599. *Organometallic and Organometalloidal Fluorine Compounds. Part XIV.* Trifluoromethyl Derivatives of Selenium.*†

By J. W. Dale, H. J. Emeléus, and R. N. Haszeldine.

Trifluoroiodomethane and selenium at 260—285° give bistrifluoromethyl selenide, $(CF_3)_2Se$, and the diselenide, $(CF_3)_2Se_2$. The latter decomposes in ultraviolet light to the monoselenide and selenium; these compounds do not form addition products with mercuric chloride or alkyl iodides. The monoselenide is stable and resistant to hydrolysis. Chlorination of the selenide or diselenide gives trifluoromethylselenenyl chloride, $CF_3{\cdot}SeCl$, and trifluoromethylselenium trichloride, $CF_3{\cdot}SeCl_3$. A monobromide is formed similarly. Oxidation of the diselenide with nitric acid, or hydrolysis of the trichloride, yields the strong monobasic trifluoromethylseleninic acid, $CF_3{\cdot}SeO_2H$. The diselenide with mercury in ultraviolet light gives bis(trifluoromethylseleno)-mercury, $(CF_3{\cdot}Se)_2Hg$, which is also obtained by shaking trifluoromethylselenenyl chloride with mercury. The mercurial and anhydrous hydrogen chloride give the hydrogen selenide, $CF_3{\cdot}SeH$. These compounds are compared with their alkyl and aryl analogues.

Direct reaction of trifluoroiodomethane with certain metals and non-metals has been applied in preparing a variety of trifluoromethyl derivatives, including those of sulphur.[1] This paper describes its extension to selenium which with trifluoroiodomethane in the optimum temperature range (260—285°) yielded bistrifluoromethyl selenide, b. p. —2°, and diselenide, b. p. 73°, in a ratio of about 4 : 1. The amount of diselenide fell rapidly above 285°, since the back-reaction, $(CF_3)_2Se_2 + I_2 \longrightarrow 2CF_3I + 2Se$, is almost quantitative at 315°: the monoselenide reacts much less readily with iodine. By contrast the reaction of trifluoroiodomethane with sulphur gives mainly disulphide with small amounts of tri- and tetra-sulphides, but no monosulphide.[1] Methyl iodide also reacts with selenium [2] but the product is trimethylselenonium iodide, which has no trifluoromethyl analogue.

Bistrifluoromethyl selenide resembled its sulphur analogue in being resistant to hydrolysis by water or aqueous alkali. This fact was used to remove traces of the diselenide, which was readily attacked by alkali. The monoselenide was, however, decomposed by 20% alcoholic potassium hydroxide at 100°:

$$CF_3{\cdot}Se{\cdot}CF_3 \xrightarrow{OH^-} CHF_3,\ F^-,\ Se^{2-},\ CO_3^{2-}$$

Parallel information on the stability of alkyl and aryl selenides is incomplete, but dimethyl selenide is not attacked by aqueous alkali at ordinary temperatures although it deposits selenium when boiled with water.[3] Di-*n*-propyl selenide and dibenzyl selenide are also stable when boiled with a 5% solution of sodium hydroxide in aqueous alcohol.[4] Dilute mineral acids did not hydrolyse bistrifluoromethyl selenide, and it was unattacked by concentrated nitric acid, in contrast to dimethyl selenide, which is said [3] to be oxidised to a salt of the selenoxide, $Me_2Se(OH)NO_3$.

Mercuric chloride did not react with bistrifluoromethyl selenide, whereas dialkyl selenides readily form addition compounds. Bistrifluoromethyl selenide also failed to form a selenonium compound with methyl iodide. These differences arise from the presence of the highly electronegative trifluoromethyl group in the molecule and are also found with other groups which delocalise the lone pairs of electrons on the selenium. Thus, diphenyl selenide and ethyl iodide do not react,[5] and dimethylphenylselenonium

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* Part XIII, *J.*, 1957, 3708.

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[1] Brandt, Emeléus, and Haszeldine, *J.*, 1952, 2552 *et seq.*; Haszeldine and Kidd, *J.*, 1954, **4228** ***et seq.***

[2] Scott, *Proc. Chem. Soc.*, 1904, **20**, 156.

[3] Jackson, *Annalen*, 1875, **179**, 1.

[4] Painter, Franke, and Gortner, *J. Org. Chem.*, 1940, **5**, 579.

