916. *The Reactions of Highly Fluorinated Organic Compounds. Part II.* Reactions of Perfluorodi*cyclo*hexyl and Perfluoro(*iso*propyl*cyclo*hexane).*

By G. B. Barlow and J. C. Tatlow.

Perfluorodi*cyclo*hexyl and chlorine or bromine at 600—650° give, principally, chloro- or bromo-undecafluoro*cyclo*hexane, respectively. With toluene at about 650° perfluorodi*cyclo*hexyl gives undecafluoro*cyclo*hexane and dibenzyl. Perfluoro(methyl*cyclo*hexane), perfluoro(ethyl*cyclo*hexane), and perfluoro-(1 : 2-di*cyclo*hexylethane) do not react in similar processes at these temperatures, whereas perfluoro(*iso*propyl*cyclo*hexane) gives undecafluoro*cyclo*hexane with toluene, and bromoundecafluoro*cyclo*hexane with bromine. It appears that, at 600—650°, C–C bonds between certain tertiary carbon atoms in fluorocarbon structures undergo homolysis, whereas C–C bonds involving primary and secondary carbon atoms split appreciably only at higher temperatures. Bromoundecafluoro*cyclo*hexane gives undecafluoro*cyclo*hexane with lithium aluminium hydride in ethereal solution.

SATURATED fluorocarbons have been extensively investigated in recent years [for summaries of fluorocarbon properties, see Grosse and Cady, *Ind. Eng. Chem.*, 1947, **39**, 367; Fowler *et al.*, *ibid.*, p. 375; Brice, " Fluorine Chemistry," Vol. I (ed., Simons), Academic Press Inc., New York, 1950, p. 423]; they are very stable substances and so far no examples have been reported of their participation in chemical reactions of the usual types.

Although the C–F bonds in fluorocarbons are resistant to chemical attack, it seemed possible that investigations of reactions at the C–C bonds might be more profitable. A few reactions of this type involving the simpler fluorocarbons have been investigated recently by Simons and his co-workers. For instance, hexafluoroethane reacts with chlorine or bromine at 900° to give chloro- and bromo-trifluoromethane respectively, octafluoropropane with bromine at 850° gives bromotrifluoromethane, and perfluoropentane and chlorine at 800° give a mixture of chlorotrifluoromethane, dichlorodifluoromethane, chloropentafluoroethane, and chlorononafluorobutane (Brice, Pearlson, and Simons, *J. Amer. Chem. Soc.*, 1949, **71**, 2499). From the reactions of hydrogen at about 800° with octafluoropropane, decafluorobutane, or mixed *cyclo*-C_6F_{12} isomers, fluoroform, difluoromethane, and pentafluoroethane are obtained (James, Pearlson, and Simons, *ibid.*, 1950, **72**, 1761); also pyrolysis of perfluoro-*n*-pentane on a platinum filament at 900—1300° gives a mixture of shorter-chain fluorocarbons (Rogers and Cady, *ibid.*, 1951, **73**, 3523).

In our investigations we hoped to effect cleavage of certain types of bonds preferentially, and thereby to avoid extensive breakdown of the structures. It was thought possible that bonds between carbon atoms at which chain-branching occurred might be broken most

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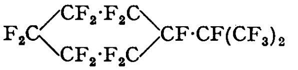
* Part I, *J.*, 1952, 1251. The sub-title of Part I should read : " The Preparation and Reactions of Some Perfluorinated Chloro*cyclo*hexanes."

readily. Accordingly, the first experiments were conducted upon perfluorodi*cyclo*hexyl (I) (Barbour, Barlow, and Tatlow, *J. Appl. Chem.*, 1952, **2**, 127), in which it was hoped to cleave the molecule between the two *cyclo*hexane rings.

(I) 

 (II)

When perfluorodi*cyclo*hexyl (I) and excess of chlorine were passed through a tube heated to about 650°, reaction occurred, and fractionation of the products gave an appreciable yield of chloroundecafluoro*cyclo*hexane identical with that prepared by fluorination of chlorobenzene (Tatlow and Worthington, *J.*, 1952, 1251). At temperatures much lower than 650° there was no reaction, whereas above 700° more extensive breakdown occurred giving short-chain fragments. Perfluorodi*cyclo*hexyl reacted similarly with bromine, the optimum temperature in this case being just below 600°, yielding bromoundecafluoro*cyclo*hexane (Brice and Simons, *J. Amer. Chem. Soc.*, 1951, **73**, 4016). The reactions of perfluorodi*cyclo*hexyl with iodine, with hydrogen, and with nitric oxide were also investigated. In the first case a fraction was obtained which may have been impure undecafluoro*cyclo*hexane, but the products from all three reactions were complex mixtures boiling over wide ranges, and from which pure components could not be isolated. It appeared that, in these cases, there was extensive cleavage of other C–C links under any conditions which resulted in the splitting of the central C–C bond.

