*The Reactions of Highly Fluorinated Organic Compounds. Part IX.** 1H-*Decafluoro*-4-*trifluoromethyl*cyclo*hexane*, *Nonafluoro*-4-*trifluoromethyl*cyclo*hex*-1-*ene*, *and Perfluoro*-(3-*methyladipic*) *Acid.*

By G. B. Barlow, M. Stacey, and J. C. Tatlow.

[Reprint Order No. 6090.]

Perfluoro-(1-methyl-4-*iso*propyl*cyclo*hexane) with bromine, chlorine, or toluene at 500—550° gave, respectively, 1-bromo- 1-chloro- and decafluoro-*cyclo*hexane or 1*H*-decafluoro-4-trifluoromethyl*cyclo*hexane. The chlorofluorocarbon was made also by vapour-phase fluorination of *p*-chlorotoluene or *p*-chlorobenzotrifluoride with cobaltic fluoride, and with lithium aluminium hydride it afforded the fluorohydrocarbon. The latter, with concentrated aqueous alkali, was dehydrofluorinated to nonafluoro-4-trifluoromethyl-*cyclo*hex-1-ene, oxidation of which gave perfluoro-(3-methyladipic) acid; from this, by decarboxylation, 1*H* : 4*H*-heptafluoro-2-trifluoromethylbutane was made. Some preliminary observations on the stability of fluorohydrocarbons to alkali are recorded.

This paper describes further applications of processes developed in this Department for the synthesis of highly fluorinated compounds and described in earlier papers in this series. We have shown that the carbon–carbon bonds between two tertiary carbon atoms in certain fluorocarbons can be broken preferentially in pyrolysis-type reactions (Barlow and Tatlow, *J.*, 1952, 4695). In an analogous manner, perfluoro-(1-methyl-4-*iso*propyl*cyclo*hexane), made by reaction of *p*-cymene with cobaltic fluoride, reacted with bromine, chlorine, or toluene when a mixture of the two was passed through a hot tube at temperatures of about 510°, 550°, and 550° respectively (owing to a calibration error, the temperatures quoted in the earlier paper are all too high by 100°; the actual temperatures used were similar to those given above). With bromine, 1-bromodecafluoro-4-trifluoromethyl*cyclo*hexane and a low-boiling product, probably 2-bromoheptafluoropropane, were formed; with chlorine the analogous chloro-derivatives were obtained. From the reaction with toluene, 1*H*-decafluoro-4-trifluoromethyl*cyclo*hexane, 2*H*-heptafluoropropane (probably), and dibenzyl were the principal products. The fluorocarbons, perfluoro-(di*cyclo*hexyl), -(*iso*propyl-*cyclo*hexane), and -(1-methyl-4-*iso*propyl*cyclo*hexane) were pyrolysed alone, or in the presence of perfluoro(methyl*cyclo*hexane) or nitrogen, at temperatures similar to those at which reaction with chlorine, bromine, or toluene occurs. In all cases, profound decomposition resulted but no recognisable products were isolated. Under these conditions, with no "reactive" carrier gas present the intermediates seemed to be capable of effecting extensive rupture of carbon–carbon bonds in themselves or in undissociated fluorocarbons present.

These reactions again illustrate that, in some fluorocarbons, bonds between tertiary carbon atoms may be cleaved more readily than bonds involving primary and secondary carbon atoms. In this particular case, though the *cyclo*hexane ring carried a second side chain, reaction occurred less readily at that point. It was suggested earlier (Part II, *loc. cit.*) that these processes are initiated by homolysis of the C–C bonds between tertiary carbon atoms (where both are not in the same ring). It appears that the bond dissociation energies for such linkages between tertiary carbon atoms, in general, are lower than for those involving primary or secondary carbon atoms. It seems likely in fact that the secondary fluorocarbon radicals formed are relatively more stable than primary ones. In accord with this are recent conclusions on the free-radical additions of fluoroalkyl iodides to fluoro-olefins (Haszeldine, *J.*, 1953, 3559, 3565), the direction of addition indicating that, here also, secondary intermediate radicals are more stable than primary.

Alternative methods for the production of 1-chlorodecafluoro-4-trifluoromethyl*cyclo*-hexane were the fluorination, in the vapour phase with cobalt trifluoride, of either *p*-chlorotoluene or *p*-chlorobenzotrifluoride. As with other chlorofluorocarbons (Tatlow and

* Part VIII, *J.*, 1955, 1184.

