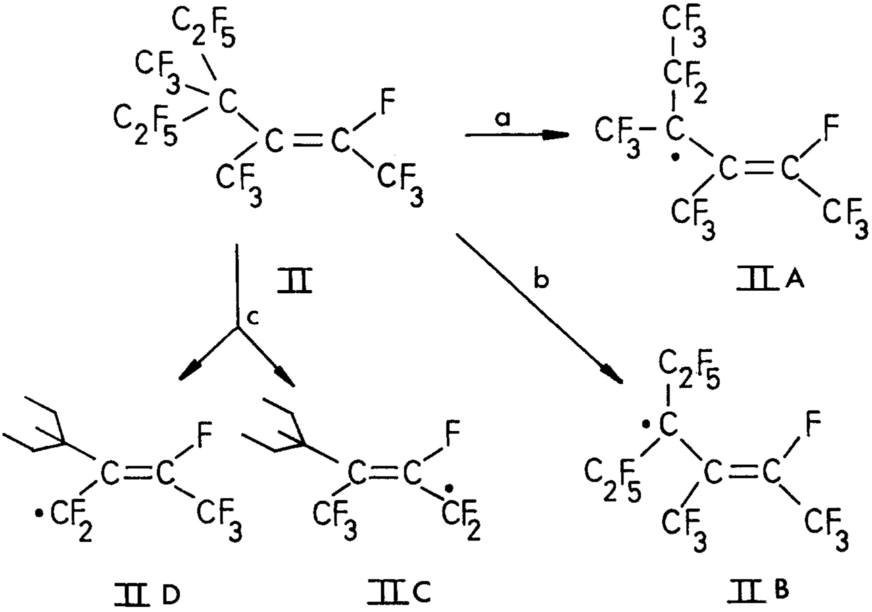
Thermal decomposition of IV proceeded at 320° (cf 500° for III) and gave two radicals, the trident radical $CF_3\ (C_2F_5)_2C^{\bullet}$ (IVA) and $CF_3\dot{C}F\ C_2F_5$ (IIIA). In the presence of bromine, and of toluene, each of these reacted to give, respectively, bromides (XI and VI) and hydrides (XII and VII). With no other reactants present, the products can be explained as arising as follows:-

X, capture of $CF_3^{\bullet}$ by IVA; V, capture of $CF_3^{\bullet}$ by IIIA; IX, capture of $F^{\bullet}$ by IVA, or of $C_2F_5^{\bullet}$ by IIIA (more likely); VIII, loss of $CF_3^{\bullet}$ from the end of a C_2F_5 group of IVA (see later); III, dimerisation of IIIA. Dimerisation of IIIA to III can proceed presumably because of the lower temperature than in the pyrolysis of III itself. However, no product of dimerisation of IVA was observed, understandably because of the steric repulsions of the bulky perfluoroalkyl groups in the trident radical (IVA), tied in with the expected instability of a quaternary C-C bond in the product.

Considering now the pyrolysis of the pentamer II and hexamer III, these at first sight have a different decomposition pattern. This however is clearly related to that proposed [6] for the thermolysis of tetramer (I) over metal surfaces, in which the first step is the formation of an allylic radical. From pentamer (II) allylic radicals could be achieved in several ways (Scheme 4) :- (a) loss of $C_2F_5^{\bullet}$ from the trident group, (b) loss of $CF_3^{\bullet}$ from the trident, (c) loss of $F^{\bullet}$ from CF_3 carried on the double bond. Intrinsically, processes (a) or (b) seem more likely in fluorocarbon chemistry [5,6], and radicals IIc and IId would not give the observed products by any obvious routes. Likewise, simple routes to the observed products are not apparent for radical IIB. However, with radical IIA, loss of $CF_3^{\bullet}$ from the end of the C_2F_5 would give the primary products, the 1,3-dienes (XIV and XV).

Analogously, with the hexamer (XVII), an identical mode of decomposition through the allylic radical XVIIA (Scheme 5), and thence loss of CF_3 from the C_2F_5 group carried on the radical centre, gives the primary product the 1,3-diene (XIX). Here, the perfluoro-1-methylpropyl group (Rf, Scheme 3) may be assumed to have higher thermal stability than the trident group. The former group is present in both products (XVIII and XIX), and though it could arise there by loss of C_2F_4 from the trident, this seems much less likely than survival of the original through the pyrolyses.

