237. *Heptafluoropropyl Derivatives of Selenium.*

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Bisheptafluoropropyl mono- and di-selenide have been prepared by reaction of selenium with silver heptafluorobutyrate. Reactions of these two compounds have been studied. Heptafluoropropylselenium trichloride and heptafluoropropylselenol, unlike their trifluoromethyl analogues, appear to be unstable.

FLUOROALKYL derivatives of selenium were first prepared by reaction of trifluoroiodomethane with the element at 260—285°.[1] A similar reaction had been shown earlier [2] to occur between selenium and the iodides $CHF_2\cdot[CF_2]_5\cdot CH_2I$ and $CHF_2\cdot[CF_2]_9\cdot CH_2I$. A mixture of the mono- and di-selenide is formed in each case. Bistrifluoromethyl diselenide has also been prepared by heating a mixture of selenium and mercuric trifluoroacetate.[3] The present paper describes the preparation of bisheptafluoropropyl mono- and di-selenide by interaction of selenium and silver heptafluorobutyrate, a reaction which probably occurs through intermediate formation of an unstable selenium heptafluorobutyrate. A number of heptafluoropropyl derivatives of selenium have been prepared with the object of comparing them with the corresponding trifluoromethyl derivatives, several of which are described here for the first time.

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[1] Dale, Emeléus, and Haszeldine, *J.*, 1958, 2939.

[2] Faurote and O'Rear, *J. Amer. Chem. Soc.*, 1956, **78**, 4999.

[3] Yarovenko, Shemanina, and Gazieva, *Zhur. obshchei Khim.*, 1959, **79**, 942; *Chem. Abs.*, 1960, **54**, 2158e.

The optimum temperature for the reaction of selenium with silver heptafluorobutyrate to yield bisheptafluoropropyl diselenide was 280°. Approximately 60% of the product at this temperature was diselenide, the balance being monoselenide, the proportion of which rose with increasing temperature. At substantially lower temperatures reaction was very incomplete. Purification of the two products by vacuum-fractionation was difficult and the mixture was therefore treated with mercury, which reacts only with the diselenide, forming the crystalline mercurial $Hg(SeC_3F_7)_2$. The latter, on treatment with iodine, gave the pure diselenide.

Bisheptafluoropropyl monoselenide, like its trifluoromethyl analogue, was stable to water and dilute alkali. It reacted slowly and incompletely with chlorine at room temperature to form heptafluoropropylselenyl chloride, heptafluoropropyl chloride and selenium chloride. Bistrifluoromethyl monoselenide also reacts slowly with chlorine, giving analogous products and also trifluoromethylselenium trichloride.[1] The latter is also formed from trifluoromethylselenyl chloride and chlorine. Chlorination of bisheptafluoropropyl diselenide also gave the selenyl chloride and no trichloride. It appears, therefore, that the latter is unstable. Heptafluoropropylselenyl chloride also decomposed slowly at room temperature, one of the products being selenium tetrachloride.

Bisheptafluoropropyl diselenide resembled its trifluoromethyl analogue in reactivity, but hydrolysis with aqueous alkali did not give fluoride and selenium quantitatively, as it does for the trifluoromethyl compound. The exact products were not identified. Formation of the mercurial $Hg(SeC_3F_7)_2$ from the diselenide and mercury parallels the formation of $Hg(SeCF_3)_2$. The new compound reacted with chlorine and bromine to form the heptafluoropropyl monohalides, whereas with iodine it gave mercuric iodide and the diselenide. Attempts to isolate the selenol C_3F_7SeH by reaction of the mercurial with dry hydrogen chloride were unsuccessful, although trifluoromethylselenol has been prepared by this route. Reaction of bisheptafluoropropylselenylmercury with methyl and ethyl iodide and with methylene iodide gave mercuric iodide and the corresponding alkyl perfluoroalkyl selenides. Analogous reactions occurred with bistrifluoromethylselenylmercury.

