624. *Organometallic Fluorine Compounds. Part II. The Synthesis of Bistrifluoromethylmercury.*

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Bistrifluoromethylmercury, $Hg(CF_3)_2$, cannot be synthesised from iodotrifluoromethane or trifluoromethylmercuric iodide by normal methods for the conversion of alkyl iodides or mercuri-iodides into mercury dialkyls, but has been obtained by reaction in absence of a solvent with silver, copper, cadmium, zinc, magnesium, or cadmium amalgam. The compound, unlike dimethylmercury, is a crystalline solid, soluble in water as well as in organic solvents, and is a weak electrolyte in aqueous solution. Both trifluoromethylmercuric iodide and bistrifluoromethylmercury are readily reduced to fluoroform.

The compound trifluoromethylmercuric iodide has been prepared from iodotrifluoromethane and mercury, though no evidence for the formation of organometallic compounds has been obtained with other metals (Emeléus and Haszeldine, preceding paper). An alternative route for the synthesis of these compounds, some of which might serve as synthetic reagents in fluorocarbon chemistry, is first to prepare bistrifluoromethylmercury which, by reaction with magnesium or zinc, might afford reactive metal fluoroalkyls. The standard method for the direct conversion of alkyl iodides into dimercurials by reaction with sodium amalgam was found to lead to complete decomposition when applied to iodotrifluoromethane. The reaction of trifluoromethylmercuric iodide with sodium (cf. Dreher and Otto, *Ber.*, 1869, **2**, 542), alkaline sodium stannite, or alkaline ferrous hydroxide (cf. Dimroth, *Ber.*, 1902, **35**, 2833) also failed to yield the dimercurial, and in the last two cases fluoroform was liberated. The reaction of trifluoromethylmercuric iodide with inorganic compounds such as potassium iodide and potassium cyanide which have been used to remove the elements of mercuric iodide from mercuri-iodides (Hein and Wagler, *Ber.*, 1925, **58**, 1499) failed to yield the dimercurial, and fluoroform was evolved from both acetone and aqueous solutions. Thus, in general, reactions in aqueous solution or in presence of an organic solvent were unsuitable because of the ready formation of fluoroform. Reaction of either trifluoromethylmercuric iodide or iodotrifluoromethane with amalgams of silver, copper, or cadmium did, however, give the dimercurial in satisfactory yield.

Bistrifluoromethylmercury, $Hg(CF_3)_2$, is a white crystalline solid with a characteristic pungent smell. It can be purified conveniently by extraction with organic solvents, followed by sublimation at atmospheric pressure. Whereas trifluoromethylmercuric iodide reacts with iodine to yield one equivalent of iodotrifluoromethane, the dimercurial yields two equivalents : $Hg(CF_3)_2 + 2I_2 = 2CIF_3 + HgI_2$. The reaction with chlorine and bromine is similar and good yields of chloro- and bromo-trifluoromethane are obtained. The dimercurial may be converted into trifluoromethylmercuric iodide by reaction with mercuric iodide at elevated temperatures, preferably in absence of a solvent, and the reaction with mercuric chloride is similar.