Worthington, *J.*, 1952, 1251; Buxton and Tatlow, *J.*, 1954, 1177; Roylance, Tatlow, and Worthington, *J.*, 1954, 4426), 1-chlorodecafluoro-4-trifluoromethyl*cyclo*hexane reacted with lithium aluminium hydride in diethyl ether, the chlorine atom being replaced by hydrogen. This gave an alternative route to 1*H*-decafluoro-4-trifluoromethyl*cyclo*hexane. Other cyclic polyfluorides (*idem, locc. cit.*; Evans and Tatlow, *J.*, 1954, 3779) undergo dehydrofluorination with concentrated aqueous potassium hydroxide, and, in this case, this type of reaction afforded nonafluoro-4-trifluoromethyl*cyclo*hex-1-ene. The olefin gave dibromo- and dichloro-addition products in the usual way. Oxidation of it with aqueous potassium permanganate afforded the branched-chain dibasic acid, perfluoro-(3-methyladipic) acid, characterised as the free acid, salts, diethyl ester, and diamide. Identical specimens of the acid and its derivatives were obtained from samples of the olefin derived ultimately from three sources, (*a*) the fluorocarbon–toluene reaction, (*b*) from *p*-chlorotoluene, and (*c*) from *p*-chlorobenzotrifluoride. Decarboxylation of the dipotassium salt of the acid, by the method of LaZerte, Hals, Reid, and Smith (*J. Amer. Chem. Soc.*, 1953, **75**, 4525), gave 1*H* : 4*H*-heptafluoro-2-trifluoromethylbutane. This fluorohydrocarbon was much less susceptible to attack by concentrated aqueous alkali than are cyclic polyfluorides, and, even under drastic conditions, only a small proportion of fluorine was removed. However, alcoholic alkali readily attacked the compound, fluoride ion (approx. 2 mol.) being eliminated under mild conditions, though no definite products were isolated, whilst under drastic conditions virtually all could be removed. It appeared that olefin formation was followed by base-catalysed addition of the alcohol across the unsaturated linkages, and subsequent further elimination of hydrogen fluoride.

The similar properties of analogous samples obtained from the three different sources suggested that isomerisation had not occurred to any serious extent in the original fluorinations. Migration of chlorine can occur during the reaction of chlorohydrocarbons with cobaltic fluoride (Roylance, Tatlow, and Worthington, *loc. cit.*) though the effect is probably more pronounced with polychlorides than with monochlorides. The purity of the volatile compounds prepared was checked by gas–liquid partition chromatography (Evans and Tatlow, *J.*, 1955, 1184). Only in one case, that of 1*H*-decafluoro-4-trifluoromethyl*cyclo*hexane, was more than one component detected. This fluorohydrocarbon gave two peaks, both being present though the relative sizes varied, in samples of the compound from all three sources. The effect may well have been due to the presence of two stereoisomeric forms.

Information available so far suggests that, in fluorohydrocarbons, isolated hydrogen atoms on secondary carbon atoms are susceptible to attack by aqueous potassium hydroxide. Several examples of olefin formation from cyclic polyfluorides are now known (see earlier papers in this series), whilst 3*H*-heptafluoroadipic acid (Barbour, MacKenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 341) readily loses fluorine with alkali. Further, the 2*H*-heptafluoropropane obtained from perfluoro(methyl*iso*propyl*cyclo*hexane) was degraded by alkaline permanganate to give trifluoroacetic acid; alkali alone effected the elimination of about 1 atom of fluorine as the ion. In contrast, the hydrogen in terminal CHF_2 groups appears to be much more resistant to attack by bases. Thus, with aqueous alkali, 1*H* : 4*H*-heptafluoro-2-trifluoromethylbutane and 1*H* : 4*H*-octafluorobutane lost, respectively, little and no fluorine. Also, 3*H*-tetrafluoropropionic acid did not give trifluoroacrylic acid (Henne and Fox, *J. Amer. Chem. Soc.*, 1954, **76**, 479). Haszeldine's preparation of 1*H*-perfluoroalkanes from perfluoroalkyl iodides (*J.*, 1953, 3761) indicates that CHF_2 groups also resist attack by alcoholic alkali. The slight attack on 1*H* : 4*H*-heptafluoro-2-trifluoromethylbutane by aqueous alkali, and the ready removal of fluorine by alcoholic alkali, suggest that the isolated fluorine at a branch point next to a CHF_2 group may be, relatively, a point of weakness.

