

### 443. The Reaction of Bromine Trifluoride and Iodine Pentafluoride with Carbon Tetrachloride, Tetrabromide, and Tetraiodide and with Tetraiodoethylene.

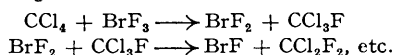
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Liquid bromine trifluoride reacts with carbon tetrachloride or tetrabromide forming mixtures of chlorofluoromethanes or bromofluoromethanes, the proportions of which depend on the reaction conditions. With carbon tetraiodide, bromofluoromethanes and carbon trifluoride result. Iodine pentafluoride converts carbon tetrabromide into a mixture of bromofluoromethanes, while with carbon tetraiodide *iodotrifluoromethane* ( $\text{CIF}_3$ ) (b. p.  $-22.5^\circ$ ) is formed in good yield. Tetraiodoethylene and iodine pentafluoride give *iodopentafluoroethane* ( $\text{C}_2\text{IF}_6$ ) (b. p.  $13^\circ$ ). Preliminary experiments show these two monoiodo-compounds to differ greatly from methyl and ethyl iodides in their reactivity, notably in their inability to form Grignard compounds under the usual conditions. By reaction of the iodo-compounds with mercury the compounds *trifluoromethylmercuric iodide*, m. p.  $112.5^\circ$ , and *pentafluoroethylmercuric iodide*, m. p.  $87.5-88.5^\circ$ , have been prepared.

THIS investigation had as its object the comparison of the reactivities of bromine trifluoride and iodine pentafluoride by a study of their reactions with fully halogenated methanes, and the synthesis of the compounds  $\text{CIF}_3$  and  $\text{C}_2\text{IF}_6$ , from which it was hoped to prepare organometallic derivatives. Previous work on the reactions of the halogen fluorides with halogenated methanes is scanty. Nutting and Petrie (U.S.P. 1,961,622, 1934) studied the reaction between bromine trifluoride and carbon tetrachloride, showing that chlorofluorides are formed. Their results have been confirmed and considerably extended. Ruff and Keim (*Z. anorg. Chem.*, 1931, 201, 245) obtained trichlorofluoromethane and a small quantity of dichlorodifluoromethane by the interaction at  $30-35^\circ$  of iodine pentafluoride and carbon tetrachloride, while Simons, Bond, and McArthur (*J. Amer. Chem. Soc.*, 1940, 62, 3477) isolated hexafluoroethane from the reaction products formed by heating iodine pentafluoride and carbon tetraiodide in a copper vessel. As is shown below, this reaction when carried out in glass yields *iodotrifluoromethane*, which probably reacts with copper, forming the fluorocarbon.

In the reaction between bromine trifluoride and carbon tetrachloride in a system at atmospheric pressure it is found that the volatile partly-fluorinated products, trichlorofluoromethane and dichlorodifluoromethane, are readily formed. To obtain good yields of chlorotrifluoromethane the reaction must be carried out in an autoclave. The bromofluoromethanes are less well known, the mono- and di-fluoro-derivatives (b. p.s  $107^\circ$  and  $24.5^\circ$ , respectively) having been prepared by Rathsburg (*Ber.*, 1918, 51, 669) by refluxing carbon tetrabromide with excess of argentic fluoride. The trifluoro-derivative (b. p.  $-59^\circ$  to  $-60.5^\circ$ ) was first prepared by Brice, Pearson, and Simons (*J. Amer. Chem. Soc.*, 1946, 68, 968) by the thermal bromination of the monohydrogen fluorocarbon. Reaction between bromine trifluoride and carbon tetrabromide occurred smoothly, and because of the comparatively high boiling points of the intermediates, the tri- as well as the mono- and di-fluoro-compounds could be prepared without the use of an autoclave. Bromine trifluoride and carbon tetraiodide reacted very readily but in this case no iodofluoromethanes were isolated. The fluorinating action of iodine pentafluoride proved to be much milder, the production of bromofluoromethanes from carbon tetrabromide paralleling Ruff and Keim's observations on the tetrachloride. Iodine pentafluoride proved also to be a suitable reagent for the fluorination of iodo-derivatives, and the production of iodotrifluoromethane by the interaction of this substance and carbon tetraiodide presented no difficulty. Hexaiodoethane is not known, but tetraiodoethylene and iodine pentafluoride yielded *iodopentafluoroethane*. This reaction was much more difficult to control.

