*The Reactions of Highly Fluorinated Organic Compounds. Part V.** 1H : 2H-*Hexafluoro*cyclo*butane and* 1H-*Pentafluoro*cyclo*but*-1-*ene.*†

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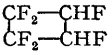
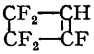
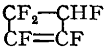
1 : 2-Dichlorohexafluoro*cyclo*butane gives, with lithium aluminium hydride, 1*H* : 2*H*-hexafluoro*cyclo*butane. Dehydrofluorination of this affords 1*H*-pentafluoro*cyclo*but-1-ene, as is shown by the formation of tetrafluorosuccinic acid upon oxidation.

This paper describes the treatment of 1 : 2-dichlorohexafluoro*cyclo*butane with lithium aluminium hydride, which was found to replace the chlorine of chloroperfluoro*cyclo*hexanes by hydrogen (Tatlow and Worthington, *J.*, 1952, 1251, and unpublished work). 1 : 2-Dichlorohexafluoro*cyclo*butane is readily made by heat-catalysed dimerisation of chlorotrifluoroethylene (Henne and Ruh, *J. Amer. Chem. Soc.*, 1947, **69**, 279; Harmon, U.S.P. 2,404,374; Buxton, Ingram, Smith, Stacey, and Tatlow, *J.*, 1952, 3830; Lacher, Tompkin, and Park, *J. Amer. Chem. Soc.*, 1952, **74**, 1693). Material made in this way has been shown to be mainly the *cis*-1 : 2-dichloride, and that from addition of chlorine to hexafluoro*cyclo*butene to be mainly the *trans*-isomer (Lacher, Büchler, and Park, *J. Chem. Phys.*, 1952, **20**, 1014).

Because it was thought that the boiling point of the corresponding dihydro-compound would be close to that of diethyl ether, the reaction of the dichloride with lithium aluminium hydride was first studied in di-*n*-butyl ether and in tetrahydrofuran. Though most of the chlorine was replaced, it was difficult to obtain a pure product if these ethers were used as solvents. In diethyl ether, however, a smooth reaction occurred, virtually all of the chlorine was eliminated, and the product, 1*H* : 2*H*-hexafluoro*cyclo*butane † (I) (b. p. 27°), could be separated from the solvent by fractional distillation. The reaction may proceed more readily in diethyl ether because of the greater solubility of lithium aluminium hydride in this solvent.


(I)


(II)


(III)

As with polyfluoro*cyclo*hexanes (Tatlow and Worthington, *loc. cit.*), the hexafluoro*cyclo*butane (I) was found to be susceptible to attack by concentrated aqueous potassium hydroxide. The product was a pentafluoro*cyclo*butene, as was confirmed by the amount of fluoride ion that appeared in the aqueous phase, corresponding to the elimination of one molecule of hydrogen fluoride. Addition of bromine across the double bond gave the corresponding dibromopentafluoro*cyclo*butane.

The olefin, of which a likely method of formation is the loss of fluoride ion from an intermediate carbonium anion resulting from separation of hydrogen under the influence of alkali, could have been either (II) or (III), depending upon whether, in the dehydrofluorination reaction, fluorine was eliminated from the $\cdot CF_2\cdot$ or the $\cdot CHF\cdot$ group flanking the $\cdot CHF\cdot$ function which provided the hydrogen. It is quite likely that such isomers would have very similar boiling points.

Oxidation of the olefin with aqueous potassium permanganate afforded only tetrafluorosuccinic acid, identified as the dianilinium salt (yield *ca.* 80%) and as the diamide. This strongly indicates that the olefin had the 1*H*-pentafluoro*cyclo*butene structure (II) and not the 3*H*-structure (III). It is possible that it contained a small proportion of (III) since the product (the unknown trifluorosuccinic acid) of the oxidation of this might be unstable, by analogy with other acids having fluorine atoms in the β-position and a hydrogen atom in the α-position relative to a carboxyl group (Henne and Zimmerschied, *J. Amer. Chem. Soc.*, 1947, **69**, 281; Buxton, Stacey, and Tatlow, *J.*, 1954, 366). However, in view of the

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† For this use of *H* to denote residual hydrogen atoms see *J.*, 1953, 5059.

volatility of the olefin, and of the fact that the optimum yield in the oxidation process may fall short of the theoretical, the identity of the olefin seems reasonably established.

Hence, in this particular dehydrofluorination reaction, hydrogen fluoride is eliminated preferentially from two adjacent •CHF• groups, the flanking $\cdot CF_2\cdot$ groups being more resistant to the removal of fluorine. It is hoped that studies upon other types of fluorohydrocarbons will reveal more about the general characteristics of this type of process.