On closer examination, the first stage of this mode of decomposition proposed for the pentamer and hexamer (II and XVII) is in fact closely related to that established for the saturated branched fluorocarbons. If the stabilities of both first-formed radicals taken together are to be maximised, and it is assumed that vinyl radicals are



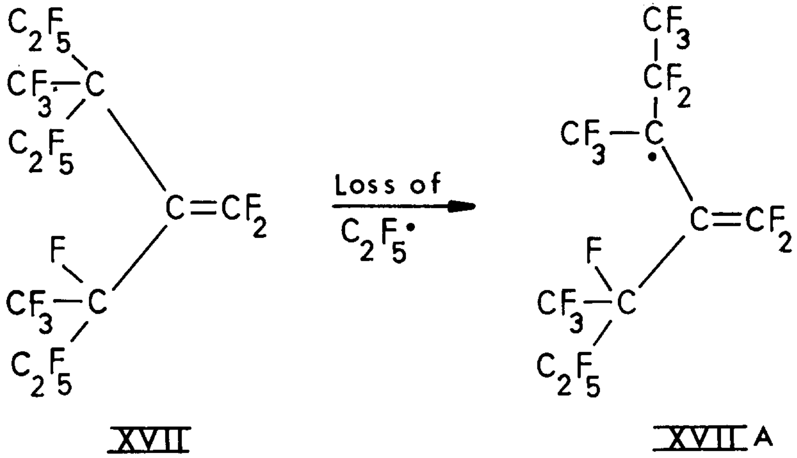
REACTIONS:

(a) LOSS OF $\cdot C_2F_5$.

(b) LOSS OF $\cdot CF_3$

(c) LOSS OF $\cdot F$

Scheme 4



Scheme 5

not very stable, then the bond between carbons most substituted by other carbons is that between the quaternary and a secondary carbon in the trident group (bond strengths roughly comparable for C-C, tertiary - tertiary, and quaternary - secondary?). The derived allylic radicals (IIA and XVIIA) could in principle rearrange, but no obvious increase in stability or easy decomposition pathway seems to be offered thereby. There is no very apparent alternative in fact to the decomposition route postulated, loss of $CF_3^{\bullet}$ to give the group $CF_2{=}\overset{|}{C}-$. The allylic radicals need not have long lifetimes and the process could be almost concerted. This possibility is supported by the failure to detect any new products when the pentamer (II) was pyrolysed in the presence of bromine or toluene. Finally, in the thermolysis of saturated fluorocarbon IV, use of the final stage of this decomposition pathway by radical IVA offers the only obvious route to olefin VIII, a major product.

Summarising, it is clear that none of these highly branched structures, saturated or olefinic, have the very high thermal stabilities of linear fluorocarbons. The trident group gives rise to particular selective bond weaknesses in molecules. If it is joined to a tertiary carbon in a perfluoroalkane that particular bond breaks very easily. If it is adjacent to a double bond, a quaternary - second C-C bond within the trident itself apparently breaks preferentially to give an allylic radical, followed by loss of terminal CF_3 to form a double bond, a decomposition route utilised also by the trident radical itself.

Reactions of products

The amination of cyclobutene (XVIII) raises a point of interest concerning the ultimate fate of the double bond. The reaction of fluoroolefins with amines is generally believed to proceed via an addition-elimination mechanism [16]. In this case, the first formal intermediate (XVIIIA) has two possible elimination pathways. It can lose fluorine, as fluoride ion, either from a relatively stable ring CF_2 group or from a tertiary CF position to give an exocyclic double bond (Scheme 3). Which of these pathways is followed is clearly the result of a delicate balance between both steric and electronic effects. It has been shown [20] that fluoride ion co-oligomerisation of hexafluoropropene and perfluorocyclobutene yields mainly the 1:1 adduct with an exocyclic double bond and in extended studies of oligomerisations of cyclic fluoroolefins [21], various products with exocyclic double bonds were found. This was explained by conformational effects, principally angle strain and fluorine-fluorine interactions. In our amination reaction, these conformational effects, the loss of F from the tertiary C-F, and the absence of vinylic fluorine in the product, clearly combine to favour the formation of amine XXI. In fact, the relatively ready elimination of the tertiary C-F may explain the exclusive orientation of the original attack by ammonia.

Considering now the diazotisation of amine XXI, if a carbonium ion intermediate is involved, it may not have the structure XXIA (Scheme 3). This is allylic and tautomeric and could be more stable as XXIB, reaction with this form being favoured further by ease of approach of the hydroxylic reagent.

