228. *Reactions of Bistrifluoromethylthiomercury and Trifluoromethylthiomercuric Chloride.*

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Bistrifluoromethylthiomercury reacts with phosphorus and arsenic chlorides to form compounds of the types R_3M, R_2MCl, and $RMCl_2$ ($R = CF_3{\cdot}S$, M = P or As), some reactions of which are recorded. The reaction of bistrifluoromethylthiomercury with mercuric chloride, aqueous potassium iodide, iodine, bromine, and nitrosyl chloride has also been studied.

Bistrifluoromethylthiomercury was first made by irradiating a mixture of bistrifluoromethyl disulphide and mercury with ultraviolet light.[1] A more convenient preparation is the reaction of carbon disulphide with mercuric fluoride at high temperatures.[2] It is a crystalline solid which dissolves in water and organic solvents and is decomposed by dry hydrogen chloride to trifluoromethanethiol, $CF_3{\cdot}SH$.[3] It also reacts with chlorine, the main product being trifluoromethanesulphenyl chloride. It seemed probable that the mercurial would be a suitable reagent for introducing the trifluoromethylthio-group into inorganic and organic molecules, and present investigations have shown this to be the case. This paper describes the reaction of the mercurial with phosphorus and arsenic trichlorides and also some of its other reactions, together with those of trifluoromethylthiomercuric chloride.

The reaction of bistrifluoromethylthiomercury with an equimolar proportion of phosphorus trichloride at room temperature gives an almost quantitative yield of trifluoromethylthiomercuric chloride, $CF_3{\cdot}S{\cdot}HgCl$. The other product is dichloro(trifluoromethylthio)phosphine, $CF_3{\cdot}S{\cdot}PCl_2$. A small amount of trifluoromethanethiol is also obtained in

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[1] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2198.

[2] Muetterties, U.S.P. 2,729,663; *Chem. Abs.*, 1956, **50**, 11,362; Man, Coffman, and Muetterties, *J. Amer. Chem. Soc.*, 1959, **81**, 3575.

[3] Haszeldine and Kidd, *J.*, 1953, 3219.

all the experiments with phosphorus and arsenic chlorides, but this is readily accounted for by the action of a small amount of water on the non-metal halide and reaction of the resulting hydrogen chloride with the mercurial. By increasing the proportion of the mercurial, two or three atoms of chlorine in the phosphorus halide can be replaced, though it is necessary to heat the reaction mixture to obtain tristrifluoromethylthiophosphine. In each case the mercurial is converted into the half-chloride and no other product is formed, other than a small amount of thiol. Reaction of the mercurial with arsenic trichloride is very similar, and this method should be applicable for introducing the trifluoromethylthio-group into alkyl- and aryl-phosphines and -arsines by reaction with a chloro-derivative. Non-fluorinated analogues of the above compounds, such as $(EtS)_3P$ [4] and $Et{\cdot}PSCl_2$ [5] are known, but have not been extensively studied.

Bistrifluoromethylthiomercury reacts in these cases as a mild fluoroalkanethiolating agent and shows a greater resemblance to diethyl- or diphenyl-mercury than to bistrifluoromethylmercury. The last does not react with phosphorus or arsenic trichloride at 100°, whereas diethylmercury yields ethyldichlorophosphine [6] and, with excess of arsenic trichloride, ethyldichloroarsine.[7] Diphenylmercury reacts similarly with phosphorus [8] and arsenic trichlorides [9] and, in each case, the mercurial is converted into mercuric chloride rather than into phenylmercuric chloride.