[5] Leicester and Bergstrom, *J. Amer. Chem. Soc.*, 1929, **51**, 3587.

iodide is formed only in very poor yield from methyl phenyl selenide and methyl iodide.[6] The triarylselenonium halides also dissociate readily at their melting points.[5, 7]

Chlorine and dialkyl selenides readily form dihalides of the type R_2SeX_2, which are stable when X = Cl or Br but unstable when X = I; diaryl selenides behave similarly on direct halogenation and no compounds of the types RSeX and $RSeX_3$ are formed, although mixed alkyl aryl selenides tend to lose alkyl halide when heated and form arylselenium monohalides.[8] Bistrifluoromethyl selenide reacted slowly with chlorine at room temperature, and rapidly at 150°, to form an approximately equimolar mixture of selenium tetrachloride and trifluoromethylselenium trichloride, together with chlorotrifluoromethane. Photochemical reaction with light of wavelength >3000 Å gave trifluoromethylselenium trichloride almost quantitatively. There was no indication of the formation of a stable dichloride, $(CF_3)_2SeCl_2$.

Bistrifluoromethyl diselenide was distinctly more reactive than the monoselenide. It was rapidly decomposed by water at 100° with deposition of selenium and, with aqueous alkali, gave fluoride, carbonate, polyselenide ion, and selenium, even below 0°. No fluoroform was produced and the intermediates were presumably the selenol, $CF_3{\cdot}SeH$, and trifluoromethylselenenic acid, $CF_3{\cdot}SeOH$, both of which immediately reacted further as in the case of their sulphur analogues.[9] The diselenide was also hydrolysed by 3N-hydrochloric acid at 100°. Hydrolysis thus occurs more readily than with bistrifluoromethyl disulphide. There is little information on the ease of hydrolysis of alkyl and aryl diselenides, though the latter must be fairly resistant since their preparation can involve strongly alkaline media. Dipropyl and dibenzyl diselenide are decomposed by boiling aqueous-ethanolic 5% sodium hydroxide.[4]

Bistrifluoromethyl diselenide formed no addition compound with mercuric chloride or iodide. Aryl diselenides form compounds such as $(C_6H_5)_2Se_2,2HgCl_2$,[10] whereas with alkyl diselenides the Se–Se bond is cleaved, affording products such as $CH_3{\cdot}Se{\cdot}HgCl$.[11]

Chlorine reacted with bistrifluoromethyl diselenide, even at −50°, converting it into the trichloride, $CF_3{\cdot}SeCl_3$, which formed almost colourless crystals. By use of a limited amount of chlorine, trifluoromethylselenenyl chloride, $CF_3{\cdot}SeCl$, was obtained. This was a cherry-red liquid (b. p. 31°) which was also obtained by dissolving the solid trichloride in the diselenide. Bromine and bistrifluoromethyl diselenide were miscible and did not react at room temperature, but at 150° selenium tetrabromide and bromotrifluoromethane were formed. At 75°, however, trifluoromethylselenenyl bromide, $CF_3{\cdot}SeBr$, resulted, and there was no tribromide in the product. Iodine, which was readily soluble in bistrifluoromethyl diselenide, reacted with it, to give trifluoroiodomethane only at temperatures in excess of 160°. Trichloromethylselenenyl chloride, $CCl_3{\cdot}SeCl$, is known, but in attempts to effect reaction with chlorine to give $CCl_3{\cdot}SeCl_3$, fission of the C–Se bond occurred. Arylselenium compounds analogous to the trifluoromethyl compounds are known, however, *e.g.*, PhSeBr, $PhSeBr_3$.[12]

Concentrated nitric acid with bistrifluoromethyl diselenide gave trifluoromethylseleninic acid, $CF_3{\cdot}SeO{\cdot}OH$ (m. p. 118·5—119°), in high yield. This was stable and non-deliquescent but volatile in water vapour. It was also obtained by exposure of trifluoromethylselenium trichloride to moist air. It is a strong acid, and the increase in strength compared with that for the alkylseleninic acids (*e.g.*, $CH_3{\cdot}SeO_2H$: K 6·4 × 10^{-6}; $C_2H_5{\cdot}SeO_2H$: K 5·3 × 10^{-6} at 25°)[13] parallels the effect noted earlier with the acids of

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[6] Baker and Moffitt, *J.*, 1930, 1722.

[7] Leicester and Bergstrom, *J. Amer. Chem. Soc.*, 1931, **53**, 4428.

[8] Jackson, *Ber.*, 1875, **8**, 109; Behaghel and Hofmann, *Ber.*, 1939, **72**, 697; Edwards, Gaythwaite, Kenyon, and Phillips, *J.*, 1928, 2293.

