817. *The Reactions of Metallic Salts of Acids with Halogens. Part III.* Some Reactions of Salts of Fluorohalogenoacetates† and of Perfluoro-acids.*

By R. N. HASZELDINE.

Reaction of silver salts of fluorohalogeno-acids † with chlorine, bromine, or iodine constitutes a general method for the synthesis of fluorohalogenohydrocarbons, and is exemplified by the preparation of the new compounds $CHClIF$, $CHBrIF$, $CClBr_2F$, CCl_2BrF, CCl_2IF, $CClBrF_2$, and $CClIF_2$. The stability of the silver salts of incompletely halogenated fluoro-acids and of fluorohalogenomethanes is considered. The silver salt reaction applied to the perfluoroalkanecarboxylic acids yields a series of perfluoroalkyl chlorides, bromides, and iodides, $CF_3{\cdot}[CF_2]_n{\cdot}X$ (X = Cl, Br, or I; n = 1—6). The sodium salts of the perfluoro-acids decompose when heated, giving high yields of the perfluoroalk-1-enes, and a mechanism for this general reaction is advanced. Conversion of chlorotrifluoroethylene into bromotrifluoroethylene is described.

SILVER TRIFLUOROACETATE with an excess of chlorine, bromine, or iodine gives high yields of the trifluoromethyl halide (Part I, *J.*, 1951, 584):

$$CF_3{\cdot}CO_2Ag + X_2 \longrightarrow CF_3X + CO_2 + AgX$$

The present communication (cf. *Nature*, 1950, **166**, 192; 1951, **168**, 1028; Abs. 75th Anniversary Meeting, Amer. Chem. Soc., New York, September, 1951) shows that the method is general, since the silver salts of the fluorohalogenoacetic acids, $CHXF{\cdot}CO_2H$ (X = H, Cl, Br, or I), $CF_2Y{\cdot}CO_2H$ (Y = H, Cl, or Br), $CCl_2F{\cdot}CO_2H$, and $CClBrF{\cdot}CO_2H$, produce the compounds shown in Table 1 when treated with the appropriate halogen (new compounds marked *).

TABLE 1.

CH_2ClF	CH_2BrF	CH_2IF	$CHCl_2F$	$CHClBrF$	$CHClIF$*	$CHBr_2F$	$CHBrIF$*	CHI_2F
$CHClF_2$	$CHBrF_2$	$CHIF_2$						
$CClBr_2F$*	CCl_2BrF*	CCl_3F	CCl_2IF*	CBr_2F_2	CCl_2F_2	$CClBrF_2$	$CClIF_2$*	

The temperature required for iodination is low when Y and Z in $CYZF{\cdot}CO_2Ag$ are strongly electronegative (*e.g.*, F), but increases when Y and Z = H, etc., until decarboxylation with simultaneous iodination is accompanied by thermal decomposition of the silver salt. The nature of Y and Z also affects the yield of the iodohalogenomethane. Thus, when Y = F, the yields fall off markedly for change of Z, in the order $F > Cl > Br$. This is attributed to the weakening of the carbon–iodine bond in $CZIF_2$ by steric effects as well as by the decrease in negativity of Z. The steric effect becomes more apparent as Y increases in size, and yields of $CZBrIF$ are low even when Z = H.

---

* Part II, *J.*, 1952, 993.

† In the sense used here, " halogen " excludes fluorine.

If the silver salt reaction involves a free-radical mechanism:

$$CYZF\cdot CO_2Ag \xrightarrow{X_2} CYZF\cdot CO_2X \longrightarrow CYZF\cdot + CO_2 + X\cdot \qquad CYZF\cdot \xrightarrow{X_2} CXYZF$$

then the ease of formation and reactivity of the $CYZF\cdot$ radical will be important in determining yields. Evidence to be presented in another paper shows that the order of radical reactivities is CBr_2F, CCl_2F, $CClF_2$, $CHClF < CHF_2$, CF_3, C_2F_5, etc. In this connection it may be noted that the $CHClF$, CCl_2F, and $CClF_2$ radicals derived from the corresponding iodides (Table 1) are substantially inert to glass and give high yields of the dimers $C_2H_2Cl_2F_2$, $C_2Cl_4F_2$, and $C_2Cl_2F_4$, whereas the CHF_2 radical undergoes some dimerisation but also gives silicon tetrafluoride and carbon dioxide. Under comparable conditions the CF_3 radical attacks glass readily to given silicon tetrafluoride and carbon monoxide and dioxide, and only small amounts of hexafluoroethane (*J.*, 1949, 2948; 1950, 3041).

Improved routes to some of the acids have been developed. Thus, Swarts's method for bromofluoroacetic acid (*Bull. Acad. roy. Belg.*, 1899, **37**, 357; *Zentr.* 1899, II, 281; see Experimental) has been replaced by the synthesis:

$$CF_2{:}CClF \xrightarrow{HCl} CClF_2\cdot CHClF \xrightarrow{Zn-EtOH} CF_2{:}CHF \xrightarrow{Br_2} CBrF_2\cdot CHBrF$$

$$CBrF_2\cdot CHBrF \xrightarrow[EtOH]{KOH-} CF_2{:}CBrF \xrightarrow{EtO^-} EtO\cdot CF_2\cdot CHBrF \xrightarrow{H^+}$$

$$CHBrF\cdot CO_2Et \longrightarrow CHBrF\cdot CO_2H$$

Chlorotrifluoroethylene is readily converted into bromotrifluoroethylene by the route shown. The ready base-catalysed addition of ethanol to the bromo-olefin again reveals the susceptibility of a polyfluoro-olefin to nucleophilic attack. The direction of addition accords with that of hydrogen chloride to give 1-bromo-2-chloro-1 : 2 : 2-trifluoroethane. The fluorobromo-ether is isomeric with that ($CBrF_2\cdot CHF\cdot OEt$) obtained by Swarts (see "Organic Reactions," John Wiley, New York, 1944, Vol. II, p. 87) from 1 : 2-dibromo-1 : 2 : 2-trifluoroethane, and thus shows that Swarts's ether arose by direct replacement of bromine by ethoxide rather than by the alternative dehydrohalogenation route:

$$CBrF_2\cdot CHBrF \xrightarrow{NaOEt} CF_2{:}CBrF \xrightarrow{EtO^-} EtO\cdot CF_2\cdot CHBrF$$

The marked lability of fluorine atoms adjacent to an ether link was noted and applied by Swarts, and is further exemplified by the acid hydrolysis of the bromofluoro-ether to ethyl bromofluoroacetate.

Bromofluoroacetic acid was also used to synthesise bromochlorofluoroacetic acid:

$$CHBrF\cdot CO_2H \longrightarrow CHBrF\cdot COCl \xrightarrow[light]{Cl_2} CClBrF\cdot COCl \longrightarrow CClBrF\cdot CO_2H$$

Dichlorofluoroacetic acid was similarly prepared from chlorofluoroacetic acid (see Experimental).