Bistrifluoromethylmercury is decomposed thermally above about 170° and is thus less stable than dimethylmercury, which is only slightly decomposed at 300° (Taylor and Jones, *J. Amer. Chem. Soc.*, 1930, **52**, 1111; Cunningham and Taylor, *J. Chem. Physics*, 1938, **6**, 359). The photochemical or pyrolytic decomposition affords trifluoromethyl radicals which will initiate the polymerisation of ethylene, tetrafluoroethylene, and other unsaturated compounds. These reactions are being further studied. The ready solubility of the dimercurial in water is of great interest, particularly as the resulting solutions have a definite, though low, conductivity even after careful purification of the solute. The conductivity does not appear to be due to hydrolysis to trifluoromethylmercuric hydroxide or mercuric hydroxide. The compound is rather weaker as an electrolyte than mercuric chloride, which is, however, appreciably hydrolysed in solution (Ley, *Z. physikal. Chem.*, 1899, **30**, 193). In certain respects it resembles mercuric cyanide, which has a specific conductivity in M/32-solution at 25° of $5{\cdot}6 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$. Both compounds show normal molecular weights in solution and neither gives a precipitate with dilute solutions of potassium iodide, silver nitrate, or alkali hydroxides. This apparently indicates the absence of mercuric ions but may be due to complex formation. The nature of the ions in solutions of bistrifluoromethylmercury and the cause of the slow change in conductivity of its fresh aqueous solutions have not yet been determined. Attempts are being made to prepare mercury complexes containing the CF_3 group, whose properties may clarify the position. A preliminary crystallographic investigation by Dr. K. Robinson of the Cavendish Laboratory indicates that the unit cell of bistrifluoromethylmercury is cubic [$a = 8{\cdot}11$ A.; 4 mols. of $Hg(CF_3)_2$ per unit cell] with mercury atoms located in the 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, and $0\frac{1}{2}\frac{1}{2}$ positions. The molecule itself is linear. The density, determined by the weighing-bottle method with perfluoromethyl*cyclo*hexane as the filling liquid, was 4·22. The *X*-ray investigation of the structure of bispentafluoroethylmercury, $Hg(C_2F_5)_2$, which has been synthesised by analogous methods (Miss J. Banus, unpublished), is more difficult than that of the fluoromethyl compound.

The reaction between trifluoromethylmercuric iodide or bistrifluoromethylmercury and metals such as magnesium and zinc was investigated to determine whether the latter were converted into reactive organometallic compounds. The formation of fluoroform on adding water to the reaction products was at first thought to show that these experiments had been successful and that the reaction $CF_3{\cdot}MI + H_2O \longrightarrow HO{\cdot}MI + CHF_3$ was taking place. This was supported by the fact that iodotrifluoromethane itself reacted with amalgams under certain conditions to give products which liberated fluoroform on addition of water. In none of the cases investigated so far, however, did the products react in other respects as if they contained zinc or magnesium organometallic compounds. The reactions with methyl cyanide, α-naphthyl *iso*cyanate, carbon dioxide, and acetone were chosen because they would have given organic fluorine compounds which would be readily detected. The liberation of fluoroform was finally traced to reduction of the mercurials present at the end of the reaction. This was established under a variety of conditions, though the possibility remains that a small part of the fluoroform came from a zinc or magnesium organometallic compound. It cannot in fact be asserted that the desired zinc and magnesium compounds are not formed or do not exist, as they may be sufficiently different chemically from the corresponding alkyl compounds to invalidate the tests used to detect them. The investigation is therefore being continued. The ease with which the trifluoromethyl mercurials were reduced by reagents such as zinc and magnesium amalgams or magnesium metal and magnesium iodide on the addition of water is unexpected since normal mercurials are quite stable in this respect and react only at elevated temperature and pressure. Only the more ionic organometallic compounds, such as the alkali-metal alkyls, are reduced by hydrogen at room temperature and atmospheric pressure.

The reaction of iodotrifluoromethane with amalgams to give a product which liberated fluoroform on the addition of water indicated that bistrifluoromethylmercury was formed. A study of this reaction enabled a method to be developed for the synthesis of the dimercurial from iodotrifluoromethane itself. Magnesium, zinc, silver, copper, and cadmium amalgams have been used. Cadmium amalgam was particularly effective and its reaction with iodotrifluoromethane constitutes the most satisfactory synthetic method so far found.

EXPERIMENTAL.