EXPERIMENTAL

Techniques - Fluorinations

These were done in standard [22] stirred nickel reactors, heated electrically and packed with cobalt (III) fluoride, ca 10 Kg in reactor A (1.3 m x 180 mm int. d.) and ca 100g in reactor B (0.45m x 40 mm int.d.).

Pyrolyses Tube A was of Pyrex glass (0.60m x 30 mm int. d.) packed with glass balls (1.5 - 2.00 mm d.) and was mounted vertically. Tube B was of nickel (0.70 m x 25 mm) packed with glass balls (1.5 - 2.00 mm d.) and mounted vertically. Each was surrounded by heating bricks and had an external thermocouple.

Gas-liquid chromatography Analytical and semi-preparative work was done in Pye Series 104 and 105 instruments. Semi-preparative columns used were of glass (9.1 m x 7 mm int. d.) with packings as follows:- column A, 1.6 m of di(2-cyanoethyl)ether/Porasil C (1:9) and 7.5 m. of dinonyl phthalate/Supasorb (1:5); column B, dinonyl phthalate/Celite (1:2); column C, silicone gum SE 30/Supasorb 60 - 80 (1:9); column D, polyethylene glycol adipate/Chromosorb P 30-60 (1:6); column E, Porasil C 80-100. Nitrogen was used as carrier gas.

Spectroscopy Mass spectra were measured on an A.E.I. MS 9 instrument and infrared on a Perkin-Elmer 257 machine. Nuclear magnetic resonance spectra were recorded on a Perkin-Elmer R12B instrument (^{1}H in δ units at 60 MHz, ^{19}F in ø units at 56.4 MHz) or on a Varian XL - 100 (^{1}H at 100.1 MHz; ^{19}F at 94.1 MHz). Tetramethylsilane was internal standard for ^{1}H measurements and trichlorofluoromethane internal standard for ^{19}F. Unless otherwise stated measurements were on neat liquids at ca. 15°.

Fluorination of Perfluoro-3,4-dimethylhex-3-ene(I) over Cobalt(III) Fluoride - The olefin (200g) was passed in a nitrogen stream (15 lh^{-1}) over cobalt (III) fluoride at 230-240° during 2 h (Reactor A). The products of the fluorination were washed successively with water, 10% sodium bicarbonate solution and dried ($MgSO_4$). Distillation (190g) using a 1m Monel metal-gauze-banded spinning band column afforded (i) a fraction b.p. 94-98° (20g) identified as unreacted starting material (I): (ii) a fraction b.p. 104-107° (145g) identified as perfluoro-3,4-dimethylhexane (III) [23] (Found: C, 21.9; F, 78.6. C_8F_{18} requires C, 21.9; F, 78.1%); m/e 419 (M-F); ^{19}F nmr spectroscopy showed bands at 70.1, 76.3, 113.1 and 180 p.p.m. in the integral ratio 3:3:2:1, consistent with the proposed structure.

Fluorination of Perfluoro-4-ethyl-3,4-dimethylhex-2-ene(II) over Cobalt(III) Fluoride - The olefin (2.0g) was passed in a stream of nitrogen (2 lh^{-1}) over CoF_3 at 148-153° (Reactor B) during 30 min. The product (1.2g) was separated by glc (column B, 75°, N_2 20 psi) to give (i) short retained very volatile material (0.05g) not further investigated: (ii) a mixture of cis and trans-perfluoro-3,4-dimethylhex-3-ene(I) (0.65g) identified by ir and nmr comparison with an authentic sample: (iii) unreacted starting material (II) (0.12g), (iv) perfluoro-3-ethyl-3,4-dimethylhexane (IV) nc (0.10g) b.p. 150-152° (Found: C, 21.8; F, 77.9. $C_{10}F_{22}$ requires C, 22.3; F, 77.7%); m/e 381 ($M-C_2F_7$), 119 (C_2F_5); ^{19}F nmr showed bands at 58.3, 67.7, 77.6-80.7, 98.7-108.1, 166.7 p.p.m. all complex multiplets, relative intensities 3:3:9:6:1, consistent with the proposed structure. Cobalt trifluoride at 120° gave only unchanged pentamer(II); at 140°, 80% unchanged pentamer (II) + tetramer (I) (10%) + IV 5%; at 160°, I (80%) + II (7%) + IV (5%); at 200°, I (90%) + II (5%). To make fluorocarbon IV, best conditions found were to fluorinate as near to 145° as possible and to separate by glc using Column A (85°, N_2 30 psi). Silver difluoride gave similar results. With elementary fluorine at up to 200°, in a vertical Pyrex column packed with Pyrex glass chips, only unchanged pentamer (II) was recovered.