The silver salts of chloro- and bromo-fluoroacetic acid and of chlorodifluoroacetic acid are unstable to water. The first two are quantitatively converted into glyoxylic acid and its silver salt, halide, and fluoride; the third yields oxalic acid, chloride, and fluoride. The most probable reaction is formation of a $CHF\cdot OH$ or $CF_2\cdot OH$ group which in an aqueous medium is unstable (*Nature*, 1951, **168**, 1028) and loses hydrogen fluoride:

$$CHBrF\cdot CO_2Ag \xrightarrow{H_2O} Br^- + HO\cdot CHF\cdot CO_2Ag \xrightarrow{-HF} CHO\cdot CO_2Ag \xrightarrow[-HF]{Br^-} CHO\cdot CO_2H + AgBr$$

$$CClF_2\cdot CO_2Ag \xrightarrow{H_2O} Cl^- + HO\cdot CF_2\cdot CO_2Ag \xrightarrow{-HF} F\cdot CO\cdot CO_2Ag \xrightarrow[-HF]{Cl^-} (CO_2H)_2 + AgCl$$

Fluorohalogenomethanes which contain one hydrogen atom (*e.g.*, $CHClF$, CHI_2F) are decomposed completely by alcoholic potassium hydroxide to halide and formate; some of those which are hydrogen-free (*e.g.*, CCl_2IF, $CClBr_2F$) are completely decomposed to halide and carbonate. Other polyhalogenomethanes ($CClIF_2$ and $CHIF_2$) give the compounds in which iodine has been replaced by hydrogen, as well as being decomposed to halide and carbonate, whereas the perfluoroalkyl iodides (*e.g.*, C_3F_7I) give the corresponding hydrogeno-compound in high yield. These observations suggest that in the fluorohalogenomethane series two mechanisms can operate : (*a*) nucleophilic attack on carbon, *e.g.*,

$$\mathrm{OH^-} \overset{\curvearrowright}{+} \mathrm{CHClF}\overset{\curvearrowright}{—}\mathrm{I} \longrightarrow \mathrm{HO{\cdot}CHClF}\ (+\mathrm{I^-}) \xrightarrow{-\mathrm{HF}} \mathrm{H{\cdot}COCl} \xrightarrow{\mathrm{KOH}} \mathrm{H{\cdot}CO_2K}$$

which predominates when the compound contains hydrogen, *i.e.*, resembles an alkyl halide; and (*b*) nucleophilic attack on iodine or bromine, *e.g.*,

$$\mathrm{OH^-} \overset{\curvearrowright}{+} \mathrm{I}\overset{\curvearrowright}{—}\mathrm{CClF_2} \longrightarrow \mathrm{HOI} + \mathrm{CClF_2^-} \xrightarrow{\mathrm{Solvent}} \mathrm{CHClF_2}$$

It appears that (*b*) only becomes important when two or more fluorine atoms are present, since chlorodifluoroiodomethane and difluoroiodomethane (where chlorodifluoromethane and difluoromethane are stable to bases) give carbonate and halide and only low yields of the hydrogeno-compounds. Thus either the intermediate ions ($\mathrm{CClF_2^-}$, $\mathrm{CHF_2^-}$) are unstable, or carbonate is formed *via* (*a*) :

$$\mathrm{OH^-} \overset{\curvearrowright}{+} \mathrm{CClF_2}\overset{\curvearrowright}{—}\mathrm{I} \longrightarrow \mathrm{HO{\cdot}CClF_2}\ (+\ \mathrm{I^-}) \xleftarrow{-\mathrm{HF}} \mathrm{F{\cdot}COCl} \xrightarrow{\mathrm{KOH}} \mathrm{F^-} + \mathrm{CO_3^{=}}$$

Increase in the positive character of the iodine or bromine atoms will facilitate (*b*), and the yield of the hydrogeno-compound is at a maximum with the perfluoroalkyl iodides.

The formation of the ether $\mathrm{CF_3{\cdot}CHF{\cdot}CF_2{\cdot}OEt}$ during hydrolysis of heptafluoroiodopropane is in accord with the intermediate formation of the $\mathrm{C_3F_7^-}$ ion :

$$\mathrm{OH^-} \overset{\curvearrowright}{+} \mathrm{I}\overset{\curvearrowright}{—}\mathrm{CF_2{\cdot}CF_2{\cdot}CF_3} \longrightarrow \mathrm{HOI} + \mathrm{C_3F_7^-}$$

$$\mathrm{F}\overset{\curvearrowleft}{—}\mathrm{CF(CF_3)}\overset{\curvearrowleft}{—}\mathrm{CF_2^-} \longrightarrow \mathrm{F^-} + \mathrm{C_3F_6} \xrightarrow{\mathrm{EtO^-}} \mathrm{CF_3{\cdot}CHF{\cdot}CF_2{\cdot}OEt}$$

For other evidence for the decomposition of fluorocarbanions into olefins see *Nature*, 1951, **168**, 1028, *J.*, 1952, 3423, and below.

The silver salt reaction, applied to the higher perfluoro-acids, $\mathrm{CF_3{\cdot}[CF_2]_{\mathit{n}}{\cdot}CO_2H}$, where $n = 1—6$, gives the corresponding halides, $\mathrm{CF_3{\cdot}[CF_2]_{\mathit{n}}{\cdot}X}$, in excellent yield. The compounds where X = Cl or Br are inert, like chloro- or bromo-trifluoromethane; those where X = I undergo free-radical reactions of the type described earlier for trifluoroiodomethane, but have the advantage that they can be manipulated in conventional apparatus.

Silver trifluoroacetate reacts with halogens *via* the intermediate $\mathrm{CF_3{\cdot}CO_2X}$ (Part II, *loc. cit.*). The reactions of phosphorus, sulphur, or mercury with silver trifluoroacetate were investigated with the object of preparing perfluoroalkyl derivatives (*J.*, 1949, 2953; 1952, 2198, 2549, 3552) without the intermediate formation of the fluoro-iodide :

$$m\mathrm{CF_3{\cdot}CO_2Ag} + 2\mathrm{M} \longrightarrow \mathrm{(CF_3{\cdot}CO_2)_{\mathit{m}}M} + \mathrm{Ag_{\mathit{m}}M}$$
$$\mathrm{(CF_3{\cdot}CO_2)_{\mathit{m}}M} \longrightarrow \mathrm{(CF_3)_{\mathit{m}}M} + m\mathrm{CO_2}$$

The perfluoroalkyl derivatives were not obtained. Phosphorus gave silver phosphide but only a trace of carbon dioxide, and the product was trifluoroacetic anhydride, which was also formed, with sulphur dioxide, when the silver salt was heated with sulphur :

$$4\mathrm{CF_3{\cdot}CO_2Ag} + 3\mathrm{S} \longrightarrow 2\mathrm{Ag_2S} + 2\mathrm{(CF_3{\cdot}CO)_2O} + \mathrm{SO_2}$$

Attempts to prepare trifluoromethyl arsenicals and phosphines by the interaction of silver trifluoroacetate and arsenic or phosphorus iodides, *i.e.*, to produce trifluoroiodomethane *in situ*, were unsuccessful.

