

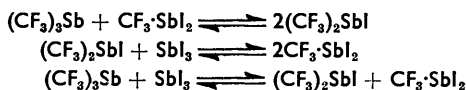
730. Organometallic and Organometalloidal Fluorine Compounds. Part XIII.* Trifluoromethyl Derivatives of Antimony.†

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Trifluoroiodomethane reacts with antimony at 165–170° to give the compounds $(\text{CF}_3)_3\text{Sb}$, $(\text{CF}_3)_2\text{SbI}$, and $\text{CF}_3\cdot\text{SbI}_2$; at higher temperatures fluorocarbons are produced. Tristrifluoromethylstibine shows markedly reduced donor properties compared with trimethylstibine, and can act as an acceptor, *e.g.*, by forming the solid $\text{C}_5\text{H}_5\text{N}\cdot\text{Sb}(\text{CF}_3)_3$. The quinequivalent derivative, $(\text{CF}_3)_3\text{SbCl}_2$, similarly forms a 1:1 compound with pyridine. The preparation and certain reactions of the compounds $(\text{CF}_3)_3\text{SbBr}_2$, $(\text{CF}_3)_2\text{SbBr}$, $\text{CF}_3\cdot\text{SbBr}_2$, $(\text{CF}_3)_2\text{SbCl}$, $(\text{CF}_3)_2\text{SbCl}_3$, and $(\text{CF}_3)_2\text{Sb}\cdot\text{Sb}(\text{CF}_3)_2$ are described, and comparisons drawn with corresponding phosphorus and arsenic derivatives.

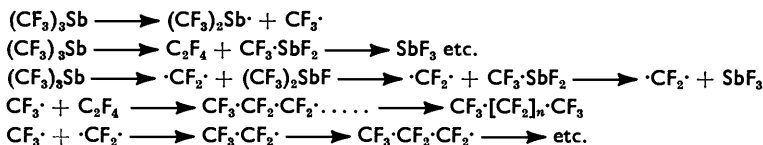
THE synthesis of numerous trifluoromethyl derivatives by direct reaction of metals or metalloids with trifluoroiodomethane has been recorded in earlier Parts of this series. The preparation and properties of a series of antimony compounds are now described.

With the necessary control of temperature and pressure, reaction of trifluoroiodomethane with antimony gives mainly tristrifluoromethylstibine with smaller amounts of iodobistrifluoromethylstibine and di-iodotrifluoromethylstibine. The proportion of the iodo-compounds can be increased by use of a mixture of antimony and antimony tri-iodide at a lower reaction temperature. This suggests that a series of equilibria is involved, *e.g.*:



The iodo-compounds disproportionate much more readily than the corresponding derivatives of phosphorus or arsenic,^{1,2} and isolation of di-iodotrifluoromethylstibine, a viscous yellow oil, proved to be particularly difficult.

If the reaction temperature is allowed to rise above the optimum of 165–175°, fluorocarbons are produced, probably by conversion of tristrifluoromethylstibine into tetrafluoroethylene or difluoromethylene radicals, followed by combination with the CF_3 radicals arising by homolytic fission of the CF_3 -Sb bond:



Carbon tetrafluoride arises by the action of antimony fluorides on trifluoroiodomethane.

Tristrifluoromethylstibine, b. p. 72° (cf. Me_3Sb , b. p. 80°), decomposes at 180°, but is stable to water at 100°; concentrated hydrochloric acid at this temperature converts it into fluoroform. As with almost all other trifluoromethyl derivatives of trivalent phosphorus, arsenic, or antimony, dilute aqueous sodium or potassium hydroxide hydrolyses tristrifluoromethylstibine to fluoroform rapidly and quantitatively at room temperature. The stibine is readily oxidised by air, but fails to react with sulphur. No reaction could be detected between tristrifluoromethylstibine (as a possible donor) and

* Part XII, *J.*, 1955, 563.