In the fluorination of halogenated methanes it is remarkable that no products are formed in which there are two or more carbon atoms in the molecule. This indicates that organic free radicals play no significant rôle in the reaction mechanism, which probably consists of a stepwise substitution by fluorine; e.g.,



The synthesis of the compounds  $\text{ClF}_3$  and  $\text{C}_2\text{IF}_5$  raises many interesting possibilities in view of the great variety of reactions shown by the analogous hydrogen compounds  $\text{CH}_3\text{I}$  and  $\text{C}_2\text{H}_5\text{I}$ . A number of the reactions of the iodofluoro-compounds are being studied and will be described later. Two mercury derivatives,  $\text{HgCF}_3\text{I}$  and  $\text{HgC}_2\text{F}_5\text{I}$ , the preparation of which is described below, serve to establish the fact that a stable bond between the  $\text{CF}_3$  or  $\text{C}_2\text{F}_5$  radicals and a metal such as mercury can be formed, though it has not yet proved possible to prepare a Grignard compound by the standard procedures.

#### EXPERIMENTAL.

*Reaction of Bromine Trifluoride with Carbon Tetrachloride.*—Bromine trifluoride, prepared from the elements and purified by distillation at atmospheric pressure in a steel retort, was distilled from a weighed copper vessel at  $110^\circ$  in a stream of dry nitrogen (4 l./hr.) into 154 g. (1 mol.) of dry carbon tetrachloride in a water-cooled copper trap. The total quantity added was 46 g. (0.33 mol.) and a vigorous reaction occurred as each drop fell into the carbon tetrachloride. The gaseous reaction products were carried off in the nitrogen stream and condensed in two Pyrex traps cooled to  $-80^\circ$  and  $-190^\circ$  respectively. The whole of the volatile product condensed at  $-80^\circ$ , and was re-evaporated in a stream of nitrogen, passed through a scrubber containing an alkaline sodium sulphite solution to remove free halogens, and recondensed. The residue in the reaction vessel was similarly treated with alkaline sodium sulphite, giving a product which was combined with the  $-80^\circ$  fraction and distilled from metallic calcium through a low-temperature column packed with Fenske rings. The following fractions were obtained: (a) 4 g., b. p.  $-27.6^\circ$ ,  $M$ , 121 ( $\text{CCl}_2\text{F}_2$ , b. p.  $-28^\circ$ ,  $M$ , 121); (b) 80 g., b. p.  $23.5^\circ$ ,  $M$ , 137 ( $\text{CCl}_3\text{F}$ , b. p.  $23.7^\circ$ ,  $M$ , 137.4); (c) 50 g., b. p.  $76^\circ$ . Fraction (c) was unchanged carbon tetrachloride.

This procedure was modified by freezing 18.5 g. (0.135 mol.) of bromine trifluoride in solid carbon dioxide in a copper vessel fitted with a reflux condenser at  $0^\circ$  and adding slowly 18.5 g. (0.225 mol.) of carbon tetrachloride. Reaction occurred on allowing the reactants to warm slowly to room temperature. The products, separated and identified as before, were:  $\text{CCl}_3\text{F}$ , 4.5 g.;  $\text{CCl}_2\text{F}_2$ , 21 g. A similar experiment, using a reflux condenser cooled to  $-80^\circ$ , gave from 16 g. (0.12 mol.) of bromine trifluoride and 20.6 g. (0.15 mol.) of trichlorofluoromethane, 17.5 g. of dichlorodifluoromethane, equivalent to a 96% yield on the trichlorofluoromethane used.

