13. *Addition of Free Radicals to Unsaturated Systems. Part XII.* Free-radical and Electrophilic Attack on Fluoro-olefins.*

By R. N. HASZELDINE and J. E. OSBORNE.

The ease of electrophilic reaction of iodine monochloride, hydrogen iodide, or hydrogen bromide with certain fluoro-olefins decreases in the order $\mathrm{CF_2{:}CH_2} > \mathrm{CF_2{:}CFCl} >$ perfluoro*cyclo*butene $>$ perfluoro*cyclo*hexene $>$ $\mathrm{CF_3{\cdot}CF{:}CF{\cdot}CF_3}$. The ease of free-radical reaction of hydrogen bromide, bromine, chlorine, or trifluoroiodomethane decreases in the order $\mathrm{CF_2{:}CH_2} > \mathrm{CF_2{:}CF_2} > \mathrm{CF_2{:}CHCl} > \mathrm{CF_2{:}CFCl} > \mathrm{CF_3{\cdot}CF{:}CF_2} > \mathrm{CF_3{\cdot}CF{:}CF{\cdot}CF_3} >$ perfluoro*cyclo*butene $>$ perfluoro*cyclo*hexene.

Syntheses of a variety of chloro-, bromo-, iodo-, and trifluoromethyl-*cyclo*butanes, -*cyclo*butenes, -*cyclo*hexanes, and -*cyclo*hexenes are described. The mode of reduction of polyfluoro-compounds by lithium aluminium hydride, and the rearrangement of fluoro-carbanions are considered.

UNSUBSTITUTED olefins such as ethylene, but-2-ene, or *cyclo*hexene react readily with electrophilic reagents such as hydrogen halides, to give simple addition products. Replacement of hydrogen by fluorine in such molecules should slow down or prevent electrophilic addition by deactivation of the double bond and/or by steric effects. A qualitative comparative study of the ease of reaction of the fluoro-olefins 1 : 1-difluoroethylene, 2-chloro-1 : 1-difluoroethylene, and perfluoro-but-2-ene, -*cyclo*hexene, and -*cyclo*butene has been made (*a*) with the electrophilic reagents hydrogen iodide, hydrogen bromide, or iodine monochloride, and (*b*) with bromine, hydrogen bromide, or trifluoroiodomethane under conditions favouring a free-radical reaction. The effect of structure on reactivity can thus be assessed.

Electrophilic Attack.—1 : 1-Difluoroethylene reacts readily with hydrogen bromide, hydrogen iodide, or iodine monochloride in the dark at room temperature to give the products (I), (II), and (III) expected from a reaction involving ionic intermediates and an olefin polarisation $\overset{\delta+}{\mathrm{CF_2}}{=}\overset{\delta-}{\mathrm{CH_2}}$. 2-Chloro-1 : 1-difluoroethylene combines with hydrogen iodide in the dark to give (IV), isomeric with (III), to the exclusion of its isomer $\mathrm{CHF_2{\cdot}CHClI}$, thus revealing a polarisation $\overset{\delta+}{\mathrm{CF_2}}{=}\overset{\delta-}{\mathrm{CHCl}}$; the reaction is much slower than that with 1 : 1-difluoroethylene. The structures of these compounds follow from their boiling points, chemical evidence (see Experimental section), and ultraviolet spectra shown in the Table.

$\mathrm{CF_2Br{\cdot}CH_3}$ (I) $\mathrm{CF_2I{\cdot}CH_3}$ (II) $\mathrm{CF_2Cl{\cdot}CH_2I}$ (III) $\mathrm{CF_2I{\cdot}CH_2Cl}$ (IV)

Ultraviolet spectra in light petroleum.

	$\lambda_{max.}$	ε	$\lambda_{min.}$	ε		$\lambda_{max.}$	ε	$\lambda_{min.}$	ε
$\mathrm{CF_2Cl{\cdot}CF_2I}$	272	295	215	17	*$\mathrm{CH_3{\cdot}CF_2I}$	267	340	207	10
$\mathrm{CF_3{\cdot}CF_2{\cdot}CF_2I}$	271	240	215	13	*$\mathrm{CF_2Cl{\cdot}CH_2I}$	263	500	212	20
$\mathrm{CF_3{\cdot}CF_2I}$	270	—	—	—	$\mathrm{CF_3{\cdot}CH_2I}$	262	265	—	—
$\mathrm{CF_3{\cdot}CH_2{\cdot}CF_2I}$	271	290	219	24	$\mathrm{CF_3{\cdot}CH_2{\cdot}CH_2I}$	261	375	213	20
*$\mathrm{CH_2Cl{\cdot}CF_2I}$	269	340	228	55	$\mathrm{CH_3{\cdot}CH_2I}$	258	435	215	20
*$\mathrm{CHFCl{\cdot}CF_2I}$	269	290	223	40					

* Prepared during present work. Other spectra taken from *J.*, 1953, 1764.

The maximum in the ultraviolet spectrum of a compound $\mathrm{R{\cdot}CF_2I}$ varies from 267 mμ when R = alkyl to 271 mμ when R = perfluoroalkyl, whereas a compound $\mathrm{R{\cdot}CH_2I}$ has a maximum between 258 mμ (R = alkyl) and 262 mμ (R = perfluoroalkyl). Ultraviolet spectra can thus be used to distinguish between $\mathrm{R{\cdot}CF_2I}$ and $\mathrm{R{\cdot}CH_2I}$ and it is clear that the compounds marked with an asterisk in the Table have the structures shown rather than

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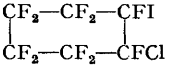
* Part XI, Haszeldine and Steele, *J.*, 1955, 3005.

those which would result from ionic addition in the opposite sense. The cases where R in $R{\cdot}CF_2I$ is $\cdot CH_2Cl$ or $\cdot CHFCl$ fit well into the series, and it is evident that substitution of hydrogen on the β-carbon atom of $\overset{\alpha}{C}{-}\overset{\beta}{C}I$ by fluorine causes a shift to longer wavelength, and that the shift is more marked when hydrogen or fluorine on the β-carbon is replaced by halogen other than fluorine. A similar effect is observed in the series $R{\cdot}CH_2I$.

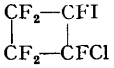
The olefins perfluorobut-2-ene, perfluoro*cyclo*hexene, and perfluoro*cyclo*butene are markedly resistant to electrophilic attack. Thus they fail to react with hydrogen bromide or iodide even at temperatures above 200°. Reaction of iodine monochloride with perfluorobut-2-ene gives only the dichloride (V); under similar conditions perfluoro*cyclo*hexene yields mainly its dichloride and only small amounts of the iodine chloride adduct (VI). By contrast, perfluoro*cyclo*butene gives mainly the adduct (VII), and for reactions involving ionic intermediates the ease of addition is thus *cyclo*-C_4F_6 > *cyclo*-C_6F_{10} > C_4F_8.