The reactions of the trifluoromethylthio-phosphines and -arsines have not yet been studied in detail. The two phosphines $(CF_3{\cdot}S)_2PH$ and $(CF_3{\cdot}S)_3P$ were prepared by the reaction of trifluoromethanesulphenyl chloride with phosphine, and there was some evidence that the latter forms an unstable compound with chlorine.[10] If such a compound is formed by dichloro(trifluoromethylthio)phosphine, it appears to be at least as unstable. Preliminary experiments on the hydrolysis of the chloro(trifluoromethylthio)-phosphines and -arsines showed that the trifluoromethylthio-group was readily split off and no acids containing this group were formed. The hydrolytic reactions were not studied in sufficient detail for a full discussion of the reaction products or mechanism. Reaction of chloro(bistrifluoromethylthio)phosphine with ethanol gave trifluoromethanethiol and probably also chloro(trifluoromethylthio)ethoxyphosphine, $CF_3{\cdot}S{\cdot}PCl(OEt)$. It is likely, therefore, that even if the trifluoromethylthio-acids are unstable, some of their derivatives may be made. The reaction of chlorobistrifluoromethylarsine with ammonia was also complicated, but no direct replacement of chlorine by the NH_2 group occurred. With chlorobistrifluoromethylphosphine this occurs readily and yields the compound $(CF_3)_2P{\cdot}NH_2$.[11]

Bistrifluoromethylthiomercury reacted with mercuric chloride in ether to form trifluoromethylthiomercuric chloride in good yield. This is a convenient preparative method which parallels that for the selenium analogue.[12] Mercuric bromide under similar conditions did not react. There was no evidence for the formation of complex ions containing the trifluoromethylthio-group on mixing bistrifluoromethylthiomercury with aqueous potassium iodide. Mercuric iodide and carbonyl sulphide were produced. Mercurials containing fluoroalkyl groups, which are more stable to hydrolysis, readily form such complexes.[13] Jellinek and Lagowski [14] have also found, by conductimetric titration of bistrifluoromethylthiomercury with tetramethylammonium or potassium iodide in acetone

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[4] Liffert and Reid, *J. Amer. Chem. Soc.*, 1938, **60**, 2370.
[5] Michaelis, *Ber.*, 1872, **5**, 6.
[6] Guichard, *Ber.*, 1899, **32**, 74; Michaelis, *Ber.*, 1880, **13**, 2174.
[7] La Coste, *Annalen*, 1881, **208**, 33.
[8] Schwarze, *J. prakt. Chem.*, 1874, **10**, 222; Michaelis and Graeff, *Ber.*, 1875, **8**, 922; Michaelis *Annalen*, 1876, **181**, 265.
[9] La Coste and Michaelis, *Annalen*, 1880, **201**, 196.
[10] Emeléus and Nabi, preceding paper.
[11] Harris, *J.*, 1958, 512.
[12] Dale, Emeléus, and Haszeldine, *J.*, 1958, 2939.
[13] Emeléus and Lagowski, *J.*, 1959, 1497.
[14] Jellinek and Lagowski, *J.*, in the press.

solution, that complexes can exist under conditions where hydrolysis is excluded. Bistrifluoromethylthiomercury was converted by iodine in carbon tetrachloride solution into bistrifluoromethyl disulphide and mercuric iodide. With bromine the products were mercuric bromide and a mixture of the disulphide and trifluoromethanesulphenyl bromide. With nitrosyl chloride there was no evidence that the nitrosyl radical formed a compound with the trifluoromethylthio-group, as it does with the trifluoromethyl group. The mercurial was instead converted into mercuric chloride, and bistrifluoromethyl disulphide was formed in high yield.

EXPERIMENTAL

Bistrifluoromethylthiomercury was prepared by irradiation of a mixture of bistrifluoromethyl disulphide with mercury.[1] All the experiments described were made in a vacuum apparatus of the usual type, and separations were done either by fractional distillation or fractional condensation, using the appropriate low-temperature baths.