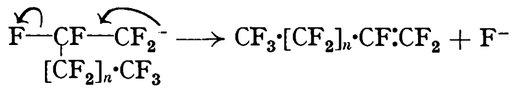
An alternative but less convenient route to trifluoroiodomethane from trifluoroacetic acid is to convert the latter into the anhydride which, with an excess of iodine, yields the fluoro-iodide, carbon dioxide, and carbon monoxide, probably by C–O fission :

$$\mathrm{(CF_3{\cdot}CO)_2O} + \mathrm{I_2} \longrightarrow \mathrm{CF_3{\cdot}CO_2I} + \mathrm{CF_3{\cdot}COI}$$

followed by the known decarboxylation and decarbonylation reactions of iodine trifluoroacetate and trifluoroacetyl iodide (Part I). Bromine or chlorine failed to convert trifluoroacetyl chloride into bromo- or chloro-trifluoromethane.

Sodium or potassium trifluoroacetate yield $\mathrm{CXF_3}$ when heated with halogen, $\mathrm{X_2}$, at temperatures higher than those required for silver trifluoroacetate (Part I). Attempts to repeat this with sodium heptafluorobutyrate gave only moderate yields of C_3F_7X, and the main product was 1 : 2-dibromohexafluoropropane (X = Br) or hexafluoropropene (X = I); sodium pentafluoropropionate similarly yielded 1 : 2-dibromotetrafluoroethane, or 1 : 2-di-iodotetrafluoroethane and perfluoro*cyclo*butane (by thermal dimerisation of tetrafluoroethylene), and only small amounts of bromopentafluoroethane or pentafluoroiodoethane. Two reactions are involved : (*a*) reaction of halogen with the sodium salt by a mechanism, probably of free-radical type [see (*b*)], analogous to that for the silver salt, leading to the formation of C_2XF_5 or C_3XF_7; and (*b*) decarboxylation (independently of halogen) of the sodium salt of the perfluoro-acid to an olefin which reacts further with bromine or, in the case of tetrafluoroethylene, with iodine. Reaction (*b*) is of general application for the preparation of alk-1-enes from the perfluoro-acid, and was independently discovered and developed by the Minnesota Mining and Manufacturing Co. (personal communication). It may be interpreted by the instability of the fluorocarbanion :

$$CF_3\cdot[CF_2]_n\cdot CF_2\cdot CF_2\cdot CO_2Na \longrightarrow CF_3\cdot[CF_2]_n\cdot CF_2\cdot CF_2^- + CO_2 + Na^+$$



$$F\text{—}\underset{[CF_2]_n\cdot CF_3}{CF}\text{—}CF_2^- \longrightarrow CF_3\cdot[CF_2]_n\cdot CF{:}CF_2 + F^-$$

and with suitable technique gives yields of 60—90%. The data shown in Table 2 for the fluoro-olefins so prepared show that cyclisation or introduction of a double bond into a fluoro-carbon produces little change in boiling point.

TABLE 2.

$CF_3\cdot[CF_2]_n\cdot CF_2\cdot CF_3$	C_3F_8	C_4F_{10}	C_6F_{14}	C_7F_{16}	C_8F_{18}
B. p.	−38°	−5°	51°	82°	103°
$CF_3\cdot[CF_2]_n\cdot CF{:}CF_2$	C_3F_6	C_4F_8	C_6F_{12}	C_7F_{14}	C_8F_{16}
B. p.	−29°	1°	57°	83°	105°
Fluoro*cyclo*alkane	—	C_4F_8	C_6F_{12}	—	—
B. p.	—	−4°	52°	—	—
Fluoro*cyclo*alkene	—	C_4F_6	C_6F_{10}	—	—
B. p.	—	1°	54°	—	—

The influence of the perfluoroalkyl group on the adjacent $CF{:}CF_2$ group is being studied. Its presence is shown by its characteristic C=C stretching vibration in the infra-red at 5·56 μ (*J.*, 1952, paper No. 849), and by oxidation to give the fluoro-acid containing two carbon atoms fewer than originally, *e.g.*,

$$CF_3\cdot[CF_2]_6\cdot CO_2Na \longrightarrow CF_3\cdot[CF_2]_4\cdot CF{:}CF_2 \xrightarrow{KMnO_4} CF_3\cdot[CF_2]_4\cdot CO_2H$$

Descent of the homologous fluoro-acid series is thus possible as well as ascent *via* the fluoro-iodides (*Nature*, 1950, 192).

EXPERIMENTAL

The silver salt reaction was carried out with the acids shown below. Molecular weights were determined by Regnault's vapour-density method.

Monofluoroacetic Acid.—To a stirred suspension of silver carbonate in water (100 ml.) was added a 3% excess of monofluoroacetic acid (10·0 g.). The mixture was heated to 70°, then cooled, and the insoluble *silver monofluoroacetate* (86%) (Found : Ag, 58·1. $C_2H_2O_2FAg$ requires Ag, 58·3%) was dried *in vacuo* over phosphoric oxide. The silver salt is more easily prepared by the addition of excess of N-silver nitrate to aqueous sodium fluoroacetate. The silver salt (9·2 g.) was heated in a sealed tube with chlorine (10% excess) from 50° to 120° during 5 hours, to give, after fractionation of the products *in vacuo*, chlorofluoromethane (52%), b. p. 8·5° (Found : C, 17·7%; *M*, 68. Calc. for CH_2ClF : C, 17·5%; *M*, 68·5). Henne (*J. Amer. Chem. Soc.*, 1937, **59**, 1400) reports b. p. −9·0°. Treatment with bromine (5% excess) similarly yielded bromofluoromethane (62%), b. p. 17·5° (Found : C, 10·6%; *M*, 113. Calc. for CH_2BrF : C, 10·6%; *M*, 113). Swarts, *Bull. Acad. roy. Belg.*, 1910, **58**, 113, reports b. p. 18—20°. Silver monofluoroacetate (8·1 g.) and iodine (150% excess), premixed in a silica flask, were slowly heated to 180—260°. The products were continuously removed by pumping through a trap cooled in liquid air to prevent decomposition of the fluoroiodomethane (55%),

b. p. 52—53°, n_D^{20} 1·490 (Found : C, 7·8; H, 1·4%; *M*, 159. Calc. for CH_2IF : C, 7·5; H, 1·3%; *M*, 160). Van Arkel and Zanetsky (*Rec. Trav. chim.*, 1937, **56**, 167) report b. p. 53·4°. The compound readily liberates iodine on exposure to light.

Chlorofluoroacetic Acid.—This was prepared in improved yield by slight modification of Young and Tarrant's procedure (*J. Amer. Chem. Soc.*, 1949, **71**, 2432). Treatment of chlorotrifluoroethylene (20 g.) with excess of ethanol and sodium ethoxide (2%) yielded 2-chloro-1 : 1 : 2-trifluoroethyl ethyl ether (96%), b. p. 88°, which was hydrolysed in a steel vessel by treatment with a three-fold excess of concentrated sulphuric acid at 0—5° during 4 hours. The temperature was raised to 50°, and the volatile material, removed by pumping through a cold trap, was washed with ice-water and distilled from phosphoric oxide, to give ethyl chlorofluoroacetate (81%), b. p. 128°, hydrolysed by 10% aqueous sodium hydroxide to chlorofluoroacetic acid (64%), b. p. 160·5—161°. The acid (10·3 g., 5% excess) was treated with anhydrous silver oxide and a little phosphoric oxide in a sealed tube with vigorous shaking, the temperature being raised slowly to 50°, to give *silver chlorofluoroacetate* (87%) (Found : Cl, 16·1; Ag, 48·7. C_2HO_2ClFAg requires Cl, 16·2; Ag, 49·2%).