EXPERIMENTAL

1H : 2H-*Hexafluoro*cyclo*butane*.—1 : 2-Dichlorohexafluoro*cyclo*butane [140 g.; b. p. 59° (made by dimerisation of chlorotrifluoroethylene)] was added continuously during 4 hr. to a mechanically stirred suspension of lithium aluminium hydride (30 g.) in diethyl ether (1000 c.c.), at *ca.* 10°, in an apparatus having a trap cooled by solid carbon dioxide–alcohol on the exit line, moisture being excluded throughout. After the addition, the mixture was refluxed for 3 hr. and was left at 10—15° for 16 hr. It was cooled in ice, and water was added very cautiously and then sulphuric acid, until the metallic hydroxides had dissolved. The ethereal layer, an ethereal extract of the aqueous phase, and the contents of the cold trap were combined and dried ($MgSO_4$ followed by P_2O_5). Care was taken during the whole operation to avoid, as far as possible, losses of volatile material. Analysis of the aqueous layer showed that 96% of the chlorine contained in the starting material was present in the ionic form. Distillation of the ethereal layer gave 1H : 2H-*hexafluoro*cyclo*butane* (36·7 g.), b. p. 26·6—27·0° (Found: F, 68·8%; *M*, 162. $C_4H_2F_6$ requires F, 69·5%; *M*, 164), and a fraction (34·5 g.), b. p. 27·0—33·5°, consisting of a mixture of this compound and ether, which was combined with similar material and re-fractionated to give more product.

Dehydrofluorination of the Dihydro-compound.—The above hexafluoro*cyclo*butane (20·0 g.) and a solution of potassium hydroxide (45 g.) in water (30 c.c.) were stirred together mechanically at 15° for 5½ hr. in an apparatus which included a trap cooled by solid carbon dioxide–alcohol. The mixture was cooled in ice-water, and water (20·0 c.c.) was added. Whilst still cold, the organic phase was separated, combined with the contents (*ca.* 1 c.c.) of the cold trap, and washed quickly with ice-cold water. Analysis of the aqueous phase for fluoride ion by the method of Belcher, Caldas, Clark, and Macdonald (*Mikrochim. Acta*, 1953, 283) showed that 17·6% of the fluorine present in the parent compound had been removed (required for elimination of one fluorine from $C_4H_2F_6$, 16·7%). The organic phase was distilled from phosphoric oxide to give 1H-*pentafluoro*cyclo*but*-1-*ene* (11·2 g.), b. p. 25—26° (Found: F, 66·5. C_4HF_5 requires F, 65·95%).

Addition of Bromine to the Cyclic Olefin.—The 1*H*-olefin (2·99 g.) and bromine (1·2 c.c.), in a quartz vessel carrying a reflux condenser cooled by solid carbon dioxide, were irradiated with ultra-violet light for 6½ hr. The mixture was washed with aqueous sodium thiosulphate, then with water, and was distilled from phosphoric oxide to give 1H-1 : 2-*dibromopentafluoro*cyclo*butane* (2·45 g.), b. p. 107—109° (Found: C, 16·1; H, 0·5; Br, 52·6; F, 31·1. $C_4HBr_2F_5$ requires C, 15·8; H, 0·3; Br, 52·6; F, 31·3%). When this product was warmed with aqueous alkali, both bromide and fluoride ions appeared in the aqueous phase.

Oxidation of the Cyclic Olefin.—The olefin (2·35 g.), potassium permanganate (15·0 g.), and water (50 c.c.) were sealed into a cooled autoclave which was then shaken at 75—80° for 12 hr. The solution was filtered, and the filtrate and washings were treated with sulphur dioxide, filtered again, acidified (H_2SO_4), and extracted exhaustively with ether. The extract was dried ($MgSO_4$), filtered, and evaporated, and the residue was dried at 80°/30 mm. The crude acidic product was dissolved in dry ether (30 c.c.), aniline (4·0 g.) in ether (30 c.c.) was added, and when precipitation was complete, the dianilinium tetrafluorosuccinate (4·84 g.), m. p. 223—224° (Found: equiv., 190), was filtered off. After two recrystallisations from ethyl alcohol–chloroform, the salt (recovery 64%) had m. p. 224—225° (Found: C, 50·8; H, 4·4; F, 20·3%; equiv., 190. Calc. for $C_{16}H_{16}O_4N_2F_4$: C, 51·1; H, 4·3; F, 20·2%; equiv., 188).

This salt (1·04 g.) and ethyl alcohol (4·0 c.c.), containing fluorosulphonic acid (0·5 c.c.), were refluxed together for 30 min. The solution was poured into ice-water, the lower layer was extracted with ether, the extracts were dried ($MgSO_4$) and filtered, and the volume was reduced to 25 c.c. Ammonia was passed through, and after 16 hr. at 10—15° the precipitate (0·44 g.) was filtered off and recrystallised from water to give tetrafluorosuccinamide (0·19 g.), m. p. 259° (Found: C, 25·3; H, 2·2; F, 40·5. Calc. for $C_4H_4O_2N_2F_4$: C, 25·5; H, 2·1; F, 40·4%). Buxton, Ingram, Smith, Stacey, and Tatlow (*loc. cit.*) report m. p. 224° for the aniline salt, and

Henne and Zimmer (*J. Amer. Chem. Soc.*, 1951, **73**, 1103) give m. p. 259·8—260·3° for the amide. An oxidation of the olefin in a sealed tube gave a similar result.

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