440. *Perfluoroalkyl Silyl Selenides.*

By E. A. V. Ebsworth, H. J. Emeléus, and N. Welcman.

The new compounds, silyl trifluoromethyl selenide and heptafluoropropyl silyl selenide, have been prepared and characterized, and some of their physical properties are described; both compounds decompose only slowly at room temperature, forming fluorosilane and unidentified products.

Silyl trifluoromethyl sulphide has recently been prepared by the reaction between iodosilane and bis(trifluoromethylthio)mercury.[1] The analogous reactions between iodosilane and bis(trifluoromethylseleno)mercury or bis(heptafluoropropylseleno)mercury yield silyl trifluoromethyl selenide and heptafluoropropyl silyl selenide:

$$2SiH_3I + Hg(SeR)_2 = 2SiH_3SeR + HgI_2 \text{ (R is } CF_3 \text{ or } C_3F_7)$$

---

[1] Downs and Ebsworth, *J.*, 1960, 3516.

The reactions are smooth at room temperature; as iodosilane vapour passes over the solid mercurial suspended on glass wool, red and yellow solids are formed, with some black material, and the required compounds are isolated from among the volatile products in yields of up to 87%.

The two silyl compounds are colourless liquids, with normal Trouton constants. Both are more stable than silyl trifluoromethyl sulphide at room temperature. The sulphur analogue decomposes at room temperature: $SiH_3{\cdot}S{\cdot}CF_3 = SiH_3F + SCF_2$. This decomposition is very slow unless traces of impurity are present, and the sulphur mercurial bis(trifluoromethylthio)mercury is particularly effective in this respect.[1] Silyl trifluoromethyl selenide decomposed to a measurable extent in the liquid phase in sealed apparatus at room temperature in 24 hours; one of the products was silyl fluoride, but no material whose properties corresponded with those expected of selenocarbonyl fluoride was obtained; the silyl trifluoromethyl selenide recovered had a yellowish tinge, which may have been due to the presence of small amounts of polymerized fluorocarbon–selenium compounds. The decomposition was, however, slight even in the presence of bis(trifluoromethylseleno)-mercury. Since disilyl selenide is rather less stable thermally than disilyl sulphide,[2] the greater stability of silyl trifluoromethyl selenide than of its sulphur analogue is surprising, and implies that selenocarbonyl fluoride is thermodynamically less stable than thiocarbonyl fluoride. Heptafluoropropyl silyl selenide is stable at room temperature for several days, though it decomposes to some extent at 60° in 48 hours; fluorosilane was the only decomposition product identified.

The value of τ in the proton resonance spectrum of silyl trifluoromethyl selenide is 0·15 p.p.m. less than that for disilyl selenide;[3] the replacement of silyl by trifluoromethyl causes a smaller shift in the same sense in the analogous silyl–sulphur compounds.[1,3] These shifts can probably be accounted for in terms of a simple inductive mechanism. The ^{29}SiH coupling constant in $SiH_3{\cdot}SeX$ increases as X is changed from SiH_3 to CF_3; again, a similar change has been observed in the analogous sulphur compounds. In the fluorine resonance spectra, replacement of the ethyl group of ethyl trifluoromethyl selenide by silyl leads to a low-field shift of about 10 p.p.m., in agreement with a recent interpretation of the fluorine chemical shifts for a number of substituted fluorocarbons;[4] the α-CF_2 chemical shift changes by about the same amount when ethyl is replaced by silyl in the heptafluoropropyl compounds. The multiplet splittings in both fluorine and proton resonance spectra of heptafluoropropyl silyl selenide are complex, but there is evidence that the couplings between the protons and both α- and β-CF_2 groups are of the order of one cycle/sec.

Heptafluoropropyl silyl selenide reacts with mercuric bromide at room temperature, to give almost quantitative yields of bromosilane. This implies that the $C_3F_7{\cdot}Se$ group should be included in the conversion series for mercury salts between bromide and iodide; since this is where selenium has been placed in the analogous series for silver salts, the Si–Se bond appears to be little affected by the fluorocarbon substituent.