When silver chlorofluoroacetate (0·010 mole) was stirred with water in a Polythene beaker for 3 weeks, silver chloride (0·006 mole), unchanged silver chlorofluoroacetate (0·001 mole), silver glyoxylate (0·002 mole) and glyoxylic acid (0·006 mole) were identified as follows. The reaction mixture gave a filtrate *A* and solid products *B*. *B* was dried *in vacuo* over phosphoric anhydride, and the silver chlorofluoroacetate in it was estimated by fusion of a portion with an excess of sodium followed by determination of fluoride. To a second portion of *B* was added dilute nitric acid, and the solution was concentrated *in vacuo* to remove chlorofluoroacetic acid; the concentrate was warmed with concentrated nitric acid and after dilution with water the residual silver chloride was weighed. In this experiment, silver glyoxylate in *B* was estimated by difference. In a second experiment, *B* was treated with a further quantity of water to complete the destruction of the silver chlorofluoroacetate, and the solid then removed by filtration was shown to consist of only silver glyoxylate and silver chloride by decomposition of the former with hydrochloric acid, filtration, and evaporation of the filtrate *in vacuo* over phosphoric anhydride; qualitative tests, and estimation as the calcium salt (see below), showed only glyoxylic acid. The filtrate *A* was freeze-dried in a Polythene beaker, and qualitative examination of the aqueous solution revealed only fluoride ion and no organic material. The residue from *A* was a viscous liquid which did not crystallise on further drying *in vacuo* over phosphoric anhydride and analysed as $CHO{\cdot}CO_2H$ (Found : C, 31·9; H, 2·7. Calc. for $C_2H_2O_3$: C, 32·4; H, 2·7%). A portion of the oil heated at 100° with sodium hydroxide was shown qualitatively to give glycollic and oxalic acids. A second portion yielded an oxime, m. p. 142° (decomp.) (lit., 143°). The remainder of the oil was dissolved in water and precipitated by addition of calcium chloride solution as calcium glyoxylate (97%), weighed as $(CHO{\cdot}CO_2)_2Ca,2H_2O$ (Doebner and Glass, *Annalen*, 1901, **317**, 417) (Found : Ca, 17·9. Calc. for $C_4H_8O_9Ca$: Ca, 18·0%). Control experiments with pure glyoxylic acid and with an artificial mixture showed that the above methods of analysis were reliable to ±3%. In a third experiment, one half of the filtrate *A* was used for estimation of fluoride as fluorosilicic acid (Found : F^-, equiv. to 97% of the silver salt decomposed), and the second portion was used for estimation of glyoxylic acid as its calcium salt (98% theor.).

The silver salt (3·1 g.), treated with chlorine or bromine as described for silver fluoroacetate, gave dichlorofluoromethane (73%) (Found : *M*, 103. Calc. for $CHCl_2F$: *M*, 103), b. p. 9° (Swarts, *Bull. Acad. roy. Belg.*, 1892, **24**. 474, reports b. p. 8·9°), and bromochlorofluoromethane (67%) (Found : *M*, 146. Calc. for CHBrClF : *M*, 147·5), b. p. 36·5° (*idem, ibid.*, 1893, **26**, 102, reports b. p. 38°), respectively. The silver salt (4·2 g.) with iodine (see silver fluoroacetate) gave *chlorofluoroiodomethane* (35%) (Found : C, 5·7; H, 0·5; F, 9·8%; *M*, 193. CHClFI requires C, 6·2; H, 0·5%; F, 9·8%; *M*, 194·5) as a light-sensitive liquid, b. p. 35°/150 mm. (*ca.* 76°/760 mm.). When shaken vigorously with mercury and exposed to ultra-violet radiation, chlorofluoroiodomethane (0·9 g.) was converted into 1 : 2-dichloro-1 : 2-difluoroethane (79%), b. p. 59°, n_D^{25} 1·390 (Found : *M*, 135. Calc. for $C_2H_2Cl_2F_2$: *M*, 135). Henne and Waalkes (*J. Amer. Chem. Soc.*, 1945, **67**, 1639) report b. p. 59°. Thermal decomposition at 230° also gave 1 : 2-dichloro-1 : 2-difluoroethane (57%).

Bromofluoroacetic Acid.—Bromotrifluoroethylene was prepared in 78% yield by debromination of 1 : 1 : 2-tribromotrifluoroethane with zinc and ethanol (Swarts, *loc. cit.*) or preferably as follows. Chlorotrifluoroethylene was converted into 1 : 2-dichlorotrifluoroethane (96%) by anhydrous hydrogen chloride and a catalytic amount of aluminium chloride at 150° in an autoclave. The product (Found : *M*, 153. Calc. for $C_2HCl_2F_3$: *M*, 153), b. p. 28°, n_D^{20} 1·335

(Henne and Ladd, *J. Amer. Chem. Soc.*, 1936, **58**, 402, report b. p. 28°), was dechlorinated by zinc and refluxing ethanol in an apparatus fitted with reflux condenser held at −45°, to give trifluoroethylene (86%), b. p. −55° (Found: *M*, 82. Calc. for C_2HF_3: *M*, 82). Swarts (*Bull. Acad. roy. Belg.*, 1899, **37**, 357) reports b. p. −51°. The olefin absorbed bromine under the influence of ultra-violet light to give quantitatively 1 : 2-dibromotrifluoroethane, b. p. 75·8° (Swarts, *loc. cit.*, reports b. p. 76°), n_D^{25} 1·418 (Found: *M*, 240. Calc. for $C_2HBr_2F_3$: *M*, 242), 18·6 g. of which were stirred and cooled in ethanol (30 ml.) to 0° in a flask fitted with reflux water-condenser. After the slow addition of *ca.* 90% of the theoretical amount of ice-cold 10% ethanolic potassium hydroxide, the whole was heated to 30° for 10 minutes, then cooled to 0°, and a further amount of base added (10% excess finally) and the temperature was raised to the b. p. The volatile products were washed with water and fractionated *in vacuo*, to give bromotrifluoroethylene (77%), b. p. −4·5° (Found: C, 14·9%; *M*, 160. Calc. for C_2BrF_3: C, 14·9%; *M*, 161). Swarts (*loc. cit.*) reports b. p. −2·5°.

Bromotrifluoroethylene (2·1 g.), heated with anhydrous hydrogen chloride (10% excess) at 150—180° for 12 hours, gave 1-*bromo*-2-*chloro*-1 : 2 : 2-*trifluoroethane* (63%), b. p. 51—52° (Found: C, 12·4; H, 0·3%; *M*, 196. $C_2HBrClF_3$ requires C, 12·2; H, 0·5%; *M*, 197·5), dehalogenated in 85% yield to trifluoroethylene.