The experiments described were usually carried out in sealed Pyrex tubes of approx. 50 c.c. capacity. The source of ultra-violet radiation was a Hanovia lamp (YEKUL; with a S250 U-type self-starting arc) placed at 12″ from the tube. Iodotrifluoromethane was prepared in 95% yield from carbon tetraiodide and iodine pentafluoride (Banks, Emeléus, Haszeldine, and Kerrigan, *J.*, 1948, 2188), and trifluoromethylmercuric iodide by the reaction of iodotrifluoromethane with mercury (Emeléus and Haszeldine, preceding paper). The amalgams were prepared by heating the components together or by electrolysis.

Reaction of Trifluoromethylmercuric Iodide with Silver Amalgam.—*Bistrifluoromethylmercury* was first prepared by the action of silver amalgam on trifluoromethylmercuric iodide. Reaction was slow at temperatures up to 120°, but above this temperature large cubic crystals, differing notably from the plate-like crystals of trifluoromethylmercuric iodide, could be seen in the solid reaction product. It is essential that conversion should be complete since the separation of the two mercurials is difficult. The optimum temperature range was 140—160°. In a typical experiment at 140° trifluoromethylmercuric iodide (2·0 g.) was heated with silver amalgam (silver, 10 g.; mercury, 25 c.c.) for 20 hours in a rocking furnace, excess of amalgam was removed, and the residual solid extracted with ether. The ethereal extract on evaporation yielded a white solid which was purified by sublimation at 70°/1 atm. The yield of pure product, m. p. 163° (sealed tube), was 80% (Found: C, 7·2; F, 33·3; Hg, 60·4%; *M*, 328. C_2F_6Hg requires C, 7·1; F, 33·6; Hg, 59·3%; *M*, 338).

Reaction of Trifluoromethylmercuric Iodide with Copper and Cadmium Amalgams.—The reaction with copper amalgam occurred readily at 120° and above, and was independent of the concentration of the amalgam provided that this was present in excess and flowed freely in the rocking furnace. The optimum amount of trifluoromethylmercuric iodide for reaction in a 50-c.c. sealed tube was 5 g., and this when heated at 120° for 12 hours gave yields varying between 60 and 80%. Silicon tetrafluoride and a small amount of tetrafluoroethylene were identified as by-products, but no hexafluoroethane was found. Fluoroform was present when ether was used as a solvent for the trifluoromethylmercuric iodide, and the yield of dimercurial was reduced (20%). The ethereal solution gave a positive test for an aldehyde. The yield of dimercurial was improved (to 50—60%) when acetone was used as solvent, but fluoroform was again detected and it was found best to use no solvent. With cadmium amalgam at 120—130° and reaction times of 10 hours yields of dimercurial of 80—90% were readily obtained and only traces of volatile by-products were formed.

Properties of Bistrifluoromethylmercury.—Bistrifluoromethylmercury, purified by slow sublimation at 70°, gave large cubic crystals with a characteristic odour which produced a burning sensation in the nostrils. These were soluble in water. When the mercurial (0·280 g.) was heated with excess of iodine (2·0 g.) for 1 hour at 100°, and subsequently for 15 minutes at 150°, the only volatile reaction product was iodotrifluoromethane (0·317 g., 97·4%). Similarly when 2-g. samples were heated with excess of chlorine and excess of bromine, chlorotrifluoromethane and bromotrifluoromethane were obtained in yields of 95 and 92%, respectively. These products were characterised tensimetrically.

The reaction of bistrifluoromethylmercury with mercuric iodide required more vigorous conditions than with normal aliphatic and aromatic dimercurials. Trifluoromethylmercuric iodide was however formed in 75% yield at 170°. With acetone as solvent, the reaction was complete in 5 hours at 140°, but the yield of the mercuri-iodide was lower (50%) and some fluoroform (0·01 g.) was detected. The reaction of bistrifluoromethylmercury (0·50 g.) with mercuric chloride at 170° for 14 hours gave a 62% yield of trifluoromethylmercuric chloride, identical with a specimen prepared from trifluoromethylmercuric hydroxide.