Pyrolysis of Perfluoro-3,4-dimethylhexane (III) - (a) Alone

The hexane (20g) was introduced dropwise during 30 min. to pyrolysis tube A at 500-520°. The products (19.1g) were collected in liquid air. The very volatile material was allowed to boil off to leave a liquid residue b.p. $\geqslant$ 0° (12.6g). Analytical glc showed only one major component and separation of a portion (1.0g) (column B, 40°, N_2 5 psi) afforded perfluoro-2-methyl butane (V) [7] (0.41g), (Found: m/e 268.984 (M-F). $C_5F_{11}^+$ requires 268.982); ^{19}F nmr (-20°) showed bands at 71.5, complex; 79.9, complex septet, J_{FF} 6 Hz; 120.1, doublet of septets, J_{FF} 11, J_{FF} 3; 185.7, complex; relative intensities 6:3:2:1, consistent with the structure. See also [24].

(b) In the presence of bromine The hexane (III) (5.0g) and bromine (10.0g) were copyrolysed at 500-520° (tube B) in a stream of nitrogen (2 lh^{-1}) during 30 min. The products were washed with 10% aqueous sodium metabisulphite solution and water, dried ($MgSO_4$) (4.0g); a sample (0.8g) then being separated (glc, column B, 45°, N_2 12 psi) to give 2-bromononafluorobutane (VI) [8] (0.35g) b.p. 43-44°, (Found: m/e 297.907 (M). $C_4F_9\,^{79}Br$ requires 279.904). ^{19}F nmr (-20°) showed bands at 76.3, 79.3, 117.8 and 141.4 all complex, in the ratio 3:3:2:1 consistent with the structure.

(c) In the presence of toluene The hexane (III) (8.2g) and dry toluene (15g) were copyrolysed as above at 510-530° during 2.2h. A part (0.8g) of the lower fluorocarbon layer (6.2g) of the product was separated (glc column B, 45°, N_2 10 psi) and identified as 2H-nonafluorobutane (VII) [9] (0.57g) (Found: m/e 200.999 (M-F), $C_4F_8H^+$ requires 200.995); ^1H nmr (-20°) showed a complex doublet at 4.9, J_{HF} 46 Hz. ^{19}F nmr showed bands at 74.9, complex; 84.4, complex; 129.0, AB system, J_{AB} 295 Hz, $\Delta\nu$ AB 668 Hz in the ratio 3:3:2 (the tertiary fluorine signal was not recorded). From the upper layer toluene and bibenzyl (1.1g) were isolated.

Pyrolysis of Perfluoro-3-ethyl-3,4-dimethylhexane (IV) - (a) Alone The fluorocarbon (2.0g) was pyrolysed (tube A) during 30 min. at 300-320° in a stream of nitrogen (2.5 lh^{-1}). The product boiling above 0° (1.7g) was collected and a portion (0.99g) was separated by glc (column A, 40-65°, N_2 20 psi) to give (i) perfluoro-2-methyl-butane (V) (0.07g):
(ii) perfluoro-2-methylbut-1-ene (VIII) nc (0.13g), (Found: m/e 230.986 (M-F). $C_5F_9^+$ requires 230.986); very strong ir C=C stretch at

1730cm^{-1}; ^{19}F nmr (sealed tube) gave bands at 61.0, complex; 64.0, complex AB; 89.3, complex; 115.6, complex; in the ratio 3:2:3:2: (iii) perfluoro-3-methyl pentane (IX) [11] (0.04g), b.p. 50-51^{o} (Found: m/e 318.979 (M-F). $C_6F_{13}^+$ requires 318.979); ^{19}F nmr bands at 74.4, 83.7, 120.2, 188.3 in the ratio 3:6:4:1, all complex multiplets: (iv) perfluoro-3,3-dimethylpentane (X) [11] (0.16g) b.p. 77-77.5^{o} (Found: m/e (M-CF_3), 318.976. $C_6F_{13}^+$ requires 318.979); ^{19}F nmr gave bands at 63.0, 81.4, 108.7, in the ratio 3:3:2 all as complex multiplets: (v) perfluoro-3,4-dimethylhexane (III) (0.18g): (vi) starting material (IV) (0.08g): V, III, and IV were identified by ir and ^{19}F nmr.