Bromotrifluoroethylene (10·9 g.) was slowly bubbled into a stirred solution of ethanol (150 ml.) containing 0·2% of sodium ethoxide at −10°, to give, after addition of water, etc., 2-*bromo*-1 : 1 : 2-*trifluoroethyl ethyl ether* (83%), b. p. 108°, n_D^{20} 1·375 (Found: C, 23·4; H, 2·9%; *M*, 200—210. $C_4H_6OBrF_3$ requires C, 23·2; H, 2·9%; *M*, 207). Temperature control is important, since if the sodium ethoxide is destroyed by reaction with the bromofluoro-ether, the addition reaction stops. By treatment with a three-fold excess of concentrated sulphuric acid at −5° in a steel vessel containing ground glass, the ether yielded ethyl bromofluoroacetate (56%), converted into bromofluoroacetic acid (61%), b. p. 106°/35 mm. (Found: equiv., 156·5. Calc. for $C_2H_2O_2BrF$: equiv., 157); Swarts, *loc. cit.*, reports b. p. 183°. *Silver bromofluoroacetate* (84%) (Found: Br, 30·1; Ag, 40·5. C_2HO_2BrFAg requires Br, 30·3; Ag, 40·9%) was prepared as was silver chlorofluoroacetate. The silver salt (0·01 mole) was decomposed by water during 14 days to give silver bromide (0·009 mole), silver glyoxylate (0·001 mole), and glyoxylic acid (0·008 mole), and, in a repeat experiment, fluoride (0·01 mole) (method as for silver chlorofluoroacetate, above).

The silver salt (3·3 g.) with bromine and chlorine (as for silver monofluoroacetate) gave (at 100°) dibromofluoromethane, b. p. 64·5° (64%) (Found: *M*, 191. Calc. for $CHBr_2F$: *M*, 192) (Swarts, *Bull. Acad. roy. Belg.*, 1910, 113, reports b. p. 65°), and (at 40°) bromochlorofluoromethane (67%). Silver bromofluoroacetate (5·1 g.), mixed with a 300% excess of powdered iodine and heated at 1 mm., gave, after preliminary fractionation in a vacuum before distillation *in vacuo* through a micro-column, *bromofluoroiodomethane* (19%), b. p. 35°/70 mm. 102—104°/760 mm. (decomp.) (Found: C, 5·9; H, 0·4; F, 8·0; I, 52·9. CHBrFI requires C, 5·0; H, 0·4; F, 7·95; I, 53·1%), whose decomposition was accelerated by light and traces of moisture. This decomposition accounts for the poor analyses for carbon, a feature characteristic of some other similar compounds.

Fluoroiodoacetic Acid.—Prepared from ethyl bromofluoroacetate (see above) by Swarts's method (*Zentr.*, 1903, I, 13) (20% yield), this acid was converted into impure silver fluoroiodoacetate with some decomposition (Found: Ag, 38·2. Calc. for C_2HFIO_2Ag: Ag, 34·7%). The salts with excess of iodine (as for silver bromofluoroacetate) gave fluorodi-iodomethane (18% yield from fluoroiodoacetic acid), b. p. 50°/50 mm. (Found: F, 6·4; I, 87·9%; *M*, 278, 280. Calc. for CHI_2F: F, 6·6; I, 88·8%; *M*, 286). Ruff, Bretschneider, Luchsinger, and Miltschitzky (*Ber.*, 1936, **69**, 299) report b. p. 100°.

Difluoroacetic Acid.—This was prepared in 61% yield from tetrafluoroethylene by hydrolysis with sulphuric acid of ethyl 1 : 1 : 2 : 2-tetrafluoroethyl ether (b. p. 58°; obtained in 94% yield by reaction of tetrafluoroethylene with ethanol and sodium ethoxide). *Silver difluoroacetate* (91% yield from 15·1 g. of acid) (Found: Ag, 53·0. $C_2HO_2F_2Ag$ requires Ag, 53·2%) was prepared by the method given below for perfluoro-acids. Like silver trifluoroacetate, silver difluoroacetate is readily soluble in water, ether, and benzene. Silver difluoroacetate (3·2 g.) and dry chlorine (10% excess) at 50° in a steel bomb gave chlorodifluoromethane (91%), b. p. −41° (Found: *M*, 86. Calc. for $CHClF_2$: *M*, 86·5). Benning and McHarness (*Ind. Eng. Chem.*,. 1940, **32**, 814) report b. p. −40·8°. The reaction also occurs readily (87% yield) at atmospheric pressure by condensing chlorine on to the silver salt (5·2 g.), allowing the mixture to warm to room temperature, and passing more chlorine into the solid while heating it gently with a free flame.

The silver salt (3·1 g.) and bromine (50% excess) at 50—60°, and finally at 100°, gave bromodifluoromethane (88%), b. p. −15° (Found: *M*, 131. Calc. for $CHBrF_2$: *M*, 131). Henne (*J. Amer. Chem. Soc.*, 1937, **59**, 1200) reports b. p. −14·5°. In an autoclave the yield was 93%, and required only a 5% excess of bromine. Silver difluoroacetate (10·1 g.), intimately mixed with powdered iodine (50% excess), was heated with a free flame under an air-condenser leading to traps cooled by liquid air. Smooth reaction occurred at *ca.* 150° to give carbon dioxide (98%) and difluoroiodomethane (93%), b. p. 20·5°, a colourless liquid liberating iodine on exposure to light (Found: C, 6·6; H, 0·5%; *M*, 178. Calc. for CHF_2I: C, 6·7; H, 0·7%; *M*, 178). Ruff (*Ber.*, 1936, **69**, 299) reports b. p. (calc.) 21·6°. When heated to 220° with mercury (2 ml.), difluoroiodomethane (4·0 g.) gave 1 : 1 : 2 : 2-tetrafluoroethane (40%) (Found: *M*, 102. Calc. for $C_2H_2F_4$: *M*, 102), silicon tetrafluoride, carbon dioxide, and hydrogen fluoride.

Bromochlorofluoroacetic Acid.—Bromofluoroacetyl chloride (73% yield from the acid) and excess of chlorine were exposed at 120° to ultra-violet light for 6 days. After dissolution in water the organic acids were extracted by ether and distilled from a trace of phosphoric oxide, to give bromochlorofluoroacetic acid (31%) and a trace of dichlorofluoroacetic acid (5%); no bromofluoroacetic acid was detected in the bromochlorofluoroacetic acid. With silver oxide and a trace of phosphoric oxide, bromochlorofluoroacetic acid gave *silver bromochlorofluoroacetate* (Found: Ag, 35·7. $C_2O_2BrClFAg$ requires Ag, 36·2%), 5 g. of which with bromine yielded *dibromochlorofluoromethane* (71%), b. p. 79·5—80·5° (Found: Br + Cl, 85·9; F, 8·4%; *M*, 224. CBr_2ClF requires Br + Cl, 86·3; F, 8·4%; *M*, 226·5). Chlorine similarly gave bromodichlorofluoromethane (see above) (63%).

