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# INSERTION REACTIONS OF DIAZO COMPOUNDS WITH SOME SELENIUM(II) ELECTROPHILES

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## Summary

Benzene- and *o*-nitrobenzene-selenenyl thiocyanate (**1** and **2**) reacted with diazomethane and several α-diazo esters to afford α-arylseleno isothiocyanates (**5a–10a**) and the isomeric thiocyanates (**6b–8b**) as the major and minor products, respectively. Analogous insertion reactions were observed with benzenesulfenyl thiocyanate (**3**) and benzeneselenenyl selenocyanate (**4**) to furnish phenylthiomethyl isothiocyanate (**11**), ethyl α-phenylthio-α-isothiocyanoacetate (**12**) and phenylselenomethyl isoselenocyanate (**13**), ethyl α-phenylseleno-α-isoselenocyanoacetate (**14**), respectively. *N*-(Phenylseleno)phthalimide formed insertion products *N*-(phenylselenomethyl)phthalimide (**16**) and ethyl α-phenylseleno-α-phthalimidoacetate (**17**) with diazomethane and ethyl diazoacetate, but effected elimination to the corresponding vinyl selenides, ethyl α-(phenylseleno)propenoate (**18**) and ethyl 2-phenylseleno-3-methyl-2-butenoate (**19**) when treated with diazo esters containing β-hydrogens. Compound **19** was similarly obtained from benzeneselenenyl iodide and the diazo ester. Attempts to effect selenoxide eliminations in compounds **7a–10a** were unsuccessful. A new, efficient preparation of **1** from the metathesis of benzeneselenenyl chloride with trimethylsilyl isothiocyanate was developed.

## Introduction

The reactions of diazo compounds with several types of divalent selenium species have been studied in recent years. These include diselenides [1–4], selenenyl halides [3–6], a selenosulfonate [7], allylic [4,8] or cyclic β-keto selenides [9], and selenoesters [10]. In general, such processes result in the insertion of the diazo compound into a selenium–carbon or selenium–heteroatom bond as in eq. 1, often in a synthetically useful manner.

(1)

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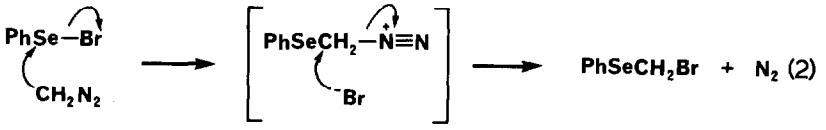
Mechanisms include electrophilic, carbene (or carbenoid), free radical and other pathways, depending upon the precise conditions and the nature of the selenium compound. The electrophilic process is exemplified by the reaction of benzeneselenenyl bromide with diazomethane (or diazoethane) at low temperatures, and was reported by Petragnani et al. [5] to proceed according to eq. 2.




In order to gain further insight into the scope and limitations of such processes, we investigated the reactions of several other selenium electrophiles of general structure RSeX, where X represents a leaving group, with diazo compounds.

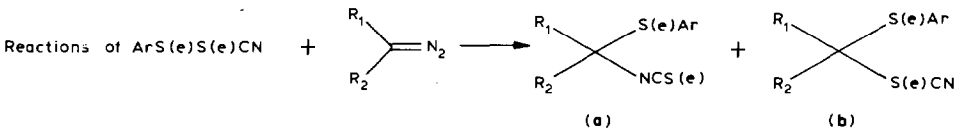
## Results and discussion

*Selenenyl and sulfenyl thio- and selenocyanates*

The insertion reactions of selenenyl thiocyanates **1** and **2**, sulfenyl thiocyanate **3** and selenenyl selenocyanate **4** with diazomethane and several α-diazo esters are summarized in Table 1. All of these reactions proceeded readily in solvents such as dichloromethane or ether at room temperature, with visible evolution of nitrogen. The products were stable, except for **13** and **14** which underwent severe discolouration upon standing for several hours under ambient conditions. Phenyl selenocyanate, on the other hand, failed to react with diazomethane even after prolonged exposure.

It appears reasonable that the mechanism of these processes is analogous to that shown in eq. 2. It therefore requires the displacement of nitrogen from the di-