[9] Haszeldine and Kidd, *J.*, 1955, 2901.

[10] Bradt and Green, *J. Org. Chem.*, 1937, **1**, 540.

[11] Bird and Challenger, *J.*, 1942, 570.

[12] Behaghel and Seibert, *Ber.*, 1932, **65**, 812.

[13] Backer and van Dam, *Rec. Trav. chim.*, 1930, **49**, 479.

phosphorus, arsenic, and antimony. The hydrolysis of trifluoromethylselenium trichloride is analogous to that of alkyl- and aryl-selenium trihalides.[11,14]

Trifluoromethylselenenyl chloride was hydrolysed readily by water with formation of the diselenide in amounts which agree with the following overall equation:

$$3CF_3{\cdot}SeCl + 2H_2O \longrightarrow CF_3{\cdot}SeO_2H + CF_3{\cdot}Se_2{\cdot}CF_3 + 3HCl$$

The seleninic acid produced was not recovered quantitatively because of losses due to its volatility with water vapour. Hydrolysis of trifluoromethylselenenyl chloride with 25% sodium hydroxide solution occurred readily and gave approximately one-third of the fluorine as fluoroform and two-thirds as fluoride. This implies that the initial reaction proceeds according to the equation for the aqueous hydrolysis; sodium trifluoromethylseleninate is decomposed by alkali with liberation of a mol. of fluoroform, and the diselenide decomposes immediately with alkali, liberating six fluoride ions per molecule.

Attempts to oxidise trifluoromethylseleninic acid to the seleninic acid, $CF_3{\cdot}SeO_3H$, were unsuccessful with nitric acid or 100-volume hydrogen peroxide. Hydrolysis of the trifluoromethylselenium trichloride with 100-volume hydrogen peroxide also gave only the seleninic acid in spite of the liberation of free chlorine, which is known to be effective for the oxidation of phenylseleninic acid to phenylselenonic acid,[15] although tolylselenonic acids are said to liberate chlorine from hydrochloric acid.[16]

Trifluoromethylselenenyl chloride reacted rapidly and quantitatively with mercury, forming bis(trifluoromethylseleno)mercury, $Hg(Se{\cdot}CF_3)_2$, which was separated by sublimation. The chlorine atom was also replaced by cyanide on reaction with silver cyanide; trifluoromethyl selenocyanate so obtained was stable to water but was decomposed by 20% aqueous alkali with quantitative formation of fluoride ion. Bistrifluoromethyl diselenide formed the mercurial $Hg(Se{\cdot}CF_3)_2$ when merely shaken with mercury, indicating a weak Se–Se bond. Formation of the sulphur analogue $Hg(S{\cdot}CF_3)_2$ requires much more vigorous conditions involving photochemical cleavage of the S–S bond of bistrifluoromethyl disulphide. Photochemical reaction of bistrifluoromethyl diselenide with mercury expedites formation of the mercurial, with bistrifluoromethyl selenide and selenium as by-products. Bis(trifluoromethylseleno)mercury formed pale yellow crystals, m. p. 51°, which sublimed *in vacuo* and were readily soluble in water or organic solvents. The compound $Hg(Se{\cdot}C_2H_5)_2$ has been prepared from ethyl hydrogen selenide, $C_2H_5{\cdot}SeH$, and mercuric oxide, but its properties have not been fully described; the methyl analogue is reported to be also formed in the reaction of methyl hydrogen selenide with mercuric cyanide.[17]

Chlorine reacted rapidly and quantitatively with the mercurial, thus:

$$Hg(Se{\cdot}CF_3)_2 + 2Cl_2 = HgCl_2 + 2CF_3{\cdot}SeCl$$

and there was no evidence for the formation of the compound $CF_3{\cdot}Se{\cdot}HgCl$ as intermediate when a deficit of chlorine was used. The sulphur analogue $CF_3{\cdot}S{\cdot}HgCl$ is produced, together with trifluoromethylsulphenyl chloride, by chlorination of bis(trifluoromethylthio)mercury.[18] Bromine and bis(trifluoromethylseleno)mercury similarly gave trifluoromethylselenenyl bromide. Reaction of bis(trifluoromethylthio)mercury with hydrogen chloride gives an almost quantitative yield of the thiol, $CF_3{\cdot}SH$,[18] but the corresponding reaction with the selenium analogue was more complicated. Reaction was negligible at room temperature, but at 50—100° low yields of the analogue, $CF_3{\cdot}SeH$, were obtained, together with the diselenide, $(CF_3)_2Se_2$, and a small amount of a high-boiling material which may have contained polyselenides. The solid residue also contained, in addition to unchanged starting material and mercuric chloride, the white crystalline intermediate

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[14] Douglass, Brower, and Martin, *J. Amer. Chem. Soc.*, 1952, **74**, 5770.