$CF_3{\cdot}CFCl{\cdot}CFCl{\cdot}CF_3$

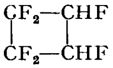
(V)



(VI)



(VII)



(VIII)

Since it has recently been shown(*J.*, 1955, 3880) that perfluoro*cyclo*butene rearranges during reaction with hydrogen iodide, the structure of (VI) and (VII) was proved, to ensure that similar rearrangement had not occurred. Photochemical chlorination of the product (VI) gave 1 : 2-dichlorodecafluoro*cyclo*hexane which is of known constitution. Photochemical chlorination of the *cyclo*butane analogue (VII) similarly gave the known 1 : 2-dichlorohexafluoro*cyclo*butane, and reaction of (VII) with lithium aluminium hydride gave 1 : 1 : 2 : 2 : 3 : 4-hexafluoro*cyclo*butane (VIII); the absence of rearrangement during the reduction was shown by conversion of (VIII) into 1 : 2-dichlorohexafluoro*cyclo*butane, and thence into perfluoro*cyclo*butene.

Free-radical Addition.—Exposure of a mixture of 1 : 1-difluoroethylene and hydrogen bromide to ultraviolet light of wavelength >2200 Å produces 2-bromo-1 : 1-difluoroethane (IX) by a free-radical chain reaction :

$$Br\cdot + CH_2{:}CF_2 \longrightarrow CH_2Br{\cdot}CF_2\cdot \xrightarrow{HBr} CH_2Br{\cdot}CHF_2 + Br\cdot \longrightarrow \text{etc.}$$

Free-radical attack is exclusively on the CH_2 group and this agrees with the direction found for attack by a trifluoromethyl radical (*J.*, 1954, 923). The photochemical reaction of hydrogen bromide in light of wavelength >3000 Å gives approximately equal amounts of (I) and (IX), *i.e.*, the ionic and the free-radical reaction proceed at about the same rate under these conditions.

The order *cyclo*-C_4F_6 > *cyclo*-C_6F_{10} > C_4F_8 observed for electrophilic attack above is changed for free-radical attack, since perfluorobut-2-ene reacts most readily with hydrogen bromide on exposure to light, to give a mixture of the hydrogen bromide adduct (X) and the dibromide.

$CH_2Br{\cdot}CHF_2$	$CF_3{\cdot}CHF{\cdot}CFBr{\cdot}CF_3$	$(CF_3)_2CF{\cdot}CFI{\cdot}CF_3$
(IX)	(X)	(XI)

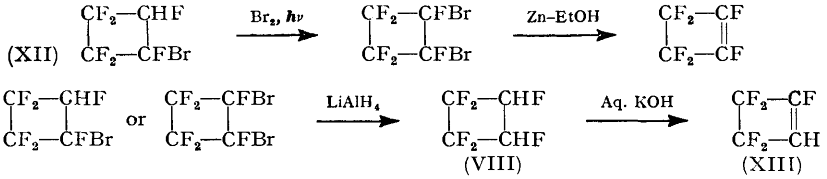
Reaction is very slow relatively to that of fluoroethylenes, and considerably slower than for unsubstituted ethylenes or butenes, and the formation of the dibromide is caused by photolysis of hydrogen bromide to give free bromine which then undergoes a slow photochemical reaction with the double bond. There is no indication of the isomerisation :

$$CF_3{\cdot}CF{:}CF{\cdot}CF_3 \xrightarrow{Br\cdot} CF_3{\cdot}CFBr{\cdot}\dot{C}F{\cdot}CF_3 \rightleftharpoons CF_3{\cdot}CF_2{\cdot}\dot{C}F{\cdot}CF_2Br \xleftarrow{Br\cdot} CF_3{\cdot}CF_2{\cdot}CF{:}CF_2$$

during photochemical reaction of bromine with perfluorobut-1- or -2-ene (cf. the rearrangement of fluoro-carbanions discussed below). Perfluorobut-1-ene reacts much faster with bromine than does perfluorobut-2-ene, as observed by Brice, LaZerte, Hals, and Pearlson (*J. Amer. Chem. Soc.*, 1953, **75**, 2698). Photochemical chlorination of perfluorobut-2-ene is much more rapid than bromination.

Trifluoroiodomethane reacts smoothly but slowly with perfluorobut-2-ene to give 2-iodo-3-trifluoromethyloctafluorobutane (XI). The attack of the trifluoromethyl radical on the olefin is markedly slower than it is on perfluoropropene (*J.*, 1953, 3559).

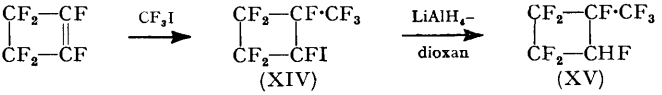
Perfluoro*cyclo*butene reacts with hydrogen bromide even less readily than perfluorobut-2-ene to give 1-bromo-1 : 2 : 2 : 3 : 3 : 4-hexafluoro*cyclo*butane (XII) (first described by Park, Sharrah, and Lacher, *J. Amer. Chem. Soc.*, 1949, **71**, 2339) and somewhat larger amounts of the dibromide. That rearrangement had not occurred during photochemical reaction (cf. reaction with hydrogen iodide, Haszeldine and Osborne, *J.*, 1955, 3880) is shown by the following reactions :



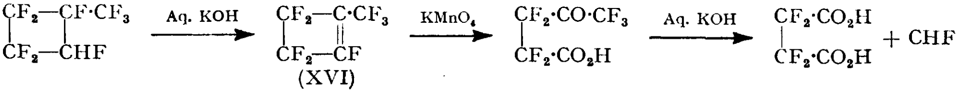
Replacement of bromine by hydrogen was effected smoothly by use of lithium aluminium hydride, which was recently employed (Tatlow and Worthington, *J.*, 1952, 1251; Buxton and Tatlow, *J.*, 1954, 1177) for replacement of chlorine by hydrogen in mono- and di-chloro-polyfluoro*cyclo*hexanes, and for the reduction of 1 : 2-dichlorohexafluoro*cyclo*butane to (VIII).

Both bromine and chlorine react with perfluoro*cyclo*butene on exposure to ultraviolet light, and that free-radical rearrangement has not occurred during formation of the 1 : 2-dibromo- or 1 : 2-dichloro-compounds is shown by debromination or dechlorination to perfluoro*cyclo*butene, and by reduction to 1 : 1 : 2 : 2 : 3 : 4-hexafluoro*cyclo*butane (VIII). The removal of the last traces of ethyl ether from the product (VIII) (b. p. 27°) was accomplished by treatment with boron trifluoride which combines with ether but not with the fluorocarbon. The structure of the product (VIII) was established by oxidation with alkaline permanganate, since perfluorosuccinic acid was produced, probably by way of 1 : 3 : 3 : 4 : 4-pentafluoro*cyclo*butene (XIII) (cf. Buxton and Tatlow, *loc. cit.*). Two CF_2 groups must thus be adjacent.