Heptafluoropropylselenyl chloride behaved as a typical acid chloride in its reaction with dimethylamine. The product, *NN*-dimethylheptafluoropropaneselenenamide, re-formed the selenyl chloride when treated with hydrogen chloride. Trifluoromethylselenyl chloride similarly gave *NN*-dimethyltrifluoromethaneselenenamide.

EXPERIMENTAL

Silver heptafluorobutyrate was prepared from silver carbonate and heptafluorobutyric acid and stored in the dark. Other materials were prepared and purified by standard procedures, vacuum-techniques being used for manipulating volatile substances. Infrared spectra were recorded on a Perkin-Elmer model 131 Infracord or a Perkin-Elmer no. 21 double-beam instrument. A Perkin-Elmer vapour fractometer (model 154) was used to check the efficiency of certain separations by vacuum-fractionation.

Mercury was determined gravimetrically as bisethylenediaminecopper tetraiodomercurate or by the thiocyanate method, and selenium as the element after oxidation in a Parr bomb.[4] Fluorine was determined by decomposition of the compound with potassium at 550° (2 hr.) in a nickel bomb, followed by distillation with perchloric acid and titration of buffered aliquot parts of the distillate with thorium nitrate in presence of sodium alizarinsulphonate.

Reaction of Silver Heptafluorobutyrate with Selenium.—In a typical experiment, dried silver heptafluorobutyrate (8 g., 25 mmoles) and selenium (4·8 g., 60 mmoles) were heated in a Carius tube at 280° for 2 hr. Preliminary separation of the products gave a mixture of the monoselenide and diselenide, carbon dioxide, and small amounts of heptafluorobutyric acid and its anhydride. The mixture was shaken for 48 hr. with a 5—6-fold excess of mercury in an evacuated tube. *Bisheptafluoropropylselenylmercury* formed white needles and was purified by vacuum-sublimation (Found: F, 37·7; Hg, 28·8; Se, 23·5. $C_6F_{14}Se_2Hg$ requires F, 38·1; Hg, 28·8; Se, 22·7%). The mercurial (2·501 g., 3·5 mmoles) and iodine (0·986 g., 3·9 mg.-atoms) were sealed in a vacuum in a Carius tube. Immediate reaction occurred. It was

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[4] Wurzschmitt and Zimmermann, *Fortschr. chem. Forsch.*, 1950, **1**, 485.

brought to completion by occasional heating to 65° during 24 hr. The product was *bisheptafluoropropyl diselenide* (1·761 g., 99%) (Found: C, 13·7; Se, 31·5; F, 53·1%; *M*, 499. $C_6F_{14}Se_2$ requires C, 14·5; Se, 31·8; F, 53·6%; *M*, 496). Vapour pressures at $-13°$ to 74·5° were given by $\log_{10} p$ (mm.) $= 7·536 - 1967/T$. The latent heat of vaporization was 9005 cal./mole, Trouton's constant 21·3, the extrapolated b. p. 149°, and the m. p. $-51°$. Decomposition, with deposition of selenium, occurred on attempted distillation at 136°/20 mm. The compound was decomposed by 15% aqueous sodium hydroxide, part of the selenium being deposited as the element and part of the fluorine forming fluoride ion. Other products were not identified.

The residual liquid, after treatment of the selenide mixture in the original preparation with mercury, was shaken with an excess of 15% aqueous sodium hydroxide. The organic layer was separated and dried. It was *bisheptafluoropropyl selenide* (2·295 g.) (Found: C, 17·4; F, 63·0; Se, 19·1%; *M*, 415. $C_6F_{14}Se$ requires C, 17·3; F, 63·7; Se, 18·9%; *M*, 417). Vapour pressures at $-45°$ to 70° were given by $\log_{10} p$ (mm.) $= 7·71 - 1803/T$. The molar heat of vaporization was 8250 cal./mole, Trouton's constant 22·1, the extrapolated b. p. 100°, and the m. p. $-108°$. The compound was inert to water and aqueous alkali and did not react with mercury in ultraviolet light.