[15] Stoecker and Krafft, *Ber.*, 1906, **39**, 2197; *J.*, 1906, **90**, 568.

[16] Doughty and Elder, 8th Intern. Congr. Appl. Chem., 1912, Vol. VI, p. 93.

[17] Siemens, *Annalen*, 1847, **61**, 360; Baroni, *Atti Accad. Lincei*, 1930, **12**, 234.

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

CF_3•Se•HgCl, which was synthesised separately by reaction of equimolar quantities of bis(trifluoromethylseleno)mercury with mercuric chloride in ether.

Trifluoromethyl hydrogen sulphide, CF_3•SeH, is colourless and boils at $-14{\cdot}5°$, which is 2° lower than the methyl analogue CH_3•SeH.[17] Alkaline hydrolysis rapidly gave all the fluorine as fluoride, together with carbonate, selenium, and alkali selenide or polyselenide.

The trifluoromethyl derivatives of selenium are thus characterised by (*a*) greater reactivity than the corresponding sulphur compounds, attributed to weaker C–Se and Se–Se bonds, (*b*) an ability to form quadrivalent selenium compounds involving halogen, *e.g.*, CF_3•$SeCl_3$, not readily formed by the corresponding sulphur compounds, and (*c*) formation of the seleninic acid, CF_3•SeO_2H, as the most stable oxy-acid, in contrast to the sulphonic acid CF_3•SO_3H. These trends are, in general, in accord with those observed with other derivatives of selenium and sulphur.

EXPERIMENTAL

Reaction of Selenium with Trifluoroiodomethane.—Experiments to determine optimum reaction conditions were made in Carius tubes (70—80 ml.) charged with about 5 g. of trifluoroiodomethane and 10 g. of roughly powdered selenium. A steel pressure-bottle (450 ml.), charged *in vacuo* with 100—150 g. of dried selenium and up to 70 g. of trifluoroiodomethane and rotated horizontally in a molten salt bath, was used in later experiments. Over sixty preparative runs were thus made. The optimum temperature range was 260—285°. Reaction was negligible at 240° while above 280° yields decreased rapidly and hexafluoroethane was formed. Under optimum conditions yields, based on trifluoroiodomethane used, were: $(CF_3)_2Se_2$, 10—15%; $(CF_3)_2Se$, 45—50%. Attempts to improve yields by adding iron powder to combine with free iodine showed little effect. The yield was increased when iodine was allowed to condense during the reaction in the unheated end of a Carius tube. Preliminary experiments showed that, in a specially designed reaction vessel, removal of iodine by reaction with mercury had a similar effect. Use of the rotating pressure vessel is most satisfactory for laboratory preparations.

Preliminary separation of the products by trap-to-trap distillation in a vacuum-apparatus of conventional type gave crude $(CF_3)_2Se_2$, b. p. 73°, crude $(CF_3)_2Se$, b. p. $-2°$, unchanged CF_3I, b. p. $-22{\cdot}5°$, and more volatile products (SiF_4, COF_2, C_2F_6, etc.).

Small amounts of the diselenide were removed from the crude bistrifluoromethyl selenide by washing it with aqueous sodium hydroxide. Separation of the monoselenide from trifluoroiodomethane by trap-to-trap distillation proved difficult but distillation in a vacuum-jacketed low-temperature fractionation column gave pure *bistrifluoromethyl selenide*, b. p. $-2°$ (Found: F, 52·9; Se, 36·2%; *M*, 217. C_2F_6Se requires F, 52·6: Se, 36·4%; *M*, 217).

Bistrifluoromethyl diselenide, b. p. 72·5—73·5°, was purified by column distillation (Found: F, 38·4; Se, 53·2%; *M*, 296. $C_2F_6Se_2$ requires F, 38·5; Se, 53·4%; *M*, 296). The residue from the distillation of the diselenide had a molecular weight of 309—315, indicating the presence of the triselenide, CF_3•Se_3•CF_3.

Reactions of Bistrifluoromethyl Selenide.—(a) *With alkali.* Bistrifluoromethyl selenide (0·483 g.) was unchanged after being sealed with 25% aqueous sodium hydroxide (4 ml.) and heated at 90—95° for 24 hr.