Dichlorofluoroacetic Acid.—Chlorofluoroacetic acid (10·0 g.) was converted into *chlorofluoroacetyl chloride* (57%), b. p. 70—72° (Found: acyl Cl, 27·7; total Cl, 54·3%; *M*, 129; $CHOCl_2F$ requires acyl Cl, 27·1; total Cl, 54·2%; *M*, 131), which was mixed with a 20% excess of chlorine in a silica tube and exposed at 80° to intense ultra-violet radiation for 14 days. After dissolution in water, the organic acids were extracted by ether and distilled, to give a mixture of chloro- (48%) and dichloro-fluoroacetic acid (31%), b. p. 95°/28 mm. (yields determined by analysis for chlorine and titration). Reaction of the mixed silver salts (from 5·1 g. of mixed acid) with bromine by the method used for chlorofluoroacetic acid yielded bromochlorofluoromethane (61% based on the silver chlorofluoroacetate), b. p. 36—37°, and *bromodichlorofluoromethane* (58% based on the silver dichlorofluoroacetate), b. p. 51—52° (Found: C, 6·4%; *M*, 181. $CBrCl_2F$ requires C, 6·6%; *M*, 182). Chlorine similarly gave dichlorofluoromethane (78% based on silver chlorofluoroacetate) (see above) and trichlorofluoromethane, b. p. 23—24° (63% based on silver dichlorofluoroacetate) (Found: *M*, 136. Calc. for CCl_3F: *M*, 137·5). Benning and McHarness (*loc. cit.*) report b. p. 23·77°. An excess of iodine, heated with the mixture of silver salts (4·6 g.), gave chlorofluoroiodomethane (29% based on silver chlorofluoroacetate) (see above), *dichlorofluoroiodomethane* (10% based on silver dichlorofluoroacetate), b. p. 44—46°/210 mm. (Found: F, 8·2; I, 55·3. CCl_2IF requires F, 8·3; I, 55·5%), and a mixture of the fluorochloro-iodides (15%) which could not be separated by distillation on the scale used. Dichlorofluoroiodomethane liberated iodine rapidly when kept and gave tetrachloro-1 : 2-difluoroethane amongst the products. After 8 hours' heating at 150°, the yield of tetrachloro-1 : 2-difluoroethane was 41%.

Bromodifluoroacetic Acid.—This acid was prepared by Swarts's method (*Zentr.*, 1903, II, 710) (8% yield) and converted into *silver bromodifluoroacetate* (Found: Ag, 38·1. $C_2O_2BrF_2Ag$ requires Ag, 38·3%) which, with an excess of bromine, yielded dibromodifluoromethane (81%), b. p. 25° (Found: *M*, 210. Calc. for CBr_2F_2: *M*, 210). The reaction with an excess of iodine gave less than 5% of a compound (not definitely identified) believed to be bromodifluoroiodomethane.

Chlorodifluoroacetic Acid.—Prepared in 65% yield by permanganate oxidation of 1 : 1 : 2 : 3-tetrachloro-3 : 3-difluoropropene, this gave a *silver* salt (77%) (Found: Ag, 45·6. $C_2O_2ClF_2Ag$ requires Ag, 45·5%) by the method used for chlorofluoroacetic acid. The silver salt (0·02 mole) decomposed in water during 14 days, to give silver chloride (0·02 mole) and oxalic acid (0·019 mole); a second experiment gave fluoride (0·039 mole).

Reaction with chlorine and bromine as described for difluoroacetic acid gave, from 5 g. of silver salt, dichlorodifluoromethane (88%), b. p. −29·5° (Found: *M*, 121. Calc. for CCl_2F_2: *M*, 121) (Bichowsky and Gilbey, *Ind. Eng. Chem.*, 1931, **23**, 366, give b. p. −29·8°), and *bromochlorodifluoromethane* (91%), b. p. −4° (Found: C, 6·9; Br + Cl, 69·6; F, 22·7%; *M*, 165. $CBrClF_2$ requires C, 7·3; Br + Cl, 69·8; F, 23·0%; *M*, 165·5). Heating with iodine at a pressure of 10 mm., so that the product was removed from the reaction vessel as rapidly as possible, gave *chlorodifluoroiodomethane* (78% from 10 g. of silver salt), b. p. 33° (Found : C, 5·6 ; Cl + I, 76·9% ; *M*, 212. $CClF_2I$ requires C, 5·65 ; Cl + I, 76·5% ; *M*, 212·5), purified by fractionation *in vacuo*. It liberated iodine rapidly on exposure to light and oxygen; when shaken with excess of mercury in a Pyrex tube exposed to ultra-violet light, chlorodifluoroiodomethane (2·1 g.) was converted into 1 : 2-dichlorotetrafluoroethane (81%) (Found : *M*, 171. Calc. for $C_2Cl_2F_4$: *M*, 171), whose structure was proved by dehalogenation with zinc and ethanol in a sealed tube at 80° to tetrafluoroethylene, identified spectroscopically. The yield of dichlorotetrafluoroethane obtained by heating the iodo-compound to 200° for 8 hours was 62%.

Chlorodifluoroiodomethane and chlorine or bromine in ultra-violet light give dichloro- (95%) or bromochloro-difluoromethane (94%).

Perfluoro-acids.—The following perfluoro-acids were prepared by the general method recorded in *Nature*, 1950, **166**, 192, and 1951, **168**, 1028, and *via* the corresponding perfluoroalkylmagnesium iodides (*ibid.*, 1951, **167**, 139 ; *J.*, 1952, 3423) : pentafluoropropionic, heptafluoro-*n*-butyric, nonafluorovaleric, undecafluoro-*n*-hexanoic, tridecafluoro-*n*-heptanoic, and pentadecafluoro-*n*-octanoic acid. The *silver* salts (see Table) were prepared by addition of the acid (10 g.) to the theoretical amount of silver carbonate suspended in water (100 ml.). The soluble silver salts of the lower perfluoro-acids are obtained by evaporation of the aqueous solution to dryness under reduced pressure. The higher perfluoro-acids and their silver salts are much less soluble in water ; complete reaction of the acids with silver carbonate was ensured by heating them at 60° for 30 minutes, and the silver salt was obtained by extraction of the suspended solid and of the aqueous solution with ether, followed by evaporation of the ethereal extracts. The salts are soluble in ether and crystallise from carbon tetrachloride or ether as greasy, pearly plates, which were dried *in vacuo* before use. Reaction of 0·01 mole with chlorine carried out (*a*) in a small stainless-steel autoclave at 50° (10% excess of chlorine), or (*b*) by passage of chlorine (20% excess) at atmospheric pressure through the vigorously stirred salt heated from 50° to 100°, gave the following : Chloropentafluoroethane (94%), b. p. −37° (Found : *M*, 154. Calc. for C_2ClF_5 : *M*, 154·5) (Calfee, Fukuhara, Young, and Bigelow, *J. Amer. Chem. Soc.*, 1940, **62**, 267, report b. p. −38°). 1-*Chloroheptafluoropropane* (91%), b. p. −1° (Found : C, 17·7% ; *M*, 204. C_3ClF_7 requires C, 17·6% ; *M*, 204·5). 1-*Chlorononafluorobutane* (89%), b. p. 30° (Found : C, 18·5% ; *M*, 253. C_4ClF_9 requires C, 18·9% ; *M*, 254·5). 1-*Chloroundecafluoropentane* (85% from 0·005 mole), b. p. 60°, n_D^{10} 1·280 (Found : C, 19·3% ; *M*, 303. C_5ClF_{11} requires C, 19·7% ; *M*, 304·5). 1-*Chlorotridecafluorohexane* (83% from 0·005 mole), b. p. 86°, n_D^{15} 1·287 (Found : C, 20·2% ; *M*, 352. C_6ClF_{13} requires C, 20·3% ; *M*, 354·5). 1-*Chloropentadecafluoroheptane* (80% from 0·005 mole), b. p. 109°, n_D^{15} 1·292 (Found : C, 20·6% ; *M*, 400, 405. C_7ClF_{15} requires C, 20·8% ; *M*, 404·5).