(b) In the presence of bromine Compound IV (2.0g) and bromine (4.0g) were co-pyrolysed in a stream of nitrogen (2.7 lh^{-}) in tube B at 305-315^{o} during 30 min. to yield a clear liquid (1.1g). Separation (glc, column A, 60^{o}, N_2 30 psi) gave (i) 2-bromononafluorobutane (VI) (0.28g), identified by ir and nmr: (ii) 3-bromo-3-trifluoromethyl-decafluoropentane (XI) nc (0.31g) b.p. 103-104^{o} (Found: C, 17.9; F, 62.2; Br, 20.1%: m/e 399.889 and 397.893 (M). $C_6F_{13}{}^{81}Br$ and $C_6F_{13}{}^{79}Br$ requires C, 18.0; F, 61.9; Br, 20.0%, M 399.895 and 397.898); ^{19}F nmr spectroscopy gave bands at 66.1, 78.6, 109.2, all as complex multiplets in the ratio 3:6:4.

(c) In the presence of toluene Fluorocarbon (IV) (1.5g) and toluene (10g) were co-pyrolysed (tube A) at 315-330^{o} in a stream of nitrogen (1.5 lh^{-1}) during 30 min. The products were collected in a glass trap cooled in liquid air and the fluorocarbon layer (0.8g) was separated off. Glc separation (column A, 65^{o}, N_2 28 psi) gave (i) 2H-nonafluorobutane (VII) (0.25g) identified by ir and nmr, and (ii) 3H-3-trifluoromethyl-decafluoropentane (XII) nc (0.27g) b.p. 52-53^{o} (Found: C, 21.4%; m/e 300.988 (M-F). C_6HF_{13} requires C, 22.5%; $C_6HF_{12}^+$ requires 300.989); ^{1}H nmr gave a complex band at 5.0; ^{19}F nmr gave bands at 62.6, 85.3, 113.2, all as complex multiplets in the ratio 3:6:4 (measurements in d_6-acetone).

Pyrolysis of the Tetramer (I) - Reactions were done in pyrolysis tube A at temperatures from 400-650^{o} and throughput rates 7.5 gh^{-1}. Below 550^{o} tetramer was recovered unchanged; decomposition was profound at above 600^{o}, but the products were highly fragmented. Pyrolysis in the presence of toluene and of bromine gave similar results.

Pyrolysis of Perfluoro-4-ethyl-3,4-dimethylhex-2-ene (II) - The olefin (45g) was pyrolysed (tube A, throughput 27 gh^{-1}) at 495-505°. The product was collected in a glass trap cooled in liquid air and very volatile materials (C_2F_6 etc.) were allowed to vent off by slowly warming to 0° (27g left). Separation (1.7g) by glc (column A, 30°, N_2 12 psi) gave (i) perfluoro-1,2,3-trimethylcyclobutene (XIII) nc (0.1g) b.p. 53-54° (Found: C, 26.8; F, 72.9. C_7F_{12} requires C, 26.9; F, 73.1%); m/e 293 (M-F); ir 1710 cm^{-1} (weak); ^{19}F nmr (sealed tube) 67.3,complex: 79.0,complex; 115.1,AB system J_{AB} 207Hz $\Delta\nu_{AB}$ 312 Hz; 169.6,complex; in the ratio 6:3:2:1 : (ii) perfluoro-2,3-dimethylpenta-1,3(E)-diene (XIV) [13] (0.42g), b.p. 62.5-63.5° (Found: C, 26.6; F, 73.1. C_7F_{12} requires C, 26.9; F, 73.1%); m/e 312 (M), very small peak at 119 (C_2F_5); ir 1750 and 1700 cm^{-1} (conjugated double bonds); ^{19}F nmr gave signals at 60.0,doublet of doublets,J=17 and 13; 62.0,complex doublet,J = 22; 68.6 and 70.0,complex AB,J_{AB} = 17; 69.6,complex; 102.7,quartet of quartets,J ≈ 22 and 6.5; respectively 3:3:1:1:3:1 integral ratio: (iii) perfluoro-2,3-dimethylpenta-1, 3(Z)-diene (XV) [13] (0.56g) b.p. 63-64° (Found: C, 26.7; F, 73.3); m/e 312 (M); ir 1745 and 1690 cm^{-1} (S); ^{19}F nmr, 58.2,quartet of doublets,J = 11.5 and 11.5; 59.9,complex; 68.2,quartet of doublets,J = 6 and 11.5; 69.4 and 70.6, complex AB,J = 17; 100.0,complex; in the ratio 3:3:3:1:1:1. See also [25].

Repeats of this pyrolysis in the presence of bromine and of toluene gave the same result with no new products detected.