Bistrifluoromethyl selenide (1·018 g.) was heated in a Carius tube with potassium hydroxide (2·5 g.) and methanol (10 ml.) at 95—100° for 19 hr. The tube was etched and 0·347 g. (65%) of fluoride was found in the hydrolysate. Fluoroform (0·221 g., 35%) was evolved.

(b) *With nitric acid.* Bistrifluoromethyl selenide (0·5 g.) did not react when sealed with concentrated nitric acid (1·5 ml.) and shaken for 4·5 hr. at 80—90°.

(c) *With methyl iodide and mercuric chloride.* Bistrifluoromethyl selenide (0·78 g.) and methyl iodide (0·55 g.) failed to react in a sealed tube at 135° in 4 hr.

There was no reaction between the monoselenide (0·468 g.) and mercuric chloride (1·84 g.) at room temperature or after 16 hr. at 130°.

(d) *With chlorine.* Bistrifluoromethyl selenide (5·0 g.) and chlorine (1·64 g.) when sealed together in a Carius tube at 20° (24 hr.) deposited small white crystals. The volatile products were removed, the tube was filled with dry nitrogen, and the end containing the solid products was heated in an oil-bath. An almost colourless solid sublimed rapidly at 100°. The pale yellow solid residue (0·99 g.) dissolved in 15% sodium hydroxide solution without gas evolution (Found: Cl, 64·0. Calc. for Cl_4Se: Cl, 64·3%). The sublimate (1·19 g.) was *trifluoromethylselenium trichloride* (Found: Cl, 42·3. CCl_3F_3Se requires Cl, 41·9%), m. p. 88—89° (sealed tube), sublimes at *ca.* 85°. Fractionation of the more volatile products gave chlorotrifluoromethane (1·50 g.) (Found: *M*, 102·5. Calc. for $CClF_3$: *M*, 104·5) and unchanged monoselenide (2·91 g.) (Found: *M*, 213. Calc. for C_2F_6Se: *M*, 216), identified by their infrared spectra. Reaction of bistrifluoromethyl selenide and chlorine at 150° is complete in 4 hr., to give an approximately equimolar mixture of selenium tetrachloride and trifluoromethylselenium trichloride.

In a second experiment bistrifluoromethyl selenide (1·54 g.) and chlorine (1·026 g.), sealed in a quartz tube, were shaken and exposed to unfiltered radiation from a Hanovia lamp with an S-250 U-type arc at 5 cm. Removal of volatile material gave only residual white selenium tetrachloride (Found: Cl, 66·3. Calc. for Cl_4Se: Cl, 64·3%), subliming at 193—200°.

In a third experiment the monoselenide (1·75 g.) and chlorine (0·341 g.) were irradiated as before for 16 hr. in a Pyrex tube. In the early stages the tube contained a red liquid and vapour ($CF_3{\cdot}SeCl$, see below) which gradually changed to a red-brown solid mixed with white fern-like crystals. The readily volatile products were removed, washed with 10% sodium hydroxide solution, and fractionated to give chlorotrifluoromethane (0·197 g.) (Found: *M*, 103. Calc. for $CClF_3$: *M*, 104·5) and bistrifluoromethyl selenide (1·25 g.) (Found: *M*, 211. Calc. for C_2F_6Se: *M*, 217). The solid residue (0·540 g.), which sublimed under dry nitrogen at 85—90° (Found: Cl, 41·3. CCl_3F_3Se requires Cl, 41·8%), was *trifluoromethylselenium trichloride* uncontaminated by selenium tetrachloride.

Reactions of Bistrifluoromethyl Diselenide.—(a) *With water, aqueous alkali, or aqueous acid.* The diselenide was immiscible with water and there was no sign of reaction on shaking them at 20° for 24 hr., even with acetone present to provide miscibility. Reaction with water occurred at 100° with deposition of selenium and etching of the tube. Reaction with aqueous alkali was rapid and complete, even below 0°, forming fluoride, polyselenide, and carbonate, but no fluoroform. This reaction was used in analysing the compound. The diselenide (0·62 g.) with 3N-hydrochloric acid at 100° for 22 hr. gave a grey-black crust of selenium and the tube was etched. The colourless gas evolved (0·21 g.) (Found: *M*, 47·5) was absorbed by 10% aqueous alkali with <1 ml. of residue and was probably carbon dioxide with a small proportion of hydrogen selenide. Complete hydrolysis of the diselenide would give 0·184 g. of carbon dioxide.

