

1369. Pentafluoroethyl Derivatives of Selenium

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Several pentafluoroethyl derivatives of selenium have been prepared by the use of the mercurial, $(C_2F_5Se)_2Hg$, or preferably the diselenide, $(C_2F_5)_2Se_2$, as starting materials. Reactions of these new compounds were studied, and some of their physical properties are described. Pentafluoroethyl selenyl trichloride is stable under excess pressure of chlorine, and the tertiary pentafluoroethylselenyl amine seems to be unstable.

PERFLUOROALKYL derivatives of metals and non-metals can be prepared mainly by two types of reaction. (1) The direct reaction between the element and the respective perfluoroiodoalkane. (2) The thermal interaction of the element and a heavy-metal salt of the appropriate perfluoroalkyl acid.

Most perfluoroalkyl compounds of many elements, notably those of phosphorus, arsenic, antimony, and sulphur, were prepared by the first method.¹ Bistrifluoromethyl mono- and di-selenide were also prepared by the interaction of trifluoroiodomethane and selenium.² Bis-pentafluoroethyl and -heptafluoropropyl mono- and di-selenides, on the other hand, were prepared by the action of mercuric or silver propionate and butyrate, respectively, on selenium metal powder.³

Bis-trifluoromethyl and -pentafluoroethyl diselenide were separated from the respective original reaction mixtures by fractional vacuum distillation, but the corresponding separation of bisheptafluoropropyl diselenide was not feasible.⁴ Bispentafluoroethyl diselenide reacted readily with the stoichiometric amount of chlorine to form pentafluoroethylselenyl chloride, and with excess of chlorine it gave pentafluoroethylselenyl trichloride. This is a pale yellow solid, stable only under pressure of chlorine, and on exposure to the atmosphere it gives a colourless, volatile solid, soluble in water to give an acid solution.

The reaction between the diselenide and mercury was stoichiometric and gave the mercurial, $(C_2F_5Se)_2Hg$, a white, crystalline solid, m. p. 39–40°. This mercurial reacted at room temperature instantaneously with iodine to give the diselenide, but the reaction

¹ (a) M. Haupttschein and A. V. Grosse, *J. Amer. Chem. Soc.*, 1951, **73**, 5461; (b) H. J. Emelús and J. D. Smith, *J.*, 1959, 375.

² J. W. Dale, H. J. Emelús, and R. N. Haszeldine, *J.*, 1958, 2939.

³ (a) N. N. Yarovenko, V. N. Shemanina, and G. B. Gazieva, *Zhur. obshchei Khim.*, 1959, **79**, 942; (b) N. Welcman, *Israel J. Chem.*, 1963, **1**, 307.

⁴ H. J. Emelús and N. Welcman, *J.*, 1963, 1268.

was completed only after warming the mixture for 100 hours at 60°. With chlorine and bromine it gave the corresponding pentafluoroethylselenyl halides.

Pentafluoroethylselenyl chloride reacted with dimethylamine to give *NN*-dimethylpentafluoroethylselenenamide. The reaction of pentafluoroethylselenyl chloride with monoethylamine depended on the ratio of the reactants; in the mole ratio 1 : 2 it gave *N*-methylpentafluoroethylselenenamide, and in the mole ratio 2 : 3 it gave *N*-methylbis-pentafluoroethylselenenimide. The chloride also reacted with ammonia in the mole ratio 2 : 3 to give bis-pentafluoroethylselenenimide. The results of its reactions with ammonia in other ratios are complex and have not yet been completely elucidated. The hydrogen-containing pentafluoroethylselenenamides showed the normal value of the Trouton constant, unlike the trifluoromethyl sulphur analogues, where the abnormal high values of the Trouton constants were attributed to association due to hydrogen bonding.⁵

Most compounds prepared were unstable towards water and alkali, but could be kept for some time if moisture was rigorously excluded. Bis-pentafluoroethyl diselenide is quite stable towards water, but decomposes readily in alkali, depositing selenium. Bis-pentafluoroethyl monoselenide is stable to most reagents and reacts only with chlorine under heat and pressure, to give pentafluoroethyl chloride, selenium tetrachloride, and other products which were unidentified.

