124. *The Reactions of Metallic Salts of Acids with Halogens. Part I. The Reaction of Metal Trifluoroacetates with Iodine, Bromine, and Chlorine.*

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Silver, sodium, potassium, mercuric, lead, and barium trifluoroacetates react with iodine to give trifluoroiodomethane. The interaction of the silver salt and bromine and chlorine yields bromo- and chloro-trifluoromethane. Trifluoroiodomethane and heptafluoroiodopropane have also been prepared by pyrolysis of trifluoroacetyl iodide and heptafluorobutyryl iodide in the presence of iodine.

Trifluoroiodomethane has been shown to be a valuable source of trifluoromethyl radicals, some of the reactions of which have already been described (*e.g.*, Haszeldine, *J.*, 1949, 2856; *Nature*, 1950, **165**, 152; Emeléus and Haszeldine, *J.*, 1949, 2948, 2953; Bennett, Brandt, Emeléus, and

Haszeldine, *Nature*, 1950, **166**, 225). Trifluoroiodomethane has hitherto been prepared from carbon tetraiodide and iodine pentafluoride and, although it can be so obtained in excellent yield, the reaction must be carefully controlled and, furthermore, elementary fluorine or chlorine trifluoride is required for the preparation of the iodine pentafluoride (Haszeldine, *J.*, 1950, 3037). Alternative routes to the synthesis of trifluoroiodomethane and other fluoro-iodides have therefore been examined, and a very convenient synthesis may now be effected by the interaction of metal trifluoroacetates and iodine :

$$CF_3{\cdot}CO_2M + I_2 \longrightarrow CF_3I + MI + CO_2$$

$$(CF_3{\cdot}CO_2)_2M' + 2I_2 \longrightarrow 2CF_3I + M'I_2 + 2CO_2$$

(see Haszeldine, *Nature*, 1950, **166**, 192, for preliminary communication).

Sodium (or potassium) trifluoroacetate is now commercially available, and may be prepared without recourse to elementary fluorine. When this salt is heated with excess of iodine at atmospheric pressure, much of the iodine is lost by sublimation, and decarboxylation with simultaneous iodination is incomplete. Thermal decomposition of the sodium trifluoroacetate also occurs and yields trifluoroacetyl fluoride and trifluoroacetic anhydride. In a simple pressure vessel, both sodium and potassium trifluoroacetates give trifluoroiodomethane in good yield.

Other salts of trifluoroacetic acid have been examined. The barium, lead, and mercuric salts react in an analogous manner to the sodium and potassium salts. In all instances it is essential that the metal trifluoroacetate and the iodine should be dry, otherwise trifluoroacetic acid is formed by the reaction

$$6CF_3{\cdot}CO_2M + 3I_2 + 3H_2O \longrightarrow 6CF_3{\cdot}CO_2H + 5MI + MIO_3$$

For this reason the hygroscopic barium and lead salts and the mercuric salt, which must be dehydrated, are unsuitable for general use.

Silver trifluoroacetate is readily prepared from the sodium salt, is stable, non-deliquescent, and does not form a hydrate. Furthermore, the interaction of this salt and iodine, which can be carried out at atmospheric pressure and moderate temperature in simple glass apparatus, gives high yields of the fluoroiodide, and forms the most convenient method for the laboratory synthesis of trifluoroiodomethane.

The interaction of silver trifluoroacetate and chlorine takes place at room temperature and yields chlorotrifluoromethane : similarly the silver salt and bromine react at moderate temperature to give bromotrifluoromethane in equally good yield. The conversion of a fluoro-acid $R{\cdot}CO_2H$ into RX is thus readily achieved, and this enables the conversion of fluoro-iodides into fluoro-acids (Haszeldine, *Nature*, 1950, **166**, 192) to be reversed :

$$\begin{tikzcd}
CF_3{\cdot}[CF_2]_n{\cdot}I \arrow[r, "C_2H_2"] & CF_3{\cdot}[CF_2]_n{\cdot}CH{:}CHI \arrow[d, "KMnO_4"] \\
CF_3{\cdot}[CF_2]_n{\cdot}CO_2Ag \arrow[u, "I_2"] & CF_3{\cdot}[CF_2]_n{\cdot}CO_2H \arrow[l]
\end{tikzcd}$$

