*The Reactions of Highly Fluorinated Organic Compounds. Part VII.**
1 : 2-*Dichlorodecafluoro*cyclo*hexane and Derived Compounds.*

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1 : 2-Dichlorodecafluoro*cyclo*hexane, prepared by addition of chlorine to perfluoro*cyclo*hexene, gave, with lithium aluminium hydride, 1*H* : 2*H*-decafluoro*cyclo*hexane. This product, together with other isomers, has been obtained also by reduction of the dichlorodecafluoro*cyclo*hexane formed by reaction of *o*-dichlorobenzene with cobaltic fluoride. 1*H* : 2*H*-Decafluoro*cyclo*hexane, when treated with aqueous alkali, afforded 1*H*-nonafluoro*cyclo*hexene, which on oxidation gave perfluoroadipic acid.

CHLOROUNDECAFLUORO*cyclo*HEXANE and ethereal lithium aluminium hydride give undecafluoro*cyclo*hexane, which undergoes dehydrofluorination with concentrated aqueous alkali to perfluoro*cyclo*hexene (Tatlow and Worthington, Part I, *J.*, 1952, 1251). We now describe a similar series of reactions in which dichlorodecafluoro*cyclo*hexane was used as the starting material; in this case the reaction with the reducing agent proceeded most readily in the cold. It was found that the dichloro-compound obtained by direct fluorination of *o*-dichlorobenzene (*loc. cit.*), when treated with lithium aluminium hydride in diethyl ether, gave a product of wide boiling range. Two fractions of reasonably constant b. p., 78—79° and 90—92°, were isolated; analysis indicated that both products had a decafluoro*cyclo*hexane structure. Accordingly, 1 : 2-dichlorodecafluoro*cyclo*hexane was prepared by addition of chlorine to perfluoro*cyclo*hexene; as has been noted previously (*loc. cit.*), the physical properties of the dichloride made thus agreed with those of the fluorination product. When the authentic 1 : 2-dichloro-compound was treated with ethereal lithium aluminium hydride the only constant-boiling fraction obtained had b. p. 91—92°, and was identical with the highest-boiling isomer obtained from the other dichlorodecafluoro-compound; it is designated as 1*H* : 2*H*-decafluoro*cyclo*hexane (I). The decafluoro*cyclo*hexane having b. p. 78° is identical with a product obtained by low-temperature fluorination of benzene, and to which has been assigned the 1*H* : 3*H*-structure (Barbour, Mackenzie, Stacey, and Tatlow, *J. Appl. Chem.*, 1954, **4**, 347; Evans and Tatlow, *J.*, 1954, 3779). In addition to position isomers of the cyclic $C_6H_2F_{10}$ structure, various stereoisomeric forms are, of course, possible. Such stereoisomers may well be present in smaller proportions in the products of both these reductions. It appears that the dichlorodecafluoro*cyclo*hexane obtained by treatment of *o*-dichlorobenzene with cobaltic fluoride is not, as stated in Part I, the pure 1 : 2-dichloride. Though it is probably mainly this compound, it does contain at least one other positional isomer, chlorine being presumably eliminated and then reintroduced into the carbon skeleton in different positions during the fluorination. This would be in accord also with the isolation of trichlorononafluoro*cyclo*hexanes from the same fluorination reaction. Apparently, those physical properties of the mixture of isomeric dichlorodecafluoro*cyclo*hexanes, which are normally used for characterisation, are virtually indistinguishable from those of the pure 1 : 2-dichloro-isomer, and mixed m. p.s give no depression. Further, preliminary experiments indicate that a dichloride with similar characteristics may be obtained also by fluorination of *p*-dichlorobenzene. The physical properties of isomeric fluorocarbons often differ very little and the same effect can apply, obviously, to chlorofluorocarbons. In contrast, it seems that isomeric fluorohydrocarbons, at least in the *cyclo*hexane series, can exhibit appreciable differences in their b. p.s. This effect arises presumably because the different molecular arrangements give rise to variations in intermolecular hydrogen bonding.