Trifluoroiodomethane reacts slowly but smoothly with perfluoro*cyclo*butene to give 1-iodo-2-trifluoromethylhexafluoro*cyclo*butane (XIV). The iodine was readily replaced by chlorine, and both the iodo- and the chloro-compound were reduced by lithium aluminium hydride in dioxan :



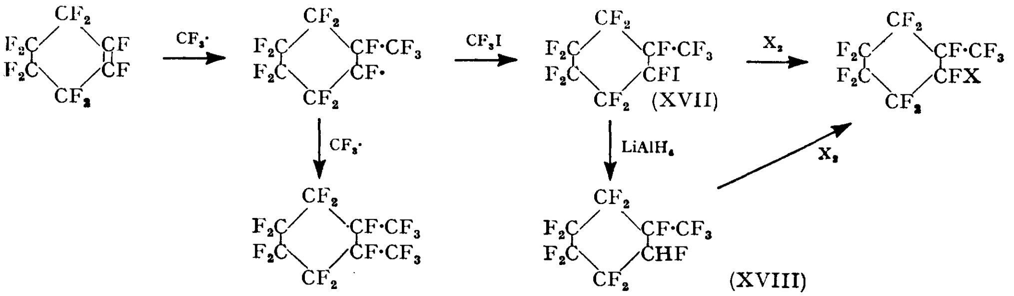
Reaction of 1-trifluoromethyl-1 : 2 : 2 : 3 : 3 : 4-hexafluoro*cyclo*butane (XV) with aqueous potassium hydroxide gave 2-trifluoromethyl*cyclo*butene (XVI) which yields a dichloride. Alkaline permanganate oxidised the *cyclo*butene (XVI) to perfluorosuccinic acid *via* the keto-acid, which was not isolated; perfluorosuccinic acid and fluoroform, produced by alkaline cleavage of the keto-acid, were also obtained from (XV) :



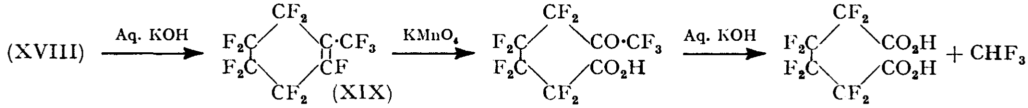
These reactions adequately prove the structures of the compounds (XIV), (XV), and (XVI).

Perfluoro*cyclo*hexene does not react at all with hydrogen bromide on irradiation at room temperature under the conditions used for perfluorobut-2-ene and perfluoro*cyclo*butene. Photochemical bromination or chlorination can be effected by prolonged irradiation, and that rearrangement had not occurred was shown by conversion of the 1 : 2-dibromo- and 1 : 2-dichloro-decafluoro*cyclo*hexanes into perfluoro*cyclo*hexene in good yield.

Trifluoroiodomethane reacts very slowly with perfluoro*cyclo*hexene, but prolonged irradiation gave a satisfactory yield of 1-iodo-2-trifluoromethyldecafluoro*cyclo*hexane (XVII), from which the 1-bromo- and 1-chloro-compound were made by photochemical halogenation. As by-product with (XVII) was obtained perfluoro-1 : 2-dimethyl*cyclo*hexane. This is clearly produced by combination of the intermediate radical with a CF_3 radical, the first time that this addition of two CF_3 radicals to a double bond has been observed. The fluorocarbon had previously been prepared by direct fluorination of *o*-xylene.



Reduction of the iodo-compound (XVII) gives (XVIII), which can be chlorinated to give 1-chlorodecafluoro-2-trifluoromethyl*cyclo*hexane, and reaction of the last compound with aqueous potassium hydroxide yields nonafluoro-1-trifluoromethyl*cyclo*hexene (XIX); this forms a dibromide and a dichloride. Only one olefin is formed, and this demonstrates that a tertiary fluorine atom is removed by aqueous base in preference to a secondary one; this was also shown by the formation of only one olefin from the analogue (XV). Alkaline permanganate oxidises the compounds (XVIII) and (XIX) to perfluoroadipic acid *via* the keto-acid, which was not isolated :



The isolation of perfluoroadipic acid shows that four CF_2 groups are adjacent, and proves the structure of the compounds (XVII), (XVIII), and (XIX).

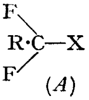
By comparison with olefins studied earlier (*J.*, 1953, 1199, 1592, 3559, *et seq.*) the following qualitative order for ease of *radical* attack can be given C_2H_4, $CH_3{\cdot}CH{:}CH_2$, $CH_3{\cdot}CH{:}CH{\cdot}CH_3$, *cyclo*-$C_6H_{10}$ $>$ $CF_2{:}CH_2$ $>$ $CF_2{:}CF_2$ $>$ $CF_2{:}CHCl$ $>$ $CF_2{:}CFCl$ $>$ $CF_3{\cdot}CH{:}CF_2$ $>$ $CF_3{\cdot}CF{:}CF_2$ $>$ $CF_3{\cdot}CF{:}CF{\cdot}CF_3$ $>$ *cyclo*-C_4F_6 $>$ *cyclo*-C_6F_{10}. It is thus evident that (*a*) replacement of vinylic hydrogen by fluorine decreases the ease of radical attack, (*b*) attachment of a perfluoroalkyl group to a vinyl-carbon atom causes a marked decrease in ease of radical attack, and (*c*) a double bond in a four- or six-membered ring is less readily attacked by a free radical than that in a straight-chain olefin. All of these effects can be attributed to electron withdrawal by fluorine, particularly by perfluoroalkyl groups adjacent to the double bond ($CF_3 \leftarrow CF{:}CF \rightarrow CF_3 \longleftrightarrow F^-CF_2{:}CF{\cdot}\overset{+}{C}F{\cdot}CF_3$, etc.), and to steric inhibition of attack.

The greater reactivity of the double bond in a four-membered ring than that in a six-membered ring is apparent in both ionic and free-radical additions and can be traced to the strain in the former ring. Another example of this reactivity is given by the isomerisation of perfluoro*cyclo*butene into perfluorobutadiene when heated (*J.*, 1955, 3880) :

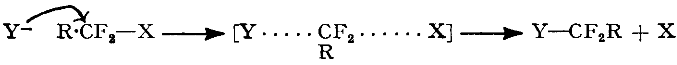
Perfluoro*cyclo*hexene does not show an analogous reaction.

Nucleophilic Attack during Reductions by Lithium Aluminium Hydride.—The marked ease of replacement of chlorine, bromine, or iodine by hydrogen in polyfluoro*cyclo*-butanes or -hexanes by use of lithium aluminium hydride merits comment, since such replacement by use of conventional reducing agents is extremely difficult if not impossible. It is suggested that the effectiveness of lithium aluminium hydride in this connection is due to (*a*) use of ether as a solvent and (*b*) the fact that hydride-ion attack on carbon can occur despite the powerful shielding effect of the fluorine atoms. Of these, (*b*) is by far the more important.

Ether probably plays a part by forming a weak molecular complex $RX \cdot OEt_2$ with the chlorine or bromine in RX of the (Lewis) acid–(Lewis) base type. Such complex formation has been demonstrated with polyfluoroiodo-compounds (*J.*, 1953, 2622) and with polyfluorobromo-compounds (unpublished results), and doubtless plays an important rôle in the formation of perfluoroalkyl Grignard compounds (*J.*, 1952, 3423; 1953, 1748; 1954, 1273) from perfluoroalkyl iodides by making the iodine more readily removable as an iodide ion.