The well-known general reaction of silver salts of acids with halogens, due to Simonini (*Monatsh.*, 1892, **13**, 320), has been extensively applied (for a recent review see Kleinberg, *Chem. Reviews*, 1947, **40**, 381). When an equivalent of the silver salt of an acid $R{\cdot}CO_2H$ is treated with two or more equivalents of halogen, the compound $R{\cdot}CO_2X$ is formed (Birckenbach, Goubeau, and Berninger, *Ber.*, 1932, **65**, 1339; Bockemüller and Hoffmann, *Annalen*, 1935, **519**, 165). The decomposition of $R{\cdot}CO_2X$ ($X = Cl$ or Br) gives RX and carbon dioxide, and the reaction of silver trifluoroacetate with halogens ($X = Cl$, Br, or I) appears to be in accord with this general reaction. Oldham and Ubbelohde (*J.*, 1941, 368) have shown that the thermal decomposition of iodine compounds $I(O{\cdot}COR)_3$ yields the ester, alkyl iodide, carbon dioxide, and iodine. The interaction of equivalent quantities of silver acetate and iodine has been investigated by Simonini (*loc. cit.*) and by Birnbaum (*Annalen*, 1869, **152**, 111), and yields methyl acetate (50—70%) and acetic acid, not methyl iodide. Trifluoromethyl trifluoroacetate has not yet been isolated as a product of the reaction of silver trifluoroacetate and iodine.

Swarts (*Anal. Soc. Fis. Quim.*, 1929, **27**, 683) investigated the reaction of silver trifluoroacetate with iodine in benzene solution, and found that it was represented by the equation

$$2CF_3{\cdot}CO_2Ag + 2I_2 + 2C_6H_6 \longrightarrow (CF_3{\cdot}CO)_2O + H_2O + AgI + C_6H_5I$$

Since, however, the reaction mixture was heated to 60°, it would appear that the products obtained were from a secondary reaction involving iodination of the solvent by the " positive " iodine of iodine trifluoroacetate and decomposition of the latter compound. Reactions carried out in solution, and the degradation of mono- and di-carboxylic fluoro-acids to the iodo-, bromo-, and chloro-compounds, will be described shortly. An alternative, but less convenient, method for the preparation of trifluoroiodomethane from trifluoroacetic acid is by the pyrolysis of the acetyl iodide. The acyl iodides of perfluoro-aliphatic acids have not yet been described, since attempts by Simons and Ramler (*J. Amer. Chem. Soc.*, **1943**, **65**, 389) to prepare trifluoroacetyl iodide by interaction of barium trifluoroacetate and phosphorus tri-iodide failed. As was predicted by these authors, however, the acyl chloride and anhydrous hydrogen iodide react to give the acyl iodide and hydrogen chloride. The reaction appears to be general and heptafluorobutyryl iodide was prepared from heptafluorobutyryl chloride.

The marked effect of fluorine on the boiling point of a compound is illustrated by the comparison of the fluoroacyl halides with their hydrocarbon analogues shown in the table below.

	B.p .		B. p.	Δ B. p.
$CF_3{\cdot}COF$ [1]	−59°	$CH_3{\cdot}COF$	20·5°	79·5°
$CF_3{\cdot}COCl$ [2]	−27	$CH_3{\cdot}COCl$	51·5	78·5
$CF_3{\cdot}COBr$ [2]	− 5	$CH_3{\cdot}COBr$	76·5	81·5
$CF_3{\cdot}COI$ [4]	23	$CH_3{\cdot}COI$	105	82
$C_3F_7{\cdot}COCl$ [3]	39	$C_3H_7{\cdot}COCl$	101·5	72·5
$C_3F_7{\cdot}COI$ [4]	77·5	$C_3H_7{\cdot}COI$	147	69·5

[1] Swarts, *Bull. Acad. Sci. roy. Belg.*, 1922, **8**, 343. [2] Simons and Ramler, *loc. cit.* [3] Haszeldine, *J.*, 1950, 2789. [4] Present communication.

Trifluoroacetyl iodide gave some hexafluoroethane on passage through a heated platinum tube, and the formation of this compound indicated that the decomposition probably proceeded *via* trifluoromethyl radicals; no trifluoroiodomethane was isolated. When pyrolysed in a stream of iodine, however, the trifluoromethyl radicals gave trifluoroiodomethane in low yield. Rapid cooling of the exit gases was used to reduce the amount of hexafluoroethane formed. Pyrolysis of heptafluorobutyryl iodide in a stream of iodine similarly gave heptafluoroiodopropane, a compound previously prepared from trifluoroiodomethane and tetrafluoroethylene (Haszeldine, *loc. cit.*).