Salt	Yield	Ag, found, %	Ag, required, %	Salt	Yield	Ag, found, %	Ag, required, %
$C_2F_5\cdot CO_2Ag$ ...	95	39·7	39·9	$C_5F_{11}\cdot CO_2Ag$	93	25·6	25·7
$C_3F_7\cdot CO_2Ag$ ...	98	33·2	33·6	$C_6F_{13}\cdot CO_2Ag$	92	22·8	22·9
$C_4F_9\cdot CO_2Ag$ ...	96	29·1	29·1	$C_7F_{15}\cdot CO_2Ag$	94	20·5	20·7

Reaction with bromine, effected as in (*a*) above (for the less volatile fluoro-bromides), or by heating a thin layer of silver salt with a 30% excess of bromine, gave bromopentafluoroethane (98%), b. p. −20° (Found : *M*, 200. Calc. for C_2BrF_5 : *M*, 199) (Brice, Pearlson, and Simons, *ibid.*, 1946, **68**, 968, report b. p. −23° to −21°), 1-bromoheptafluoropropane (97%), b. p. 12° (Found : *M*, 248. Calc. for C_3BrF_7 : *M*, 249) (Brice *et al.*, *loc. cit.*, report b. p. 12° for a mixture of isomers), 1-*bromononafluorobutane* (95%), b. p. 44° (Found : C, 16·3% ; *M*, 298. C_4BrF_9 requires C, 16·1% ; *M*, 299), 1-*bromoundecafluoropentane* (91%), b. p. 74·5° (Found : C, 17·2% ; *M*, 345. C_5BrF_{11} requires C, 17·2% ; *M*, 349), 1-*bromotridecafluorohexane* (90% from 0·005 mole), b. p. 100° (Found : C, 17·7% ; *M*, 393, 397. C_6BrF_{13} requires C, 18·0% ; *M*, 399), and 1-*bromopentadecafluoroheptane* (86% from 0·005 mole), micro-b. p. 123—124° (Found : C, 18·7. C_7BrF_{15} requires C, 18·7%).

Fluoro-iodides were prepared from the silver salts by use of an autoclave or by heating with a free flame an intimate mixture of silver salt and powdered iodine (200% excess) (cf. Part I). The temperature of the reflux condenser and the pressure in the reaction flask (600 mm. to 2 mm.) were controlled so that the iodo-compound was removed rapidly. The by-products from the reactions will be discussed later. The products were pentafluoroiodoethane (94%), b. p. 13° (Found : *M*, 246. Calc. for C_2F_5I : *M*, 246) (Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2188, report b. p. 13°), heptafluoroiodopropane (90%), b. p. 39·5° (Found : *M*, 296. Calc. for C_3F_7I : *M*, 296) (Haszeldine, *J.*, 1949, 2856 ; 1950, 2789, reports b. p. 39—

40°), *nonafluoro*-1-*iodobutane* (89%), b. p. 67° (Found: C, 13·5%; *M*, 345. C_4F_9I requires C, 13·9%; *M*, 346), *undecafluoro*-1-*iodopentane* (89%), b. p. 95°, n_D^{20} 1·320 (Found: C, 15·1%; *M*, 393. $C_5F_{11}I$ requires C, 15·2%; *M*, 396), *tridecafluoro*-1-*iodohexane* (90% from 0·005 mole), b. p. 117°, n_D^{20} 1·322 (Found: C, 16·2. $C_6F_{13}I$ requires C, 16·1%), and *pentadecafluoro*-1-*iodoheptane* (85% from 0·005 mole), b. p. 137—138°, n_D^{30} 1·323 (Found: C, 16·8. $C_7F_{15}I$ requires C, 16·9%).

Reactions with Alcoholic Potassium Hydroxide.—One-g. samples of the following compounds were completely destroyed by 15 ml. of potassium hydroxide solution (15% in 95% ethanol) after 48 hours at 35°, to give (*a*) fluoride and halide: CH_2IF, CH_2BrF, CH_2ClF, (*b*) fluoride, halide, and formate: $CHClIF$, $CHCl_2F$, $CHClBrF$, CHI_2F, or (*c*) fluoride, halide, and carbonate: $CClBrIF$, $CClBr_2F$, CCl_2BrF, CCl_2IF. Under similar conditions $CHClF_2$ and CH_2F_2 were stable, and $CClIF_2$ and $CHIF_2$ yielded $CHClF_2$ (24%) and CH_2F_2 (19%) and halide and carbonate. Heptafluoroiodopropane (5·0 g.), with alcoholic potassium hydroxide at 100°, gave heptafluoropropane (70%), ethyl 1 : 1 : 2 : 3 : 3 : 3-hexafluoropropyl ether (5%) (identical with the ether prepared by the sodium ethoxide-catalysed reaction of ethanol with hexafluoropropene), and fluoride (15%).

Miscellaneous Reactions with Silver Trifluoroacetate.—(a) *With phosphorus.* Silver trifluoroacetate (4·0 g.), heated to 180° for 12 hours with an excess of yellow phosphorus (6 g.; freed from the oxide by dipping into carbon disulphide), gave silver phosphide, a trace of carbon dioxide, and trifluoroacetic anhydride (61%), b. p. 40° (Found: *M*, 209. Calc. for $C_4F_6O_3$: *M*, 210), which dissolved in aqueous sodium hydroxide without evolution of fluoroform. (Tristrifluoromethylphosphine would have given fluoroform.) A similar reaction at 310° for 12 hours gave trifluoroacetic anhydride (67%) identified as above, and *ca.* 5% of carbon dioxide and silicon tetrafluoride. (b) *With sulphur.* Silver trifluoroacetate (3·0 g.), mixed with an excess of sulphur (7 g.) and heated at 300° for 12 hours, gave silver sulphide, trifluoroacetic anhydride (81%), b. p. 40° (*M*, 210), which dissolved completely in water, subsequently made alkaline without liberation of fluoroform or fluoride, and sulphur dioxide (84%), b. p. −10° (*M*, 64). (Bistrifluoromethyl sulphide is stable to water and base; bistrifluoromethyl disulphide gives fluoride with base.) (c) *With mercury.* In a single experiment, mercury was heated with silver trifluoroacetate at 300° for 12 hours, giving carbonyl fluoride and silicon tetrafluoride, but not bistrifluoromethylmercury. (d) *With arsenic and phosphorus iodides.* Single attempts to prepare trifluoromethyl-arsines or -phosphines in good yield by the reaction of the silver salt, arsenic or phosphorus, and iodine were unsuccessful.