Since only very slight dissociation of chlorine or bromine molecules into atoms occurs at 600—700°, it was thought that the reactions of perfluorodi*cyclo*hexyl with these reagents might be initiated by the splitting, presumably homolytic, of the fluorocarbon molecule. Strong evidence in support of this was obtained when the fluorocarbon (I) was treated with toluene at *ca.* 650°. Reaction of atoms or radicals with toluene molecules, with the abstraction of hydrogen atoms from the side chains and subsequent dimerisation of the residual, fairly stable benzyl radicals to give dibenzyl, has been used extensively by Szwarc; bond dissociation energies have been measured thus for various types of compounds (Szwarc, *Chem. Reviews*, 1950, **47**, 75; Szwarc and Sehon, *J. Chem. Phys.*, 1951, **19**, 656). Toluene, when passed through the reaction tube at 650—700°, was recovered unchanged, but a mixture of perfluorodi*cyclo*hexyl and excess of toluene, at 640—660°, gave undecafluoro*cyclo*hexane and dibenzyl. From the product of the reaction of the fluorocarbon with an equimolecular proportion of toluene there were isolated undecafluoro*cyclo*hexane and stilbene. The formation of the latter is to be expected, in the absence of an excess of toluene.

These reactions indicate that, if Szwarc's toluene carrier-gas technique is as applicable in fluorocarbon chemistry as it is to fission of other types of bonds, homolysis of the C–C bond between the rings of the perfluorodi*cyclo*hexyl molecule takes place at 600—650°, and apparently occurs more readily than does cleavage of the other bonds in the molecule. This suggests that, in general, some types at least of bonds between two tertiary carbon atoms are more readily broken than bonds involving primary and secondary carbon atoms.

Support for this hypothesis was found in the reactions of other fluorocarbons. Perfluoro-(methyl*cyclo*hexane), -(ethyl*cyclo*hexane), and -(1 : 2-di*cyclo*hexylethane) did not react with toluene at about 650°. However, the new fluorocarbon perfluoro(*iso*propyl*cyclo*hexane) (II) reacted with toluene in a similar process and, though a more complex mixture resulted than in the case of perfluorodi*cyclo*hexyl, some undecafluoro*cyclo*hexane was isolated, together with dibenzyl. There was also a gaseous product, probably heptafluoropropane. It appeared that the presence of traces of impurities in the toluene adversely affected this reaction. With bromine at 600°, perfluoro(*iso*propyl*cyclo*hexane) (II) gave bromoundecafluoro*cyclo*hexane and a low-boiling product, probably 2-bromoheptafluoropropane. The former product resembled chloroundecafluoro*cyclo*hexane in that with ethereal lithium aluminium hydride it gave undecafluoro*cyclo*hexane (see Part I, *loc. cit.*).

These reactions of fluorocarbons show that there are differences in stability between various types of C–C bonds in such compounds. Certain bonds between two tertiary carbon atoms break at *ca.* 650° and are more reactive than bonds between carbon atoms one or both of which are linked to fewer than three other carbon atoms (Simons and his co-workers, *locc. cit.*, used temperatures of 800—900° to split C–C bonds between primary or secondary carbon atoms of short-chain fluorocarbons).

It is hoped to extend the investigation to various types of fluorocarbons including those possessing quaternary carbon atoms. Already we have found that the bond between the tertiary carbons in perfluoro-(1-methyl-4-*iso*propyl*cyclo*hexane) is susceptible to this type of reaction, whereas that in perfluoro-(1 : 2-dimethyl*cyclo*hexane) is not. The reactivity of a bond obviously will depend to an appreciable extent on the structure of the molecule as a whole; in the latter fluorocarbon, for instance, both tertiary carbon atoms are in the same six-membered ring, rupture of which may well be difficult.

Reactions of C–C bonds in fluorocarbons are of considerable interest, not only as synthetic processes but also because they may well yield fundamental information upon fluorocarbon bond strengths and radical-type reactions. A number of fluorinated compounds can readily be prepared by the use of such reactions, and this would represent a novel use for the chemically stable fluorocarbons.

EXPERIMENTAL

Preparation of Fluorocarbons.—(a) *Perfluorodi*cyclo*hexyl.* Prepared as described by Barbour, Barlow, and Tatlow (*loc. cit.*), this compound, after purification by sublimation *in vacuo* and recrystallisation from light petroleum (b. p. 60—80°), had m. p. 75°, b. p. 179°.