Preparation of Heptafluoropropylselenyl Chloride.—Bisheptafluoropropylselenylmercury (0·481 g., 0·69 mmole) and an excess of chlorine (0·125 g., 1·75 mmoles) reacted in a Carius tube to yield *heptafluoropropylselenyl chloride* (Found: C, 11·7; Cl, 12·8; Se, 28·4%; *M*, 282. C_3F_7ClSe requires C, 12·7; Cl, 12·5; Se, 27·9%; *M*, 283·5). Vapour pressures at $-50°$ to 16° were given by $\log_{10} p$ (mm.) $= 7·88 - 1742/T$. The molar heat of vaporization was 7970 cal./mole, Trouton's constant 22·9, the extrapolated b. p. 74°, and the m. p. $-89°$. Some chlorine (0·0315 g.) was recovered. A white water-soluble residue was mercuric chloride (Found: Hg, 71·9. Calc. for Cl_2Hg: Hg, 73·8%), probably contaminated by a little selenium tetrachloride formed from the heptafluoropropylselenium monochloride. The latter, on storage, slowly deposited selenium tetrachloride (Found: Cl, 62·7. Calc. for Cl_4Se: Cl, 64·2%). There was no evidence for the formation of heptafluoropropylselenium trichloride in this reaction or when the separated monochloride was treated with chlorine.

Bisheptafluoropropyl monoselenide (1·331 g., 3·2 mmoles) and chlorine (0·455 g., 6·4 mmoles) reacted slowly in a sealed tube at room temperature to form heptafluoropropylselenyl chloride (0·155 g.) (Found: *M*, 285) and selenium tetrachloride (Found: Cl, 63·5%). Unused monoselenide (0·712 g.) and heptafluoropropyl chloride (0·196 g.) (Found: *M*, 203. Calc. for C_3F_7Cl: *M*, 204·5) were also isolated. The selenyl chloride was characterized by its infrared spectrum. Bisheptafluoropropyl diselenide (0·534 g., 1·1 mmoles) and chlorine (0·077 g., 1·1 mmoles) reacted in a sealed tube, to yield heptafluoropropylselenyl monochloride (0·545 g.) (Found: *M*, 282).

Preparation of Heptafluoropropylselenyl Bromide.—Bisheptafluoropropylselenylmercury (1·105 g., 1·6 mmoles) and bromine (0·507 g., 3·2 mmoles) reacted rapidly in a sealed tube at room temperature, to yield *heptafluoropropylselenyl bromide* (0·628 g.) (Found: C, 10·5; Br, 24·2; Se, 23·7%; *M*, 327. C_3F_7BrSe requires C, 10·9; Br, 24·4; Se, 24·1%; *M*, 328). Vapour pressures at $-22°$ to 25° were given by $\log_{10} p$ (mm.) $= 7·852 - 1829/T$. The molar heat of vaporization was 8374 cal./mole, Trouton's constant 22·7, and the extrapolated b. p. 95°. The compound decomposed slowly at room temperature.