Experimental

Fluorinations with Cobaltic Fluoride.—For a description of the apparatus and general reaction conditions used see Barbour, Barlow, and Tatlow (*J. Appl. Chem.*, 1952, **2**, 127).

(a) p-*Cymene*. This hydrocarbon (43·8 g.; input rate 30 c.c./hr.) was passed through a reaction

vessel maintained at 260—280°. After being poured into ice-water, neutralised, separated, dried, and filtered, the product was fractionated through a 1′ column packed with Dixon gauze spirals. After removal of the low-boiling breakdown products, there was obtained perfluoro-(1-methyl-4-*iso*propyl*cyclo*hexane) (66·0 g.), b. p. 144—146°, n_D^{16} 1·3006. Haszeldine and Smith (*J.*, 1950, 3617) gave b. p. 146·5°, n_D^{25} 1·2965.

(b) p-*Chlorotoluene*. This compound (248·4 g. in all; input rate 20 c.c./hr.) was fluorinated in three runs at 290—310°. After being worked up as described above, the products were combined and fractionated to give, as constant-boiling fractions, perfluoro(methyl*cyclo*hexane) (90·0 g.), b. p. 75·5—75·8°, n_D^{17} 1·285, and 4-*chlorotridecafluoro*(*methyl*cyclo*hexane*) (107·1 g.), b. p. 102—103°, n_D^{17} 1·314 (Found: C, 22·9; F, 67·4%; *M*, 373. C_7ClF_{13} requires C, 22·9; F, 67·4%; *M*, 366·5).

(c) p-*Chlorobenzotrifluoride*. This material (359 g. in all; input rate 20 c.c./hr.) was fluorinated in three runs at 290—310°, to give perfluoro(methyl*cyclo*hexane) (155·0 g.), b. p. 75·5—75·8°, and 4-chlorotridecafluoro(methyl*cyclo*hexane) (168·4 g.), b. p. 101·7—103·1°, n_D^{18} 1·314.

Reactions of Perfluoro-(1-*methyl*-4-iso*propyl*cyclo*hexane*).—These reactions were carried out in a packed hard-glass tube as described by Barlow and Tatlow (*loc. cit.*). Temperatures were measured by chromel–alumel and iron–constantan thermocouples connected to a " Cambridge " potentiometer. In general, the tube and packing were attacked slowly by the reactants, and after a number of runs some etching was visible. The toluene used was " sulphur-free " which had been passed through the tube at 650° and then fractionated.

(a) *With toluene*. The fluorocarbon (52·9 g.; input rate 10 c.c./hr.) and toluene (140 c.c.; input rate 50 c.c./hr.) were passed into the reaction tube which was at 540—555°. When the contents of the trap warmed to room temperature, a low-boiling fraction (*ca.* 7 c.c.), b. p. $< -10°$, probably 2*H*-heptafluoropropane, was obtained. The residue was fractionated through a 1′ column, to give 4H-*tridecafluoro*(*methyl*cyclo*hexane*) (7·9 g.), b. p. 85·1—86·3° (Found: C, 25·5; H, 0·5; F, 74·0%; *M*, 331. C_7HF_{13} requires C, 25·3; H, 0·3; F, 74·4%; *M*, 332). After removal of excess of toluene, the still residue afforded, by the usual isolation techniques, dibenzyl (7·2 g.), m. p. and mixed m. p. 52°.

The gaseous product was treated with potassium hydroxide (10 g.), potassium permanganate (20 g.), and water (40 c.c.) in a rocking autoclave for 18 hr. at 120°. The aqueous phase was reduced (sulphur dioxide), neutralised, and evaporated, and the residue extracted with alcohol. Potassium trifluoroacetate (2·8 g.) was obtained, identified after esterification and subsequent ammonolysis as trifluoroacetamide, m. p. and mixed m. p. 73° (Found: C, 21·2; H, 1·6. Calc. for $C_2H_2ONF_3$: C, 21·25; H, 1·8%), for which Swarts (*Bull. Acad. roy. Belg.*, 1922, **8**, 343) gave m. p. 74·8°. When the gaseous compound was shaken at 10—15° for 16 hr. with concentrated aqueous potassium hydroxide, fluoride ion (0·9 mol.) appeared in the aqueous phase.