EXPERIMENTAL.

Preparation of Silver Trifluoroacetate.—Sodium trifluoroacetate was dissolved in the minimum amount of water and added to a concentrated aqueous solution of silver nitrate. The solution was filtered to remove traces of silver chloride and extracted with ether overnight. This was sufficient to remove most of the silver trifluoroacetate, but a further small quantity was obtained by concentration of the aqueous solution on a steam-bath until on cooling a few crystals could be observed, followed by further extraction with ether. The ethereal extracts were evaporated to dryness on the steam-bath, then powdered, and the drying completed in a vacuum-desiccator over silica gel.

Silver trifluoroacetate was also prepared from the free acid by addition of silver oxide to a 50% aqueous solution and evaporation to dryness *in vacuo*. A slight excess of silver oxide did not affect the subsequent reactions of the silver salt.

Interaction of Silver Trifluoroacetate and Iodine.—In a typical experiment, silver trifluoroacetate (100 g.) was intimately mixed with excess of iodine (300 g.) in a 2-l. Pyrex flask fitted with wide-bore air- and water-condensers and connected by wide-bore rubber tubing to two traps cooled by liquid air. The reaction was initiated by application of a free flame at the upper edge of the mixture. Fumes of iodine were evolved, and a stream of faintly pink gas could be observed passing through the condensers. The reaction was readily controlled by intermittent application of the flame and was allowed to spread slowly throughout the whole reaction mixture. Excessive heating led to a too rapid gas evolution with loss of iodine into the condensers, and for this reason the use of a heating bath is to be recommended only for work on a small scale.

The traps contained carbon dioxide, iodine, and trifluoroiodomethane, and the last was easily separated by distillation *in vacuo*; alternatively, the carbon dioxide and iodine were removed by washing with dilute aqueous alkali. The fluoro-iodide (81 g., 91%), b. p. −22°, prepared by this method was identical with that obtained from carbon tetraiodide and iodine pentafluoride (b. p. −22·5°) (Found : I, 64·6%; *M*, 196. Calc. for CF_3I : I, 64·8%; *M*, 196). Yields of 89—94% were consistently obtained.

When equimolar amounts of silver trifluoroacetate and iodine were mixed and heated as above, the yield of trifluoroiodomethane was reduced to 80—84%. No other products were isolated, and it is believed that the decrease in yield is due not to side reactions but to mechanical difficulties such as the incomplete mixing of the iodine and silver salt.

Interaction of Silver Trifluoroacetate and Bromine.—To silver trifluoroacetate (11 g.) in four Pyrex tubes cooled in liquid air was added bromine (16 g.). The tubes were then evacuated and sealed. On warming to room temperature, a reaction was apparent and silver bromide was deposited. The reaction was completed by warming the mixture to 50° for 2 hours. The volatile products were washed with aqueous alkali, and distillation gave bromotrifluoromethane (6·5 g., 88%) (Found : Br, 53·2%; *M*, 149. Calc. for $CBrF_3$: Br, 53·7%; *M*, 149), b. p. −58°. Banks, Emeléus, Haszeldine, and Kerrigan (*J.*, 1948, 2188) report b. p. −57·8°. The reaction can also be carried out at atmospheric pressure by heating a mixture of silver trifluoroacetate and bromine on a water-bath.

Interaction of Silver Trifluoroacetate and Chlorine.—Silver trifluoroacetate (11 g.) and chlorine (6·5 g.) were sealed in four tubes and allowed to warm to room temperature. A vigorous reaction ensued and silver chloride was formed. The volatile products of reaction were washed with alkali, and on fractionation yielded chlorotrifluoromethane (4·7 g., 90%) (Found : *M*, 104·5. Calc. for $CClF_3$: *M*, 104·5), b. p. −82°.

Reaction of Sodium and Potassium Trifluoroacetate with Iodine.—Sodium and potassium trifluoroacetate were dried *in vacuo* on a water-bath before use. Vigorous heating with a free flame was needed to bring about the reaction of the sodium salt (27·2 g.) and iodine (100 g.) at atmospheric pressure. Much of the iodine sublimed and distilled from the salt before reaction occurred. The products of reaction were trifluoroiodomethane (3·9 g., 10%), carbon dioxide, carbonyl fluoride, silicon tetrafluoride, trifluoroacetyl fluoride (b. p. *ca.* −60°), and trifluoroacetic anhydride (b. p. 40°). By reaction of the last two compounds with aqueous alkali, neutralisation to bromothymol-blue with dilute sulphuric acid, and evaporation to dryness followed by extraction with absolute ethanol, a total of 6 g. (22%) of sodium trifluoroacetate was recovered.