† Presented at Amer. Chem. Soc. Meeting, New York, 1954, Abs., p. 35M.

¹ Bennett, Emeléus, and Haszeldine, *J.*, 1953, 1565; 1954, 3598, 3896.² Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2552; Emeléus, Haszeldine, and Walaschewski, *J.*, 1953, 1552.

aluminium chloride, mercury chloride, or palladium chloride. The effect on antimony of the electron-attracting trifluoromethyl groups, which have at times pseudohalogen characteristics, is clearly demonstrated by the increased sensitivity to hydrolysis and by the formation of a 1:1 compound with pyridine, $C_5H_5N, Sb(CF_3)_3$, where antimony is clearly an acceptor; by contrast, trimethylstibine is a donor which forms complexes readily with palladium or platinous chloride.³ Trimethylstibine does not form a complex with tris(trifluoromethyl)stibine. Antimony trichloride also shows acceptor properties and yields complexes with ammonia, quinoline, dimethyl sulphide, and other organic donors.⁴

Tris(trifluoromethyl)stibine shows four strong bands, at 8.43, 8.75, 8.91, and 9.17 μ , in the C-F stretching vibration region and a strong band at 13.85 μ attributed to CF_3 deformation [cf. $(CF_3)_3P$ 13.3; $(CF_3)_3As$ 13.6 μ].

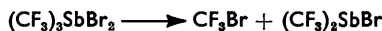
Tris(trifluoromethyl)stibine reacts smoothly and exothermally with chlorine at -45° to give tris(trifluoromethyl)antimony dichloride, $(CF_3)_3SbCl_2$; reaction at higher temperatures causes loss of chlorotrifluoromethane. There is a marked contrast between the labile, liquid tris(trifluoromethyl)antimony dichloride and trimethylantimony dichloride, a white solid decomposing only at 150–200°. Tris(trifluoromethyl)antimony dichloride is hydrolysed immediately with aqueous alkali according to the equation:



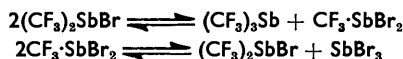
The properties of tris(trifluoromethyl)antimonic acid and its salts have been described earlier.⁵ Tris(trifluoromethyl)antimony dichloride forms a 1:1 complex with pyridine. Antimony pentachloride, but not phosphorus pentachloride, is known to form many stable 1:1 complexes, including those with water, ether, and pyridine.⁶ Antimony pentabromide⁷ can exist as the six-co-ordinated etherate $Et_2O, SbBr_5$, whereas phosphorus pentabromide⁸ is in the four-co-ordinate form $PBr_4^+Br^-$. Attempts to form complexes of tris(trifluoromethyl)antimony dichloride with phosphorus pentachloride, aluminium chloride, or auric chloride were unsuccessful, although the compound $SbCl_5, AuCl_3$, formulated as $SbCl_4^+AuCl_4^-$, has been described.⁹

Mercury reconverts tris(trifluoromethyl)antimony dichloride into tris(trifluoromethyl)stibine quantitatively.

The reaction of bromine with tris(trifluoromethyl)stibine is more difficult to control. At -30° tris(trifluoromethyl)antimony dibromide is formed, whereas reaction at 20° gives bromobis(trifluoromethyl)stibine, dibromotrifluoromethylstibine, and bromotrifluoromethane. Tris(trifluoromethyl)antimony dibromide decomposes when kept at room temperature:



Bromobis(trifluoromethyl)stibine disproportionates only slowly when kept:



Iodobis(trifluoromethyl)stibine is best prepared from tris(trifluoromethyl)stibine by reaction with iodine or antimony tri-iodide; it readily disproportionates on exposure to heat or light to give products analogous to those from the bromo-compound.

The iodine atom is reactive, as in the corresponding phosphorus or arsenic compounds,

³ Morgan and Yardley, *J.*, 1925, **127**, 184.