The mercurial was treated with dry hydrogen chloride in order to prepare pentafluoroethylselenol, but in the reaction products only bis-pentafluoroethyl diselenide and some unidentified volatile substances could be found. In this respect the pentafluoroethyl compounds resemble the heptafluoropropyl derivatives,⁴ trifluoromethylselenol having been isolated.

All pentafluoroethyl derivatives of selenium show strong absorption in the 1100—1300 cm^{-1} region due to carbon-fluorine stretching vibrations, and at 750 cm^{-1} , which could be ascribed to deformation modes of perfluoroalkyl groups.

The ^{19}F nuclear magnetic resonance spectra showed the expected two peaks with the CF_2 peak at a higher field except in bis-pentafluoroethylselenomercury, in which it was at a lower field. The chemical shift of CF_3 remains practically unaffected by changes in the radicals bound to the selenium and this is in accord with the results of n.m.r. studies on similar substances.⁶

EXPERIMENTAL

All reagents were either of analytical grade or were purified by standard methods. Silver pentafluoropropionate was prepared from silver carbonate and pentafluoropropionic acid. The preparation of bis-pentafluoroethylselenomercury was effected by a procedure described elsewhere.⁴

Separation of Bis-pentafluoroethyl Monoselenide.—The *monoselenide* was separated from the liquid that remained after the removal of the mercurial, washed with concentrated (15%) aqueous sodium hydroxide (to remove traces of pentafluoropropionic acid), and dried over anhydrous sodium sulphate. The monoselenide is a colourless liquid (Found: *M*, 313.5. $\text{C}_4\text{F}_{10}\text{Se}$ requires *M*, 317). Vapour pressures in the temperature range from -41 to 21.5° are given by $\log_{10}p(\text{mm.}) = 8.06 - 1650/T$. Its molar heat of vaporisation is 6650 cal./mole, Trouton's constant 20.9, the extrapolated boiling point 45° , and the melting point -122° (Found: C, 15.0; F, 59.65. $\text{C}_4\text{F}_{10}\text{Se}$ requires C, 15.15; F, 59.95%). The monoselenide is stable towards water, alkalis, dilute acids, and chlorine at room temperature. Monoselenide (0.819 g., 2.5 mmoles) and chlorine (0.183 g., 2.5 mmoles) were vacuum-sealed in a small Carius tube. No reaction occurred during 3 weeks at room temperature or at 50° . At 100° the tube walls were covered after 2 days with white selenium tetrachloride and the liquid in the tube contained some pentafluoroethyl monochloride and pentafluoroethylselenyl monochloride. No further identification of the decomposition products was made.

Preparation of Bis-pentafluoroethyl Diselenide.—Bis-pentafluoroethylselenomercury (2.0 g.,

⁵ H. J. Emeléus and S. N. Nabi, *J.*, 1960, 1103.

⁶ E. Pitcher, A. D. Buckingham, and F. G. A. Stone, *J. Chem. Phys.*, 1962, **36**, 124.

3.33 mmoles) and a slight excess of finely ground iodine (1.0 g., 3.9 mmoles) were sealed under a vacuum and kept at 60° for 120 hr. *Bispentafluoroethyl diselenide* (1.145 g., 2.9 mmoles) (90%), a greenish yellow liquid, was formed (Found: C, 12.25; F, 47.95. $C_4F_{10}Se_2$ requires C, 12.1; F, 48.0%). Vapour pressures at -1 to 45° were given by $\log_{10}p(\text{mm.}) = 8.65 - 2090/T$. The molar heat of vaporisation was 8400 cal./mole, the extrapolated b. p. 90°, Trouton's constant 22.6 cal./mole/degree, and the m. p. -100°. The compound is insoluble in water and decomposes slowly in water even at room temperature, depositing selenium; it decomposes easily in alkali.