(b) *With mercuric chloride or iodide.* The diselenide [(*a*) 0·428 g., (*b*) 0·471 g.] was recovered unchanged after being heated at 200° (48 hr.) in a sealed tube with (*a*) mercuric chloride (0·975 g.) or (*b*) mercuric iodide (0·721 g.).

(c) *With chlorine.* Bistrifluoromethyl diselenide (1·106 g.) was sealed in a Carius tube with chlorine (0·378 g.). Reaction below room temperature gave a red liquid with suspended crystals. Readily volatile products were pumped off, to leave *trifluoromethylselenium trichloride* (Found: Cl 41·7; Se, 31·5. CCl_3F_3Se requires Cl, 41·8; Se, 31·1%), m. p. 88—89° after sublimation. Hydrolysis by aqueous alkali gave fluoroform (0·0406 g.) (Found: *M*, 73. Calc. for CHF_3: *M*, 70). The theoretical yield from the sample for analysis (0·178 g.) would be 0·049 g. if hydrolysis occurred according to the equation:

$$CF_3{\cdot}SeCl_3 + 5NaOH = 3NaCl + Na_2SeO_3 + CHF_3 + 2H_2O$$

The volatile red liquid was mainly trifluoromethylselenenyl chloride containing some diselenide (Found: Se, 44·5; Cl, 17·0. Calc. for $CClF_3Se$: Se, 43·1; Cl, 19·35%).

Bistrifluoromethyl diselenide (1·462 g.) with an excess of chlorine (1·794 g.) at room temperature rapidly gave a 97% yield of trifluoromethylselenium trichloride and only a trace of selenium tetrachloride. The volatile products were washed with aqueous alkali to remove chlorine and gave 8 ml. of a colourless gas (Found: *M*, 110. Calc. for $CClF_3$: *M*, 104·5).

In an experiment with a deficit of chlorine the diselenide (2·467 g.) and chlorine (0·725 g.) gave trifluoromethylselenium trichloride (0·625 g.) and a red liquid which was fractionated in a small column, to give *trifluoromethylselenenyl chloride* (1·760 g.) (Found: F, 31·3; Cl, 19·2; Se, 42·8%; *M*, 185. $CClF_3Se$ requires F, 31·1; Cl, 19·4; Se, 43·0%; *M*, 183·5), b. p. 31—31·5°. The residue solidified to pale yellow crystals (Found: Cl, 41·7. Calc. for CCl_3F_3Se: Cl, 41·8%).

Reactions of Trifluoromethylselenium Trichloride.—(a) *With bistrifluoromethyl diselenide.*

The diselenide (1·91 g.) and the trichloride (1·65 g.), mixed at room temperature, gave 3·33 g. of trifluoromethylselenenyl chloride (b. p. 30—31·5°).

(b) *With water.* The trichloride (0·540 g.) was placed in one end of an almost horizontal Carius tube with about 0·5 ml. of water in the other; the tube was then partly evacuated and sealed. In 8 hr. the crystals had deliquesced completely. Hydrochloric acid and water were pumped off (Found: 0·229 g. of HCl, 99% of that for complete hydrolysis of the trichloride). The solid was volatile with water vapour.

Trifluoromethylselenium trichloride (0·110 g.) when exposed to moist air on a watch-glass gave in 36 hr. chloride-free water-soluble white crystals (0·0313 g.) which were unchanged in weight on a further 10 hours' exposure to air or on being dried over phosphoric oxide. The *trifluoromethylseleninic acid* (Found: Se, 43·8; F, 31·3. CHO_2F_3Se requires Se, 43·7; F, 31·5%), m. p. 118·5—119°, rapid decomp. at 205°, was decomposed by sodium–potassium alloy for analysis. The yield in duplicate experiments with this procedure was about 40%, because of volatility of the acid with water vapour. The titration curve in aqueous solution was typical of a strong monobasic acid (Found: equiv., 183. $CF_3{\cdot}SeO{\cdot}OH$ requires equiv., 183).

The acid was also prepared by shaking bistrifluoromethyl diselenide (1·053 g.) with concentrated nitric acid (5 ml.) in a Carius tube (24°, 12 hr.). Products volatile at −15° were pumped off and the solid residue was heated *in vacuo* to 35—40° to remove unchanged nitric acid (*ca.* 0·5 ml.). The residue was kept in an evacuated desiccator over phosphoric oxide for 9 days to give trifluoromethylseleninic acid (mixed m. p. 117·9—118·2°) with an infrared spectrum identical with that of the hydrolysis product from trifluoromethylselenium trichloride. The white silver salt of the acid was moderately soluble in water.