⁴ Rose, *Pogg. Ann.*, 1830, **20**, 160; Schiff, *Annalen*, 1864, **131**, 116; Adhikari, Ray, and Roy, *J. Indian Chem. Soc.*, 1931, **8**, 715.

⁵ Emeléus and Moss, *Z. anorg. Chem.*, 1955, **282**, 24.

⁶ Anschutz and Evans, *Annalen*, 1887, **239**, 291; Williams, *Trans. Faraday Soc.*, 1876, **30**, 463.

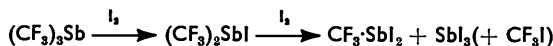
⁷ Raynaud, *Bull. Soc. chim. France*, 1920, **27**, 411.

⁸ Van Driel and Macgillavry, *Rec. Trav. chim.*, 1943, **62**, 167.

⁹ Sidgwick, "The Chemical Elements and Their Compounds," Clarendon Press, Oxford, 1950, p. 191.

but disproportionation often occurs faster than a simple replacement reaction. Silver chloride gives chlorobistrifluoromethylstibine, a compound that disproportionates readily to tristrifluoromethylstibine and antimony trichloride.

Further reaction of iodobistrifluoromethylstibine with iodine at room temperature gives di-iodotrifluoromethylstibine:



Mercury or, better, zinc reacts with iodobistrifluoromethylstibine to give tetrakis-trifluoromethylstibine. The boiling points of this and other stibines are compared with the corresponding nitrogen, phosphorus, and arsenic compounds in the annexed Table.

Boiling points of some trifluoromethyl compounds.

Element (M):	N	P	As	Sb
(CF ₃) ₃ M	-11°	17°	33°	72°
(CF ₃) ₂ MI	—	73	92	ca. 129
CF ₃ ·MI ₂	—	153	183	>200
(CF ₃) ₂ MCl	—	21	46	ca. 88
(CF ₃) ₂ MBr	—	—	60	113
CF ₃ ·MBr ₂	—	—	118	155
[(CF ₃) ₂ M·] ₂	20°/95 mm.	84	107	ca. 136
(CF ₃) ₃ MCl ₂	—	94	98	ca. 101
(CF ₃) ₂ MCl ₃	—	107	95	13°/5 mm.*

* Vapour pressure of the solid.

Cf. Me₃SbCl, b. p. 155—160°; Me₂SbBr, b. p. 175—180°; (Me₂Sb)₂, b. p. 190°.

Trifluoromethyl derivatives of trivalent antimony boil 30—50° higher than the corresponding arsines and 50—60° higher than the phosphines. The analogous methylstibines are often solids at room temperature and have much higher boiling points. The relatively slight increase in boiling point in the series (CF₃)₃MCl₂ as the element (M) increases in atomic weight is noteworthy.

Tetrakis-trifluoromethylstibine is a pale yellow liquid unlike its methyl analogue, which is a bright red solid melting to a yellow oil.

Tetrakis-trifluoromethylstibine liberates almost the whole of its fluorine as fluoroform on hydrolysis with aqueous alkali, and only 1—2% [cf. 9% for (CF₃)₂P·P(CF₃)₂ and 16% for (CF₃)₂As·As(CF₃)₂]^{1,2} as fluoride. Reaction of tetrakis-trifluoromethylstibine with an excess of bromine or iodine at higher temperatures yields bromotrifluoromethane or trifluoroiodomethane; chlorine cleaves the Sb—Sb bond at -78° to form the trichloride (CF₃)₂SbCl₃. In many ways, tetrakis-trifluoromethylstibine is a more convenient source of bistrifluoromethylantimony derivatives than is iodobistrifluoromethylstibine.