Reaction between Bispentafluoroethyl Diselenide and Chlorine.—(a) *In a 1:1 molar ratio.* Bispentafluoroethyl diselenide (1.015 g., 2.56 mmoles) reacted in an evacuated Carius tube with chlorine (0.165 g., 2.30 mmoles) at room temperature to give *pentafluoroethylselenyl chloride* (0.922 g., 3.95 mmoles) (Found: C, 10.5; Cl, 15.0; F, 40.25%; M , 231. C_2ClF_5Se requires C, 10.3; Cl, 15.2; F, 40.7%; M , 233.5). Vapour pressures at -58 to 15.5° were given by $\log_{10}p(\text{mm.}) = 7.78 - 1580/T$. The molar heat of vaporisation was 6370 cal./mole, the extrapolated b. p. 50°, Trouton's constant 20.5 cal./mole/degree, and the m. p. -118°.

(b) *With an excess of chlorine.* Bispentafluoroethyl diselenide (0.110 g., 0.275 mmoles) reacted in an evacuated Carius tube with an excess of chlorine (0.110 g., 1.55 mmoles), to form an orange-yellow liquid at room temperature which froze at 0° to a pale yellow solid which was stable only under pressure of chlorine. This was *pentafluoroethylselenyl trichloride* (Found: C, 8.1; Cl, 34.95. $C_2Cl_3F_5Se$ requires C, 7.9; Cl, 34.55%).

Reactions of Pentafluoroethylselenyl Chloride.—(a) *With dimethylamine.* Pentafluoroethylselenyl chloride (0.556 g., 2.38 mmoles) reacted in a Carius tube with dimethylamine (0.215 g., 4.76 mmoles), to form *NN-dimethylpentafluoroethylselenamide* (0.550 g., 2.3 mmoles) (96%), a pale yellow liquid (Found: C, 19.65; H, 2.4; N, 5.75%; M , 242.5. $C_4H_8F_5NSe$ requires C, 19.8; H, 2.5; N, 5.8%; M , 242). Vapour pressures at -17 to 47° were given by $\log_{10}p(\text{mm.}) = 8.07 - 1820/T$. The molar heat of vaporisation was 7300 cal./mole. Trouton's constant 20.75 cal./mole/deg., the extrapolated boiling point 79°, and the m. p. -75°.

(b) *With monomethylamine in the molar ratio 1:2.* Pentafluoroethylselenyl chloride (0.922 g., 3.95 mmoles) reacted in a Carius tube with monomethylamine (0.248 g., 7.9 mmoles), to give *N-methylperfluoroethylselenamide* (0.826 g., 3.62 mmoles) (91%) (Found: C, 16.0; H, 1.6; N, 6.05%; M , 230. $C_3H_4F_5NSe$ requires C, 15.8; H, 1.75; N, 6.145%; M , 228). Vapour pressures at -30 to 45° were given by $\log_{10}p(\text{mm.}) = 7.82 - 1765/T$. The molar heat of vaporisation was 7100 cal./mole, Trouton's constant 19.95, and the extrapolated b. p. 83°.

(c) *With monomethylamine in the molar ratio 2:3.* Pentafluoroethylselenyl chloride (1.233 g., 5.3 mmoles) and monomethylamine (0.241 g., 7.8 mmoles) reacted at room temperature in an evacuated Carius tube and furnished *N-methylbis(pentafluoroethylselenenimide)* (0.675 g., 1.6 mmoles) (62%), a pale yellow non-volatile liquid, m. p. -45° (Found: C, 14.1; H, 0.7; N, 3.25. $C_5H_3F_{10}NSe_2$ requires C, 14.25; H, 0.95; N, 3.4%). Vapour pressures at 9 to 50.5° were given by $\log_{10}p(\text{mm.}) = 7.84 - 2000/T$. The molar heat of vaporisation was 8040 cal./mole, Trouton's constant 19.90, and the extrapolated b. p. 131°.

(d) *With ammonia in the molar ratio 2:3.* Pentafluoroethylselenyl chloride (1.15 g., 5 mmoles) and ammonia (0.131 g., 7.7 mmoles) reacted at room temperature in an evacuated Carius tube, to give *bispentafluoroethylselenenimide* (0.896 g., 2.2 mmoles) (87%), a yellowish, non-volatile liquid (Found: C, 11.7; H, 0.25; N, 3.4. $C_4HF_{10}NSe_2$ requires C, 11.45; H, 0.45; N, 3.45%). Vapour pressures at -3 to 49° were given by $\log_{10}p(\text{mm.}) = 7.7 - 2000/T$. The molar heat of vaporisation was 8040 cal./mole, Trouton's constant 19.3, and the extrapolated b. p. 144°.