(b) *Perfluoro*(iso*propyl*cyclo*hexane*). Cumene (65 g.; input rate 26·0 g./hr.) was passed into the cobalt trifluoride reactor, kept at 300—320°. After completion of the addition, the apparatus was swept out with nitrogen, and the product was poured into ice-water, separated, washed with water, and dried (Na_2CO_3). The combined products from four such experiments were fractionated through a 1′ column to give, after removal of decomposition products, *perfluoro*(iso*propyl*cyclo*hexane*) (320 g.), b. p. 124·3—125·2°/749 mm., n_D^{17} 1·302 (Found : F, 75·2%; *M*, 443. C_9F_{18} requires F, 76·0%; *M*, 450).

(c) *Perfluoro-(methyl*cyclo*hexane), -(ethyl*cyclo*hexane), and -(di*cyclo*hexylethane).* Perfluoroethyl*cyclo*hexane (cf. Haszeldine and Smith, *J.*, 1950, 2689), b. p. 101°, n_D^{17} 1·289 (Found : F, 75·9%; *M*, 403. Calc. for C_8F_{16} : F, 76·0%; *M*, 400), perfluoromethyl*cyclo*hexane (cf. Fowler *et al.*, *Ind. Eng. Chem.*, 1947, **39**, 292), b. p. 76·0°, n_D^{15} 1·285, and perfluoro-(1 : 2-di*cyclo*hexylethane) (cf. Barbour, Barlow, and Tatlow, *loc. cit.*), m. p. 71—72°, b. p. 208°, were prepared by the method described above (yields 54, 70, and 63%, respectively).

Apparatus for carrying out High-temperature Reactions of Fluorocarbons.—The apparatus comprised a vertical Pyrex-glass tube [70 cm. long (heated section); 2·5 cm. diam.] fitted with an electrical heating-jacket which gave a uniform temperature. Down the centre of the tube there was a coaxial glass tube in which a chromel–alumel thermocouple could be inserted, enabling temperature readings to be taken along the length of the heated section of the reaction tube. The free space in the latter was packed with short lengths of small-bore Pyrex tube. Reactants were fed into the top of the tube at constant rates and the products were collected in traps cooled by solid carbon dioxide–alcohol.

Toluene (input rates up to 50 g./hr.) when passed through this tube at temperatures of 700° or below was recovered unchanged; handling losses were small, and no solid residue remained after distillation.

*Reaction of Perfluorodi*cyclo*hexyl with Toluene.*—Perfluorodi*cyclo*hexyl (40·0 g.; input rate 25·0 g./hr.) and toluene (132 g.; input rate 82·5 g./hr.) were passed simultaneously into the reaction tube kept at 645—660°. The crude product from the trap was fractionated through a 1′ column to give, after removal of breakdown products, undecafluoro*cyclo*hexane (13·2 g.), b. p. 62·4—63·4°, m. p. and mixed m. p. 48° (Found : F, 74·8. Calc. for C_6HF_{11} : F, 74·1%); Tatlow and Worthington (*loc. cit.*) gave b. p. 63·0—63·5°, m. p. 46—48°.

Further distillation of the crude product, after removal of a small intermediate fraction, gave toluene (113 g.), b. p. 110—111°, then a trace of unchanged perfluorodi*cyclo*hexyl, m. p. 75°, leaving a solid residue, which after three recrystallisations from ethyl alcohol gave dibenzyl (6·7 g.), m. p. and mixed m. p. 53° (Found : C, 92·3; H, 7·5. Calc. for $C_{14}H_{14}$: C, 92·3; H, 7·7%).

An experiment with a toluene input rate of 9·15 g./hr. gave undecafluoro*cyclo*hexane (9·8 g.) and, from the still residue, after three recrystallisations from light petroleum (b. p. 60—80°), stilbene (1·0 g.), m. p. and mixed m. p. 123—124° (Found : C, 93·2; H, 6·9. Calc. for $C_{14}H_{12}$: C, 93·3; H, 6·7%), characterised as its dibromide, m. p. 235° (Found : C, 49·5; H, 3·5; Br, 46·8. Calc. for $C_{14}H_{12}Br_2$: C, 49·4; H, 3·6; Br, 47·0%), for which Wislicenus and Seeler (*Ber.*, 1895, **28**, 2693) recorded m. p. 237°.