(b) *With chlorine*. The fluorocarbon (38·2 g.; input rate 20 g./hr.) and chlorine (*ca.* 6 l./hr.) were allowed to react at 540—555°. The product was washed with ice-cold aqueous sodium hydroxide, then water, and was dried. A low-boiling product, b. p. 0°, probably 2-chloroheptafluoropropane, was given off during this process. Fractionation of the liquid residue afforded 4-chlorotridecafluoro(methyl*cyclo*hexane) (11·4 g.), b. p. 100·7—101·7°, n_D^{14} 1·315 (Found: C, 23·2; F, 67·8%; *M*, 364).

(c) *With bromine*. Bromine (25 g.), in a stream of nitrogen (5 l./hr.), and the fluorocarbon (54.9 g.; input rate 18 g./hr.), at 510°, gave two pure compounds, 2-bromoheptafluoropropane (10·1 g.), b. p. 15—16°, and 4-*bromotridecafluoro*(*methyl*cyclo*hexane*) (8·8 g.), b. p. 115·2—116·1° (Found: C, 20·2; F, 59·7%; *M*, 407. C_7BrF_{13} requires C, 20·45; F, 60·1%; *M*, 411).

(d) Passage of this fluorocarbon, or of perfluorodi*cyclo*hexyl or perfluoro(*iso*propyl*cyclo*-hexane), through the tube at 550—600° alone or mixed with one another or with perfluoro-(methyl*cyclo*hexane), gave, in all cases, mixed products from which no pure compounds could be isolated. Dilution of the fluorocarbon with nitrogen effected no improvement. A typical product had b. p. 25—130°, with no flat portions on the distillation curve.

4H-*Tridecafluoro*(*methyl*cyclo*hexane*) *from the* 4-*Chloro-analogue*.—4-Chlorotridecafluoro-(methyl*cyclo*hexane) (186 g.; obtained from *p*-chlorotoluene), in ether (100 c.c.), was added, during 90 min., to a stirred suspension of lithium aluminium hydride (12·5 g.) in ether (200 c.c.). The heat of reaction caused a gentle reflux, and, after the addition, the mixture was refluxed for 3 hr. further. Water was then added cautiously, followed by nitric acid until the precipitates had dissolved, and, after being separated, washed with water, dried ($MgSO_4$), and filtered, the organic layer was fractionally distilled. 4*H*-Tridecafluoro(methyl*cyclo*hexane) (73 g.), b. p. 86·6—88·0° (Found: C, 25·1; H, 0·6; F, 74·9%; *M*, 332), was obtained.

A sample of the chloro-compound made from *p*-chlorobenzotrifluoride, when treated likewise, gave a similar product (44%), b. p. 86·2—88·0° (Found: C, 25·5; H, 0·5; F, 74·0%).

Examination of the three samples of the hydrofluorocarbon by gas–liquid partition chromatography gave two peaks in each case. For the sample derived from the reaction of the fluorocarbon and toluene, the peaks had roughly equal heights. The samples derived ultimately from *p*-chlorotoluene and *p*-chlorobenzotrifluoride gave peaks in the same places, but in both cases the smaller one was only about ¼ of the height of that from the other sample, the larger peaks being almost identical in all cases.

Nonafluoro-4-trifluoromethylcyclohex-1-ene.—4-*H*-Tridecafluoro(methyl*cyclo*hexane) (24·0 g.) was boiled under reflux with potassium hydroxide (20 g.) in water (25 c.c.) for 5 hr. After being separated, washed with water, dried (P_2O_5), and filtered, the product was fractionated through a 1′ column. *Nonafluoro-4-trifluoromethylcyclohex-1-ene* (12·0 g.), b. p. 75·4—75·9°, n_D^{20} 1·293 (Found: C, 26·9; F, 72·6%; *M*, 312. C_7F_{12} requires C, 26·9; F, 73·1%; *M*, 312), was obtained. Each of the three samples of the hydrofluorocarbon gave a product with these properties. Gas-chromatographic examination revealed only a single identical peak in each case.