Fluorination of Perfluoro-2,3-dimethylpenta-1,3-diene Isomers (XIV and XV) - A mixture of the olefins (4.5g) was fluorinated in the usual way over CoF_3 (Reactor B) at 310-330° in a stream of nitrogen (1.4lh^{-1}) during 30 min. The products (3.2g) were collected in a glass trap cooled in liquid air. A portion (1.12g) of the mixture, which consisted of a major product with some minor breakdown products was purified by glc (column A, 50°, N_2 16 psi) to give perfluoro-2,3-dimethylpentane (XVI) [11] (0.7g) b.p. 83-84° (Found: C, 21.7; F, 78.7. C_7F_{16} requires C, 21.6; F, 78.4%); m/e 369 (M-F); ^{19}F nmr peaks at 69.1-71.3, 80.3, 113.1, 175.8 and 179.8 all complex multiplets and in the ratio 9:3:2:1:1

Cyclisation of Perfluoro-cis and trans-2,3-dimethylpenta-1,3-diene isomers (XIV and XV) - A mixture (approx. 1:1) of the dienes (1.7g) was heated in a sealed Carius Tube (volume 75cm^3) at 290-300° for 130 h to yield a colourless liquid (1.28g). Separation by glc (column A, 30°, N_2 12 psi) gave (i) perfluoro-1,2,3-trimethylcyclobutene (XIII) (0.10g); (ii) perfluoro-2,3-dimethylpenta-1,3(E)-diene (0.4g) and (iii) perfluoro-2,3-dimethylpenta-1,3(Z)-diene (0.49g) all identified by comparison of their ir spectra with authentic samples.

Pyrolysis of Perfluoro-2-(1'-ethyl-1'-methylpropyl)-3-methylpent-1-ene (XVII) - Tetrafluoroethylene hexamer fraction was distilled through a 0.5m fractionating column packed with Dixon gauzes and the major isomer (XVII) (>95% pure) collected at 160-165°. This (14.0g) was passed through pyrolysis tube A at 495 - 505° during 1.4h. From the liquid product (10.7g) a sample (1.2g) was separated by glc (column A, 50°, N_2 20 psi) to give (i) (0.25g), a multi-component mixture: (ii) perfluoro-1-methyl-2-(1'-methylpropyl)cyclobut-1-ene (XVIII) nc (0.61g), b.p. 97-98° (Found: C, 26.3; F, 74.1. C_9F_{16} requires C, 26.2; F, 73.8%); m/e 412 (M); ir weak band at 1690 cm^{-1} (C=C); ^{19}F nmr 61.8, doublet, J = 17; 73.4, complex; 80.2, doublet, J = 12; 111.5, complex; 115.2, complex; 120.7, AB J = 300, $\Delta\nu$ = 437; 180.7, complex; in the ratio 3:3:3:2:2:2:1: (iii) a mixture (0.5g) with strong ir bands at 1720 and 1745cm^{-1}.

The combined products of several pyrolyses (35g) were carefully fractioned using a Fischer-Spaltrohr HMS 500 column to give two fractions essentially pure; (i) perfluoro-2-methyl-3-(1'methylpropyl)buta-1,3-diene (XIX) nc (1.1g) b.p. 93-94°; (Found: C, 25.9%; m/e 411.970 (M). C_9F_{16} requires C, 26.2%; M 411.974); ir 1720, 1745 cm^{-1} (strong); ^{19}F nmr 63.3, (69.9 - 71.5), (68.2, 72.9, 77.0, and 78.6), 83.9, (119.1 - 122.5), 174.5 all complex multiplets in the ratio 3:3:4:3:2:1 : (ii) perfluoro-1-methyl-2-(1'-methylpropyl)cyclobut-1-ene (XVIII) (17.8g), b.p. 97-98.5°, ir identical to that of the sample from glc.

Characterisation of Perfluoro-1-methyl-2-(1'methylpropyl)-cyclobut-1-ene (XVIII) - (a) Fluorination over CoF_3 The cyclobutene (15.1g) was fluorinated (Reactor B) at 310° in a stream of nitrogen (1 lh^{-1}). The products (4.7g) were washed with water, dried ($MgSO_4$) and distilled in vacuum from P_2O_5. A sample (1.0g) was separated from minor components by glc (column B, 60°, N_2 15 psi) to give perfluoro-1-methyl-2-(1'methylpropyl)cyclobutane (XX) nc (0.62g) b.p. 107-108° (Found: C, 23.7; F, 76.5. C_9F_{18} requires C, 24.0; F, 76.0%); m/e 431 (M-F); 231 (M - C_4F_9); 100 (C_2F_4): ^{19}F nmr spectrum was complex but showed bands at 70.8-75.8, 82.8, 108-134, 183.9-191.9, in the ratio 6:3:6:3.