*Reactions of Perfluorodi*cyclo*hexyl with Chlorine and Bromine* (*with* R. E. WORTHINGTON).—Perfluorodi*cyclo*hexyl (88·0 g.; input rate 25·0 g./hr.) was passed through the tube at 650°, together with a stream of chlorine (5 l./hr.). The crude product was washed with aqueous sodium hydroxide, then with water, and dried (P_2O_5). Distillation through a 1′ column gave breakdown products (17·0 g.), b. p. 50—78·4°, and then chloroundecafluoro*cyclo*hexane (39·7 g.), b. p. 78·4—78·6°, m. p. 28°, mixed m. p. with a specimen (m. p. 31°) prepared by Tatlow and Worthington (*loc. cit.*) 31° (Found : F, 66·3%; *M*, 323. Calc. for C_6ClF_{11} : F, 66·0%; *M*, 316·5).

At 585—595°, perfluorodi*cyclo*hexyl (40·0 g.; input rate 25·0 g./hr.) and bromine (13·5 g.) in nitrogen (4·5 l./hr.) gave decomposition products (2·5 g.), b. p. 89·5—91·8°, and bromoundecafluoro*cyclo*hexane (18·6 g.), b. p. 91·8—92·5°, n_D^{12} 1·3300 (Found : C, 20·0; F, 58·1%; *M*, 342. Calc. for C_6BrF_{11} : C, 20·0; F, 57·9%; *M*, 361). Brice and Simons (*loc. cit.*) recorded b. p. 90—92°, n_D^{20} 1·3205.

*Reactions of Perfluorodi*cyclo*hexyl with Hydrogen, Iodine, and Nitric Oxide.*—These reactions were carried out under the general conditions described above. From the reactions with hydrogen at 575° and above, complex mixtures, b. p. $<$82°, were obtained. There were indications of flats on the distillation curves at 61—62°, but a pure fraction could not be obtained. With iodine at 550—600°, perfluorodi*cyclo*hexyl gave a mixture of iodine-containing fragmentation products. Nitric oxide and perfluorodi*cyclo*hexyl at 580—600° gave complex mixtures (b. p. $<$100°) from which no pure compounds could be isolated.

*Reaction of Perfluoro(*iso*propyl*cyclo*hexane) with Toluene.*—The fluorocarbon (38·4 g.; input rate 21·0 g./hr.) and toluene (121 g.; 66·0 g./hr.) were passed into the tube at 650—670°. The crude product from the trap was fractionated as before. There was a low-boiling product (b. p. below −10°), probably heptafluoropropane, and after removal of breakdown products undecafluoro*cyclo*hexane was obtained. The fraction was not completely pure, there being a gradual rise in the b. p. during the distillation. The central cut (4·0 g.), b. p. 62—64°, was rather low-melting, but when cooled in ice left only a small residue of liquid. This was removed, and the residual solid sublimed to give the pure product, m. p. 48°. Further distillation of the original crude product gave toluene, unchanged fluorocarbon (*ca.* 1 g.), and a solid residue. After two recrystallisations from ethyl alcohol this afforded dibenzyl (7·4 g.), m. p. and mixed m. p. 53—54°.

*Reaction of Perfluoro(*iso*propyl*cyclo*hexane) with Bromine.*—At 590—600° this fluorocarbon (28·8 g.; input rate 16·1 g./hr.) with bromine (15·5 g.), introduced in a stream of nitrogen (4·5 l./hr.), gave a colourless liquid, probably 2-bromoheptafluoropropane (7·0 g.), b. p. 14·2—14·6°, and bromoundecafluoro*cyclo*hexane (9·6 g.), b. p. 92·0—92·3°, n_D^{17} 1·328 (Found : *M*, 366. Calc. for C_6BrF_{11} : *M*, 361), identical with the material mentioned previously.

*Treatment of Bromoundecafluoro*cyclo*hexane with Lithium Aluminium Hydride.*—The bromo-compound (36·1 g.) in dry ether (10 c.c.) was added slowly to a stirred suspension of lithium aluminium hydride (3·2 g.) in ether (50 c.c.), a spontaneous reaction occurring. After being refluxed for 1 hour the mixture was treated with water, then dilute sulphuric acid, and the ethereal layer was separated, washed, dried (P_2O_5), filtered, and fractionated in a 1′ column to give undecafluoro*cyclo*hexane (4·2 g.), b. p. 62—63°, m. p. 45—47°, identical with the other specimens.

*Attempted Reactions with Perfluoro-(methyl*cyclo*hexane), -(ethyl*cyclo*hexane), and -(1 : 2-di*cyclo*hexylethane).*—These fluorocarbons, if treated with toluene at or below 670°, were recovered unchanged, and no dibenzyl was found in the products. At 700° with perfluoro-(1 : 2-di*cyclo*hexylethane) there was evidence of slight reaction; a little low-boiling product but no dibenzyl was formed, most of the fluorocarbon being recovered unchanged.

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

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