Phenylsulfinylselenyl Chloride ($PhSO_2SeCl$): A New Reagent for the Formation of C–Se and N–Se Bonds. Generation and *In Situ* Diels–Alder Trapping of Selenonitrosoarene Intermediates (Ar–N=Se)

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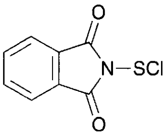
The novel electrophilic selenium transfer reagent phenylsulfinylselenyl chloride, $PhSO_2SeCl$, **3** has been prepared and reacted with enolisable carbonyl compounds to yield α-selenoketones and diselenides; reaction of reagent **3** with arylamines in the presence of triethylamine and dimethylbutadiene affords 1,2-selenazine derivatives, providing the first evidence for Diels–Alder trapping of selenonitroso intermediates, Ar–N=Se.

Compounds which can be employed as sulfur transfer reagents are well documented;[1] however, there are few reports of the analogous selenium reagents which are synthetically viable. We were interested in selenium analogous of *N*-chlorosulfanylphthalimide **1** which has been used to effect the transfer of a sulfur atom in the synthesis of thionitroso intermediates (R–N=S),[2] novel thiirane derivatives,[3] alkynyl vinyl sulfides,[4] sulfur heterocycles,[5] and functionalised thiones.[6] Our initial studies focused on bis(phenylsulfonyl) diselenide **2**, which is readily prepared from diselenium dichloride and the sodium salt of phenylsulfinic acid,[7] and we have previously employed **2** as a selenium transfer reagent in a low yielding synthesis of bis(tetrathiafulvalenyl)selenide.[8]

Here we report the synthesis of the novel reagent phenylsulfinylselenyl chloride ($PhSO_2SeCl$) **3** and explore its reactions with enolisable carbonyl compounds and with amines. Chlorination of the diselenide **2** occurred rapidly at room temperature in dichloromethane to afford compound **3** as an off-white, air- and moisture-sensitive solid in quantitative yield (Scheme 1) which was kept under an atmosphere of dry nitrogen and used within 1 h of preparation. The results of addition of reagent **3** to enolisable carbonyl compounds **4a–f** to form α-selenoketones **5** are reported in Table 1. Ketones **4a–c** yielded phenylsulfinylselenenyl derivatives **5a–c** in high yield, whereas ketones **4e** and **4f** gave no isolable selenated products. Reaction of **3** with acetone **4d** gave almost exclusively the diselenide **6**, and upon standing at room temperature for 48 h the α-selenoketones **5a–c** underwent similar dimerisation to the corresponding diselenides.



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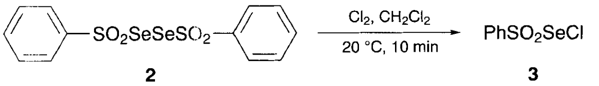
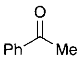
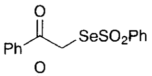
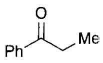
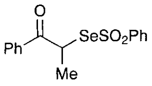
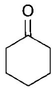
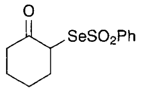
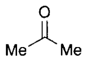
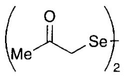
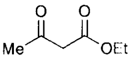
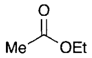
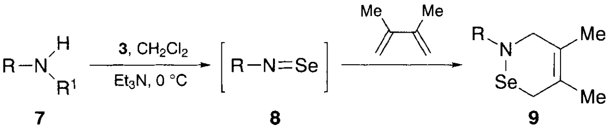


Scheme 1

Table 1 Reaction of carbonyl compounds **4a–f** (10 equiv.) with reagent **3** (CH_2Cl_2, 0 °C for **4a–c, e, f**; neat, 0 °C for **4d**)

Entry	4	Yield (%)	Product 5 or 6
a		93	
b		87	
c		87	
d		45	 **6**
e		0	No reaction
f		0	No reaction