Reaction of Bistrifluoromethylthiomercury with Phosphorus Trichloride.—Phosphorus trichloride (0·426 g., 3·09 mmoles) and bistrifluoromethylthiomercury (1·250 g., 3·10 mmoles) reacted in a sealed tube at room temperature and gave trifluoromethylthiomercuric chloride (1·038 g.) (Found: Cl, 10·7. Calc. for $CClF_3SHg$: Cl, 10·55%) and trifluoromethanethiol (0·011 g.) (Found: *M*, 100. Calc. for CHF_3S: *M*, 102). The first of these products was also analysed in all subsequent experiments and, for the second, the molecular weight was determined and the infrared spectrum checked. The only other volatile product of the above reaction was *dichloro(trifluoromethylthio)phosphine* (Found: C, 5·9; Cl, 34·7; S, 15·9%; *M*, 203. CCl_2F_3PS requires C, 5·9; Cl, 35·0; S, 15·8%; *M*, 203). It was analysed by decompostion with 15% aqueous sodium hydroxide, oxidation with hydrogen peroxide, acidification with nitric acid, and precipitation of chloride as silver chloride. The filtrate was evaporated repeatedly with hydrochloric acid to remove fluoride, and sulphur then determined as barium sulphate. Vapour pressures of the compound (20—90°) were given by $\log_{10} p$ (mm.) = 7·345 − 1655/*T*. The b. p. was 98°, the latent heat of vaporisation 7568 cal./mole, and Trouton's constant 20·4.

Phosphorus trichloride (0·217 g., 1·58 mmoles) and bistrifluoromethylthiomercury (1·275 g., 3·17 mmoles) in a sealed tube at room temperature (40 hr.) gave trifluoromethylthiomercuric chloride (1·045 g.), trifluoromethanethiol (0·031 g.), and *chloro(bistrifluoromethylthio)phosphine* (Found: C, 8·4; Cl, 13·7; S, 13·5%; *M*, 267. $C_2ClF_6PS_2$ requires C, 8·9; Cl, 13·2; S, 23·8%; *M*, 269). Vapour pressures (20—100°) were given by $\log_{10} p$ (mm.) = 7·312 − 1721/*T*. The b. p. was 115°, the latent heat of vaporisation 8198 cal./mole, and Trouton's constant 21·1. A mixture of phosphorus trichloride (0·194 g., 1·33 mmoles) and bistrifluoromethylthiomercury (1·69 g., 4·20 mmoles) when heated in a sealed tube at 50° (72 hr.) gave trifluoromethylthiomercuric chloride (1·302 g.), trifluoromethanethiol (0·027 g.), and *tristrifluoromethylthiophosphine* (Found: C, 10·3; S, 29·2%; *M*, 330. $C_3F_9PS_3$ requires C, 10·8; S, 28·8%; *M*, 334). With these proportions of reactants at room temperature a mixture of the above products was formed.

Reaction of Bistrifluoromethylthiomercury with Arsenic Trichloride.—Arsenic trichloride (0·497 g., 2·74 mmoles) and bistrifluoromethylthiomercury (1·103 g., 2·74 mmoles) reacted in an evacuated sealed tube at room temperature (48 hr.) and gave trifluoromethanethiol (0·023 g.) (Found: *M*, 99. Calc. for CHF_3S: *M*, 102) (identity was confirmed by infrared spectrum), and trifluoromethylthiomercuric chloride (0·917 g., 2·72 mmoles). The only other volatile product was *dichloro(trifluoromethylthio)arsine* (0·63 g.) (Found: C, 4·9; Cl, 29·0; S, 12·9%; *M*, 224. CCl_2F_3AsS requires C, 4·9; Cl, 28·7; S, 13·0%; *M*, 247). Vapour pressures (20—100°) were given by $\log_{10} p$ (mm.) = 7·75 − 1939/*T*. The b. p. was 125°, the latent heat of vaporisation 8885 cal./mole, and Trouton's constant 22·3. The m. p. was −34°. A similar preparation with arsenic trichloride (0·364 g., 2·01 mmoles) and bistrifluoromethylthiomercury (1·625 g., 4·03 mmoles) gave trifluoromethylthiomercuric chloride (1·345 g.), trifluoromethanethiol (0·015 g.), and *chloro(bistrifluoromethylthio)arsine* (0·597 g.) (Found: C, 7·7; Cl, 11·6; S, 20·3%; *M*, 319. $C_2ClF_6AsS_2$ requires C, 7·7; Cl, 11·4; S, 20·5%; *M*, 312). Vapour pressures (20—100°) were given by $\log_{10} p$ (mm.) = 8·03 − 2066/*T*. The b. p. was 128°, the latent heat of vaporisation 9490 cal./mole, and Trouton's constant 23·7. The m. p. was −50°. Arsenic trichloride (0·319 g., 1·76 mmoles) and bistrifluoromethylthiomercury (2·306 g., 5·73 mmoles), after being heated in a sealed tube at 50° (72 hr.), gave trifluoromethylthiomercuric chloride (1·702 g.), trifluoromethanethiol (0·004 g.), and, after several refractionations, *tristrifluoromethylthioarsine* (0·60 g.) (Found: C, 9·4; S, 26·0%; *M*, 374. $C_3F_9AsS_3$ requires C, 9·5; S, 25·5%; *M*, 378).