(*A*)

If nucleophilic attack on the carbon atom of a molecule (*A*) is considered, where X = Cl, Br, or I, and R = perfluoroalkyl, the fluorine atoms ought to facilitate such attack, since by their inductive effect they should increase the positive character of the carbon atom and so enhance the ease of attack by a negative ion. Normally this effect, which would enable rapid nucleophilic replacement of X to occur, is more than offset by two factors : (i) the decrease in the ease with which X^- can be lost as the final stage of a bimolecular reaction :



$$Y^- \; R\cdot CF_2{-}X \longrightarrow [Y\cdots\cdots \underset{R}{CF_2}\cdots\cdots X] \longrightarrow Y{-}CF_2R + X^-$$

this is again a direct consequence of the inductive and hyperconjugative effects of the fluorine atoms; (ii) the shielding of the carbon by the small but remarkably effective strongly electronegative fluorine atoms which both by their steric effect and by their field effect adequately prevent access of the nucleophilic reagent to the carbon atom. It is thus suggested that lithium aluminium hydride acts as source of hydride ion which, by virtue of its small size, can overcome the factor (ii) above :

$$H^- + R\cdot CF_2{-}X \longrightarrow R\cdot CHF_2 + X^-$$

The attack doubtless occurs through hydride-ion shift in a cyclic complex, possibly of the type postulated for hydride-ion shift during the reduction of carbonyl compounds by Grignard solutions (*J.*, 1953, 1748), and it is not suggested that free hydride ions are present in ethereal lithium aluminium hydride. The ready replacement of halogen by hydrogen in *cyclo*-butanes or -hexanes by use of lithium aluminium hydride supports the above ideas, since shielding of the carbon by the attached fluorine atoms is decreased in the cyclic compounds and ease of attack by H^- is thereby increased. If the above ideas are correct it is clear that the stability of perfluorocarbons is due more to the shielding effect than to the negativity of the fluorine atoms.

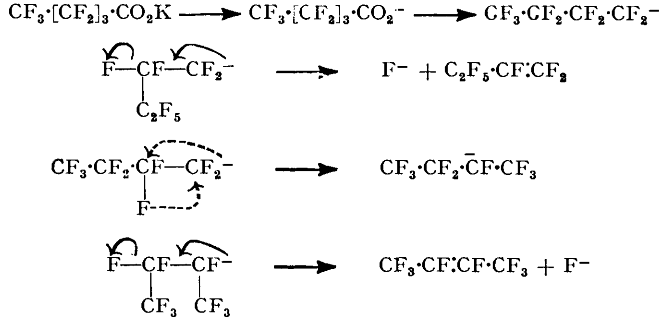
Fluoro-carbanion Rearrangement.—The conversion of a fluoro-acid into an olefin containing a terminal double bond by pyrolysis of its anhydrous sodium salt :

$$CF_3\cdot[CF_2]_n\cdot CF_2\cdot CF_2\cdot CO_2Na \longrightarrow CF_3\cdot[CF_2]_n\cdot CF{:}CF_2 + NaF + CO_2$$

has been established as a general reaction capable of application to acids containing chlorine as well as fluorine, and to dibasic acids (*Nature*, 1951, **168**, 1028; *J.*, 1952, 4259; 1954, 4026; 1955, 3880; see Brice *et al.*, *loc. cit.*, for reference to American work). Brice *et al.* studied the effect of variation of the metal on the course of the pyrolysis, and noted that potassium perfluoropentanoate gave two olefins :

$$CF_3\cdot[CF_2]_3\cdot CO_2K \longrightarrow CF_3\cdot CF{:}CF\cdot CF_3\ (80\%) + CF_3\cdot CF_2\cdot CF{:}CF_2\ (20\%)$$

Our independent work, done in order to study the preparation of the perfluorobut-2-ene required for the reactions described above, is in agreement with this result, except that the ratio of the olefins obtained (approx. 1 : 1) is appreciably different. The important fact is that two olefins are obtained, however, and this we interpret as evidence for fluorocarbanion rearrangement (see *Nature*, 1951, **168**, 1028, for the original suggestions about fluorocarbanion reactivity) :



This suggests that potassium fluoride must act as catalyst for the fluoro-carbanion isomerisation, whereas sodium fluoride does not, and some support for this is given by the fact that pyrolysis of an equimolar mixture of sodium and potassium perfluoropentanoate gives essentially the same ratio of perfluorobut-2-ene to perfluorobut-1-ene (47 : 45) as does pyrolysis of the potassium salt alone (48 : 43), whereas pyrolysis of the pure sodium salt yields only perfluorobut-1-ene. If the potassium salt decomposed preferentially, the potassium fluoride so produced might react with sodium perfluoropentanoate by a solid-state reaction to give more potassium salt :

$$KF + C_4F_9{\cdot}CO_2Na \rightleftharpoons C_4F_9{\cdot}CO_2K + NaF$$

Pyrolysis of the potassium salt would thus displace this equilibrium to the right.

Potassium fluoride does not catalyse the rearrangement of perfluorobut-1-ene into the but-2-ene, so rearrangement must occur before the olefin is formed. Studies of the salt of acids of longer chain length will be reported later.

EXPERIMENTAL

Reactions were carried out in sealed Pyrex or silica tubes unless otherwise stated. Precautions were taken to exclude air, moisture, or material which might catalyse ionic or free-radical reactions. The olefins used were spectroscopically pure and free from peroxides, and were distilled *in vacuo* before use. Reaction products were manipulated in a conventional vacuum system.

Reactions of 1 : 1-*Difluoroethylene.*—(a) *With hydrogen iodide.* The olefin (1·7 g.) and anhydrous hydrogen iodide (6·0 g.), kept at 20° in the dark (6 days), gave 1 : 1-*difluoro*-1-*iodoethane* (5·0 g., 98%), b. p. 45°, n_D^{19} 1·4183 (Found : C, 12·2; H, 1·8%; *M*, 193. $C_2H_3IF_2$ requires C, 12·5; H, 1·6%; *M*, 192). The isomeric 1 : 1-difluoro-2-iodoethane boils at 89·5° (Booth and Burchfield, *J. Amer. Chem. Soc.*, 1935, **57**, 2070). The above reaction time was unnecessarily long, and subsequent experiments showed that reaction is rapid (2 hr.) even at −30°, particularly if solid iodine, which catalyses the reaction, is added.

(b) *With hydrogen bromide.* Difluoroethylene (1·71 g.) and hydrogen bromide (2·28 g.), kept at 20° in the dark (95 hr.), gave 1-*bromo*-1 : 1-*difluoroethane* (3·9 g., 100%), b. p. 14·4° (isoteniscope) (Found : C, 16·3; H, 2·3%; *M*, 144. $C_2H_3BrF_2$ requires C, 16·6; H, 2·1%; *M*, 145). The isomeric 2-bromo-1 : 1-difluoroethane, which boils at 57·3° (Henne and Midgley, *ibid.*, 1936, **58**, 884), was not formed.

The difference in b. p. of 44° between the isomers $CF_2X{\cdot}CH_3$ and $CHF_2{\cdot}CH_2X$ (X = I or Br) is noteworthy; a similar effect is apparent when X = Cl (cf. $CF_2Cl{\cdot}CH_3$, b. p. −9°, and $CHF_2{\cdot}CH_2Cl$, b. p. 35°).

(c) *Photochemical reaction with hydrogen bromide.* The olefin (0·68 g.) and hydrogen bromide (0·95 g.), irradiated in a silica tube (1·2 hr.), gave unchanged starting materials (10%), 2-bromo-1 : 1-difluoroethane (1·3 g., 85% based on olefin), b. p. 56·5—57·0° (Found : *M*, 145), and only a very small amount of 1-bromo-1 : 1-difluoroethane produced by an ionic reaction.

In a second experiment, difluoroethylene (1·54 g.) and hydrogen bromide (1·90 g.) in a Pyrex tube (which cuts off light of wavelength <3000 Å) were irradiated for 17 hr., to give unchanged starting materials (30%), 2-bromo-1 : 1-difluoroethane (1·12 g.), b. p. 57·0—57·5° (Found : *M*, 145), and 1-bromo-1 : 1-difluoroethane (1·13 g.), b. p. 14—15° (Found : *M*, 145).