Having established that reagent **3** was a convenient source of electrophilic selenium for the formation of carbon–selenium bonds, we examined the reaction of **3** with amines, and have thereby developed a route to transient organic selenonitroso species, R–N=Se. Although analogous thionitroso species (R–N=S) have been widely studied recently within our group and elsewhere,[2] a selenonitroso species has been only tentatively observed in a matrix at 100 K,[9] and has never been trapped in a subsequent reaction. Our route to R–N=Se species, which is based on recent chemistry employing the reaction of sulfur dichloride with amines to yield thionitroso groups,[10] is outlined in Scheme 2. A mixture of reagent **3**, amine, or trimethylsilylated amine **7a–g**, triethylamine and dimethylbutadiene was stirred in dry dichloromethane at 0 °C for 0.5 h to yield the corresponding 1,2-selenazine derivatives **9a–e**, albeit in low yield, which are presumably formed by Diels–Alder reaction of

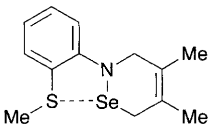


Scheme 2

Table 2 Reaction of trimethylsilyated amines **7** with reagent **3** to produce the corresponding 1,2-selenazine derivatives **9** (Scheme 2)

Entry	7, R=	7, R¹=	Yield 9 (%)[a]	Stability of 9[b]
a	4-Br-C_6H_4	H	12	2–3 h
b	4-Br-C_6H_4	TMS	15	2–3 h
c	4-Me-C_6H_4	H	14	2–3 h
d	4-Me-C_6H_4	TMS	20	2–3 h
e	2-SMe-C_6H_4	H	18	3 d
f	2-SeMe-C_6H_4	H	0	—
g	$PhOCH_2CH_2$	TMS	0	—

[a] Based on material isolated pure, as judged by ^1H NMR and mass spectra, after column chromatography on alumina utilising hexane as the eluent. [b] Stability at 0 °C as determined by ^1H NMR.



9e′

an intermediate selenonitroso species **8**. No adducts were isolated using amines **7f** and **7g** (Table 2).

Adducts **9a–d** are unstable; however, the presence of the *ortho*-thiomethyl substituent in **9e** considerably increases the stability of the 1,2-selenazine system, presumably by virtue of a non-bonded, five-membered ring S---Se interaction (structure **9e′**).† Similar non-bonded S---S interactions have been shown to increase the stability of related sulfur heterocycles.[10b,11] Attempts to utilise analogous Se---Se and O---Se interactions to stabilise 1,2-selenazine derivatives were unsuccessful: no products were purified from analogous reactions of amines **7f**[12] and **7g**. It is noteworthy that in the mass spectrum of **9e** a fragment of *m/z* 174 is seen which corresponds to *N*-phenyl-3,4-dimethyl-3-pyrroline (*i.e.* loss of Se and SMe) whereas for the analogous 1,2-thiazine[10b] such a clean fragmentation does not occur, while for many other *N*-aryl-1,2-thiazines retro-Diels–Alder reaction occurs in the mass spectrometer and the Ar–N=S fragment is observed.[2a,13]

In summary, we have developed an expedient route to the new electrophilic selenium transfer reagent **3** which can be formally viewed as a synthetic equivalent of the inaccessible $SeCl_2$.[14] Reagent **3** undergoes reactions similar to those of analogous sulfur reagents with enolisable carbonyl compounds and with arylamines, furnishing novel functionalised α-selenoketones, diselenides and 1,2-selenazine derivatives, the latter compounds providing the first evidence for Diels–Alder trapping of selenonitroso intermediates.

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Footnote

† *Spectroscopic data* for **9e**: *m/z* (CI) for ^{80}Se (%): 300 (M^+, 20), 254 (20), 220 (25), 174 (50%) and 140 (100%); ^1H NMR δ ($CDCl_3$) 8.0 (1H, m), 7.7–7.6 (2H, m), 7.4 (1H, m), 4.1 (2H, broad s, CH_2N), 3.35 (2H, broad m, CH_2Se), 2.0 (3H, s, SMe) and 1.8 (6H, s, 2 × Me).

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