Reaction of Trifluoromethylselenenyl Chloride.—(a) *With water.* Trifluoromethylselenenyl chloride (0·488 g.) was sealed in an evacuated Carius tube with 1 ml. of water frozen at the bottom. When the monochloride melted and came into contact with the ice there was a mild reaction and drops of a pale yellow liquid were formed. The volatile products were removed, leaving a white crystalline residue, identified by mixed m. p. as trifluoromethylseleninic acid. The yellow oil which separated from the water layer in the volatile fraction was bistrifluoromethyl diselenide (0·249 g.), b. p. 72—73° (Found: F, 38·1. Calc. for $C_2F_6Se_2$: F, 38·5%). The theoretical yield of diselenide for the reaction, $3CF_3{\cdot}SeCl + 2H_2O = (CF_3)_2Se_2 + CF_3{\cdot}SeO{\cdot}OH + 3HCl$, was 0·262 g. The presence of selenium in the aqueous layer was confirmed by reduction with hydrazine.

(b) *With aqueous alkali.* Trifluoromethylselenenyl chloride (0·241 g.) with 20% aqueous sodium hydroxide (3 ml.) at 100° for 4 hr. gave fluoroform (0·029 g., 32%), chloride (Found: Cl, 19·1. Calc. for $CClF_3Se$: Cl, 19·4%), and fluoride (0·0498 g., 68%).

(c) *With silver cyanide.* Trifluoromethylselenenyl chloride (3·02 g.) and dried silver cyanide (10 g.) in a sealed tube below 0° gave smoothly *trifluoromethyl selenocyanate* (2·86 g.), b. p. 84°/758 mm. It was decomposed for analysis by sodium–potassium alloy (Found: Se, 45·2; F, 32·5%; *M*, 175. C_2F_3NSe requires Se, 45·4; F, 32·8%; *M*, 174).

Reaction of Bistrifluoromethyl Diselenide with Bromine.—Bistrifluoromethyl diselenide (0·806 g.) and dry bromine (1·690 g.) were heated in a sealed tube at 100—155° for 20 hr. The readily volatile products were removed, leaving a red-brown solid (1·27 g.) (Found: Br, 80·0; Se, 19·6. Calc. for Br_4Se: Br, 80·2; Se, 19·8%). The volatile material gave selenium tetrabromide (*ca.* 0·02 g.) and bromotrifluoromethane (0·499 g.) contaminated with unchanged diselenide.

Under milder conditions (70—75°, 12 hr.) bistrifluoromethyl diselenide (6·86 g.) and bromine (7·4 g.) gave, after fractionation, *trifluoromethylselenenyl bromide* (8·3 g.), b. p. 53·5—54·3° (Found: Br, 35·4; Se, 34·2%; *M*, 229. $CBrF_3Se$ requires Br, 35·1; Se, 34·6%; *M*, 228). Attempts to prepare trifluoromethylselenium tribromide by varying the reaction conditions and the proportion of bromine were unsuccessful.

When the monobromide (1·32 g.) was shaken with water (5 ml.) bistrifluoromethyl diselenide (0·548 g.), b. p. 72—72·7°, was formed. This is a 96% yield for the reaction, $3CF_3{\cdot}SeBr + 2H_2O = (CF_3)_2Se_2 + CF_3{\cdot}SeO_2H + 3HBr$.

Trifluoromethylselenenyl bromide (0·564 g.) was sealed with mercury (2 ml.) and shaken for a few minutes at room temperature. The product was bistrifluoromethyl diselenide (0·358 g.) (Found: *M*, 293. Calc. for $C_2F_6Se_2$: *M*, 296).

Reaction of Bistrifluoromethyl Diselenide with Iodine.—Bistrifluoromethyl diselenide (0·680 g.) was heated at 150—160° for 66 hr. with dried iodine (0·926 g.). Diselenide (0·666 g.) (Found:

M, 297) and iodine (0·910 g.) were recovered. The recovered material, reheated at 315—320° for 48 hr., gave trifluoroiodomethane (0·520 g.) (Found: *M*, 198. Calc. for CIF_3: *M*, 196).