The trifluoromethyl derivatives of trivalent antimony are thus prepared from trifluoroiodomethane with distinctly greater difficulty than the corresponding phosphorus or arsenic compounds, and are appreciably less stable thermally; the metal-carbon bond becomes weaker as the atomic weight of the metal or metalloid increases within the group. The reactions of tristrifluoromethylstibine with the halogens, by addition and/or substitution, resemble those of tristrifluoromethyl-phosphine or -arsine. Antimony reaches the quinquivalent state more easily than arsenic, however, and this is shown in its trifluoromethyl derivatives. Tristrifluoromethylarsenic dichloride is known, but attempts to make the bromide (CF₃)₃AsBr₂ failed.² The existence of tristrifluoromethylantimony dibromide but not of antimony pentabromide suggests that quinquivalent antimony is more stable in its trifluoromethyl derivatives than in its fully inorganic halides. Quinquivalent antimony appears to be most stable in its alkyl compounds, however, since trimethylantimony di-iodide has been reported.¹⁰ All attempts to make tristrifluoromethylantimony di-iodide failed; there was no reaction between tristrifluoromethylstibine and

¹⁰ Landolt, *Annalen*, 1852, **84**, 44.

iodine at low temperatures, and cleavage to give trifluoroiodomethane occurred at higher temperatures (*ca.* 20°). The ease of such cleavage increases with the atomic weight of the group VB elements: tristrifluoromethylphosphine reacts with iodine at 180° and tristrifluoromethylarsine at 100°.

EXPERIMENTAL

Reactions were carried out in sealed tubes unless otherwise stated, and conventional vacuum-techniques were used for the manipulation of volatile products. Where possible, the antimony compounds were analysed by treatment with 10% aqueous potassium hydroxide at 70° for 24 hr. to give fluoroform quantitatively; this was distilled *in vacuo* and weighed. Ionic fluorine was determined by titration with thorium nitrate, and covalent fluorine by fusion with sodium followed by steam-distillation of the acidified solution and titration with thorium nitrate. Antimony was determined by the iodine or bromate method. Molecular weights were determined by Regnault's method.

Reaction of Antimony with Trifluoroiodomethane.—Preliminary experiments showed that Pyrex tubes were unsuitable as reaction vessels since extensive attack on the glass occurred. The most suitable apparatus was found to be a 300 ml. steel cylinder to which were added coarsely ground antimony (50–100 g.) and trifluoroiodomethane (75–120 g.). The cylinder was sealed and rotated in a horizontal position for 3–10 hr. whilst immersed in an oil-bath. Little reaction occurred at <160°, and 165–175° was the optimum temperature with this size of apparatus. This is distinctly lower than the temperature required for the preparation of the corresponding phosphorus or arsenic compounds. Rotation of the cylinder prevents sintering of the antimony tri-iodide which cuts down the surface area of the antimony considerably and so prevents further reaction. Use of a high pressure (>50 atm. calc.) was found necessary for good yields.

In a typical experiment, antimony (100 g.) and trifluoroiodomethane (75 g.) heated at 165–170° for 7 hr. gave a mixture (30 g.) of trifluoromethylantimony compounds containing approx. 90% of tristrifluoromethylstibine and 10% of iodobistrifluoromethylstibine; with a different ratio, antimony (50 g.) and trifluoroiodomethane (110 g.) gave 18 g. of crude product (90% yield based on trifluoroiodomethane consumed). Distillation of the crude product obtained from several experiments of the above type gave *tristrifluoromethylstibine* (Found: CF₃, 63.2; Sb, 37.1%; *M*, 328. C₃F₉Sb requires CF₃, 63.0; Sb, 37.0%; *M*, 329), b. p. 72°, *iodobistrifluoromethylstibine* (Found: CF₃, 35.7; I, 32.8; Sb, 31.7. C₂F₆ISb requires CF₃, 35.7; I, 32.8; Sb, 31.5%), b. p. 16°/8 mm., m. p. –42°, and impure di-iodotrifluoromethylstibine (Found: CF₃, 14.0; I, 56.2; Sb, 26.8. Calc. for CF₃I₂Sb: CF₃, 15.5; I, 57.1; Sb, 27.4%), m. p. 4–8°, b. p. >200° (with disproportionation).