Reaction of Dichloro(trifluoromethylthio)phosphine with Chlorine.—The phosphine (0·470 g., 2·31 mmoles) and chlorine (0·164 g., 2·31 mmoles) were sealed in a 20 ml. tube and left at −78° (12 hr.). A pale yellow solid and some liquid were present. Volatile material was removed at −22° and fractionated. It gave a liquid which condensed at −63° (0·252 g.) (Found: Cl, 47·2; S, 11·5%; *M*, 150). This is consistent with a mixture of phosphorus trichloride (0·072 g.) and dichloro(trifluoromethylthio)phosphine (0·180 g.). The volatile fraction was trifluoromethanesulphenyl chloride (Found: *M*, 136. Calc. for $CClF_3S$: *M*, 136·5), whose identity was confirmed by the infrared spectrum. The solid was phosphorus pentachloride (Found: Cl, 86·0. Calc. for Cl_5P: Cl, 85·0%).

Hydrolysis of Chloro(trifluoromethylthio)-phosphines and -arsines.—(a) *Chloro(bistrifluoromethylthio)phosphine.* The phosphine (0·430 g.) and water (0·029 g.) were shaken for 24 hr. and gave a viscous liquid and a more mobile phase. The volatile products were trifluoromethanethiol (0·160 g.) (Found: *M*, 100. Calc. for CHF_3S: *M*, 102) and unchanged chloro(bistrifluoromethylthio)phosphine (Found: Cl, 13·9; S, 24·6. Calc. for $C_2ClF_6PS_2$: Cl, 13·2; S, 23·9%). The viscous involatile liquid showed no infrared absorption bands due to the trifluoromethylthio-group. It gave a strongly acid solution in water, which contained chloride and reduced mercuric chloride solution.

(b) *Dichloro(trifluoromethylthio)phosphine.* The chlorophosphine (0·391 g.) and water (0·070 g.) were shaken as before and gave hydrogen chloride (0·142 g.), which, from the infrared spectrum, contained a small amount of thiol. A fraction which condensed at −132° (0·180 g.) had *M* 98 and was trifluoromethanethiol. The infrared spectrum showed the presence of a little carbonyl sulphide. The involatile product gave qualitative tests for phosphorous acid and showed no infrared absorption due to the trifluoromethylthio-group.

(c) *Dichlorotrifluoromethylthioarsine.*—The arsine (0·572 g.) and water (0·083 g.) formed a homogeneous solution when shaken together. Fractionation of the volatile products gave a fraction which condensed at −196° (0·073 g.), had *M* 71, and was shown, by its infrared spectrum, to contain carbonyl sulphide, silicon tetrafluoride, and trace of the thiol. Hydrogen chloride was absent. A fraction which condensed at −132° (0·040 g.) had *M* 81, and, from the infrared spectrum, contained the thiol and carbonyl sulphide. Dichloro(trifluoromethylthio)arsine (0·287 g.; *M*, 242) was recovered unchanged. The residual liquid of low volatility gave no infrared absorption due to the trifluoromethylthio-group. With water it gave a solution containing chloride and arsenite.