EXPERIMENTAL

Silyl Trifluoromethyl Selenide.—Preparation. Iodosilane (0·380 g.) was passed as vapour over solid bis(trifluoromethylseleno)mercury suspended on glass wool. Red and yellow solids were formed, and the tube became just warm, while some black material was formed on its walls; the volatile products were distilled twice over a fresh sample of bis(trifluoromethylseleno)mercury (1·2205 g.) to complete the conversion, and, on fractional distillation, *silyl trifluoromethyl selenide* was obtained (0·3055 g.) (Found: *M*, 179; Se, 43·4; *Si*-H, 1·67%. CH_3F_3SeSi requires *M*, 179; Se, 44·1; *Si*-H, 1·68%). The yield, based upon the amount of iodosilane taken, was 70%.

---

[2] Emeléus, MacDiarmid, and Maddock, *J. Inorg. Nuclear Chem.*, 1955, **1**, 194.

[3] Ebsworth and Turner, unpublished work.

[4] Pitcher, Buckingham, and Stone, *J. Chem. Phys.*, 1962, **36**, 124.

Properties. The compound is a colourless liquid, m. p. $-125{\cdot}8°$; it is involatile at $-96°$, and has a v. p. at $-26°$ of 15 mm. Between $-60°$ and $+4°$ the vapour pressures are given by the equation $\log_{10} p$ (mm.) $= -1460/T + 7{\cdot}615$. The b. p. (extrapolated over 30°) is 35°, the latent heat is 6700 cal./mole, and Trouton's constant 22. The compound was unchanged after 36 hr. in the vapour phase at room temperature. After 24 hr. in the liquid phase at room temperature, 0·165 g. gave 0·20 g. of material volatile at $-96°$, which on fractional distillation gave ~0·008 g. of fluorosilane (identified spectroscopically) and a less volatile material containing disiloxane (identified spectroscopically) and some fluorocarbon derivative; 0·145 g. of silyl trifluoromethyl selenide was recovered (*M*, 180), that had a yellowish tinge but unchanged infrared spectrum. Silyl trifluoromethyl selenide (0·1450 g.) was kept at room temperature in the presence of ~0·10 g. of bis(trifluoromethylseleno)mercury for 24 hr. in the liquid phase; the solid blackened, and on fractional distillation the volatile substances recovered were fluorosilane (~0·007 g.; identified spectroscopically) and silyl trifluoromethyl selenide (*M*, 178; identity confirmed spectroscopically).

Heptafluoropropyl Silyl Selenide.—Preparation. Iodosilane (0·7915 g.) was allowed to pass as vapour over bis(heptafluoropropylseleno)mercury suspended on glass wool; yellow and red solids were formed, together with some black matter on the walls of the tube. *Heptafluoropropyl silyl selenide* was obtained from the volatile products by fractional distillation (1·2292 g.) (Found: *M*, 278; Se, 28·1; *Si*-H, 1·07%. $C_3H_3F_7SeSi$ requires *M*, 279; Se, 28·3; *Si*-H, 1·08%). The compound is a colourless liquid, melting at $-98°$; its v. p. at 0° is 36 mm., and vapour pressures between $-40°$ and $+20°$ are given by the equation $\log_{10} p$ (mm.) $= -1729/T + 7{\cdot}833$. The b. p. (extrapolated over 50°) is 76°, the latent heat of vaporization is 7900 cal./mole, and Trouton's constant 23.

Stability. The compound was recovered unchanged after 72 hr. at room temperature in the liquid phase. After being kept at 58° for 48 hr., however, 0·1070 g. gave a drop of yellowish liquid, involatile at room temperature, together with 0·005 g. of a substance (*M*, 64) whose infrared spectrum showed that it consisted of fluorosilane (*M*, 50) and some fluorocarbon-containing substance.

Reaction with mercuric bromide. Silyl heptafluoropropyl selenide (0·1849 g.) was kept with mercuric bromide (0·4773 g.) for 48 hr. at room temperature. From the volatile products, bromosilane was recovered (0·0699 g.) (Found: *M*, 110. Calc. for SiH_3Br: *M*, 111). Its v. p. was: at $-34°$ 151 mm., at $-45°$ 81 mm. (Calc.:[5] at $-34°$ 153 mm., at $-45°$ 84 mm.). Approximately 0·005 g. of a more volatile material was also obtained; the infrared spectrum indicated the presence of C–F and Si–H bonds. The amount of bromosilane recovered represents 95% of that calculated from the equation, $2SiH_3{\cdot}Se{\cdot}C_3H_7 + HgBr_2 = 2SiH_3Br + Hg(SeC_3F_7)_2$.