(d) *With iodine monochloride.* Difluoroethylene (1·11 g.) and iodine monochloride (2·10 g.), kept in the dark (4 days) at room temperature, gave unchanged olefin (0·26 g.) and 1-*chloro*-1 : 1-*difluoro*-2-*iodoethane* (2·90 g., 74% based on olefin), b. p. 97·5°, n_D^{20} 1·465 (Found : C, 10·5; H, 1·0. $C_2H_2ClIF_2$ requires C, 10·6; H, 0·9%). The direction of addition is shown by the ultraviolet spectra and by the fact that the infrared spectrum of the product differs from that of its isomer described below. The product was uncontaminated by its isomer.

Reaction of 2-*Chloro*-1 : 1-*difluoroethylene with Hydrogen Iodide.*—The olefin (0·73 g.) and hydrogen iodide (0·90 g.), kept at 30° (1 day), gave only 0·05 g. of product, b. p. >0°. In a second experiment, the olefin (3·11 g.) and hydrogen iodide (2·3 g.) were kept at 20° (6 days), to give 0·72 g. of product of b. p. >0°. The combined products were distilled, giving only 2-*chloro*-1 : 1-*difluoro*-1-*iodoethane*, b. p. 101°, n_D^{18} 1·468 (Found : C, 10·5; H, 1·1. $C_2H_2ClIF_2$ requires C, 10·6; H, 0·9%).

The direction of addition follows from the reaction of the chlorofluoroiodoethane (0·43 g.) with zinc (0·7 g.) and ethanol (0·7 ml.) in a sealed tube at 20° (19 hr.) to give only 1 : 1-difluoroethylene (80%) (Found : *M*, 64. Calc. for $C_2H_2F_2$: *M*, 64), identified by means of its infrared spectrum. The ultraviolet spectrum of the iodo-compound is also in accord with the proposed structure.

Reaction of Perfluorocyclohexene.—(a) *With hydrogen halides.* The olefin (2·4 g.) and hydrogen bromide (0·8 g.), heated at 240—250° (22 hr.), failed to react and the hydrogen bromide was recovered unchanged.

Hydrogen iodide (1·19 g.), perfluoro*cyclo*hexene (2·45 g.), and iodine (0·2 g.; to act as catalyst), heated at 240—250° (22 hr.) and then distilled *in vacuo*, gave unchanged hydrogen iodide (87%) and perfluoro*cyclo*hexene, examination of which by ultraviolet spectroscopy failed to detect any iodo-compound possibly present in low concentration.

Irradiation of perfluoro*cyclo*hexene (2·5 g.) and hydrogen bromide (1·6 g.) in a silica tube at room temperature (12 days) gave unchanged hydrogen bromide (63%), hydrogen, bromine, and the perfluoro*cyclo*hexene. Careful examination of the last material failed to reveal the presence of bromo-compounds. This does not necessarily mean that hydrogen bromide will not react photochemically with perfluoro*cyclo*hexene, but only that it fails to react under conditions where the other olefins studied will react.

(b) *With chlorine or bromine.* The olefin (2·8 g.) and a slight excess of chlorine, shaken in a silica tube and exposed to ultraviolet light (25 hr.), gave 1 : 2-dichlorodecafluoro*cyclo*hexane (81%), b. p. 109°, m. p. 37°, and unchanged olefin (15%). The dichloro-compound was spectroscopically identical with a known specimen. Roylance, Tatlow, and Worthington (*J.*, 1954, 4426) report m. p. 39—41° for this compound. Perfluoro*cyclo*hexene and chlorine react only slowly in the dark at the temperature used for the photochemical chlorination (50°).

The olefin and bromine similarly react only very slowly at room temperature or at 80° in the absence of light. Exposure of perfluoro*cyclo*hexene (2·9 g.) and bromine (20% excess) in a silica tube to intense ultraviolet light (48 hr.) at 80° gave unchanged olefin (1·0 g.) and 1 : 2-dibromodecafluoro*cyclo*hexane (83% based on olefin used), micro-b. p. 139°, m. p. 30—32° after sublimation. Tatlow and Worthington (*J.*, 1952, 1251) report b. p. 140°, m. p. 32°.

The 1 : 2-dichloro- and -dibromo-decafluoro*cyclo*hexane prepared as above were combined and heated (90°) and shaken with zinc (4 g.) and ethanol (15 ml.) in a sealed tube (8 hr.), to give perfluoro*cyclo*hexene (85%), spectroscopically identical with a known specimen.

(c) *With iodine monochloride.* Mixtures of perfluoro*cyclo*hexane (3·0—5·5 g.) and iodine monochloride (2·2—4·7 g.) were heated in sealed tubes under a wide variety of conditions of temperature (50—205°), reactant ratio, and time. In most cases where reaction occurred at all, approx. 65% of the perfluoro*cyclo*hexene was recovered, and 30% of it was converted into the dichloride, b. p. 110°. Small quantities of an iodo-compound with a b. p. higher than 110° were detected in reactions at the higher temperatures (150—200°). The fractions of highest b. p. from all the experiments were combined and distilled, to give 1-*chloro*-2-*iododecafluoro*-cyclo*hexane* (0·2 g., 1%), micro-b. p. 140° (Found : C, 16·7. C_6ClIF_{10} requires C, 16·9%).

A similar series of experiments gave the 1-chloro-2-iododecafluoro*cyclo*hexane, (micro-) b. p. 142°, in 3% yield. The compound (0·9 g.) was mixed with a 10% excess of chlorine in a sealed 5 ml. tube, which was kept in the dark (4 days), then exposed to ultraviolet light

(24 hr.). Distillation gave 1 : 2-dichlorodecafluoro*cyclo*hexane (78%), spectroscopically identical with a known specimen.

(d) *With trifluoroiodomethane.* Perfluoro*cyclo*hexene (4·2 g.) and trifluoroiodomethane (100% excess) were exposed to intense ultraviolet radiation from a Hanovia lamp 2 cm. from the silica reaction tube. Even with this vigorous treatment and a temperature of 60—65°, the reaction was very slow, and after 24 days 70% of the olefin was recovered unchanged. The material with b. p. >60° was removed and the unchanged trifluoroiodomethane and perfluoro*cyclo*hexene were again irradiated (3 weeks). Distillation of the combined products gave unchanged olefin (44%), *decafluoro-*1-*iodo-*2-*trifluoromethyl*cyclo*hexane* (68% based on olefin used), (micro-) b. p. 132° (Found : C, 18·3%; *M*, 455. C_7IF_{13} requires C, 18·3%; *M*, 458), and perfluoro-1 : 2-dimethyl*cyclo*hexane (11% based on olefin used), b. p. 101—102° (Found : C, 24·0%; *M*, 400. Calc. for C_8F_{16} : C, 24·0%; *M*, 400). Haszeldine and Smith (*J.*, 1950, 2689) report b. p. 100—102° for the perfluorodimethyl*cyclo*hexane.

*Some Reactions of Polyhalogeno-trifluoromethyl*cyclo-*hexanes and -hexenes.*—The reactions of chloropolyfluoro*cyclo*hexanes with lithium aluminium hydride have been studied by Tatlow and Worthington (*J.*, 1952, 1251).