To prepare more fully fluorinated products a 200-c.c. stainless-steel autoclave fitted with a pressure gauge and needle valve was used. The bromine trifluoride was put into the autoclave in a separate container and the reactants were not mixed until the autoclave was sealed. The yields of four experiments recorded below show that under these conditions, which preclude the escape of the volatile partly fluorinated products as formed, moderate yields of monochlorotrifluoromethane result.

Wt. of $\text{CCl}_4$ , g.	Wt. of $\text{BrF}_3$ , g.	Wt. of $\text{CClF}_3$ , g.	Wt. of $\text{CCl}_2\text{F}_2$ , g.	Wt. of $\text{CCl}_4$ , g.	Wt. of $\text{BrF}_3$ , g.	Wt. of $\text{CClF}_3$ , g.	Wt. of $\text{CCl}_2\text{F}_2$ , g.
78	78	34.4	19.4	38.5	41	21.9	4.1
40	35	16	11.5	40	33.7	21.8	5.9

*Reaction of Bromine Trifluoride with Carbon Tetrabromide.*—As carbon tetrabromide is a solid it was fluorinated in bromine solution, 111 g. (0.33 mol.) being dissolved in 1000 g. of bromine in a 1-l. flask fitted with a stirrer and cooled in ice. With the slow addition of 15.2 g. (0.11 mol.) of bromine trifluoride, only a trace of volatile material collected in cooled traps connected with the flask. The bulk of the bromine was distilled off through a column, and the residue was washed with alkaline sodium sulphite solution, dried, and distilled. The products were tribromodifluoromethane, 85 g., b. p.  $106^\circ$  (Found: Br, 88.2. Calc. for  $\text{CBr}_2\text{F}_2$ : Br, 88.75%), and ca. 1 c.c. of dibromodifluoromethane (Found:  $M$ , 211. Calc. for  $\text{CBr}_2\text{F}_2$ :  $M$ , 211). The vapour-pressure data of a carefully purified sample of tribromodifluoromethane in the range  $43$ – $103^\circ$  are represented by the equation  $\log p$  (mm.) =  $7.60757 - 1796.45/T - 0.003284 \log T$ , giving a calculated b. p. of  $106.2^\circ$ , a latent heat of vaporisation at the b. p. of 5.96 kcal./mol., and a value of Trouton's constant of 22.1.

By varying the proportion of reactants it was possible to raise the yield of dibromodifluoromethane; e.g., using 166 g. (0.5 mol.) of carbon tetrabromide in 1000 g. of bromine, reaction at  $0^\circ$  with 46 g. (0.33 mol.) of bromine trifluoride gave 79 g. of  $\text{CBr}_2\text{F}_2$ , 14 g. of  $\text{CBr}_3\text{F}$ , and 150 c.c. (gas) of  $\text{CBrF}_3$ . By dispensing with the solvent the yield of the trifluoro-compound was much increased. By adding 13.7 g. (0.1 mol.) of bromine trifluoride dropwise to 33.2 g. (0.1 mol.) of solid carbon tetrabromide, 2.1 l. (gas) of the trifluoro-compound were obtained, the yield being 94% of theoretical. A sample of this material was carefully purified by fractionation in the vacuum apparatus, and the vapour pressure was found to be represented in the range  $-117^\circ$  to  $-55^\circ$  by the equation  $\log p$  (mm.) =  $16.0750 - 1250.75/T - 3.1651 \log T$ . The calculated b. p. is  $-57.8^\circ$ , the latent heat of vaporisation at the b. p. 5.43 kcal./mol. and Trouton's constant 21.1.

*Reaction of Bromine Trifluoride with Carbon Tetraiodide.*—Carbon tetraiodide was prepared by Walker's method (*J.*, 1904, 85, 1090) and dried in a high vacuum over phosphoric oxide for several hours. The reaction was carried out in a 250-c.c. two-necked flask with a reflux condenser, low-temperature traps, and a dropping device for adding bromine trifluoride. To 65 g. (0.125 mol.) of carbon tetraiodide cooled in ice were added dropwise during two hours 33 g. (0.24 mol.) of bromine trifluoride. A flame was seen as each drop came into contact with the tetraiodide. After the reaction the volatile products remaining in the flask were swept out in nitrogen, condensed, scrubbed with alkaline sodium sulphite solution, and stored as gas (vol., 1.8 l.). The residue in the flask contained iodine and its monobromide and pentafluoride, but no carbon tetraiodide. Two pure products,  $\text{CBr}_2\text{F}_2$  (4.5 g.) and  $\text{CF}_4$  (3.2 g.), were separated from the gaseous mixture formed in the reaction. There was no evidence of the formation of iodofluoromethanes.

