537. *The Reactions of Fluorocarbon Radicals. Part III. The Synthesis of Heptafluorobutyric Acid.*

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The interaction of heptafluoroiodopropane and acetylene yields 3 : 3 : 4 : 4 : 5 : 5 : 5-heptafluoro-1-iodopent-1-ene, which, on treatment with permanganate, gives heptafluorobutyric acid. Salts and derivatives of the acid are described, and the synthesis of long-chain fluoro- and fluorohalogeno-acids is discussed.

In Part I (Haszeldine, *J.*, 1949, 2856), the interaction of trifluoroiodomethane and tetrafluoroethylene was shown to yield compounds of general formula $CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I$, and several members of this series were briefly described. The isolation and reactions of individual members of this polymer series will be described in a later communication. The present communication describes the conversion of the compound where $n = 1$ (*i.e.*, C_3F_7I) into heptafluorobutyric acid, and illustrates the use of trifluoroiodomethane in synthetic organic fluorine chemistry.

The carbon–iodine bond in heptafluoroiodopropane splits homolytically when the compound is irradiated with ultra-violet light or heated, in a manner analogous to that shown for trifluoroiodomethane and pentafluoroiodoethane (Haszeldine and Emeléus, *Research*, 1948, **1**, 715). Under these conditions an addition–polymerisation reaction occurs with acetylene (cf. Haszeldine, *Nature*, 1950, **165**, 152) to give mainly the first member of the series $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}[CH{:}CH]_n{\cdot}I$:

$$C_3F_7I \longrightarrow C_3F_7{\cdot} + {\cdot}I$$
$$C_3F_7{\cdot} + CH{:}CH \longrightarrow C_3F_7CH{:}CH{\cdot}$$
$$C_3F_7CH{:}CH{\cdot} + C_3F_7I \longrightarrow C_3F_7CH{:}CHI + C_3F_7{\cdot}$$

It has been shown (Part II, Haszeldine, *J.*, in press; *Nature*, 1950, **166**, 192) that the double bond adjacent to a perfluoroalkyl group such as CF_3 or C_2F_5 is susceptible to permanganate oxidation; similarly, treatment of the heptafluoroiodobutene with alkaline potassium permanganate gives heptafluorobutyric acid in good yield. The latter resembles trifluoroacetic acid, since it is a strong acid (approaching a mineral acid) and has a low boiling point (121°) compared with the corresponding unhalogenated acid (163·5°); it has an odour similar to that of pentafluoropropionic acid (Haszeldine and Leedham, unpublished observations).

Heptafluorobutyric acid shows many of the reactions of a carboxylic acid, and has been characterised by the formation of the following crystalline salts of organic bases: piperazinium bisheptafluorobutyrate, nitron heptafluorobutyrate, and benzylamine heptafluorobutyrate. The acid forms well-defined metallic salts of which the sodium, potassium, mercuric, and silver compounds have been obtained pure. Silver heptafluorobutyrate is soluble in ether and benzene, as is silver perchlorate and silver trifluoroacetate (Swarts, *Bull. Soc. chim. Belg.*, 1939, **48**, 176). The mercuric salt, which is very soluble in water, gives a basic salt when heated in aqueous solution.

Ethyl heptafluorobutyrate was prepared in high yield by the standard procedure, and with ammonia gave the amide. Interaction of the amide and phosphoric oxide afforded the nitrile which is readily hydrolysed by aqueous alkali and which has a boiling point (1°) almost 120° below that of butyronitrile (b. p. 118°) (cf. $CF_3{\cdot}CN$, b. p. −64°, and $CH_3{\cdot}CN$, b. p. 82°).

Tetradecafluorobutyric anhydride and heptafluorobutyryl chloride were prepared in almost quantitative yield. The anhydride acetylated a phenol (β-naphthol) in the normal manner, although the product was readily hydrolysed. The acid chloride gave amides in the normal manner, the amide, anilide, and benzylamide being prepared. The characterisation of the perfluoro-carboxylic acids by the melting points of the amides must be carried out with care since the melting points of pentafluoropropionamide (95—96°) and heptafluorobutyramide (102—103°) are rather close, although appreciably different from that of trifluoroacetamide (75°).

Kauck and Diesslin (Abstracts, American Chemical Society 116th Meeting, Atlantic City, September, 1949, 9K) have described the synthesis of heptafluorobutyric acid by the electrochemical fluorination of butyric acid in liquid hydrogen fluoride, followed by hydrolysis of the acid fluoride so formed. Reid and Smith (*ibid.*, 9K) and Husted and Ahlbrecht (*ibid.*, 10K) give 119° as the boiling point of the fluoro-acid and state that the anhydride, acyl halide, salts, esters, amide, and anilide have been prepared.