Bistrifluoromethylmercury was slowly decomposed at temperature above 160° : after 14 hours at 170° about 40% had undergone reaction. Silicon tetrafluoride and carbon dioxide, formed by attack on the glass, were found in the products, but no hexafluoroethane was present. Globules of mercury were also produced. No decomposition to volatile reaction products could be detected when bistrifluoromethylmercury was dissolved in water and set aside for several hours at 20°. When the dimercurial (0·5 g.) was dissolved in water and heated to 130° for 12 hours, 80% was recovered unchanged. A faint opalescence was visible in the aqueous solution, but the very small amount of volatile material isolated was insufficient for identification. If it was fluoroform it corresponded in amount to less than 0·5% decomposition.

Conductivity of Aqueous Solutions of Bistrifluoromethylmercury.—Bistrifluoromethylmercury, prepared as described earlier, was purified by treating its solution in water with silver nitrate to convert the small amount of unchanged trifluoromethylmercuric iodide present into the nitrate. The faint precipitate of silver iodide was removed by filtration, and the solution extracted several times with ether, which leaves strong electrolytes, such as the nitrate, in the aqueous phase. The ethereal solution was evaporated and the residue sublimed several times at 70°, dissolved in conductivity water, and extracted with pure ether. After evaporation the residue was sublimed 4 times. There was no residue in these sublimations.

The conductivity of a freshly prepared solution of bistrifluoromethylmercury decreased slowly with time, reaching a steady value in 2—3 days. Thus the specific conductivity of an M/4-solution at 25° was initially 15 × 10^{-6} ohm^{-1} cm.$^{-1}$ and decreased to a constant value of 12 × 10^{-6}ohm^{-1} cm.$^{-1}$ in 2 days. When the solution was diluted, the initial conductivity again decreased to an equilibrium value. The specific conductivity of the solvent was 1·53 × 10^{-6} ohm^{-1} cm.$^{-1}$. Equilibrium values of the conductivity are recorded in the table.

Molarity.	M/4.	M/8.	M/16.	M/32.
Specific conductivity × 10^6 (ohm^{-1} cm.$^{-1}$)	12	9	6	4
Molar conductivity × 10^2	5	7	10	13

The graph of the molar conductivity against the square root of concentration is not a straight line. When the bistrifluoromethylmercury was extracted from the aqueous solution with ether (90% recovery), and the aqueous solution evaporated to dryness *in vacuo* at room temperature, no trifluoromethylmercuric hydroxide could be detected. The aqueous solution remained neutral during evaporation. There was also no evidence for the formation of mercuric hydroxide or fluoroform at room temperature. On addition of dilute solutions of potassium iodide, silver nitrate, or alkali hydroxide to aqueous solutions of bistrifluoromethylmercury no precipitate was formed, which suggests that mercuric ions were not present. Hydrogen sulphide, however, precipitated mercuric sulphide slowly when passed through an aqueous solution of the dimercurial.

Reaction of Trifluoromethylmercuric Iodide and Bistrifluoromethylmercury with Zinc and Magnesium Metals and Amalgams.—Trifluoromethylmercuric iodide (2·0 g.) was heated with zinc powder (4·0 g.) for 12 hours at 140° and water added to the reaction mixture. Fluoroform (21%) was steadily evolved during 2 hours. Zinc amalgam, fluoride, and iodide were present and no mercuri-iodide was recovered. If dry ether was added to the reaction mixture instead of water, only unchanged trifluoromethylmercuric iodide (40%) was isolated. Raising the temperature increased the amount of mercuri-iodide decomposed, but a fluoro-organozinc compound was not isolated. Similar results were obtained with magnesium shavings and with zinc and magnesium amalgams. If water was added to the reaction products fluoroform was evolved, but, if the reaction product was extracted with ether, the addition of water to either the ethereal extracts or the residual solid failed to liberate fluoroform. Evaporation of the ethereal solution yielded unchanged trifluoromethylmercuric iodide.