The solid residue in the cylinder contained antimony tri-iodide, isolated by sublimation *in vacuo* (Found: I, 75.4; Sb, 24.0. Calc. for SbI₃: I, 75.7; Sb, 24.3%), m. p. 168°. Qualitative tests for fluoride were positive, but there were no quinquevalent antimony compounds present, and treatment of the solid with aqueous alkali failed to liberate fluoroform.

Reaction at temperatures above the optimum caused extensive side-reactions; at 200°, for example, about 75% of the liquid product was fluorocarbon [Found: F, 76.1. Calc. for (CF₂)_{*n*}: F, 76.0%], b. p. range –40° to 150°, showing the typical infrared spectrum and chemical and thermal stability of this type of compound.

Reaction of fresh antimony with trifluoroiodomethane at the optimum temperature gave *ca.* 10% of the liquid product as iodobistrifluoromethylstibine; if the antimony, now containing antimony tri-iodide, was used in subsequent reactions with trifluoroiodomethane, the iodobistrifluoromethylstibine content of the liquid product increased to 25%. The yield of the iodostibine was higher at 165° than at 175°.

The first experiment with fresh antimony in a clean reaction vessel always gave low yields, but the second experiment with fresh antimony gave good yields; this is attributed to the decomposition of trifluoroiodomethane on the walls and to the deposition of antimony tri-iodide on the walls of the vessel, thus providing a protective coating for the second experiment.

Tristrifluoromethylstibine.—The vapour pressure *p* of this colourless mobile liquid is given by the expression $\log_{10} p$ (mm.) = 7.031 – 1811/*T*, where *T* is the temperature in °K, whence the b. p. is 71.7° and Trouton's constant is 24.0. The m. p. is –58°. The liquid is oxidised in air with formation of white fumes of carbonyl fluoride and carbon dioxide, and the exothermic

reaction will ignite a 0.2 ml. sample of the liquid, or produce a mild explosion in the vapour. Tristrifluoromethylstibine is stable at 160° *in vacuo* and is not decomposed on exposure to daylight.

Tristrifluoromethylstibine (2.19 g.) is insoluble in water (5 ml.) and is recovered unchanged after being heated with it at 100° for 8 hr. The stibine (1.70 g.) was unaffected by concentrated hydrochloric acid (5 ml.) at 20°, but completely destroyed by it after 6 hr. at 100° to give fluoroform (0.99 g., 90%) and fluoride. The stibine was hydrolysed quantitatively to fluoroform and antimonite by 2*N*-aqueous potassium hydroxide at 20° during 24 hr.

Trifluoromethylstibine failed to react with sulphur between -40° and 100°, though sulphur is appreciably soluble in the stibine at 100°. There was no reaction with aluminium chloride or palladous chloride at 20° (24 hr.).

Pyridine (0.027 g.) and tristrifluoromethylstibine (0.192 g.) reacted as the mixture warmed from -80°, to give white crystals soluble in the excess of the stibine as the temperature increased. The unchanged tristrifluoromethylstibine was removed at 0° by pumping, to leave *tristrifluoromethylstibine-pyridine* (Found: CF₃, 50.5. C₅H₅NF₉Sb required CF₃, 50.8%) as a white solid, m. p. 39°. The vapour pressure of the liquid is given by the equation $\log_{10} p$ (mm.) = 8.713 - 2740/*T* whence the b. p. is approx. 127°. The high value of 31 obtained for Trouton's constant from this equation suggests that the compound dissociates in the vapour phase, as often found with weak complexes.