Reactions of Bispentafluoroethylselenomercury. (a) *With methyl iodide.* The mercurial (1.5 g., 2.5 mmoles) and methyl iodide (0.7 g., 4.93 mmoles) reacted in a Carius tube at room temperature, to give *methyl pentafluoroethyl selenide*, a colourless liquid (Found: C, 16.85; H, 1.5; F, 44.45%; M , 208.5. $C_3H_3F_5Se$ requires C, 16.9; F, 1.4; F, 44.6%; M , 213). Vapour pressures at -39 to 13° were given by $\log_{10}p(\text{mm.}) = 8.11 - 1.666/T$. The latent heat of vaporisation was 6700 cal./mole, the extrapolated boiling point 46°, Trouton's constant 21.1 cal./mole/deg., and the m. p. -108°.

(b) *With ethyl iodide.* Bispentafluoroethylselenomercury (1.5 g., 2.5 mmoles) was sealed in a vacuum in a small Carius tube with ethyl iodide (0.78 g., 5.0 mmoles). No reaction occurred at room temperature, but red mercuric iodide was deposited on heating the tube at 60° for 4 hr. The yield of liquid, colourless *ethyl pentafluoroethyl selenide* was 1.0 g. (4.4 mmoles, 88%) (Found: C, 21.3; H, 2.3; F, 41.65. $C_4H_5F_5Se$ requires C, 21.15; H, 2.2; F, 41.85%). Vapour pressures at -32 to 38° were given by $\log_{10}p(\text{mm.}) = 8.21 - 1815/T$. The latent heat of vaporisation

was 7300 cal./mole, the extrapolated boiling point 67°, Trouton's constant 21.5 cal./mole/deg., and the freezing point -122°.

(c) *With di-iodomethane.* Bis(pentafluoroethyl)selenomercury (3.1 g., 5 mmoles) and diiodomethane (1.34 g., 5 mmoles) when sealed under a vacuum in a Carius tube reacted only when the tube was heated at 110° for 48 hr. A colourless substance, m. p. -23°, was *bis(pentafluoroethyl)selenyl methane* (Found: C, 14.7; H, 0.5. $C_5H_2F_{10}Se_2$ requires C, 14.65; H, 0.5%).

(d) *With chlorine.* Bis(pentafluoroethyl)selenomercury (1.2 g., 2 mmoles) and chlorine (0.345 g., 4.86 mmoles) reacted immediately in a Carius tube upon warming to room temperature and yielded pentafluoroethylselenyl chloride (0.9 g., 3.85 mmoles). The solid that remained in the tube was mostly mercuric chloride, but contained also some pentafluoroethylselenyl trichloride, which melted at room temperature and atmospheric pressure.

(e) *With bromine.* Bis(pentafluoroethyl)selenomercury (4.2 g., 7 mmoles) and bromine (2.1 g., 13 mmoles) were sealed in a Carius tube, which was kept for several days at room temperature, but heated to 50° intermittently. Reddish-brown, liquid *pentafluoroethylselenyl bromide* was formed (Found: C, 8.65; Br, 28.8; F, 34.3%; *M*, 275. C_2BrF_5Se requires C, 8.65; Br, 28.8; F, 34.2%; *M*, 278). Vapour pressures at the temperature interval from -31 to 20° were given by $\log_{10}p(\text{mm.}) = 8.26 - 1800/T$. The latent heat of vaporisation was 7250 cal./mole, the extrapolated b. p. 63°, Trouton's constant 21.5 cal./mole/deg., and the freezing point -95°.

(f) *With hydrogen chloride.* Bis(pentafluoroethyl)selenomercury (3.3 g., 5.5 mmoles) and dry hydrogen chloride (0.4 g., 10.9 mmoles) were heated for several hours at 100° in an evacuated Carius tube. On opening the tube bis(pentafluoroethyl) diselenide (0.934 g.) was obtained with some very volatile unidentified substances.