Reaction of Heptafluoropropyl- and Trifluoromethyl-selenyl Chloride with Dimethylamine.—Heptafluoropropylselenyl chloride (0·226 g., 0·8 mmole) and dimethylamine (0·072 g., 1·6 mmoles) reacted immediately in a sealed tube at room temperature, to yield NN-*dimethylheptafluoropropylselenenamide* (0·219 g.) (Found: C, 21·8; H, 2·45; N, 5·0; Se, 43·9%; *M*, 291. $C_5H_6F_7NSe$ requires C, 20·5; H, 2·05; N, 4·8; Se, 45·5%; *M*, 292) and dimethylamine hydrochloride (0·0634 g.) (Found: Cl, 42·9. Calc. for C_2H_8ClN: Cl, 43·5%). The amide was a colourless liquid with a vapour pressure, at $-45°$ to 48°, given by $\log_{10} p$ (mm.) $= 7·16 - 1610/T$. The molar heat of vaporization was 7370 cal./mole, Trouton's constant 19·6, the extrapolated b. p. 103°, and the m. p. $-94°$. The amide (0·066 g., 0·22 mmole) and hydrogen chloride (0·0170 g., 0·47 mmole) reacted below room temperature to form heptafluoropropylselenyl chloride (0·0594 g.) (Found: *M*, 283). Its identity was checked by the infrared spectrum. The solid residue (0·0177 g.) was dimethylamine hydrochloride (Found: Cl, 43·1%).

Trifluoromethylselenyl chloride (0·220 g., 1·2 mmoles) and dimethylamine (0·108 g., 2·4 mmoles) reacted readily, to give NN-*dimethyltrifluoromethylselenenamide* (0·208 g.) (Found: *M*, 190. $C_3H_6F_3NSe$ requires *M*, 192). Vapour pressures at $-45°$ to 48° were given by

$\log_{10} p$ (mm.) = 7·15 − 1470/T. The molar heat of vaporization was 6740 cal./mole, Trouton's constant 19·5, and the extrapolated b. p. 71°. The other product (0·0910 g.) was dimethylamine hydrochloride (Found: Cl, 43·7%).

Reaction of Bisheptafluoropropylselenyl- and Bistrifluoromethylselenyl-mercury.—(*a*) *With methyl iodide.* Bisheptafluoropropylselenylmercury (2·215 g., 3·2 mmoles) and methyl iodide (1·600 g., 11 mmoles) at room temperature in 4 days gave *heptafluoropropyl methyl selenide* (0·811 g.) (Found: C, 18·4; H, 1·58; F, 49·8; Se, 29·7%; *M*, 261. $C_4H_3F_7Se$ requires C, 18·2; H, 1·15; F, 50·5; Se, 30·0%; *M*, 263) and mercuric iodide (1·358 g.) (Found: Hg, 43·3. Calc. for I_2Hg: Hg, 44·1%). Vapour pressures of the selenide at −41° to 51° were given by $\log_{10} p$ (mm.) = 7·95 − 1608/T. The molar heat of vaporization was 7358 cal./mole, Trouton's constant 21·6, and the extrapolated b. p. 68°. Bistrifluoromethylselenylmercury (3·725 g., 7·5 mmoles) and methyl iodide (2·118 g., 15 mmoles) reacted similarly, to give *methyl trifluoromethyl selenide* (2·329 g.) (Found: C, 16·9; H, 1·93; F, 33·8; Se, 47·9%; *M*, 162. $C_2H_3F_3Se$ requires C, 14·8; H, 1·84; F, 35·0; Se, 48·5%; *M*, 163). Vapour pressures at −64° to 21° were given by $\log_{10} p$ (mm.) = 7·66 − 1448/T. The molar heat of vaporization was 6630 cal./mole, Trouton's constant 21·9, and the extrapolated b. p. 29·6°.

(*b*) *With methylene iodide.* Bisheptafluoropropylselenylmercury (2·375 g., 3·4 mmoles) and methylene iodide (0·913 g., 3·4 mmoles) did not react in a sealed tube at 20°. At 120° (48 hr.) the products were mercuric iodide and *bisheptafluoropropylselenylmethane* (Found: C, 15·6; H, 0·6; F, 51·1; Se, 31·8. $C_7H_2F_{14}Se_2$ requires C, 16·5; H, 0·4; F, 52·1; Se, 31·0%). The vapour pressure at 20° was ~2 mm. Bistrifluoromethylselenylmercury (4·568 g., 9·2 mmoles) and methylene iodide (2·208 g., 8·2 mmoles) reacted at 120° in 16 hr. to give *bistrifluoromethylselenylmethane* (2·410 g.) (Found: C, 11·4; H, 0·62; F, 36·9; Se, 50·1%; *M*, 309. $C_3H_2F_6Se_2$ requires C, 11·6; H, 0·62; F, 36·8; Se, 51·0%; *M*, 310). Vapour pressures at 0° to 86° were given by $\log_{10} p$ (mm.) = 7·746 − 1850/T. The molar heat of vaporization was 8480 cal./mole, Trouton's constant 22·3, and the extrapolated b. p. 108°.

