Metathesis of N-Silyl Compounds with Selenenyl Chlorides. First Preparation of a Selenenyl Azide and a Triselenenamide
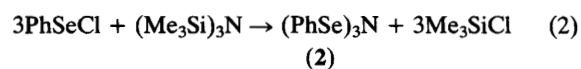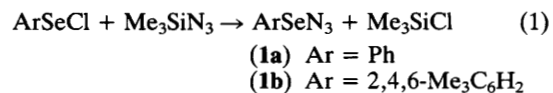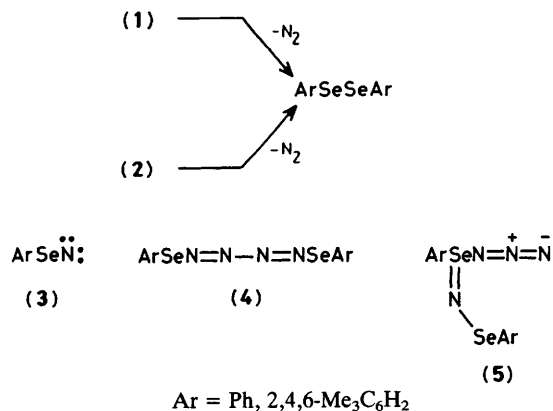
Thomas G. Back* and Russell G. Kerr

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

The reaction of trimethylsilyl azide with mesityleneselenenyl chloride afforded mesityleneselenenyl azide, and tris(trimethylsilyl)amine reacted with benzeneselenenyl chloride to produce tribenzeneselenenamide.
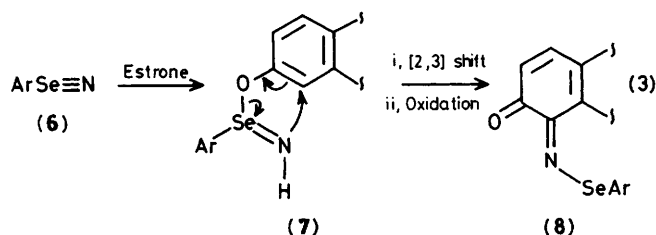
The metathesis of selenenyl chlorides with Si–N,[1,2] Si–CN,[3] Si–NCS,[4] and Si–X[2] (X = Br, I) compounds provides a convenient synthesis of selenenamides, phenyl selenocyanate, selenenyl thiocyanates, and selenenyl bromides and iodides, respectively. The attractiveness of this approach stems from the rapid and quantitative formation of the products and the facile removal of the volatile chlorosilane byproduct. We now report the preparation of the first selenenyl azide (**1b**) *via* the metathesis of the corresponding selenenyl chloride with trimethylsilyl azide (equation 1), and the novel triselenenam-ide (**2**) from the similar reaction of benzeneselenenyl chloride with tris(trimethylsilyl)amine (equation 2).

$$\text{ArSeCl} + \text{Me}_3\text{SiN}_3 \rightarrow \text{ArSeN}_3 + \text{Me}_3\text{SiCl} \qquad (1)$$

$$\text{(1a)} \quad \text{Ar} = \text{Ph}$$
$$\text{(1b)} \quad \text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$$

$$3\text{PhSeCl} + (\text{Me}_3\text{Si})_3\text{N} \rightarrow (\text{PhSe})_3\text{N} + 3\text{Me}_3\text{SiCl} \qquad (2)$$

$$\text{(2)}$$

Scheme 1

$Ar = Ph, 2,4,6-Me_3C_6H_2$

the species (3) with various alkenes[5] or dimethyl sulphoxide (DMSO),[6] to no avail. This indicates that selenenyl azides either react *via* mechanisms other than those involving nitrene intermediates, or that nitrenes (3) react further to afford diselenides faster than they react with these trapping agents. For instance, it is possible that species (3) attacks the azide (1) to produce intermediates such as (4) or (5), from which nitrogen extrusion leads to the observed diselenides.