Thus, two general methods appear to be available for the preparation of long-chain perfluoro-acids. The first by the electrochemical fluorination of the corresponding halogen-free acid, and the second by the use of members of the polymer series $CF_3{\cdot}[CF_2]_n{\cdot}I$, derived from trifluoroiodomethane and pentafluoroiodoethane and tetrafluoroethylene by application of the procedure described in the present communication:

$$\left.\begin{array}{l} CF_3I + C_2F_4 \longrightarrow CF_3{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I \\ C_2F_5I + C_2F_4 \longrightarrow CF_3{\cdot}CF_2{\cdot}[CF_2{\cdot}CF_2]_n{\cdot}I \end{array}\right\} CF_3{\cdot}[CF_3]_n{\cdot}I$$

$$CF_3{\cdot}[CF_2]_n{\cdot}I \xrightarrow{C_2H_2} CF_3{\cdot}[CF_2]_n{\cdot}CH{:}CHI \xrightarrow{KMnO_4} CF_3{\cdot}[CF_2]_n{\cdot}CO_2H$$

An alternative route lies through the reaction of the fluoro-iodides with ethylene, followed by dehydroiodination and oxidation (unpublished results):

$$CF_3{\cdot}[CF_2]_n{\cdot}I \xrightarrow{C_2H_4} CF_3{\cdot}[CF_2]_n{\cdot}CH_2{\cdot}CH_2I \longrightarrow CF_3{\cdot}[CF_2]_n{\cdot}CH{:}CH_2 \xrightarrow{KMnO_4} CF_3{\cdot}[CF_2]_n{\cdot}CO_2H$$

Yet another method utilises the fact that trifluoroiodomethane and similar fluoro-iodides can be converted into the Grignard reagents which, on carboxylation, yield the expected acid (unpublished observations):

$$CF_3{\cdot}[CF_2]_n{\cdot}I \xrightarrow{Mg} CF_3{\cdot}[CF_2]_n{\cdot}MgI \xrightarrow{CO_2} CF_3{\cdot}[CF_2]_n{\cdot}CO_2H$$

The interaction of trifluoroiodomethane, pentafluoroiodoethane, or of the fluoro-iodides $CF_3{\cdot}[CF_2]_n{\cdot}I$ with other fluoro-halogenoethylenes can yield compounds $CF_3{\cdot}[CF_2]_n{\cdot}[CX_2{\cdot}CY_2]{\cdot}I$ (X and Y = H, F, Cl, Br), and clearly application of the procedures described above will lead to the synthesis of a large number of fluorinated acids.

EXPERIMENTAL.

Preparation of Heptafluoroiodopropane.—This fluoro-iodide, b. p. 39·8°, was prepared by the interaction of trifluoroiodomethane and tetrafluoroethylene as described in Part I (and forthcoming communication).

Reaction of Heptafluoroiodopropane with Acetylene.—Heptafluoroiodopropane (3·0 g.) and acetylene (0·35 g.) were heated in a Pyrex tube of *ca.* 50 ml. capacity at 220° for 12—24 hours. Under these conditions a slight excess of acetylene was present at the end of reaction, no cuprene was formed, and the fluoro-iodide was quantitatively converted into an almost colourless liquid (3·2 g.) with b. p. >50°. The crude product (32·4 g.) from ten such experiments was distilled through an efficient fractionating column and gave 3 : 3 : 4 : 4 : 5 : 5 : 5-*heptafluoro*-1-*iodopent*-1-*ene* (29·2 g.), b. p. 101·5—103°/772 mm., n_D^{25} 1·381 (Found : I, 39·0; F, 41·0%; *M*, 316. $C_5H_2IF_7$ requires I, 39·4; F, 41·3%; *M*, 322).

Oxidation of 3 : 3 : 4 : 4 : 5 : 5 : 5-*Heptafluoro*-1-*iodopent*-1-*ene*.—The fluoroiodopentene (4·0 g.) was sealed in a Carius tube with potassium permanganate (8·0 g.), potassium hydroxide (4·0 g.), and water (40 ml.), and was shaken vigorously whilst heated to 85—90°. After 2 hours the products from two such tubes were combined and examined. Heptafluoropropane (0·1 g.; *M*, 170) was stored for further examination (see below). The aqueous solution was treated with sulphur dioxide, acidified with sulphuric acid, and extracted with ether. After the ether had been removed through a Vigreux column, the residual acid was neutralised to bromothymol-blue with potassium hydroxide, and the solution evaporated to dryness. The solid obtained by extraction with hot absolute alcohol, followed by removal of the alcohol, was cooled and treated with concentrated sulphuric acid. Distillation through a short column gave heptafluorobutyric acid (2·65 g., 51%).