Infrared Spectra.—Infrared spectra were recorded by using a Perkin–Elmer model 21 double-beam spectrometer, fitted with sodium chloride optics. The observed frequencies and their assignments are given below.

$SiH_3{\cdot}SeCF_3$	$SiH_3{\cdot}SeC_3F_7$	Assignment
2200s	2200s	SiH stretching
	1340s	?CF stretching of CF_3-groups[6]
1260w		?
1155 1110 1070 vs	1240 1225 1220 1125 vs	CF stretching
1015s	1040m	?
980s	950w	?
900 880 vs	900 890 vs	SiH_3 deformation
	830vs	Characteristic of C_3H_7–Se group[7]
800s	800w	?
740s	740s	CF_3-deformation
	665w	?

Nuclear Magnetic Resonance Spectra.—These were recorded by means of a Varian Associates V4500A spectrometer operating at 40 Mc./sec. with sample-spinning and flux-stabilizer. Samples were studied in Pyrex tubing of 5 mm. outside diameter, and positions of bands were measured with a Muirhead–Wigan decade oscillator. The measurements from the proton resonance spectra are given. The resonance for the trifluoromethyl derivative showed the expected quartet structure, but that for the heptafluoropropyl compound had seven components, separated by 1·5 c./sec. This can be explained in terms of two sets of overlapping

---

[5] Stock and Somieski, *Ber.*, 1917, **50**, 1739.

[6] Hauptschein, Stokes, and Nordiff, *J. Amer. Chem. Soc.*, 1952, **74**, 4005.

triplets, with the smaller coupling equal to half the larger. The two sets of triplets could arise from coupling with fluorines of the α- and β-CF_2 groups.

	$CF_3{\cdot}Se{\cdot}SiH_3$	$C_3F_7{\cdot}Se{\cdot}SiH_3$	$(SiH_3)_2Se$[3]
Chemical shift (τ) *	5·70	5·71	5·86
J(^{29}Si–H) (c./sec.)	230 ± 1	Not observed	226 ± 2
J(H–F) (c./sec.)	1·6 ± 0·1	? 3·0, 1·5	—

* Measured in dilute solution relative to cyclohexane (τ 8·56) as solvent and internal standard.

In the fluorine resonance spectra, the CF_3 compound gave a quartet at 25·5 p.p.m. to high field of trichlorofluoromethane as internal standard and solvent; the fluorine chemical shift for $CF_3{\cdot}Se{\cdot}C_2H_5$ under the same conditions is 35·2 p.p.m.[7] The α- and β-CF_2 and CF_3 fluorine chemical shifts in $C_3F_7{\cdot}Se{\cdot}SiH_3$ are 77·9, 121·3, and 79·5 p.p.m., respectively, as against 88·6, 123·7, and 82·5 for $C_3F_7{\cdot}Se{\cdot}C_2H_5$; [7] the multiplet structure of each resonance is extremely complicated. That for the β-CF_2 group, for instance, shows at least 20 peaks, with average separation between nearest neighbours of ~1 c./sec. The CF_3 resonance shows a clear triplet structure, with separation of 9·4 c./sec.; since, however, the ratio J/σ between the α-CF_2 and the CF_3 groups is relatively large, this separation gives no more than an estimate of the coupling constant, which is 9·8—9·9 c./sec. in other C_3F_7Se derivatives.[7] It is possible to detect two quartet structures in the α-CF_2 resonance, with separations of *ca.* 9 and *ca.* 3 c./sec.; this suggests that the H–F coupling involving the α-fluorine atoms is larger than that involving the β-fluorines, but a detailed analysis of the spectrum would have to be made before this could be substantiated.

One of the authors (N. W.) thanks the Israel Institute of Technology for a Scholarship.

University Chemical Laboratory, Cambridge. [*Received, January* 10*th*, 1962.]

---

[7] Welcman, Ph.D. Thesis, Cambridge, 1961.