The structure of 1*H* : 2*H*-decafluoro*cyclo*hexane (I) was confirmed by oxidation with neutral aqueous permanganate. Though the reaction was slow, cleavage of the molecule

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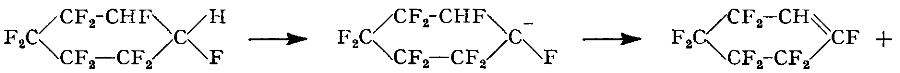
* Part VI, *J.*, 1954, 3779.

between the ·CHF· groups occurred with the formation, in poor yield, of perfluoroadipic acid, identified as the free acid and the dianilinium salt. This observation may help to explain the formation of fluoro-dibasic acids by the oxidation of polyfluoro*cyclo*hexane mixtures (Barbour, Mackenzie, Stacey, and Tatlow, *loc. cit.*, p. 341).

1*H* : 2*H*-Decafluoro*cyclo*hexane (I), like undecafluoro*cyclo*hexane, was attacked by concentrated aqueous alkali, one mol. only of hydrogen fluoride being eliminated, to give a nonafluoro*cyclo*hexene. The b. p. (64—65°) of this compound differed slightly from that (71—72°) of the hydro-olefin, which is a mixture of 3*H*- and 4*H*-nonafluoro*cyclo*hexene, obtained by the action of alkali on 1*H* : 3*H*-decafluoro*cyclo*hexane (*idem, ibid.*, p. 347). Oxidation of the olefin (b. p. 65°) afforded perfluoroadipic acid, identified as organic salts and as the diamide, no other acid being detected. This showed that the olefin was 1*H*-nonafluoro*cyclo*hex-1-ene (II). If any other constituent was present it could have been only in very small concentration. The likeliest impurity would be perfluoro*cyclo*hexa-1 : 3-diene which has a very similar b. p. (63—64°; Evans and Tatlow, *loc. cit.*). Thus, in the reaction of 1*H* : 2*H*-decafluoro*cyclo*hexane with aqueous alkali, only one mol. of hydrogen fluoride is eliminated, one of the ·CHF· groups providing the fluorine, as is also the case in the comparable reaction with 1*H* : 2*H*-hexafluoro*cyclo*butane (Buxton and Tatlow, *J.*, 1954, 1177).

It seems likely that the elimination of hydrogen fluoride from a fluorohydrocarbon with the formation of an unsaturated compound proceeds through an intermediate fluorocarbonium anion. If a hydrogen atom in a polyfluoride is sufficiently acidic to be removed by alkali, the residual anion could rearrange to give an olefin by elimination, as fluoride ion, of a fluorine atom from an adjacent carbon atom :


(I) (II)

Similar schemes have been postulated to explain the formation of olefins by pyrolysis of salts of fluoro-acids (Hals, Reid, and Smith, *J. Amer. Chem. Soc.*, 1951, **73**, 4054; LaZerte, Hals, Reid, and Smith, *ibid.*, 1953, **75**, 4525; Haszeldine, *J.*, 1952, 4259), and by the decompositions of fluorine-containing Grignard reagents (Haszeldine, *J.*, 1952, 3423; Henne and Francis, *J. Amer. Chem. Soc.*, 1951, **73**, 3518; 1953, **75**, 992; Tarrant and Warner, *ibid.*, 1954, **76**, 1624) and of perfluoroalkyl lithium compounds (Pierce, McBee, and Judd, *ibid.*, p. 474). The same type of mechanism may apply in the cases of some at least of the many examples of dehydrohalogenation (halogen being Cl, Br, or I) reactions of fluorohalogenohydrocarbons that have been reported.

1*H*-Nonafluoro*cyclo*hexene (II) gave a dibromo-addition product with bromine under ultra-violet irradiation. Treatment with aqueous alkali removed both bromine and fluorine from this saturated compound. That both halogens came from the ·CBrF· group was indicated by oxidation of the crude unsaturated mixture; perfluoroadipic acid was obtained.