(*a*) To a stirred solution of lithium aluminium hydride (1·0 g.) in dry ether (20 ml.) was slowly added (2 hr.) decafluoro-1-iodo-2-trifluoromethyl*cyclo*hexane (4·1 g.) in dry ether (10 ml.). After being kept (1 hr.) and heated under reflux (1 hr.) the excess of lithium aluminium hydride was destroyed by cautious addition of 25% sulphuric acid (10 ml.), followed by water (30 ml.). The dried ethereal layer and extracts of the aqueous solution were distilled to give 1-H-*decafluoro-*2-*trifluoromethyl*cyclo*hexane* (62%), b. p. 86° (isoteniscope) (Found : C, 25·2; H, 0·3%; *M*, 330. C_7HF_{13} requires C, 25·3; H, 0·3%; *M*, 332).

(*b*) A mixture of 1-*H*-decafluoro-2-trifluoromethyl*cyclo*hexane (3·1 g.), potassium hydroxide (1·5 g.), and water (3 ml.) was heated in a sealed tube at 85° for 3 hr. Water was added, and the organic layer was separated and distilled from phosphoric anhydride, to give *nonafluoro-*1-*trifluoromethyl*cyclo*hexene* (78%), b. p. 75° (Found : C, 26·8%; *M*, 310. C_7F_{12} requires C, 26·9%; *M*, 312).

(*c*) Nonafluoro-1-trifluoromethyl*cyclo*hexene (1·2 g.), potassium permanganate (4 g.), and water (15 ml.) were heated and shaken at 80° (15 hr.) in a sealed tube. Removal of the excess of permanganate with sulphur dioxide and ether-extraction in the usual way (see Part II, *loc. cit.*), followed by distillation of the dried (Na_2SO_4) ethereal extracts, gave a residual white solid which was dried over phosphoric anhydride. A portion of the solid had m. p. 133° after sublimation *in vacuo*. The rest of the solid was exactly neutralised by aqueous sodium hydroxide, and the aqueous solution was freeze-dried to give disodium perfluoroadipate (75% total yield), identified by means of its infrared spectrum.

(*d*) 1-*H*-Decafluoro-2-trifluoromethyl*cyclo*hexane (2·1 g.) was sealed in a silica tube with water (2 ml.) and a 10% excess of chlorine and irradiated for 48 hr. Distillation of the dried (P_2O_5) organic layer gave 1-*chlorodecafluoro-*2-*trifluoromethyl*cyclo*hexane* (78%), b. p. 103° (Found : C, 22·8%; *M*, 365. C_7ClF_{13} requires C, 22·9%; *M*, 366·5), and unchanged starting material (5%).

The same chloro-compound was produced in 85% yield by reaction of decafluoro-1-iodo-2-trifluoromethyl*cyclo*hexane (1·5 g.) with chlorine (30% excess) in a sealed tube on exposure to ultraviolet light (3 days). The iodo-compound (2·7 g.) and a 20% excess of bromine, kept in the dark (2 days), then irradiated (2 days), gave 1-*bromodecafluoro-*2-*trifluoromethyl*cyclo*hexane* (78%), b. p. 115° (Found : C, 20·4%; *M*, 407. C_7BrF_{13} requires C, 20·4%; *M*, 411).

(*e*) Nonafluoro-2-trifluoromethyl*cyclo*hexene (1·0 g.) and chlorine (10% excess), strongly irradiated in a 10 ml. silica tube at 80° (4 days), gave 1 : 2-*dichlorononafluoro-*1-*trifluoromethyl*cyclo*hexane* (65%), micro-b. p. 130° (Found : C, 21·9. $C_7Cl_2F_{12}$ requires C, 21·9%), and unchanged olefin (15%).

Similar reaction with bromine for 7 days gave 1 : 2-*dibromononafluoro-*1-*trifluoromethyl*cyclo*hexane* (57%), b. p. 160° (Found : C, 17·8. $C_7Br_2F_{12}$ requires C, 17·8%), and recovered olefin (28%).

*Reaction of Perfluorobut-*2-*ene.*—(a) *With hydrogen iodide.* The olefin (1·68 g.), iodine (0·5 g.), and hydrogen iodide (1·22 g.) failed to react after being heated at 140° (16 hr.).

(b) *With hydrogen bromide.* There was no reaction between perfluorobut-2-ene (1·12 g.) and hydrogen bromide (0·55 g.) when heated at 175° (16 hr.), 200° (23 hr.), or 280° (47 hr.).

The olefin (1·72 g.) and hydrogen bromide (0·73 g.) in a silica tube were exposed to ultraviolet light for 51 hr.; 84% of the olefin underwent reaction. The free bromine which had been produced was removed by reaction with mercury, and the colourless liquid was distilled, to give 2-*bromo*-1 : 1 : 1 : 2 : 3 : 4 : 4 : 4-*octafluorobutane* (60% based on olefin used), b. p. 53—54°, n_D^{17} 1·307 (Found : C, 17·3; H, 0·6%; *M*, 278. C_4HBrF_8 requires C, 17·1; H, 0·4%; *M*, 281), and 2 : 3-dibromo-octafluorobutane (40% based on olefin used), b. p. 96°, n_D^{18} 1·354.

(c) *With iodine monochloride.* No reaction occurred at room temperature or at 130° (16 hr.). The olefin (1·93 g.) and iodine monochloride (3·1 g.) were heated at 200° (16 hr.) to give a 70% reaction of the olefin. Distillation gave 2 : 3-dichloro-octafluorobutane (90% based on olefin used), b. p. 60—60·5°, identified by means of its infrared spectrum.

A third experiment with perfluorobut-2-ene (1·87 g.) and iodine monochloride (4·2 g.) at 140° (100 hr.) gave only 2 : 3-dichloro-octafluorobutane (90%) and unchanged olefin (43%).

Examination of the still residues from the above experiments by ultraviolet spectroscopy showed that only traces of an organic iodo-compound were present.

(d) *With bromine or chlorine.* Perfluorobut-2-ene (3·7 g.) and bromine (10% excess), irradiated in a silica tube for 5 days, gave 2 : 3-dibromo-octafluorobutane (75%), b. p. 95—96°, n_D^{20} 1·355, and unchanged olefin (18%). Infrared spectroscopic examination of the dibromide and of the unchanged olefin showed that no isomerisation to perfluorobut-1-ene had occurred.

Perfluorobut-2-ene (2·9 g.) and chlorine (20% excess), irradiated in a silica tube (3 days), gave 2 : 3-dichloro-octafluorobutane (88%), b. p. 62°, identified spectroscopically, and unchanged olefin, shown to be spectroscopically free from perfluorobut-1-ene.

(e) *With trifluoroiodomethane.* The butene (2·6 g.) and trifluoroiodomethane (5·1 g.), on exposure to ultraviolet radiation in a silica tube (14 days), gave unchanged olefin (23%) and *octafluoro*-2-*iodo*-3-*trifluoromethylbutane* (79%), b. p. 85—86·5° (isoteniscope) (Found : C, 15·4%; *M*, 395. C_5IF_{11} requires C, 15·2%; *M*, 396).