Reaction of Tristrifluoromethylstibine with Halogens.—(a) *With chlorine.* Tristrifluoromethylstibine (0.874 g.) was treated with nine successive portions of chlorine (0.189 g., total) at -40° to -50°. Each addition caused an exothermic reaction, and the mixture was cooled before addition of the next portion of chlorine to prevent explosive decomposition. Distillation *in vacuo* gave *tristrifluoromethylantimony dichloride* (1.053 g.) (Found: CF₃, 51.8; Cl, 17.7; Sb, 29.9%; *M*, 401. C₃Cl₂F₉Sb requires CF₃, 51.8; Cl, 17.7; Sb, 30.4%; *M*, 400) as a colourless liquid, m. p. -34°, whose vapour pressure is given by the equation $\log_{10} p$ (mm.) = 7.290 - 2024/*T* between -30° and 50°, whence the extrapolated b. p. is 101°. The chloro-compound decomposes slowly at 20°, more rapidly at 50° and above to give chlorotrifluoromethane. It is stable in dry air.

Tristrifluoromethylantimony dichloride (0.122 g.) and mercury (10.4 g.), shaken for 15 min., gave tristrifluoromethylstibine (0.099 g.) (Found: *M*, 326. Calc. for C₃F₉Sb: *M*, 329), and mercury chlorides.

Reaction of the chloro-compound (0.660 g.) with pyridine (0.054 g.) followed by pumping for 30 min. gave the white infusible solid *tristrifluoromethylantimony dichloride-pyridine* (0.301 g.) (Found: CF₃, 42.9. C₅H₅NCl₂F₉Sb requires CF₃, 43.2%).

(b) *With bromine.* Tristrifluoromethylstibine (0.798 g.) dissolved bromine (0.362 g.) slowly at -30°, to give the unstable yellow *tristrifluoromethylantimony dibromide* (Found: CF₃, 42.8; Br, 32.9; Sb, 24.9. C₃Br₂F₉Sb requires CF₃, 42.4; Br, 32.7; Sb, 24.9%), m. p. -16°, purified by trap-to-trap distillation *in vacuo*. Bromotrifluoromethane is not liberated during this reaction.

Reaction of the stibine (13.8 g.) with bromine (7.2 g.) by mixing at -30° then warming to 20° gave, after 17 hr., tristrifluoromethylstibine (5.40 g.), *bromobistrifluoromethylstibine* (4.9 g.) (Found: CF₃, 40.7; Br, 23.7. C₂BrF₆Sb requires CF₃, 40.7; Br, 23.6%), b. p. 113°, *dibromotrifluoromethylstibine* (1.9 g.) (Found: CF₃, 19.9; Br, 45.0. CBr₂F₃Sb requires CF₃, 19.7; Br, 45.6%), b. p. 34°/2.5 mm., *ca.* 155°/760 mm., bromotrifluoromethane, and antimony tribromide.

(c) *With iodine.* Powdered iodine (0.383 g.) gave a pale violet solution in tristrifluoromethylstibine (1.171 g.), deepening to brown, when shaken with it in a sealed 50 ml. tube. The colour soon faded and after 30 min. all the iodine had dissolved, to give an orange-yellow solution with deposition of a red solid and evolution of a gas. Fractionation, carried out immediately to minimise disproportionation of the products, gave trifluoroiodomethane (Found: *M*, 195. Calc. for CF₃I: *M*, 196), tristrifluoromethylstibine, iodobistrifluoromethylstibine (0.314 g., 54%) with an infrared spectrum identical with that of the material described earlier, crude di-iodotrifluoromethylstibine (14%) (Found: CF₃, 16.3; I, 55.5; Sb, 26.0. Calc. for CF₃I₂Sb: CF₃, 15.5; I, 57.1; Sb, 27.4%) as a yellow oil, and antimony tri-iodide. This is the best method for preparation of iodobistrifluoromethylstibine.

Tristrifluoromethylstibine (0.20 g.) and antimony tri-iodide (3.0 g.), heated at 120° for 7 days in a 15 ml. sealed tube, gave iodobistrifluoromethylstibine, identified spectroscopically, along with unchanged tristrifluoromethylstibine and antimony tri-iodide.