(b) Pyrolysis of Perfluoro-1-methyl-2-(1'methylpropyl)cyclobutane (XX) in the Presence of Bromine The cyclobutane (3.5g) and bromine (5.0g) were co-pyrolysed (Tube B) at 505-535° in a stream of nitrogen (2 lh^{-1}) during 1h. The product (2.1g) after being washed with 10% aqueous sodium metabisulphite solution, water,was dried ($MgSO_4$): a portion (1.1g) of the product (2.1g) was separated by glc (column E, 50°, N_2 20 psi) and gave (i) 2-bromononafluorobutane (VI) (0.12g) identified by comparison of its ir and ^{19}F nmr spectra with those of an authentic sample: (ii) a mixture (0.16g) with a strong ir band at $1785cm^{-1}$: (iii) unreacted starting material (0.52g).

(c) Cyclisation of Perfluoro-2-methyl-3-(1'methylpropyl)buta-1,3-diene (XIX) The diene (0.9g) was heated in a sealed Carius tube (vol. $80cm^3$) at 230° for 150 h to yield a colourless liquid (0.72g) which on separation by glc (column A, 40°, N_2 20 psi) gave (i) perfluoro-1-methyl-2-(1'-methylpropyl)cyclobut-1-ene (XVIII) (0.45g) and (ii) starting material (XIX) (0.13g), both identified by comparison of their ir and nmr spectra with those of authentic samples.

Reaction of Perfluoro-1-methyl-2-(1'methylpropyl)cyclobut-1-ene (XVIII) with Ammonia - Ammonia ($1.13cm^3$) was distilled slowly into a well-stirred solution of compound XVIII (10g) in dry diethyl ether ($150cm^3$) at -50°. When the addition was complete the solution was allowed to warm slowly (ca. 3 h) to 0°. The resulting solution was washed with iced water, dried ($MgSO_4$) and most of the ether distilled off to leave a pale yellow liquid (9.7g). Separation of a portion (0.7g) by glc (column C, 105°, N_2 14 psi) gave (i) ether (0.1g) and (ii) E and Z-1-trifluoromethyl-2-(1'trifluoromethylpentafluoropropyliden-1'-yl)tetrafluorocyclobutylamine (XXI) nc (0.45g), b.p. 124-126° (Found: C, 26.2; H, 0.5; F, 69.4, N, 3.9. $C_9H_2F_{15}N$ requires C, 26.4; H, 0.5; F, 69.7; N, 3.4%); m/e 409 (M); 340 ($M-CF_3$), 190 ($M - C_4F_9$), 147 ($M - C_6F_{10}$); the ir spectrum had bands at 3460, 3380 and 1615 cm^{-1} (NH). Nmr measurements were done in solution in CCl_4, the ^1H spectrum having one complex peak at 2.28. The ^{19}F spectrum had bands corresponding to 2 isomers. Those for one form were at 59.7, complex; 73.04, complex; 81.7, complex; 105 - 115, 2 unresolved ABs; 125.3, AB, J = 217 $\Delta\nu$ = 243; in the ratio 3:3:3:2:2:2. Those for the other were at 59.1, 73.04, 82.6, 105 - 115, 125.3, in the same ratio. The stereoisomers were present in approximately equal proportions.

Diazotisation of E and Z-1-Trifluoromethyl-2-(1'-trifluoromethylpentafluoropropyliden-1'-yl)tetrafluorocyclobutylamine (XXI) - A chilled aqueous solution of sodium nitrite (2.7g) in water (15cm^3) was added dropwise to a well stirred solution of XXI (7.5g) in 15% sulphuric acid (75cm^3). The solution was maintained at -5^o throughout the addition (30 min.) and was further stirred for 1h at 0^o. The mixture was then heated under reflux for 2h and nitrogen was evolved. When the evolution had ceased the mixture was cooled and the pale yellow organic layer (6.2g) separated. Analytical glc showed a number of minor short-retained components and a major product. Distillation in vacuo followed by glc (column D, 120^o, N_2 15 psi) afforded 2-(2'-trifluoromethyltetrafluorocyclobut-1'en-1'-yl)octafluorobutan-2-ol (XXII) nc (3.6g) b.p. 114-115^o (Found: C, 25.7; F, 69.6. m/e 390.979 (M-F). $C_9HF_{15}O$ requires C, 26.3; F, 69.5%. M-F, 390.980); ir 3600 (OH), 1685 (weak) cm^{-1}.