Reactions of Chloro(bistrifluoromethylthio)phosphine.—(i) *With ammonia.* The chlorophosphine (0·228 g.) and ammonia (0·030 g.) reacted quickly in a sealed tube after removal from a cooling bath at −78°. A small quantity of the chlorophosphine was recovered (*M*, 269) The infrared spectrum of this showed no bands due to the amino-group. All the ammonia was used. The solid residue was soluble in water, and the solution contained ammonium chloride and fluoride.

(ii) *With ethanol.* The chlorophosphine (0·410 g.) and ethanol (0·071 g.) in a sealed tube at 20° (36 hr.) gave trifluoromethanethiol (0·152 g.) (Found: *M*, 100. Calc. for CHF_3S: *M*, 102). A volatile fraction which condensed in a trap at −63° (0·228 g.) was probably impure *chloro(trifluoromethylthio)ethoxyphosphine* (Found: Cl, 18·7; S, 17·2%; *M*, 195. $C_3H_5OClF_3PS$ requires Cl, 16·7; S, 15·1%; *M*, 212). Its infrared spectrum showed bands at 1040 and 960 cm.$^{-1}$, characteristic of the P–OEt group, and also those of the trifluoromethylthio-group. A small amount of solid was left in the reaction tube which showed infrared bands characteristic of the trifluoromethylthio-group.

Reactions of Bistrifluoromethylthiomercury.—(a) *With mercuric chloride.* Bistrifluoromethylthiomercury (0·301 g.) and mercuric chloride (0·204 g.), each in ether (10 ml.), were mixed and shaken at room temperature. The product, after removal of ether, was sublimed in a vacuum at 40—50° and was trifluoromethylthiomercuric chloride (0·45 g.) (Found: Hg, 61·0; Cl, 10·4. Calc. for CF_3ClSHg: Hg, 61·2; Cl, 10·55%).

(b) *With mercuric bromide.* The mercurial (0·400 g.) and mercuric bromide (0·358 g.) in a similar experiment gave, after removal of ether and vacuum sublimation, mercuric bromide (mixed m. p. 232—235°; m. p. of $HgBr_2$, 235°). The *X*-ray powder photograph was identical with that of mercuric bromide. A second, more volatile fraction in the sublimation was bistrifluoromethylthiomercury (m. p. 35°). Its identity was checked by infrared spectrum and it contained no bromide.

(c) *With aqueous potassium iodide.* Bistrifluoromethylthiomercury (0·200 g., 0·50 mmole) and potassium iodide (0·166 g., 1·0 mmole) reacted rapidly in water (2 ml.) at room temperature to form carbonyl sulphide (0·053 g.) (Found: *M*, 60. Calc. for COS: *M*, 60) (identity confirmed by infrared spectrum) and mercuric iodide (0·215 g.). Similar experiments with aqueous potassium chloride or bromide and the mercurial in a 2 : 1 molar ratio also gave approx. 90% of the carbonyl sulphide expected from the complete breakdown of the trifluoromethylthio-groups. Tristrifluoromethylthiomercuric chloride (0·400 g., 1·2 mmoles) and potassium iodide (0·400 g., 2·4 mmoles) in water (2 ml.) gave carbonyl sulphide (0·064 g., 1·1 mmoles) and mercuric iodide (0·525 g.).

(d) *With bromine and iodine.* The mercurial (0·458 g.) and iodine (0·578 g.) in carbon tetrachloride solution at room temperature gave bistrifluoromethyl disulphide (Found: *M*, 201. Calc. for $C_2F_6S_2$: *M*, 202) (identity checked by the infrared spectrum) and mercuric iodide (0·508 g., m. p. 259°). Reaction in absence of a solvent was similar but less complete. Bistrifluoromethylthiomercury (0·533 g.) and bromine (0·422 g.) at 20° gave mercuric bromide (0·470 g., m. p. 236°), free bromine (0·037 g.), and a mixture (*M*, 184) which, from the infrared spectrum, contained trifluoromethanesulphenyl bromide and bistrifluoromethyl disulphide. In a repeat experiment at 0° this mixture had *M* 190 and contained Br, 24·5%, indicating a mixture of 55% of the sulphenyl bromide and 45% of disulphide. It could not be separated by trap-to-trap distillation in the vacuum system. A reaction in carbon tetrachloride solution gave similar results.