Iodobistrifluoromethylstibine decomposes rapidly when heated, particularly in light. A sample (0.206 g.) kept for 6 months in the dark at 20° gave trifluoromethylstibine (0.055 g.), unchanged iodobistrifluoromethylstibine (0.101 g.), di-iodotrifluoromethylstibine (0.004 g.), and antimony tri-iodide (0.039 g.). Traces of air or alkali catalyse the disproportionation.

Di-iodotrifluoromethylstibine is a viscous bright yellow liquid which freezes to a pale yellow solid. It is stable to water but decomposed readily by aqueous potassium hydroxide with evolution of fluoroform. Disproportionation occurs slightly less readily at room temperature than for iodobistrifluoromethylstibine, but is rapid on attempted distillation at atmospheric pressure.

Chlorobistrifluoromethylstibine.—Iodobistrifluoromethylstibine (0.534 g.) and silver chloride (2.02 g.), kept in a sealed tube at room temperature for 24 hr., gave crude chlorobistrifluoromethylstibine (0.411 g.) (Found: CF_3 , 46.8%; M , 292. Calc. for $\text{C}_2\text{ClF}_6\text{Sb}$: CF_3 , 46.8%; M , 295). A satisfactory chlorine analysis could not be obtained for this compound, and attempts to purify it further were unsuccessful since it disproportionates rapidly to trifluoromethylstibine and antimony trichloride. Chlorobistrifluoromethylstibine is a colourless liquid of vapour pressure 20 mm. at 17° and b. p. approx. 88°; it is hydrolysed only slowly by hot water to give antimony trioxide, and rapidly by aqueous sodium hydroxide to give fluoroform, chloride, and antimonite.

Tetrakistrifluoromethylstibine.—Reaction of iodobistrifluoromethylstibine, or of the crude liquid products from the reaction of trifluoroiodomethane with antimony, with an excess of zinc powder or mercury gave *tetrakistrifluoromethylstibine* almost quantitatively [Found: F 43.6% (42.9% as CHF_3 , 0.7% as F^-); Sb, 46.7%; M , 514. $\text{C}_4\text{F}_{12}\text{Sb}_2$ requires F, 43.9; Sb 47.0%; M , 518], b. p. 16.8°/4.1 mm., 28.3°/10.3 mm., 34°/14.1 mm., approx. 136°/760 mm. The reaction with mercury is relatively slow and is incomplete after 3 days' shaking. Tetrakistrifluoromethylstibine is a pale yellow liquid which deepens in colour when heated, and freezes to a colourless solid. It slowly decomposes at room temperature, particularly in light. It is readily oxidised by air and is insoluble in, and denser than, water. Hydrolysis with aqueous potassium hydroxide liberated the fluorine as fluoroform and fluoride ion, and yielded antimony and antimonite. For determination of antimony the compound was first decomposed by treatment with an excess of bromine at 20° (24 hr.) to give bromotrifluoromethane and antimony tribromide; the antimony content of the solid was determined in the usual way.

Tetrakistrifluoromethylstibine (3.23 g.) dissolved in trichlorofluoromethane (9 g.) at -78° to a colourless solution to which chlorine was added portionwise until a pale yellow colour in the liquid revealed the presence of a slight excess. The exothermic reaction produced a white solid, isolated by removal of the more volatile products *in vacuo* at -46°, then purified by fractionation *in vacuo* and shown to be *bistrifluoromethylantimony trichloride* (Found: CF_3 , 37.8; Cl, 28.6; Sb, 33.1. $\text{C}_2\text{Cl}_3\text{F}_6\text{Sb}$ requires CF_3 , 37.7; Cl, 29.1; Sb, 33.2%), b. p. 13°/5 mm., m. p. 27°. The solid slowly decomposes to give chlorotrifluoromethane at 25°, but can be stored indefinitely at -78°.

Reaction of tetrakistrifluoromethylstibine with an excess of iodine in a sealed tube at 90° for 24 hr. gave antimony tri-iodide and trifluoroiodomethane essentially quantitatively. Bromine attacks the distibine at room temperature to liberate bromotrifluoromethane and antimony tribromide quantitatively.

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