*Reaction of Perfluoro*cyclo*butene.*—(a) *With iodine monochloride.* Perfluoro*cyclo*butene (2·62 g.) and iodine monochloride (5·5 g.) were heated at 140° (2 days), then 170° (3 days), to give unchanged olefin (1·73 g.), 1-*chlorohexafluoro*-2-*iodo*cyclo*butane* (0·95 g.), b. p. 99—100°, n_D^{15} 1·4059 (Found : C, 14·6. C_4ClIF_6 requires C, 14·8%), and 1 : 2-dichlorohexafluoro*cyclo*butane (0·30 g.), b. p. 59°.

In a second experiment the olefin (8·7 g.) and iodine monochloride (18 g.) were heated at 180° (1 day), to give unchanged olefin (2·7 g.), 1-chlorohexafluoro-2-iodo*cyclo*butane (77% based on olefin used), and 1 : 2-dichlorohexafluoro*cyclo*butane (10%). Ultraviolet spectrum of 1-chlorohexafluoro-2-iodo*cyclo*butane in light petroleum : $\lambda_{max.}$ 270 (ε 300); $\lambda_{min.}$ 223 (ε 45).

(b) *With hydrogen bromide.* No reaction occurred when perfluoro*cyclo*butene and hydrogen bromide were heated at 180° (6 days) or at 220° (4 days).

The olefin (3·8 g.) and hydrogen bromide (2·5 g.), irradiated for 3 days, gave 1-bromo-1 : 2 : 2 : 3 : 3 : 4-hexafluoro*cyclo*butane (33% based on olefin used), b. p. 96°, n_D^{20} 1·389 (Found : C, 19·8%; *M*, 243. Calc. for C_4HBrF_6 : C, 19·8%; *M*, 243), 1 : 2-dibromohexafluoro*cyclo*butane (49% based on olefin used), b. p. 62° (Found : C, 14·9%; *M*, 318. Calc. for $C_4Br_2F_6$: C, 15·0%; *M*, 322), and unchanged olefin (35%). The identity of the recovered olefin was confirmed by spectroscopic examination. Park, Sharrah, and Lacher (*J. Amer. Chem. Soc.*, 1949, **71**, 2339) report b. p. 56°/632 mm. for the bromohexafluoro*cyclo*butane.

(c) *With hydrogen iodide.* See Haszeldine and Osborne (*J.*, 1955, 3880).

(d) *With chlorine or bromine.* Perfluoro*cyclo*butene (2·8 g.) and a 10% excess of chlorine, on exposure to ultraviolet light (1 day), gave 1 : 2-dichlorohexafluoro*cyclo*butane (71%) and unchanged olefin (21%).

Perfluoro*cyclo*butene (3·1 g.) and bromine (10% excess), similarly treated, gave 1 : 2-dibromohexafluoro*cyclo*butane (65%) and unchanged olefin (24%). Infrared spectroscopic examination of the recovered olefin showed it to be identical with the starting material.

(e) *With trifluoroiodomethane.* The olefin (3·6 g.) and trifluoroiodomethane (100% excess) in a 50 ml. silica tube, exposed to ultraviolet light (25 days), gave unchanged olefin (30%) and *hexafluoro*-1-*iodo*-2-*trifluoromethyl*cyclo*butane* (67% based on olefin used), b. p. 85—87° (Found : C, 17·0%; *M*, 360. C_5IF_9 requires C, 16·8%; *M*, 358). Spectroscopic examination of the recovered olefin showed it to be identical with the starting product.

*Reactions of Perfluoro*cyclo-*butanes and -butenes.*—(a) 1-*Chlorohexafluoro*-2-*iodo*cyclo*butane.* The iodo-compound (4·9 g.) in ethyl ether (10 ml.) was added slowly (3 hr.) to a suspension of lithium aluminium hydride (2 g.) in ether (30 ml.) under a reflux condenser, and the mixture refluxed for 2 hr. Dilute sulphuric acid (20 ml.) was added cautiously to the cooled mixture, followed by water. The ethereal layer, combined with two ethereal extracts of the aqueous phase, were dried (P_2O_5), then distilled through a short packed column. The fraction of b. p. 25—29° (mainly 27°) (62%) was transferred to an apparatus for manipulation of volatile compounds and further purified by distillation, to give 1 : 1 : 2 : 2 : 3 : 4-hexafluoro*cyclo*butane

(51%), b. p. 27° (isoteniscope) (Found: C, 29·0; H, 1·1%; *M*, 164. Calc. for $C_4H_2F_6$: C, 29·3; H, 1·2%; *M*, 164). Buxton and Tatlow (*loc. cit.*) report b. p. 26·6—27·0°. There was no unchanged iodo-compound, and perfluoro*cyclo*butene was not detected as a product.

1-Chlorohexafluoro-2-iodo*cyclo*butane (1·0 g.), sealed with chlorine (10% excess) in a 5 ml. tube and irradiated (8 hr.), gave 1 : 2-dichlorohexafluoro*cyclo*butane (95%), b. p. 59—60° (Found: *M*, 233. Calc. for $C_4Cl_2F_6$: *M*, 233), identified by means of its infrared spectrum.

(b) 1-*Bromo*-1 : 2 : 2 : 3 : 3 : 4-*hexafluoro*cyclo*butane*. The bromo-compound (2·3 g.) in ether (2 ml.) was treated with lithium aluminium hydride (1 g.) in ether (12 ml.) under conditions similar to those of (a) above. Distillation of the ethereal extracts gave 1 : 1 : 2 : 2 : 3 : 4-hexafluoro*cyclo*butane (63%) (Found: *M*, 163).

The bromo-compound (1·2 g.) and bromine (30% excess) in a 10 ml. silica tube, exposed to intense ultraviolet radiation (4 days), gave 1 : 2-dibromohexafluoro*cyclo*butane (71%), b. p. 95—96° (Found: *M*, 320. Calc. for $C_4Br_2F_6$: *M*, 322), and unchanged monobromo-compound (15%). The dibromo-compound so produced was readily debrominated by zinc and dioxan in a sealed tube at 80° (3 hr.), to give perfluoro*cyclo*butene (81%), identified spectroscopically.

(c) 1 : 2-*Dibromohexafluoro*cyclo*butane*. The dibromo-compound (2·9 g.) was treated with lithium aluminium hydride as in (b) above, to give 1 : 1 : 2 : 2 : 3 : 4-hexafluoro*cyclo*butane (60%) (Found: *M*, 164). As in (a) and (b) above, loss of product occurred by failure to achieve complete separation from ether on the scale used. Reaction of the ether–hexafluoro*cyclo*butane mixture, b. p. 29—32°, with an excess of boron trifluoride rendered further separation possible, since boron trifluoride forms a complex only with the ether.

(d) 1 : 2-*Dichlorohexafluoro*cyclo*butane*. The dichloride (8·6 g.) in ether (5 ml.) was added (2 hr.) to lithium aluminium hydride (2 g.) in ether (40 ml.). The mixture, treated as in (*a*) above, gave 1 : 2 : 2 : 3 : 3 : 4-hexafluoro*cyclo*butane (74%), b. p. 27° (Found: *M*, 164), and no unchanged chloro-compound.

(e) 1 : 1 : 2 : 2 : 3 : 4-*Hexafluoro*cyclo*butane*. The products obtained from reductions of the type described above were combined, treated with boron trifluoride to remove any traces of ether, then redistilled.

A portion (1·7 g.), chlorine (1·6 g.), and water (1 ml.) in a 10 ml. silica tube were exposed to ultraviolet light (5 days), to give 1 : 2-dichlorohexafluoro*cyclo*butane (87%), b. p. 59° (isoteniscope) (Found: *M*, 234. Calc. for $C_4Cl_2F_6$: *M*, 233).