*Reaction of Iodine Pentafluoride with Carbon Tetrabromide.*—Iodine pentafluoride was prepared from the elements. There was no reaction at room temperature between 52 g. (0.23 mol.) of iodine penta-

fluoride and 120 g. (0.36 mol.) of carbon tetrabromide when these were mixed in a quartz flask, the neck of which was cooled to give a reflux, and connected to cooled traps. Reaction occurred on heating gradually to 90° and after 3 hours at this temperature the volatile products remaining in the flask were swept into the traps by a stream of nitrogen. From the residue 2 g. of tribromofluoromethane (b. p. 105°) were isolated. The gaseous products (7.01 l.) gave 6.73 l. of dibromodifluoromethane (an 83% yield on the  $\text{CBr}_4$  used) and 0.5 c.c. (liquid) of tribromofluoromethane, together with a small amount of carbon tetrafluoride.

*Reaction of Iodine Pentafluoride with Carbon Tetraiodide.*—To a 250-c.c. Pyrex flask containing 80 g. (0.153 mol.) of carbon tetraiodide were added 30 g. (0.135 mol.) of iodine pentafluoride. The flask was clamped in a vibrator, and connected by rubber tubing to a series of traps cooled in liquid air. Shortly after mixing the reactants a vigorous reaction with gas evolution started. This was completed, when it had moderated, by heating to 90–100° for 30 minutes. The residue in the flask consisted of iodine, iodine pentafluoride, and some unidentified material which was possibly a thermal decomposition product from carbon tetraiodide. The volatile reaction products were washed with 5% aqueous sodium hydroxide solution to remove silicon tetrafluoride, iodine, and acid vapours. The gaseous products were fractionated and gave 2.53 l. (gas) of *iodotrifluoromethane* (Found: I, 64.2; M, 196.  $\text{CIF}_3$  requires I, 64.8%; M, 196) and 73 c.c. (gas) of trifluoromethane, which was characterised by vapour-pressure measurements. The second product may have arisen from the presence of iodoform in the carbon tetraiodide. The vapour-pressure curve of iodotrifluoromethane was measured, the data in the range –85° to –23° being represented by the equation  $\log p$  (mm.) = 7.5665 – 1174.29/T. The calculated b. p. is –22.5°, the latent heat of vaporisation at the b. p. 5.357 kcal./mol., and Trouton's constant 21.4. Unsuccessful attempts were made to isolate di-iododifluoromethane and tri-iodofluoromethane by reducing the ratio of iodine pentafluoride to carbon tetraiodide and by slower addition of the pentafluoride.

*Reaction of Iodine Pentafluoride with Tetraiodoethylene.*—Di-iodoacetylene was prepared by Dehn's method (*J. Amer. Chem. Soc.*, 1911, **33**, 1598) and converted into tetraiodoethylene by refluxing with iodine in toluene solution (Datta and Prasad, *ibid.*, 1917, **39**, 451). To 100 g. (0.19 mol.) of tetraiodoethylene in a 500-c.c. silica flask fitted with a reflux condenser and cooled in ice, were added dropwise, during 9 hours, 180 g. (0.81 mol.) of iodine pentafluoride. Too rapid addition of the pentafluoride resulted in an explosion, the iodoethylene decomposing into carbon and iodine. A smooth reaction occurred under the correct conditions and the volatile products were condensed in the usual way in cooled traps. Towards the end of the reaction the temperature was raised gradually to 130°.