Commercial fluorosulphonic acid is a very effective catalyst for the direct esterification of fluoro-carboxylic acids, or their anilinium salts, by aliphatic alcohols. Since the esters may be converted without isolation into acid amides this permits a rapid conversion of salts into amides for identification purposes (see also Barbour *et al.*, *loc. cit.*). Diethyl octafluoroadipate was made in this way from the acid and from the dianilinium salt. It was reduced by ethereal lithium aluminium hydride to the corresponding octafluorohexane-1 : 6-diol. This has been reported by McBee, Marzluff, and Pierce (*J. Amer. Chem. Soc.*, 1952, **74**, 444) and we confirmed their observation that it is not appreciably acidic.

EXPERIMENTAL

1 : 2-*Dichlorodecafluoro*cyclo*hexane from Perfluoro*cyclo*hexene.*—(*a*) The olefin (71·5 g.) was contained in a quartz vessel which carried a reflux condenser cooled by solid carbon dioxide. The vessel was irradiated by ultra-violet light and a very slow stream of chlorine was passed in fine bubbles through the olefin for 24 hr. Distillation of the product from two such reactions

gave, after removal of an intermediate fraction (9·0 g.), b. p. 53—108°, 1 : 2-dichlorodecafluoro*cyclo*hexane (144·0 g.), b. p. 108°, m. p. 34°.

(*b*) During 3 hr. the olefin (29·9 g.) was swept by a stream of chlorine into a vertical hard-glass tube heated to 560°, the products being condensed in traps cooled in solid carbon dioxide. After being washed with ice-cold aqueous sodium hydroxide, then with water, and dried (P_2O_5), the product was distilled to give unchanged olefin (11·2 g.) and 1 : 2-dichlorodecafluoro*cyclo*hexane (10·1 g.), b. p. 107·5—108·5°, m. p. 36°.

1H : 2H-*Decafluoro*cyclo*hexane from* 1 : 2-*Dichlorodecafluoro*cyclo*hexane*.—A liquid mixture of the dichloro-compound [120 g., prepared by method (*a*) above] and ether (10 c.c.) was added slowly to a suspension of lithium aluminium hydride (15 g.) in ether (400 c.c.) at 0°. The mixture was kept at 0° for 3 hr., mechanical stirring being continued throughout. It was then added slowly, with stirring, to water (400 c.c.) at 0°, nitric acid (250 c.c.; 2·5N) was added, and the ether layer was separated, washed, dried ($MgSO_4$), and filtered. Examination of the original aqueous layer showed that 95% of the chlorine, but no detectable fluorine, from the chlorofluorocarbon was present in the ionic form. Distillation of the organic layer through a 1′ column gave, after removal of ether and an intermediate fraction (20 g.; b. p. 35—91°, rising steadily), 1H : 2H-*decafluoro*cyclo*hexane* (47·2 g.), b. p. 91—92°/753 mm., m. p. 46°, n_D^{50} 1·291 (Found : C, 27·1; H, 0·9; F, 71·8. $C_6H_2F_{10}$ requires C, 27·3; H, 0·8; F, 71·9%).

*Decafluoro*cyclo*hexane from Dichlorodecafluoro*cyclo*hexane obtained from* o-*Dichlorobenzene*.—Dichlorodecafluoro*cyclo*hexane [187 g., obtained by passage of *o*-dichlorobenzene over cobaltic fluoride (Tatlow and Worthington, *loc. cit.*)] and ether (20 c.c.) were added at 0° during 3 hr. to lithium aluminium hydride (33·0 g.), in ether (800 c.c.), and the mixture was left for 2 hr. at 0°, mechanical stirring being applied throughout. After 16 hr. at 10—15°, water (330 c.c.) was added carefully, followed by concentrated nitric acid (100 c.c.), and the organic layer was separated, washed, dried ($MgSO_4$), and filtered. Distillation of the material through a 4′ column afforded : (i) b. p. 54—78° (29·3 g.); (ii) 1*H* : 3*H*-decafluoro*cyclo*hexane (8·5 g.), b. p. 78—79°, m. p. 34—36°, n_D^{46} 1·286 (Found : C, 27·7; H, 1·0; F, 72·3%); (iii) b. p. 79—90° (40·0 g.), mainly solid material; and (iv) 1*H* : 2*H*-decafluoro*cyclo*hexane (44·2 g.), b. p. 90—92°, m. p. 47°, n_D^{51} 1·290 (Found : C, 27·2; H, 1·1; F, 72·2%). This sample of the 1*H* : 2*H*-polyfluoride was less pure than that mentioned above; it was probably contaminated with other material having b. p. close to 90°.