(e) *With nitrosyl chloride.* Bistrifluoromethylthiomercury (0·201 g.) and nitrosyl chloride (0·065 g.) reacted below room temperature and gave bistrifluoromethyl disulphide (0·096 g., 95%). A fraction which condensed in liquid nitrogen (0·035 g.; *M*, 40) was mainly nitric oxide mixed with a little trifluoromethanesulphenyl chloride, detected by its infrared spectrum. Mercuric chloride (0·133 g., m. p. 274—276°) was also produced.

Reactions of Trifluoromethylthiomercuric Chloride.—(i) *With silver nitrate.* The chloride (0·300 g.) and silver nitrate (0·150 g.) were separately dissolved in water (10 ml.) acidified with nitric acid, and the solutions mixed. Silver chloride was filtered off, and the filtrate freeze-dried. The residue was sublimed in vacuum at 100° and gave *trifluoromethylthiomercuric nitrate* (0·235 g., 65%) (Found: Hg, 56·6. CO_3NF_3SHg requires Hg, 56·7%).

(ii) *With silver acetate.* The mercurial (0·324 g.) and silver acetate (0·161 g.) similarly gave silver chloride and a solid residue after the filtrate had been freeze-dried. When this was sublimed in vacuum a small amount of unchanged chloride sublimed at 40°. The sublimate at 70° was *trifluoromethylthiomercuric acetate* (0·21 g., 60%), which was free from chloride (Found: Hg, 57·3. $C_3H_3O_2F_3SHg$ requires Hg, 57·2%).

Infrared Spectra.—Measurements were made on a Perkin-Elmer Model 21 double-beam spectrometer fitted with sodium chloride or potassium bromide prisms. The spectra of the phosphines and arsines were measured in the vapour phase with a 10 cm. cell, and solid mercurials were examined as mulls with Nujol and hexachlorobutadiene. The chief bands observed are listed below, the letters having their usual significance.

$CF_3{\cdot}S{\cdot}PCl_2$: 2290 w, 1303 w, 1325 w, 1182 s, 1172 s, 1118 s, 1100 s, 1020 w, 754 m.
$(CF_3{\cdot}S)_2PCl$: 2285 w, 1933 w, 1883 w, 1865 w, 1324 w, 1303 w, 1183 s, 1173 s, 1120 s, 1100 s, 753 m
$(CF_3{\cdot}S)_3P$: 2270 w, 1323 w, 1300 w, 1262 w, 1183 s, 1170 s, 1126 s, 1097 s, 1013 w, 754 m.
$(CF_3{\cdot}S)AsCl_2$: 2260 w, 1378 w, 1368 w, 1183 s, 1165 s, 1113 s, 1098 s, 757 m.
$(CF_3{\cdot}S)_2AsCl$: 2280 w, 1180 s, 1166 s, 1097 s, 735 m.
$(CF_3{\cdot}S)_3As$: 2290 w, 1300 w, 1163 s, 1125 s, 1097 s, 1027 w, 756 m.
$(CF_3{\cdot}S)HgCl$: 1307 w, 1300 w, 1215 w, 1165 s, 1135 s, 1090 s, 1073 s, 752 m.
$(CF_3{\cdot}S)HgNO_3$: 1387 s, 1308 m, 1215 w, 1185 s, 1135 s, 1098 s, 808 w, 754 m.
$(CF_3{\cdot}S)HgOAc$: 2940 w, 1600 m, 1387 m, 1325 m, 1219 w, 1092 s, 1018 w, 753 m.

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