(*c*) *With ethyl iodide.* Bisheptafluoropropylselenylmercury (6·162 g., 8·85 mmoles) and ethyl iodide (2·760 g., 17·7 mmoles) reacted very slowly at room temperature, to give mercuric iodide and *ethyl heptafluoropropyl selenide* (3·720 g.) (Found: C, 21·8; H, 2·1; F, 47·3; Se, 28·0%; *M*, 277. $C_5H_5F_7Se$ requires C, 21·6; H, 1·8; F, 48·0; Se, 28·5%; *M*, 277). Vapour pressures at −30° to 60° were given by $\log_{10} p$ (mm.) = 8·007 − 1880/T. The molar heat of vaporization was 8610 cal./mole, Trouton's constant 23·5, and the extrapolated b. p. 23·5°. Bistrifluoromethylselenylmercury (3·545 g., 7·1 mmoles) and ethyl iodide (2·012 g., 13 mmoles) at 120° gave, in 8 hr., mercuric iodide and *ethyl trifluoromethyl selenide* (1·976 g.) (Found: C, 21·1; H, 2·98; F, 31·6; Se, 45·1%; *M*, 177. $C_3H_5F_3Se$ requires C, 20·3; H, 2·83; F, 32·2; Se, 44·6%; *M*, 177). Vapour pressures at −50° to 19° were given by $\log_{10} p$ (mm.) = 7·89 − 1650/T. The molar heat of vaporization was 7560 cal./mole, Trouton's constant 22·9, the extrapolated b. p. 56·6°, and the m. p. −125°. The solid in the reaction tube (0·0177 g.) was dimethylamine hydrochloride (Found: Cl, 43·1%).

Infrared Spectra.—The chief bands observed are listed below.

$(C_3F_7)_2Se$: 1340vs, 1280vs, 1245vs, 1230vs, 1180s, 1160s, 1130vs, 1080m, 1045s, 945w, 900s, 830vs, 750s, 740vs, 675vs.

$(C_3F_7)_2Se_2$: 1340s, 1280w, 1245vs, 1230vs, 1200w, 1160w, 1130s, 1080w, 1040w, 940w, 830s, 795w, 750w, 740s, 670s.

C_3F_7SeCl: 1340vs, 1275m, 1245vs, 1230vs, 1160s, 1130vs, 1085m, 1045s, 900m, 835vs, 800w, 750w, 740vs, 670m.

C_3F_7SeBr: 1340vs, 1280m, 1245vs, 1230vs, 1200s, 1160m, 1130vs, 1085m, 1040m, 945w, 900m, 832vs, 750w, 740vs, 675vs.

$C_3F_7SeNMe_2$: 2910m, 1450w, 1330s, 1270m, 1235vs, 1220vs, 1190m, 1120s, 1080w, 1040m, 960m, 940m, 895w, 830m, 740s, 670m.

C_3F_7SeMe: 2950m, 1435m, 1340vs, 1290s, 1240vs, 1220vs, 1195s, 1120vs, 1090m, 1045s, 925s, 905s, 845vs, 800w, 740vs, 665s.

C_3F_7SeEt: 2940m, 1450w, 1340vs, 1240vs, 1220vs, 1200s, 1120vs, 1090m, 1040s, 950w, 910s, 840vs, 800w, 740vs, 670m.

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