Oxidation of 1H : 2H-*Decafluoro*cyclo*hexane*.—The fluorohydrocarbon (3·0 g.; b. p. 91°), potassium permanganate (12·0 g.), and water (40 c.c.) were heated at 95° for 16 hr. in a rocking autoclave. The residual mixture was decolorised with sulphur dioxide and filtered, the filtrate being acidified (H_2SO_4) and extracted exhaustively with ether. The extract was dried ($MgSO_4$), filtered, and evaporated, to leave a crude residue (0·9 g.) which, after two recrystallisations from dry benzene, afforded perfluoroadipic acid (0·49 g.), m. p. 134° (Found : C, 24·9; H, 0·9; F, 52·1. Calc. for $C_6H_2O_4F_8$: C, 24·8; H, 0·7; F, 52·4%). Treatment of the pure acid with aniline in ether followed by recrystallisation from acetone–chloroform gave the dianilinium salt (68%), m. p. 213° (Found : C, 45·6; H, 3·1; F, 31·7. Calc. for $C_{18}H_{16}O_4N_2F_8$: C, 45·4; H, 3·4; F, 31·9%). Tatlow and Worthington (*loc. cit.*) gave m. p. 133—134° and 212° for the acid and salt, respectively.

1H-*Nonafluoro*cyclo*hex*-1-*ene*.—1*H* : 2*H*-Decafluoro*cyclo*hexane (33·0 g., b. p. 91°) was refluxed for 11 hr. with potassium hydroxide (70 g.) in water (70 c.c.). Estimation of the fluoride ion in the aqueous phase showed that approximately 1 mol. of hydrogen fluoride had been removed. The organic layer was separated, dried (P_2O_5), and distilled through a 1′ column to give 1H-*nonafluoro*cyclo*hex*-1-*ene* (24·2 g.), b. p. 64—65°/750 mm., n_D^{12} 1·310 (Found : C, 29·5; H, 0·5; F, 69·0. C_6HF_9 requires C, 29·5; H, 0·4; F, 70·1%). The olefin (in 0·13M-solution in CCl_4) gave a C=C band in the infra-red at 1707 cm.$^{-1}$ [cf. decafluoro*cyclo*hexene and octafluoro*cyclo*hexa-1 : 4-diene which gave bands at 1734 cm.$^{-1}$ (Evans and Tatlow, *loc. cit.*)].

Oxidation of 1H-*Nonafluoro*cyclo*hexene*.—The olefin (2·55 g.), potassium permanganate (30·7 g.), and water (60 c.c.) were heated at 100° for 14 hr. in a rocking autoclave, to give, after isolation as described previously, crude perfluoroadipic acid. One portion was converted by the usual method into the dianilinium salt (66% based on olefin), m. p. 214° (Found : C, 45·0; H, 3·5; N, 6·0%; equiv., 238). A second part gave, by treatment in aqueous solution with *S*-benzyl*iso*thiuronium chloride followed by recrystallisation of the precipitate from water, the *bis*-(S-*benzyl*iso*thiuronium*) salt (72% based on olefin), m. p. 244—245° (Found : C, 42·4; H, 3·8; S, 10·4. $C_{22}H_{22}O_4N_4S_2F_8$ requires C, 42·4; H, 3·6; S, 10·3%).