The ^{1}H nmr spectrum showed one broad peak at 3.7. ^{19}F nmr peaks were present at 61.0, s; 74.2, complex; 79.9, s; 112.7,complex; 115.8,complex; 121.9, AB J = 308 $\Delta\nu$ = 387; in the ratio 3:3:3:2:2:2 (measured in solution in $CDCl_3$).

REFERENCES

1 W.T. Miller, J.H. Fried, and H. Goldwhite, J. Amer. Chem. Soc., 82 (1960) 3091.

2 H.C. Fielding and A.J. Rudge, (to I.C.I. Ltd.) B.P. 1,082,127 (1967) W.R. Deem, (to I.C.I. Ltd.) B.P. 1,302,350 (1973): D.P. Graham, J. Org. Chem., 31 (1966) 955.

3 H.C. Fielding, Organofluorine Chemicals and their Industrial Applications (Editor R.E. Banks), Horwood, Chichester (1979) 214: J.C. Tatlow, ibid., p 19.

4 G.B. Barlow and J.C. Tatlow, J. Chem. Soc., (1952) 4695: G.B. Barlow, M. Stacey and J.C. Tatlow, ibid, (1955) 1749: B.R. Letchford, C.R. Patrick and J.C. Tatlow, Tetrahedron, 20 (1964) 1381.

5 V.E. Platonov and G.G. Yakobson, Synthesis, (1976) 374.

6 R.D. Chambers,A.A.Lindley, H.C. Fielding, J.S. Moilliet and G. Whittaker, J. Chem. Soc. Chem. Comm., (1978) 475: See also [25].

7 E.J. Barber, L.L. Burger, and G.H. Cady, J. Amer. Chem. Soc., 73 (1951) 4241.

8 M. Hauptschein, M. Braid, and A.H. Fainberg, J. Amer. Chem. Soc., 80 (1958) 851.

9 W.T. Miller, M.B. Freedman, J.H. Fried and H.F. Koch, J. Amer. Chem. Soc., 83 (1961) 4105.

10 G. Whittaker, unpublished work.

11 W.C. Askew, T.M. Reed III and J.C. Mailen, Radiat. Res., 33 (1968) 282.

12 J. Burdon and D.H. Whiffen, Spectrochim Acta, 12 (1958) 139.

13 P.W.L. Bosbury, R. Fields and R.N. Haszeldine, J. Chem. Soc. Perkin I, (1978) 422.

14 R.D. Chambers and R.H. Mobbs, Advances in Fluorine Chemistry, Butterworths, London, 4 (1965) 50.

15 W.T. Miller U.S.P. 2,691,036 (1954); 2,751,414 (1956): J.D. LaZerte, U.S.P. 2,704,769 (1955).

16 R.L. Pruett, J.T. Barr, K.E. Rapp, C.T. Bahner, J.D. Gibson and R.H. Lafferty, J. Amer. Chem. Soc., 72 (1950) 3646: C.O. Parker, ibid., 81 (1959) 2183: P. Robson, J. Roylance, R. Stephens, J.C. Tatlow, and R.E. Worthington, J. Chem. Soc., (1964) 5748.

17 W. Kirmse, Angew. Chem. International Ed., 15 (1976) 251.

18 L.C. Krogh, T.S. Reid and H.A. Brown, J. Org. Chem., 19 (1954) 1124.

19 J.S. Broughton, R. Stephens and J.C. Tatlow, unpublished results.

20 M.J.R. Fraticelli, Ph.D. Thesis, Cornell University, Ithaca, New York (1965).

21 R.D. Chambers, G. Taylor, and R.L. Powell, J. Chem. Soc. Perkin I, (1980) 426; 429; 435.

22 M. Stacey and J.C. Tatlow, Advances in Fluorine Chemistry, Butterworths, London, 1 (1960) 166.

23 W.T. Miller, J.O. Stoffer, G. Fuller, and A.C. Currie, J. Amer. Chem. Soc., 86 (1964) 51.

24 Recently, this fluorocarbon has been used as a radical source in re-arrangements; R.D. Chambers, W.K.R. Musgrave, and C.R. Sargent, J. Chem. Soc. Perkin I, (1981) 1071.

25 The full paper corresponding to [6] has now appeared; J.Chem. Soc. Perkin I, (1981) 1064: further, the preparation is described of XIII XIV and XV as a mixture by another route. Spectral characteristics are in agreement with ours.