When potassium trifluoroacetate (30·5 g.) was heated at atmospheric pressure with a large excess of iodine (500 g.), the yield of trifluoroiodomethane was 40%.

Sodium trifluoroacetate (13·6 g.) heated to 270° in a sealed tube with iodine (70 g.) gave a 58% yield of the fluoro-iodide.

Sodium trifluoroacetate (27·2 g.) was mixed with iodine (200 g.) in a 100-ml. stainless-steel autoclave and heated during 4 hours to a maximum temperature of 280°. Trifluoroiodomethane (24·1 g.) was isolated in 61% yield. The potassium salt under identical conditions gave a 55% yield of the fluoro-iodide. It may not be necessary to use a temperature as high as 280°.

Reaction of Barium, Mercuric, and Lead Trifluoroacetates with Iodine.—These salts were first described by Swarts (*Bull. Soc. chim. Belg.*, 1939, **48**, 176). Barium trifluoroacetate was prepared by addition of 60% aqueous trifluoroacetic acid to an equivalent amount of barium hydroxide, and evaporation to dryness on a water-bath. Dehydration was completed in a vacuum-desiccator over phosphoric anhydride, with pumping, for several weeks. Mercuric and lead trifluoroacetates were similarly prepared from mercuric and lead oxides and 30% trifluoroacetic acid. Reaction with iodine was effected in an autoclave as described for sodium and potassium trifluoroacetates. The barium, mercuric, and lead salts were heated to 280°, 250°, and 250° to give 32, 35, and 26% yields of trifluoroiodomethane, respectively.

Trifluoroacetyl Iodide and Heptafluorobutyryl Iodide.—Trifluoroacetyl chloride (26 g.) was prepared from sodium trifluoroacetate and phosphorus trichloride, sealed in 12 tubes with anhydrous hydrogen iodide (50 g.), and heated to 120° for 8 hours. The products of reaction were given a preliminary distillation through a series of cooled traps to remove hydrogen chloride and hydrogen iodide, followed by fractionation to give *trifluoroacetyl iodide* (28 g., 62%) (Found : I, 56·9%; *M*, 222. C_2F_3OI requires I, 56·7%; *M*, 224), a liquid, b. p. 23°, which fumes in air.

Heptafluorobutyryl iodide (5·1 g., 57%) (Found : C, 15·1; I, 39·4%; *M*, 318. C_4F_7OI requires C, 14·8; I, 39·2%; *M*, 324), b. p. 77—78°, n_D^{25} 1·353, was similarly prepared from heptafluorobutyryl chloride (6·4 g.) and anhydrous hydrogen iodide (13 g.).

Pyrolysis of Trifluoroacetyl Iodide and Heptafluorobutyryl Iodide.—The apparatus consisted of a cylindrical Pyrex tube containing iodine and heated electrically, through which a stream of nitrogen was passed. Iodine vapour was thereby carried through a wide-bore exit tube and into a platinum tube 30'' long and of ½'' internal diameter heated to 550—600°. Once it had been established that iodine was flowing through the tube, trifluoroacetyl iodide, slightly diluted by nitrogen, was added through a T-piece and mixed with the iodine before entering the tube. The optimum conditions were not investigated. On leaving the furnace, the exit gases were cooled as rapidly as possible by a series of wide-bore traps cooled in liquid air. Trifluoroacetyl iodide (8 g.), added during 2 hours with a nitrogen dilution of 4 l./hr., gave 15, 20, and 22% yields of trifluoroiodomethane in consecutive experiments. Trifluoroacetyl iodide, pyrolysed alone at 550°, gave no trifluoroiodomethane; hexafluoroethane (10%) was detected and some trifluoroacetyl iodide was recovered unchanged.

Similarly, heptafluorobutyryl iodide (4·8 g.), added at 2 g./hr., gave heptafluoroiodopropane (16%), b. p. 40°, *M* 296, identical with the material prepared earlier from trifluoroiodomethane and tetrafluoroethylene.

Professor A. L. Henne of Ohio State University reports (private communication) that he has independently prepared trifluoroiodomethane from silver trifluoroacetate and iodine.

The author is indebted to Imperial Chemical Industries Limited, General Chemicals (Widnes), for a gift of sodium trifluoroacetate.

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[*Received, October* 14*th*, 1950.]