In two further experiments a total of 32 g. of the fluoroiodopentene was oxidised by the addition of solid potassium permanganate (30 g.), portionwise during 2 hours, to the fluoro-iodide (16 g.), potassium hydroxide (4 g.), and water (40 ml.) in a flask fitted with reflux condenser, and shaken vigorously in a vibro-shaker. Three further portions of potassium hydroxide (4 g.) and water (40 ml.) were added during the reaction. The reaction temperature (thermometer in the liquid) was kept at 60°. The volatile products of reaction were condensed in a trap cooled by liquid air. Heptafluorobutyric acid (13·5 g., 63%) was isolated from the reaction product as described above. The total fluoro-acid prepared (16·15 g.) was distilled through a 15-plate column, to yield pure heptafluorobutyric acid (Found : C, 22·2; H, 0·7%; equiv., 213·8. Calc. for $C_4HO_2F_7$: C, 22·4; H, 0·5%; equiv., 214·0).

Properties of Heptafluorobutyric Acid.—Heptafluorobutyric acid is a colourless liquid, b. p. 120·8—121·0°, n_D^{16} 1·295, which fumes in air and is soluble in water, ethanol, acetone, ether, benzene, and carbon tetrachloride.

The volatile product of the oxidation was heptafluoropropane (1·2 g., 7%) (Found : *M*, 170. Calc. for C_3HF_7 : *M*, 170), b. p. −17°. Brice, Pearlson, and Simons (*J. Amer. Chem. Soc.*, 1946, **68**, 968) report b. p. −21°. After combination with the material obtained earlier (1·3 g. total), it was brominated thermally by passage of a mixture with excess of bromine vapour through a 45-cm. Pyrex tube, packed with short lengths of Pyrex tubing, at 620°. The product was washed with dilute alkali, fractionated *in vacuo*, and shown to be bromoheptafluoropropane (93% yield) (Found : C, 14·2%; *M*, 249. Calc. for C_3BrF_7 : C, 14·45%; *M*, 249), b. p. 12°. Brice, Pearlson, and Simons (*loc. cit.*) report b. p. 11—12°.

Reactions and Derivatives of Heptafluorobutyric Acid.—Piperazine (0·1 g.) was dissolved in the minimum amount of water and added to heptafluorobutyric acid (0·4 g.). Ether was added and the solid was removed by filtration and recrystallised from ethanol, to yield *piperazinium bisheptafluorobutyrate* (0·3 g.), m. p. 247° (decomp.) (Fisher hot plate) (Found : C, 28·3; H, 2·6; N, 5·3. $C_{12}H_{12}O_4N_2F_{14}$ requires C, 28·0; H, 2·3; N, 5·45%).

Benzylamine heptafluorobutyrate (0·15 g.), m. p. 100—102°, was prepared from benzylamine (0·1 g.) and heptafluorobutyric acid (0·2 g.) in ethereal solution and was recrystallised from benzene (Found : C, 41·7; H, 3·1. $C_{11}H_{10}O_2NF_7$ requires C, 41·1; H, 3·1%).

A freshly prepared solution (6%) of nitron in aqueous acetic acid (10%) was slowly added to a solution of heptafluorobutyric acid (0·1 g.) in water; the precipitate was removed by filtration and recrystallised several times from aqueous ethanol, to give *nitron heptafluorobutyrate* (Found : N, 10·5. $C_{24}H_{17}O_2N_4F_7$ requires N, 10·65%).

Mercuric oxide dissolved in a slight excess of heptafluorobutyric acid (0·5 g.) during 48 hours, giving a viscous solution which, when left in a vacuum-desiccator for 2 weeks, yielded *mercuric heptafluorobutyrate* (Found : C, 15·3. $C_8O_4F_{14}Hg$ requires C, 15·3%), a white solid, very soluble in water in which it is appreciably hydrolysed. When heated in aqueous solution it yielded a basic salt.

Heptafluorobutyric acid (3·0 g.) was kept at room temperature for 12 hours in a 10% excess of ethyl alcohol and concentrated sulphuric acid (0·2 ml.), then heated under reflux for 3 hours. Ice-water was added and the ester layer taken into a vacuum system where it was dried. When removed from the system and distilled, *ethyl heptafluorobutyrate* (3·01 g., 88%) (Found : C, 30·2; H, 2·6. $C_6H_5O_2F_7$ requires C, 29·75; H, 2·05%) had b. p. 94·5—95°, n_D^{25} 1·301, n_D^{15} 1·306.