The dianilinium salt was esterified with ethyl alcohol, fluorosulphonic acid being used as catalyst (2 hours' refluxing), and the crude ester which separated when the mixture was poured into water was extracted with ether, the solution was dried ($MgSO_4$), ammonia gas was bubbled through, and the resultant precipitate was recrystallised to give perfluoroadipic acid diamide (70%), m. p. 236—238°, for which McBee, Wiseman, and Bachman (*Ind. Eng. Chem.*, 1947, **39**, 415) gave m. p. 237°.

Addition of Bromine to the Cyclic Olefin.—1*H*-Nonafluoro*cyclo*hex-1-ene (4·81 g.) and bromine (3·15 g.) were sealed in a hard-glass tube and irradiated with ultra-violet light for 19 hr. The product was washed with aqueous sodium metabisulphite, separated, dried (P_2O_5), and distilled to give (i) recovered olefin (0·85 g.), b. p. 64—66°, n_D^5 1·316; and (ii) 1H-1 : 2-*dibromononafluoro*cyclo*hexane* (3·58 g.), b. p. 147—150° (88—90°/95 mm.), n_D^6 1·394 (Found : C, 18·1; H, 0·2. $C_6HBr_2F_9$ requires C, 17·8; H, 0·25%). This compound had decomposed slightly after being kept for several days and, if it was washed with water, small amounts of bromide ion were found in the aqueous phase.

The dibromononafluoro-compound (1·96 g.), sodium hydroxide (0·67 g.), and water (10 c.c.) were shaken together in a sealed tube at 10—15° for 42 hr. Estimations of the ionic halogens present in the aqueous phase showed that both bromine and fluorine (approx. 0·7 and 0·4 atomic proportion, respectively) had been removed. The organic layer (1·2 g.), potassium permanganate (15 g.), and water (50 c.c.) were heated at 105° for 17 hr. in a rocking autoclave. Isolation and precipitation as described before afforded bis-(*S*-benzyl*iso*thiuronium) perfluoroadipate (44% based on $C_6HBr_2F_9$), m. p. 244—245° (Found : C, 41·9; H, 3·6; N, 9·1%).

2 : 2 : 3 : 3 : 4 : 4 : 5 : 5-*Octafluorohexane*-1 : 6-*diol*.—Perfluoroadipic acid (10 g.), ethyl alcohol (15·0 c.c.), and commercial fluorosulphonic acid (1·0 c.c.) were mixed, a vigorous reaction occurring, and the mixture was refluxed for 45 min. It was then poured into water (50 c.c.) and the lower layer was extracted with ether. The extracts were washed, dried ($MgSO_4$), filtered, and evaporated, and the residue was distilled to give diethyl perfluoroadipate (9·0 g.), b. p. 102—103°/11 mm., n_D^{20} 1·355.

The di-ester (5·0 g.) in dry ether (10 c.c.) was added slowly to a mechanically-stirred suspension of lithium aluminium hydride (1·5 g.) in ether (20 c.c.) so that the solvent was kept steadily refluxing. After being stirred for a further hour, the mixture was cooled to 0°, and water was added dropwise, followed by 30% sulphuric acid (20 c.c.). The ether layer and ethereal extracts of the aqueous phase were dried ($MgSO_4$), filtered, and evaporated. The residue was recrystallised from chloroform to give the diol (3·0 g.), m. p. 67·5—68·5° (Found : C, 27·0; H, 2·4; F, 58·4. Calc. for $C_6H_6O_2F_8$: C, 27·5; H, 2·3; F, 58·0%). McBee, Marzluff, and Pierce (*loc. cit.*) recorded m. p. 68°. Considerable difficulty was experienced in getting accurate carbon analyses on this compound. Potentiometric titrations showed that the diol was not appreciably acidic.

Treatment with *p*-nitrobenzoyl chloride in pyridine at 100° for 1 hr. followed by isolation as usual gave, after recrystallisation from light petroleum (b. p. 60—80°) containing a little ethyl alcohol, the *di*-p-*nitrobenzoate* (72%), m. p. 105—106° (Found : C, 43·0; H, 2·1; F, 27·4. $C_{20}H_{12}O_8N_2F_8$ requires C, 42·9; H, 2·2; F, 27·1%).

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