The nitrene (3) could also display behaviour more characteristic of the corresponding selenazyl (6) [*i.e.* (3) ⟷ (6)]. Indeed, when the azide (1b) was permitted to decompose in the presence of estrone, the selenoimine (8) was formed in 12% yield, presumably by attack of the 3-OH group at the selenium atom of (6), followed by the known[7] [2,3]-sigmatropic rearrangement of the resulting intermediate (7) and oxidation by an as yet unidentified process, possibly mediated by the same selenazyl (see equation 3).§ The cycloaddition of (1) and (6), followed by nitrogen extrusion, provides an alternative pathway for diselenide formation.

The metathesis of tris(trimethylsilyl)amine with three equivalents of benzeneselenenyl chloride was carried out in THF at room temperature for 24 h. Concentration of the reaction mixture afforded 89% of tribenzeneselenenamide (2) as a low-melting orange solid, which had a satisfactory elemental analysis and a ^{77}Se n.m.r. signal at δ −295 p.p.m.,† consistent with that of *N,N*-dialkylselenenamides.[8] Diphenyl diselenide was produced quantitatively when compound (2) was refluxed for 1 h in THF (Scheme 1). This transformation is probably mediated by free-radicals formed by the homolytic cleavage of the Se–N bond. By analogy, tribenzenesulphenamide is known to undergo facile S–N scission which results in some remarkable free-radical chemistry.[9]

These examples indicate that the selenium–silicon metathesis is a powerful method for preparing Se–N compounds which are otherwise inaccessible.

When trimethylsilylazide was treated with an equimolar amount of benzeneselenenyl chloride in dry tetrahydrofuran (THF) at or below room temperature, the red colour of the selenenyl chloride was rapidly discharged and nitrogen evolution was observed. Upon removal of the solvent, a quantitative yield of diphenyl diselenide was obtained, suggesting the formation of (1a) as an unstable intermediate, followed by its immediate decomposition as shown in Scheme 1.

Repetition of the reaction with the more hindered mesityleneselenenyl chloride resulted in a slower metathesis which required *ca.* 2 h at room temperature to go to completion. However, removal of the solvent and rapid recrystallization of the residue from chloroform–hexane afforded an orange solid (84% yield), m.p. 58—61 °C (decomp.), to which we assign the selenenyl azide structure (1b) on the basis of the following evidence. The product had a strong, new azide absorption in its i.r. spectrum at 2106 cm⁻¹, clearly distinct from the silyl azide starting material at 2139 cm⁻¹. Its ^{77}Se n.m.r. spectrum displayed a signal at δ 146 p.p.m.,† readily distinguishable from the corresponding diselenide (δ −926 p.p.m.) and selenenyl chloride (δ −154 p.p.m.). The ^1H n.m.r. spectrum of a freshly prepared sample revealed only a small amount (<10% by integration) of the diselenide as a contaminant.‡

Compound (1b) gradually lost nitrogen and afforded the corresponding diselenide nearly quantitatively (>90%) after standing for 5 days at room temperature, or after photolysis or pyrolysis at 110 °C for shorter periods. Since azides are known to decompose *via* nitrene intermediates, we attempted to trap

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† All ^{77}Se n.m.r. signals are reported in $CDCl_3$ relative to an external Na_2SeO_3 reference; positive values indicate chemical shifts downfield from the reference; negative values are upfield.

‡ ^1H-n.m.r. data (Ar = 2,4,6-Me₃C₆H₂): (1b) δ 7.20 (s, 2H), 2.45 (s, 6H), 2.24 (s, 3H); ArSeSeAr: δ 6.69 (s, 2H), 2.17 (s, 9H); ArSeCl: δ 6.92 (s, 2H), 2.62 (s, 6H), 2.29 (s, 3H).

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§ We thank a referee for suggesting this trapping experiment.