A solution of ethyl heptafluorobutyrate (2·80 g.) in anhydrous ether was cooled in ice and saturated with dry ammonia. Evaporation at room temperature, and recrystallisation of the residual solid from aqueous ethanol or chloroform, followed by sublimation at 80°/760 mm., gave *heptafluorobutyramide*, m. p. 102—103° (2·20 g., 89%) (Found : C, 22·6; H, 1·1; N, 6·6. $C_4H_2ONF_7$ requires C, 22·5; H, 0·9; N, 6·6%).

The amide (2·10 g.) was mixed with a large excess of phosphoric oxide and carefully heated. The volatile products were collected in a trap cooled in liquid air and transferred to the vacuum system. Fractionation gave *heptafluorobutyronitrile* (1·71 g., 89%) (Found : N, 7·4%; *M*, 195. C_4NF_7 requires N, 7·2%; *M*, 195), b. p. 1°/757 mm.

Heptafluorobutyronitrile (1·5 g.) was readily hydrolysed by aqueous potassium hydroxide, and evaporation and purification by extraction with absolute ethanol gave *potassium heptafluorobutyrate* (1·7 g.) (Found : K, 15·5. $C_4O_2F_7K$ requires K, 15·5%). The potassium salt (1·6 g.) was converted into *silver heptafluorobutyrate* (1·8 g.) by dissolution in water, addition of excess of 50% silver nitrate, extraction with ether, evaporation of the ether, and drying *in vacuo* (Found : Ag, 33·5. $C_4O_2F_7Ag$ requires Ag, 33·6%).

Heptafluorobutyric acid (2·0 g.), heated with excess of phosphoric oxide, gave *tetradecafluorobutyric anhydride* (1·8 g., 94%) [Found : *M* (Regnault bulb), 410; equiv., 204·8. $C_8O_3F_{14}$ requires *M*, 410;

equiv., 205·0], b. p. 108°, $n_D^{15.5}$ 1·287, n_D^{25} 1·282. The molecular weight of the anhydride is normal and indicates that it is not associated in the vapour state.

Tetradecafluorobutyric anhydride (0·2 g.) was added to β-naphthol (0·06 g.) and anhydrous sodium heptafluorobutyrate (0·1 g.) in a small tube which was sealed and heated at 100° for 20 minutes. The clear liquid crystallised on cooling and, after removal of excess of anhydride and acid by evacuation, was extracted with dry light petroleum. Evaporation and sublimation of the residual solid gave *β-naphthyl heptafluorobutyrate*, (0·1 g.), m. p. 58°. Hydrolysis with sodium hydroxide and back-titration with hydrochloric acid (cf. Bourne, Tatlow, and Tatlow, *J.*, 1950, 1367) gave the heptafluorobutyryl content (Found: C_3F_7·CO, 57·5. $C_{14}H_7O_2F_7$ requires C_3F_7·CO, 57·9%).

Heptafluorobutyric acid (2·0 g.) was gently heated with excess of phosphoric pentachloride in a small flask to which was attached a fractionating column. The temperature was slowly raised until *heptafluorobutyryl chloride* (2·05 g., 97%) was obtained (Found: C, 20·6; Cl, 15·1%; *M*, 231. C_4OClF_7 requires C, 20·6; Cl, 15·3%; *M*, 232·5), b. p. 39°, n_D^{15} 1·291. With ammonia, heptafluorobutyryl chloride gave heptafluorobutyramide.

Heptafluorobutyryl chloride (0·2 g.) was added to excess of aniline in benzene (2 ml.). After filtration, the benzene solution was washed with water and evaporated to dryness at room temperature. The residual solid was purified by sublimation at 80°/760 mm., followed by recrystallisation from aqueous ethanol. *Heptafluorobutyranilide* (0·1 g.) had m. p. 92—93° (Found: C, 42·0; H, 2·5. $C_{10}H_6ONF_7$ requires C, 41·5; H, 2·1%).

By the procedure described above, excess of benzylamine yielded N-*benzylheptafluorobutyramide* (0·1 g., from 0·2 g. of chloride) (Found: N, 4·3; F, 43·3. $C_{11}H_8ONF_7$ requires N, 4·6; F, 43·9%), m. p. 55—56°, sublimes 80°/760 mm.

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