The volatile reaction products were fractionated in a vacuum apparatus and found to consist of silicon tetrafluoride and carbon dioxide (from attack on the silica vessel), tetrafluoroethylene, an unidentified fraction, and iodopentafluoroethane (12 g., 26%). The residue in the flask consisted of iodine, carbon, and unchanged iodine pentafluoride. No higher-boiling iodofluoro-compounds were present. The tetrafluoroethylene was identified by its molecular weight, vapour-pressure curve, and its reaction with chlorine to yield dichlorotetrafluoroethane (M, 170, b. p. 5°; cf. Henne, *J. Amer. Chem. Soc.*, 1934, **56**, 1726). *Iodopentafluoroethane* was identified by its molecular weight and iodine content (Found: I, 51.2; M, 246.  $\text{C}_2\text{IF}_5$  requires I, 51.6%; M, 246). The b. p. of a purified sample was 13°.

*Reaction of Iodotrifluoromethane with Mercury.*—A known quantity of iodotrifluoromethane was condensed in vacuum into a Carius tube of 45–55 c.c. capacity containing a known weight of mercury, and the tube was sealed. A series of experiments was made with tubes of either Monax glass or silica, exposed either to daylight or to a mercury arc, or with the tube heated at a definite temperature in a rocking furnace. During irradiation the tube was clamped in a 50-cycle vibrator. After reaction the tube was cooled in liquid air, opened, and its volatile contents removed to a vacuum system for examination. The volatile residues contained unchanged iodotrifluoromethane, recovery of which varied from 70 to 94% in a series of fourteen experiments under varied conditions. This unchanged material was condensed in vacuum by passing through a trap cooled in melting pentane and was characterised by determination of molecular weight and vapour pressure. A second fraction of the volatile material passed through the pentane-bath and was condensed in liquid air. This was shown to consist of hexafluoroethane (a pure sample of which was isolated) admixed with an impurity of lower molecular weight, which may have been tetrafluoroethylene.

The residue in the Carius tube was scraped out, mercury was removed by filtration, and the remaining material was extracted with acetone. The residue consisted of finely divided mercury and mercurous iodide. The acetone solution on evaporation gave a white crystalline substance admixed with a little mercuric iodide. It was purified by sublimation and identified by analysis as *trifluoromethylmercuric iodide*, m. p. 112.5° (Found: C, 3.42; I, 31.95; F, 14.2; Hg, 50.5.  $\text{CIF}_3\text{Hg}$  requires C, 3.02; I, 32.02; F, 14.37; Hg, 50.6%). The yield of this compound varied from about 5 to 8%, a high proportion of iodotrifluoromethane being recovered unchanged. The compound is decomposed by ultra-violet light, and it is best to use a Monax tube at 1 ft. from the arc (a Hanovia fluorescence lamp fitted with an S. 250 type self-starting arc), with an irradiation time of 24–48 hours. Satisfactory yields were also obtained in the rocking-tube furnace, with up to 48 hours' heating at 180–190°.

*Reaction of Mercury with Iodopentafluoroethane.*—The same procedure in filling and opening the Carius tube was used as in the preparation of trifluoromethylmercuric iodide. A mixture of 4.18 g. of iodopentafluoroethane was heated for 12 hours at 205° with 65 g. of mercury in a rocking furnace. At the end of the reaction, white needle-shaped crystals separated from the excess of iodofluoride. The volatile material removed from the tube contained 94% of the iodopentafluoroethane taken. The residue in the tube was extracted with ether, and crude *pentafluoroethylmercuric iodide* recovered from the solvent. This material was sublimed and formed white plates, m. p. 87.5–88.5° (Found: C, 5.7; I, 27.5; Hg, 44.5.  $\text{C}_2\text{IF}_5\text{Hg}$  requires C, 5.4; I, 28.3; Hg, 44.9%). Irradiation of the reactants under the conditions already described for trifluoromethylmercuric iodide gave from 1.80 g. of iodopentafluoroethane and 40 g. of mercury, 0.04 g. of the resublimed mercurial, 67% of the iodofluoro-compound being recovered unchanged.