Reaction of Bistrifluoromethyl Diselenide with Mercury.—The diselenide (0·618 g.) was sealed in a quartz Carius tube with mercury (2 ml.) and shaken (20 hr.) at 4 cm. from the mercury arc lamp. The volatile products were bistrifluoromethyl diselenide (0·175 g.) (Found: *M*, 294. Calc. for $C_2F_6Se_2$: *M*, 296) and 0·035 g. of a gas (Found: *M*, 223) which was probably bistrifluoromethyl selenide (*M*, 217). The residue in the tube was extracted with ether, and the product obtained on evaporation was sublimed in a vacuum at 50°, to give *bis(trifluoromethylseleno)mercury* (0·395 g.) as yellow needles with an unpleasant pungent odour. It was decomposed for analysis by sodium–potassium alloy at 525° (Found: F, 22·8; Se, 31·5. $C_2F_6Se_2Hg$ requires F, 23·0; Se, 31·8%). The resublimed crystals melted sharply at 51°. A yield of 96% was obtained by using more efficient shaking and subliming the product directly instead of extracting it with ether. A further quantity of this compound was recovered from the residues left from the mercury treatment of crude bistrifluoromethyl diselenide fractions from the selenium–trifluoroiodomethane reaction.

Reaction of Bis(trifluoromethylseleno)mercury.—(a) *With chlorine.* Bis(trifluoromethylseleno)mercury (2·60 g.) was sealed in a Carius tube with chlorine (0·735 g.). Reaction was rapid below room temperature. The volatile product after 20 hr. at 16° was trifluoromethylselenenyl chloride (1·910 g.) (Found: F, 30·9; Cl, 19·2; Se, 42·8. Calc. for $CClF_3Se$: F, 31·1; Cl, 19·4; Se, 43·0%).

(b) *With bromine.* Bromine (4·02 g.) and bis(trifluoromethylseleno)mercury (6·25 g.) were shaken in a Carius tube at 25° for 4 hr. The volatile product was trifluoromethylselenenyl bromide, b. p. 53·7—54·4° (4·82 g.). The residue in the tube (4·38 g.; m. p. 233°) was mercuric bromide.

(c) *With hydrogen chloride.* In a typical experiment the mercurial (9·0 g.) and anhydrous hydrogen chloride (1·32 g.) were heated in a Carius tube at 95—103° for 100 min. Fractionation of the product gave 0·742 g. of material, condensed at −140° (Found: *M*, 148. CHF_3Se requires *M*, 149). Refractionation gave *trifluoromethyl hydrogen selenide* (Found: F, 37·9; Se, 52·5. $CF_3{\cdot}SeH$ requires F, 38·3; Se, 53·0%), b. p. −14·5°/758 mm., unattacked by dry air at 20° but rapidly decomposed by water.

(d) *With mercuric chloride.* Bis(trifluoromethylseleno)mercury (0·212 g.) and mercuric chloride (0·116 g.) were dissolved in ether, which was then evaporated. The solid, which differed in appearance from the mercurial and melted to a clear liquid at 185—190°, was $CF_3{\cdot}Se{\cdot}HgCl$.

Analytical Procedures.—For analysis, certain of the more stable compounds [*e.g.*, $(CF_3)_2Se$] were heated at 500—550° with an excess of sodium or sodium–potassium alloy in a Carius tube. Unchanged alkali metal was destroyed with a few ml. of methanol. The contents of the tube were transferred to a Willard and Winter fluoride distillation apparatus and warmed with 10 ml. of 100-vol. hydrogen peroxide to oxidise inorganic selenide and polyselenides, and, in part, selenium to selenite. The contents of the flask were concentrated to 20 ml., concentrated sulphuric acid (40 ml.) was added, and the fluoride determined in the usual way. The residue in the distillation flask was transferred to a 500 ml. Erlenmeyer flask, the distillation flask being rinsed with hot nitric acid (5 ml.) to dissolve residual grey selenium. The liquid was evaporated to fumes of sulphuric acid, nitric acid (5 ml.) was added, and the evaporation repeated. The cooled sulphuric acid solution was diluted to 100 ml. and filtered and the filtrate digested for 1 hr. at 80—90° with concentrated hydrochloric acid (20 ml.) to reduce selenate to selenite. To the cooled solution was added slowly hydrazine hydrate (6—7 ml.) in water (20 ml.). After digestion on a steam bath for 2 hr. to convert selenium into the grey form, the latter was filtered off, dried at 100—120°, and weighed.

Compounds decomposed by alkaline hydrolysis [*e.g.*, $(CF_3)_2Se_2$] were treated with hydrogen peroxide after hydrolysis and the above procedure for determining fluorine and selenium was repeated.

Halogens were usually determined as silver halide on a separate sample, contamination by sparingly soluble silver selenite or silver trifluoromethyl seleninate being avoided by washing with hot water or warm dilute nitric acid.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, February 11th,* 1958.]