In a typical experiment bistrifluoromethylmercury (1·0 g.) and zinc dust (2·0 g.) were heated to 165° for 3 hours, and water was added to the reaction mixture. Fluoroform was slowly evolved, and after 30 minutes a 20% yield was obtained based on the mercury compound destroyed. Immediate ether-extraction of the filtered aqueous solution gave a 35% recovery of the dimercurial. Similar results were obtained with zinc amalgam and with magnesium. If the unchanged mercurial was removed from the reaction product by ether extraction, then the addition of water did not liberate fluoroform. The volatile products from the above reactions included silicon tetrafluoride, carbon dioxide, tetrafluoroethylene, and an unidentified fraction of molecular weight 150.

Reactions of Iodotrifluoromethane with Silver, Copper, and Cadmium Amalgams.—These provide a method of preparing bistrifluoromethylmercury without first isolating trifluoromethylmercuric iodide. Silver amalgam of the same composition as before reacted very slowly with iodotrifluoromethane (3·0 g.) at room temperature, but after 10 hours at 80° a 68% yield of bistrifluoromethylmercury was obtained, based on the fluoroiodide used (4%). At the optimum temperature of 200—250° for 24 hours the weight of dimercurial isolated per experiment had increased (0·17 g.) but the yield (15%) had decreased based on the fluoro-iodide used (between 40 and 50%). The volatile reaction products were silicon tetrafluoride and carbon dioxide, formed by attack on the reaction vessel.

Experiments on the reaction of iodotrifluoromethane (6·0 g.) and copper amalgam at the optimum temperature of 160—180° for 10—40 hours gave a yield of 40—60% (1·0—1·5 g.) based on the fluoro-iodide used (30—60%) in successive experiments. The yield of the dimercurial fell off rapidly at temperatures greater than 200°, and silicon tetrafluoride, carbon dioxide, small amounts of hexafluoroethane, and probably carbon monoxide were formed. Efficient shaking in a vibro-shaker was essential, otherwise the yields were low and variable. When iodotrifluoromethane (4·5 g.) and copper amalgam were irradiated with the mercury arc for 50 hours at room temperature, a 52% yield of the dimercurial based on the fluoro-iodide used (25%) was obtained. The yields were variable when both heat and irradiation were used, and between 20 and 60% of the iodotrifluoromethane underwent reaction at temperatures of 80—200° for 10—20 hours to yield 0·2—0·5 g. of bistrifluoromethylmercury.

Cadmium amalgam reacted with iodotrifluoromethane at room temperature without extensive decomposition and was the most suitable reagent for preparing bistrifluoromethylmercury. The fluoro-iodide (3·0 g.) was condensed into the Pyrex reaction tube containing cadmium amalgam (3·0 g. of cadmium, 20 c.c. of mercury). After 24 hours' shaking a white solid was present and the liquid phase had disappeared. The yield of pure dimercurial was consistently between 35 and 40%, based on the fluoro-iodide used (50—60%).

Reaction of Iodotrifluoromethane with Other Amalgams.—Sodium amalgam (0·6%) reacted vigorously with iodotrifluoromethane on gentle shaking and extensive decomposition to sodium fluoride and iodide occurred. No dimercurial or hexafluoroethane could be isolated. Ether and benzene were used in attempts to moderate the reaction, but the two sodium salts were again formed and a small yield (5—7%) of fluoroform was obtained. Addition of water to the reaction products did not liberate fluoroform and it is unlikely, therefore, that trifluoromethylsodium was present.