Reactions of Trifluoroacetic Anhydride and Trifluoroacetyl Chloride with Halogens.—Trifluoroacetic anhydride (3·0 g.) with an excess of iodine (12 g.) at 350° for 12 hours gave carbon monoxide, carbon dioxide, and trifluoroiodomethane (63%), b. p. −22° (Found: *M*, 196. Calc. for CIF_3: *M*, 196).

Trifluoroacetyl chloride (2·2 g.) was heated with an excess of chlorine at 280° for 7 hours; the volatile products were completely absorbed by aqueous sodium hydroxide (to which chlorotrifluoromethane is stable). An experiment with bromine at 340° for 12 hours gave a similar result.

Reaction of Sodium Heptafluorobutyrate and Pentafluoropropionate with Bromine or Iodine.—The reaction of bromine (300% excess) with dried sodium heptafluorobutyrate (10·0 g.), heated strongly with a free flame, was slow and much of the bromine distilled through the reflux condenser and was trapped in liquid-air traps. The products were 1-bromoheptafluoropropane (18%) (Found: *M*, 249. Calc. for C_3BrF_7: *M*, 249) and 1 : 2-dibromohexafluoropropane (27%), b. p. 71° (Found: C, 11·5%; *M*, 310. Calc. for $C_3Br_2F_6$: C, 11·6%; *M*, 310), identified by infra-red spectroscopy. Reaction in an autoclave at 260° for 12 hours gave 32% of bromoheptafluoropropane and 34% of dibromohexafluoropropane. Reaction with iodine at atmospheric pressure similarly gave heptafluoroiodopropane (9%), b. p. 39—40° (Found: *M*, 296. Calc. for C_3IF_7: *M*, 296), and hexafluoropropene (41%), b. p. −29° (Found: *M*, 150. Calc. for C_3F_6: *M*, 150), identified by comparison of its infra-red spectrum with that of a known specimen. In an autoclave at 250° for 4 hours the yields were 5% and 37%.

Sodium pentafluoropropionate (3·0 g.), heated with an excess of bromine in a small autoclave at 260° for 8 hours, gave bromopentafluoropropane (8%) and 1 : 2-dibromotetrafluoroethane (43%), b. p. 45—47° (Found: *M*, 258. Calc. for $C_2Br_2F_4$: *M*, 260), whose identity was confirmed by its infra-red spectrum. Iodine similarly yielded pentafluoroiodoethane (7%), 1 : 2-di-iodotetrafluoroethane (35%), b. p. 112° (Emeléus and Haszeldine, *loc. cit.*, report b. p. 112°), and perfluoro*cyclo*butane (13%), b. p. *ca.* −2° (Found: *M*, 200. Calc. for C_4F_8: *M*, 200).

Thermal Decomposition of Sodium Salts of Perfluoro-acids.—*Sodium heptafluorobutyrate.*

The salt (8·7 g.) was spread evenly down a horizontal silica tube (2 cm. in diameter), closed at one end, with the other end leading *via* two traps cooled by liquid air to an oil-pump. The pressure in the tube was reduced to 50 mm., maintained by a manostat, and the silica tube was slowly moved into a furnace heated to 280°. Steady evolution of gas occurred and the rate of reaction was controlled by the speed of movement into the furnace. The temperature of the furnace was finally raised to 320°. The condensed products were carbon dioxide and hexafluoropropene (92%), b. p. −29° (Found : *M*, 150. Calc. for C_3F_6 : *M*, 150), identified by its infra-red spectrum. A second experiment, carried out at atmospheric pressure in nitrogen, gave a 90% yield of olefin. The reaction is slow at 200—220°, but is rapid and essentially quantitative at 230—280°. The residue in the reaction tube (which need not be of silica) was sodium fluoride. Decarboxylation can be effected by a free flame or oil-bath, but the yields are lower (75—85%), and temperature control is advisable.

Sodium pentafluoropropionate (5·7 g.) at 270°/150 mm. yielded tetrafluoroethylene (84%) (Found : *M*, 100. Calc. for C_2F_4 : *M*, 100) and perfluoro*cyclo*butane (4%) (Found : *M*, 200. Calc. for C_4F_8 : *M*, 200), identified spectroscopically.

Sodium nonafluorovalerate (3·7 g.) was converted, at 290°/100 mm., into *octafluorobut-*1*-ene* (77%), b. p. 0·8° (Found : C, 23·8% ; *M*, 200. C_4F_8 requires C, 24·0% ; *M*, 200), distinguished from its isomeric perfluoro*cyclo*butane and octafluorobut-2-ene by its infra-red spectrum and particularly the band at 5·56 μ. Miller *et al.* (*Ind. Eng. Chem.*, 1947, **39**, 333, 401) report the preparation of octafluorobut-1-ene, but give no physical properties. Minnesota Mining and Manufacturing Co. report b. p. −2° to −1° at 730 mm. (personal communication). Permanganate oxidation of octafluorobut-1-ene yielded pentafluoropropionic acid (56%), characterised as its amide.

Sodium tridecafluoro-*n*-heptanoate (3·3 g.) similarly gave *dodecafluorohex-*1*-ene* (65%), b. p. 57° (Found : C, 24·1% ; *M*, 297. C_6F_{12} requires C, 24·0% ; *M*, 300), showing absorption at 5·56 μ. Permanganate oxidation gave nonafluorovaleric acid (52%).

Sodium pentadecafluoro-octanoate (3·8 g.) yielded *tetradecafluorohept-*1*-ene* (60%), b. p. 82—83° (Found : C, 23·7% ; *M*, 348. C_7F_{14} requires C, 24·0% ; *M*, 350), showing strong absorption at 5·56 μ. Permanganate oxidation yielded undecafluorohexanoic acid (49%).

Sodium heptadecafluorononanoate (2·2 g.) at 300°/5 mm. gave *hexadecafluoro-oct-*1*-ene* (47%), micro-b. p. 105° (Found : C, 23·9% ; *M*, 392, 396. C_8F_{16} requires C, 24·0% ; *M*, 400), oxidised by permanganate to tridecafluoro-*n*-heptanoic acid (61%). Oxidation of this and the other olefins described above was effected by treatment at 100—130° with a 20% excess of alkaline potassium permanganate in a 100-ml. autoclave. The aqueous solution was treated with sulphur dioxide, acidified with sulphuric acid and extracted with ether in the usual way. After removal of the ether through a Vigreux column, the residual acid was distilled or recrystallised from carbon tetrachloride.

UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE.

[*Received, April 8th,* 1952.]