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PRELIMINARY NOTE

Organosilicon isoselenocyanates

Almost all reported organometallic selenocyanates have been derivatives of heavy metals, such as Hg, Tl, Sn, Pb, Bi[1,2]. Comparable species for lighter metals and metalloids, except for $H_3SiNCSe$, reported by Ebsworth and Mays[3], and impure $(C_6H_5)_3GeNCSe$, reported by Aynsley *et al.*[2], are unknown. This paper is a report on the preparation and properties of some organosilicon isoselenocyanates.
Two preparative methods have been used to prepare these compounds:

$$R_3SiCl + KSeCN \rightarrow R_3SiNCSe + KCl \qquad (1)$$

$$R_3SiCl + AgSeCN \rightarrow R_3SiNCSe + AgCl \qquad (2)$$

Potassium selenocyanate reacts vigorously with organochlorosilanes at room temperature, but the amount of heat evolved in the reaction makes a solvent desirable. Those solvents used include acetone, acetonitrile (both of which dissolve KSeCN), carbon disulfide, ether, and benzene. Yields in this preparation are low due to a competing side reaction:

$$KSeCN \rightarrow KCN + Se \qquad (3)$$

This decomposition proceeds rapidly in the presence of chlorosilanes. Selenium deposits on walls of the flask and the surface of unreacted KSeCN as an amorphous red solid. If the reaction is carried out in acetonitrile or acetone, white KCl precipitates immediately, followed in a few seconds by formation of red selenium. Examination of the infrared spectrum of the undistilled organosilicon product shows a very strong selenocyanate band at 2060 cm^{-1}, but no band at 2190 cm^{-1} due to cyanide[1], indicating that potassium selenocyanate is the source of the selenium.

In a typical preparation, 4.088 g (0.028 moles) KSeCN (purified by precipitation from CH_3CN) were weighed into a 50 ml Erlenmeyer flask. To this was added 2.30 ml (0.019 moles) $(CH_3)_3SiCl$ in 10.0 ml anhydrous ether. The flask was stoppered

TABLE 1

SILYL ISOSELENOCYANATES
vs = very strong; m = medium; w = weak; sh = shoulder.

Compound	*Method of preparation*	*m.p. (°C)*	*b.p. (°C)*	*NCSe Infrared peaks (cm^{-1})*	
$H_3SiNCSe$[3]	2 (H_3SiI + AgSeCN)	−15.1	20/9 mm	2068 (vs)	
$(CH_3)_3SiNCSe$	1,2		175–177	2055 (vs)	625 (m)
$(C_2H_5)_3SiNCSe$	1,2		195–200/100 mm	2065 (vs) 2090 (sh)	600 (w)[a]
$(C_6H_5)_3SiNCSe$	1	97–99		2070 (vs)	620 (w)[a]

[a] These peaks are partially masked by peaks arising from vibrations due to the organic groups on the silicon.

and placed in a dessicator. Within one minute the white KSeCN began to turn reddish; after ten minutes the solid layer was a deep red-black. The system was allowed to stand for 24 hours, after which the liquid was filtered and distilled to give 1.28 g of a clear colorless liquid, b.p. 175–177°, for a 26.8% yield. (Found: C, 27.3; H, 5.3; N, 7.5. C_4H_9NSeSi calcd.: C, 27.0; H, 5.1; N, 7.9%.)

$(CH_3)_3SiCl$ and $(C_2H_5)_3SiCl$ are converted to the selenocyanate by heating with silver selenocyanate, but the corresponding isothiocyanates do not react with silver selenocyanate, indicating that the selenocyanate group falls between Cl and NCS in the Me_3Si-Conversion Series[1]. Ebsworth reports that NCSe falls between Br and Cl in the H_3Si-Conversion Series[3].

The physical properties of the silyl isoselenocyanates are reported in Table 1.

Infrared peaks in these spectra may be assigned by comparison to reported spectra of other organosilyl pseudohalides[1,4] and also other organometallic selenocyanates[1,2,3,5]. The extremely strong asymmetric stretching band appears at about 2060 cm^{-1}, while the much weaker symmetric stretching band appears at about 620 cm^{-1}. Peaks arising from the NCSe deformation mode and the Si–N stretching mode apparently appear below 400 cm^{-1}, making them inaccessible to the available instrument; a peak at 468 cm^{-1}, previously assigned to the NCSe bending mode[1], apparently arises from the Si–Cl stretch of chlorosilane impurity. On the basis of the infrared spectrum[1] and the analogy of $(CH_3)_3SiNCSe$ to $(CH_3)_3SiNCO$ and $(CH_3)_3SiNCS$, both known to be bonded through nitrogen[6], these compounds are presumed to be isoselenocyanates rather than selenocyanates.

One major difference between the silyl isoselenocyanates and other silyl pseudohalides is the weakness of the carbon–selenium bond. Hydrolysis leads to immediate formation of amorphous red selenium:

$$2\,R_3SiNCSe + H_2O \rightarrow (R_3Si)_2O + HCN + Se \qquad (4)$$

In all probability HNCSe is formed initially, but this compound, which has never been isolated, apparently decomposes immediately to HCN and Se. The ease of this hydrolysis and the toxic nature of the products makes caution absolutely necessary in handling organosilyl selenocyanates.

The C–Se bond can be cleaved by other reactions. Although $(CH_3)_3SiNCSe$ and $(C_2H_5)_3SiNCSe$ can be distilled with only slight decomposition, pyrolysis at higher temperatures leads to deposit of Se and formation of the corresponding cyanides. Preliminary experiments indicate that this reaction is reversible and that $(CH_3)_3SiNCSe$ can be formed in good yield from $(CH_3)_3SiCN$ and Se. Likewise, the silyl isoselenocyanates will react with triphenylphosphine analogously to the deselenation of KSeCN reported by Nicpon and Meeks[7]. $(C_6H_5)_3PSe$ and the organosilyl cyanides have been identified as products of this reaction:

$$Me_3SiNCSe + (C_6H_5)_3P \rightarrow Me_3SiCN + (C_6H_5)_3PSe \qquad (5)$$

Both reactions are presently being studied in great detail, particularly with respect to their application to the proposed cyanide–isocyanide equilibrium in $(CH_3)_3SiCN$ and $(C_2H_5)SiCN$[1].

The reactivity of KSeCN and the unexpected stability of the organosilyl isoselenocyanates makes it probable that the reaction described in Eqn. (1) is quite general, and could be very easily extended to other organometalloid systems. Such compounds would probably show interesting properties and might be useful for certain synthetic reactions.

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