Magnesium amalgam, prepared by heating magnesium (4 g.) with mercury (20 c.c.), was shaken vigorously for 5 hours in sealed tubes with iodotrifluoromethane (3·0 g.) at room temperature. Heat was evolved and the amalgam was partly converted into a fine powder. Unchanged fluoro-iodide (48%) and a small amount of silicon tetrafluoride were isolated from the volatile products. On addition of water to the residue, hydrogen and fluoroform (24% yield) were evolved. Magnesium fluoride and iodide were also identified. The fluoroform could result either from the reduction of bistrifluoromethylmercury or from the decomposition of an organomagnesium compound. The first possibility was supported by the isolation of bistrifluoromethylmercury in low yield (3—20%) from the initial reaction product by extraction with dry ether and ensuring that moisture was excluded during the subsequent evaporation and sublimation. Unsuccessful attempts were made to cause any trifluoromethylmagnesium iodide present in the reaction product to react with methyl cyanide, acetone, α-naphthyl *iso*cyanate, and carbon dioxide. Similar results were obtained with zinc amalgam and iodotrifluoromethane (3·0 g.). Yields of up to 30% of the dimercurial were obtained, similar yields of fluoroform resulted on the addition of water, and all tests for the presence of an organozinc compound were negative. If ether was used as a solvent for iodotrifluoromethane during the reactions with magnesium or zinc amalgams, fluoroform was present in the volatile products, the majority of the fluoro-iodide was destroyed, and the addition of water did not liberate fluoroform. The reaction of iodotrifluoromethane (6·0 g.) with zinc amalgam (4 g. of zinc, 20 c.c. of mercury) which occurs on gentle rocking for 4 days affords 35—40% yields of bistrifluoromethylmercury based on the fluoroiodide used (40%).

Reaction of Trifluoromethylmercuric Iodide with Sodium Stannite and with Sodium Iodide.—A solution of sodium stannite was prepared by dissolving stannous chloride (0·7 g.) in water (10 c.c.) and adding a solution of sodium hydroxide (1·6 g.) in water (8 c.c.), and was slowly added with stirring to a solution of trifluoromethylmercuric iodide (1·0 g.) in water (30 c.c.) and alcohol (1 c.c.). A precipitate of finely divided mercury was obtained, and after 1 hour the solution was filtered and extracted with ether. No bistrifluoromethylmercury was present. The gas evolved during the reaction was shown to be fluoroform (63% yield).

Trifluoromethylmercuric iodide (2·0 g.) was dissolved in acetone (70 c.c.), sodium iodide (7·0 g.) added, and the solution heated under reflux for 1 hour. Portions of the yellow solution, filtered to remove a faint grey precipitate, were poured into water (400 c.c.) or allowed to evaporate at room temperature. Ether-extraction gave an oil, containing only carbon and hydrogen, which was apparently derived from the acetone. Bistrifluoromethylmercury was not detected. Potassium iodide reacted in aqueous solution as described in Part I.

Reduction of Trifluoromethyl Mercurials by Amalgams.—Trifluoromethylmercuric iodide (1·0 g.), zinc amalgam (0·5 g. of zinc, 5 c.c. of mercury), zinc dust (0·2 g.), and a globule of mercury were placed in a reaction tube which was evacuated. Water was added, and the volatile products, which were evolved steadily, were collected. The yield of fluoroform after a reaction time of 1 hour was 74%, and 3% of the mercurial was recovered unchanged by ether-extraction. With magnesium amalgam the yield of fluoroform was 81% in ½ hour. It was also found that a mixture of magnesium and magnesium iodide in presence of water produced fluoroform from trifluoromethylmercuric iodide.

Bistrifluoromethylmercury was reduced very slowly (4% in 3·5 hours) by a pure zinc amalgam in presence of water at room temperature, but the addition of zinc powder increased the reaction rate greatly. Thus, when water was added to a mixture of zinc powder (0·4 g.) + mercury (2 c.c.) (heated to give some zinc amalgam) and bistrifluoromethylmercury (0·5 g.), no unchanged mercurial could be detected after 2 hours, and a 95% yield of fluoroform was obtained. Addition of an iodide to zinc or magnesium amalgam and mercury also increased the rate of reduction of bistrifluoromethylmercury in presence of water.

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