A second portion (2·9 g.), water (20 ml.), potassium permanganate (2 g.), and potassium hydroxide (2 g.) in a 50 ml. autoclave were shaken and heated (80°) for 8 hr. The filtered solution was treated with sulphur dioxide, acidified with sulphuric acid, and extracted with ether in the usual way. The dried (P_2O_5) ethereal extract was evaporated to dryness and the residual hygroscopic solid neutralised with aqueous sodium hydroxide; freeze-drying gave disodium tetrafluorosuccinate (73%), identified by means of its infrared spectrum.

A third portion (1·8 g.), potassium hydroxide (2 g.), and water (2 ml.) were shaken vigorously in a sealed tube (12 hr.), water (10 ml.) was added, and the volatile products were distilled *in vacuo*, giving 1 : 3 : 3 : 4 : 4-pentafluoro*cyclo*butene (77%), b. p. 25° (isoteniscope) (Found: *M*, 134. Calc. for C_4HF_5: *M*, 134). Buxton and Tatlow (*loc. cit.*) report b. p. 25—26° for this compound.

(f) *Hexafluoro*-1-*iodo*-2-*trifluoromethyl*cyclo*butane*. The iodo-compound (5·9 g.) in dioxan (10 ml.) was added during 2 hr. to a vigorously stirred suspension of lithium aluminium hydride (2 g.) in dioxan (50 ml.). After being stirred for a further hour the mixture was heated to 60° (1 hr.), then cooled. Dilute sulphuric acid (30 ml.) was added slowly, then water (100 ml.), and the volatile products, combined with those which had passed through the reflux condenser and been condensed in a trap cooled by liquid oxygen, were transferred to a vacuum-system. Distillation gave 1-H-*hexafluoro*-2-*trifluoromethyl*cyclo*butane* (79%), b. p. 36° (isoteniscope) (Found: C, 25·6; H, 0·4%; *M*, 231. C_5HF_9 requires C, 25·9; H, 0·4%; *M*, 232).

(g) 1-H-*Hexafluoro*-2-*trifluoromethyl*cyclo*butane*. This compound (3·7 g.) was shaken with powdered potassium hydroxide (4 g.) and water (4 ml.) for 5 hr. Distillation of the volatile products *in vacuo* gave *pentafluoro*-1-*trifluoromethyl*cyclo*butene* (83%), b. p. 24° (isoteniscope) (Found: C, 28·3%; *M*, 212. C_5F_8 requires C, 28·3%; *M*, 212).

Pentafluoro-1-trifluoromethyl*cyclo*butene (1·1 g.), mixed with chlorine (0·5 g.) and exposed to ultraviolet light (24 hr.), gave 1 : 2-*dichloropentafluoro*-1-*trifluoromethyl*cyclo*butane* (91%), b. p. 80° (isoteniscope) (Found: C, 21·1%; *M*, 283. $C_5Cl_2F_8$ requires C, 21·2%; *M*, 283).

Pentafluoro-1-trifluoromethyl*cyclo*butene (2·7 g.), potassium permanganate (2 g.), water (15 ml.), and potassium hydroxide (2·1 g.) were shaken vigorously in an autoclave and heated to 75° (8 hr.). The excess of permanganate was removed, and the acid produced was isolated by ether-extraction in the usual way. The solid remaining after evaporation of the ether was perfluorosuccinic acid (69%), identified by conversion into its disodium salt; the infrared spectrum of the last compound was compared with that of a known specimen.

Perfluorosuccinic acid was also isolated (61%) by reaction of 1-*H*-hexafluoro-2-trifluoromethyl*cyclo*butane (3·0 g.) with permanganate under the above conditions. Fluoroform was also detected as a reaction product by means of its infrared spectrum.

Pyrolysis of Sodium and Potassium Perfluoropentanoate (cf. *J.*, 1952, 4259).—The acid was prepared from perfluoro-*n*-butyl iodide by reaction with acetylene and oxidation (*J.*, 1950, 3037, 2789; 1953, 1548, 3761) and also by electrolysis of pentanoyl fluoride in anhydrous hydrogen fluoride. The sodium and potassium salts were obtained by exact neutralisation of the acid, followed by freeze-drying.

Anhydrous sodium perfluoropentanoate (3·9 g.) in a platinum cylinder with open ends was placed in a platinum tube closed at one end and connected at the other to a trap cooled in liquid oxygen and thence to a pump. The tube was evacuated to 10 mm. and the closed end was then slowly pushed into a furnace at 270°. Gas was evolved steadily and collected in the trap. After 2 hr. the contents of the trap were transferred to a vacuum-apparatus and purified by distillation, to give carbon dioxide and perfluorobut-1-ene (91%), b. p. 0·3° (isoteniscope) (Found : *M*, 200. Calc. for C_4F_8 : *M*, 200). Infrared spectroscopic examination showed the presence of a $-CF{:}CF_2$ bond (absorption at 5·57 μ) (*J.*, 1952, 4423; 4259) and that the product was uncontaminated by perfluorobut-2-ene. The olefin combined readily with bromine, when mixed with it in a sealed tube at 25° (5 hr.), to give 1 : 2-dibromo-octafluorobutane (97%), b. p. 95° (Found : *M*, 358. Calc. for $C_4Br_2F_8$: *M*, 360).

Anhydrous potassium perfluoropentanoate (4·1 g.) was pyrolysed under conditions as near to identical as possible with those used for the sodium salt above. The volatile products were carbon dioxide and a mixture of perfluorobutenes (89%) (Found : *M*, 200. Calc. for C_4F_8 : *M*, 200). Infrared spectroscopic examination showed the presence of perfluorobut-2-ene (band at 5·77 μ) and perfluorobut-1-ene (band at 5·57 μ). The mixed olefins were then sealed with successive portions of 0·1 g. of bromine and kept for an hour at 25° before refractionation *in vacuo* to separate the dibromide produced and recover the unchanged olefinic material. The recovered olefinic material was then examined by infrared spectroscopy to follow the extent of removal of perfluorobut-1-ene which, as demonstrated by Brice *et al.* (*loc. cit.*) preferentially reacts with the bromine. Reaction with successive small portions of bromine in this way removed all the perfluorobut-1-ene (43% yield) with removal of a negligible amount of perfluorobut-2-ene which remained unattacked (48% yield). Perfluorobut-2-ene combined with bromine when exposed to ultraviolet light at room temperature (5 days), to give 2 : 3-dibromo-octafluorobutane (75%), b. p. 96° (Found : *M*, 360. Calc. for $C_4Br_2F_8$: *M*, 360). Both dibromo-compounds were reconverted into their respective olefins almost quantitatively by reaction with zinc and ethanol.

A mixture of potassium perfluoropentanoate (2·0 g.) and sodium perfluoropentanoate (2·1 g.) was pyrolysed under the above conditions. Infrared spectroscopic examination of the olefin revealed two double-bond bands. The spectrum was almost identical with that of the mixed perfluorobut-1- and -2-ene obtained as above. The mixture was separated in the same way, to give perfluorobut-2- (47%) and -1-ene (45%).

Perfluorobut-1-ene (1·3 g.) was spectroscopically unchanged after being heated with anhydrous potassium fluoride (1·0 g.) at 270° for 8 hr.

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