Infrared Spectra.—These were recorded on a Perkin-Elmer model 131 Infracord, and the main bands observed are listed below.

$(C_2F_5Se)_2Hg$ (in $CHCl_3$) 1310s, 1170w, 1100s, 1080s, 930vs. $(C_2F_5)_2Se$ 1330m, 1320m, 1235vs, 1185w, 1165m, 1125m, 1115m, 1030vw, 960vw, 930s, 805w, 750m. $(C_2F_5)_2Se_2$ 1330m, 1260vw, 1235vs, 1180m, 1120m, 1105m, 1030w, 935s, 805w, 750m. C_2F_5SeCl 1335m, 1240vs, 1170w, 1120m, 950s, 775vw, 750w. C_2F_5SeBr 1330m, 1180vs, 1160w, 1110s, 950s, 750w. $C_2F_5SeCH_3$ 3000vw, 1450vw, 1330w, 1300vw, 1265vw, 1230vs, 1145w, 1120s, 1030w, 960m, 925vw, 805w, 750w. $C_2F_5SeC_2H_5$ 3050vw, 1460vw, 1430vw, 1340w, 1260w, 1235vs, 1145w, 1120s, 1030w, 955m, 805m, 750w. $(C_2F_5Se)_2CH_2$ 1330m, 1230vs, 1145w, 1110m, 950s, 748w. $C_2F_5SeN(CH_3)_2$ 3580vw, 3000vw, 2950w, 2820vw, 1450w, 1325m, 1215vs, 1130m, 1105s, 1035vw, 950w, 935s, 740w. $C_2F_5SeN(CH_3)H$ 3700vw, 3500vw, 3000vw, 1460vw, 1335s, 1220vs, 1130m, 1110s, 1050w, 945s, 755m. $(C_2F_5Se)_2NCH_3$ 3600vw, 3000vw, 1335s, 1230vs, 1185vw, 1150w, 1120s, 945vs, 750m. $(C_2F_5Se)_2NH$ 3400vw, 1330s, 1255vw, 1220vs, 1150m, 1120s, 945vs, 750m.

Nuclear Magnetic Resonance Spectra.—These were recorded for ^{19}F resonances on a Varian DP-60 spectrometer operating on 56.4 Mc./sec. at high resolution conditions, and are quoted as chemical shifts measured against trichlorofluoromethane ($\phi = 0$) as solvent (30% by volume) and internal standard. Chemical shifts and coupling constants are given in the Table.

| Compound | Chemical shift (p.p.m.) | | Coupling constants (c/sec.) | |
|-----------------------|-------------------------|--------|-----------------------------|----------------|
| | CF_3 | CF_2 | $J(CF_2-CF_3)$ | $J(CF_3-CF_2)$ |
| $(C_2F_5Se)_2Hg$ * | 85.4 | 70.6 | 4.1 | 4.2 |
| $(C_2F_5)_2Se$ | 84.1 | 85.8 | 4.4 | Not observed |
| $(C_2H_5)_2Se_2$ | 82.9 | 90.8 | 1.5 | 2.0 |
| C_2F_5SeCl | 83.0 | 96.4 | 3.5 | 3.5 |
| C_2F_5SeBr | 82.7 | 92.9 | 3.4 | 3.4 |
| $C_2F_5SeCH_3$ † | 84.4 | 95.3 | 4.2 | 3.7 |
| $C_2F_5SeC_2H_5$ | 84.8 | 92.5 | 3.9 | 3.8 |
| $(C_2F_5Se)_2CH_2$ | 84.8 | 94.0 | 4.0 | 3.4 |
| $C_2F_5SeN(CH_3)_2$ † | 85.1 | 96.4 | 3.1 | 2.9 |
| $C_2F_5SeN(CH_3)H$ | 84.1 | 99.9 | 3.9 | 3.7 |
| $(C_2F_5Se)_2NHC_3$ | 84.1 | 100.9 | 3.4 | 3.5 |
| $(C_2F_5Se)_2NH$ | 83.7 | 103.0 | 3.7 | 3.6 |

* In CCl_4 solution. † $J(F-H) = 1.0$.

One of the authors (H. R.) thanks the National Council for Research and Development for a grant.