Addition of Halogen to this Olefin.—The olefin described above (1·53 g.) and bromine (0·25 c.c.) were sealed in a hard-glass tube and irradiated by an ultraviolet lamp for 16 hr. After being washed, dried (P_2O_5), and distilled, the product afforded 1 : 2-*dibromononafluoro-4-trifluoromethylcyclohexane* (1·32 g.), b. p. 156—159° (Found: C, 17·9. $C_7Br_2F_{12}$ requires C, 17·8%).

A similar reaction with chlorine gave 1 : 2-*dichlorononafluoro-4-trifluoromethylcyclohexane* (50%), b. p. 129—131° (Found: F, 58·9. $C_7Cl_2F_{12}$ requires F, 59·5%).

Oxidation of the Olefin.—Nonafluoro-4-trifluoromethyl*cyclo*hex-1-ene (30·0 g.), potassium permanganate (120 g.), and water (300 c.c.) were heated at 115° for 16 hr. in a rocking autoclave. Isolation by the usual technique (see earlier papers) gave an acidic solid, which, after being dried *in vacuo*, was recrystallised from dry benzene to give the very hygroscopic *perfluoro-(3-methyladipic) acid* (22·1 g.), m. p. 60—61° (Found: C, 24·5; H, 0·9; F, 55·3%; equiv., 172. $C_7H_2O_4F_{10}$ requires C, 24·7; H, 0·6; F, 55·9%; equiv., 170).

Derivatives of Heptafluoro-3-trifluoromethyladipic Acid.—With *S*-benzylthiuronium chloride in concentrated aqueous solution, the acid gave the *di-(S-benzylthiuronium) salt* (from water), m. p. 208° (Found: C, 41·5; H, 3·4; S, 9·7. $C_{23}H_{22}O_4N_4S_2F_{10}$ requires C, 41·1; H, 3·3; S, 9·5%).

The acid (11·0 g.), ethyl alcohol (*ca.* 20 c.c.), and commercial fluorosulphonic acid (1·0 c.c.) were refluxed together for 1 hr. The product was worked up as usual, and, since esterification appeared to be incomplete, it was re-treated as before. Isolation followed by distillation afforded the *diethyl ester* (8·0 g.), b. p. 112°/14 mm., n_D^{12} 1·361 (Found: C, 33·6; H, 2·5; F, 48·0. $C_{11}H_{10}O_4F_{10}$ requires C, 33·3; H, 2·5; F, 48·0%).

Ammonia gas was passed through a solution of the ester in ether. After 16 hr., the precipitate was filtered off and recrystallised from water to give *heptafluoro-3-trifluoromethyladipdiamide* (70%), m. p. 168—169° (Found: C, 24·6; H, 1·2: F, 56·2. $C_7H_4O_2N_2F_{10}$ requires C, 24·9; H, 1·2; F, 56·2%).

Acid derived from each of the three samples of olefin was subjected to these procedures. In each case, the product had the above characteristics, and, in the cases of the solids, no depressions were observed when mixed m. p.s were carried out.

1H : 4H-*Heptafluoro-2-trifluoromethylbutane.*—Heptafluoro-3-trifluoromethyladipic acid was titrated with aqueous potassium hydroxide to pH 5, and the solution obtained was evaporated to dryness. The resultant dipotassium salt (5·3 g.), after 4 hr. in refluxing ethylene glycol (8·0 c.c.), afforded 1H : 4H-*heptafluoro-2-trifluoromethylbutane* (1·7 g.), b. p. 63—65° (Found: C, 23·7; H, 0·8. $C_5H_2F_{10}$ requires C, 23·8; H, 0·8%).

Gas-chromatographic analysis of this compound revealed a single peak only.

Treatment of the compound (0·17 g.) with potassium hydroxide (0·2 g.), in water (0·2 c.c.), at 100° for 14 hr. in a small rocked bomb, effected the elimination of only 0·0036 g. of fluoride ion. When about a stoicheiometric proportion of potassium hydroxide in ethyl alcohol (*ca.* 2N) was used, for 20 min. at 100°, fluoride ion (approx. 2 mol.) was eliminated, but the product was unchanged starting material together with a complex high-boiling residue. After 20 min. at 100° with excess of alcoholic alkali, virtually all of the fluorine had been eliminated from the fluorohydrocarbon.

THE CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM, 15.

[*Received, February 2nd,* 1955.]