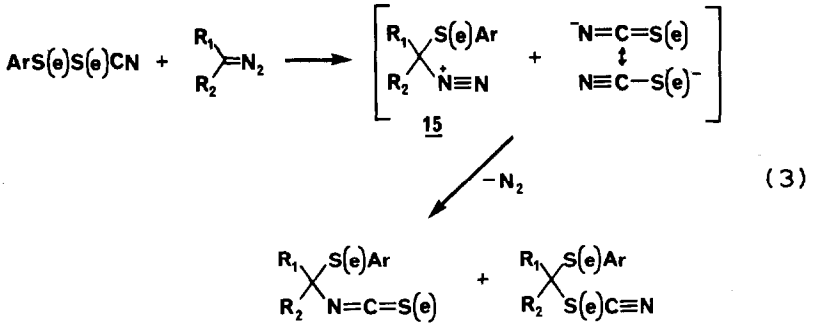
TABLE 1




| Electrophile | $R_1$ | $R_2$ | Product(s) | Isolated yield of a (%) and [b (%)] |
|---|---|---|---|---|
| PhSeSCN (**1**) | H | H | **5** | 85 [a] |
| **1** | H | $CO_2Et$ | **6** | 70 [18] [a] |
| **1** | H | $CO_2Et$ | **6** | 16 [71] [b] |
| **1** | H | $CO_2Et$ | **6** | 82 [12] [c] |
| **1** | Me | $CO_2Et$ | **7** | 60 [4] [c] |
| **1** | i-Pr | $CO_2Et$ | **8** | 65 [7] [c] |
| *o*-$NO_2$PhSeSCN (**2**) | Me | $CO_2Et$ | **9** | 52 |
| **2** | i-Pr | $CO_2Et$ | **10** | 58 |
| PhSSCN (**3**) | H | H | **11** | 72 |
| **3** | H | $CO_2Et$ | **12** | 61 |
| PhSeSeCN (**4**) | H | H | **13** | 68 |
| **4** | H | $CO_2Et$ | **14** | 98 |

[a] Electrophile prepared in situ from PhSeCl and KSCN. [b] Electrophile prepared in situ from PhSeCl and NaSCN. [c] Electrophile prepared via metathesis (eq. 4).

azonium intermediate **15** by the ambidentate thio- or selenocyanate anion in the product-forming step (eq. 3).



(3)

In general, the isothio- or isoselenocyanate products (series **a**, Table 1) dominated, and the corresponding thio- or selenocyanates (series **b**) were either obtained in low yield or were not detected at all. The isomeric products were readily distinguished by significant differences in their IR spectra, with the former compounds (series **a**) exhibiting a broader absorption at lower frequencies than their counterparts in series **b** [11,12]. Furthermore, $\alpha$-hydrogens (when present) appeared further downfield in the $^1$H NMR spectra of series **a**, presumably as a result of the closer proximity of the electronegative nitrogen atom.

The isomer distribution in the reaction of benzeneselenenyl thiocyanate (**1**) with ethyl diazoacetate proved remarkably sensitive to the method of preparation of the selenium electrophile. When it was produced in situ by treating benzeneselenenyl chloride with a 10% excess of potassium thiocyanate in dichloromethane, the isothiocyanate **6a** was the major product. However, when sodium thiocyanate was employed in lieu of the potassium salt, the isomer ratio was essentially reversed. This indicates that the nature of the alkali metal counterion plays an important role in determining the course of the reaction *.

When the product mixture obtained from the use of KSCN (rich in **6a**) was subsequently treated with NaSCN, the ratio of **6a**/**6b** remained essentially unchanged. Similarly, the mixture rich in **6b** was not significantly altered by exposure to KSCN. These results indicate that the different isomer distributions are not due to further sodium or potassium thiocyanate-mediated equilibration of an initial kinetically-controlled product mixture. The isomerization of thio- to isothiocyanates is well known in other systems [13]. The precise reasons for the contrasting chemoselectivity in these experiments is not entirely clear, but it is worth noting that the same selenenyl thiocyanate **1** also behaves capriciously with respect to chemo-, as well as regio- and stereoselectivity in its additions to olefins [14].

We also devised a simple and highly efficient preparation of **1**, which obviates the need for employing a metal thiocyanate precursor. Commercially available trimethylsilyl isothiocyanate and benzeneselenenyl chloride react rapidly in dichloromethane to produce the desired selenenyl thiocyanate quantitatively via the metathe-

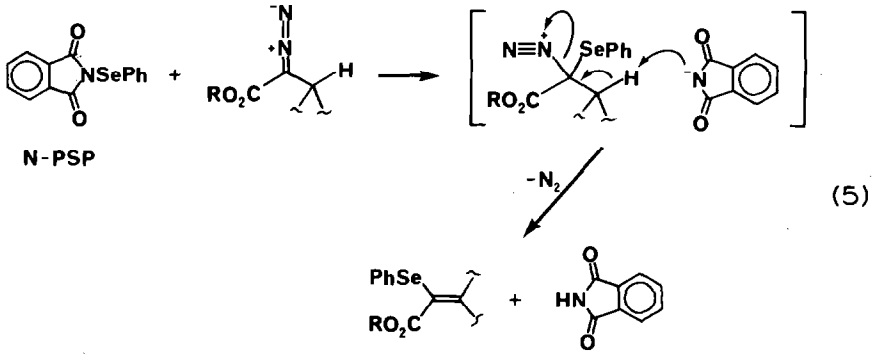
* Most of the metal cation precipitates in the form of KCl or NaCl during the preparation of **1** (i.e. $PhSeCl + M^+ SCN^- \rightarrow PhSeSCN + M^+ Cl^- \downarrow$). However, the use of excess thiocyanate $M^+ SCN^-$, which is partly soluble in dichloromethane, ensures its presence during the subsequent reaction of **1** with the diazo compound.

sis reaction shown in eq. 4. The sole byproduct, trimethylsilyl chloride, is easily removed with the solvent. A similar procedure has recently been reported for the preparation of phenyl selenocyanate [15]. When pure **1** thus prepared was permitted to react with ethyl diazoacetate, the isothiocyanate **6a** was strongly favoured.

$$PhSeCl + Me_3SiNCS \longrightarrow \underset{\underline{1}}{PhSeSCN} + Me_3SiCl \qquad (4)$$

*N-(Phenylseleno)phthalimide*

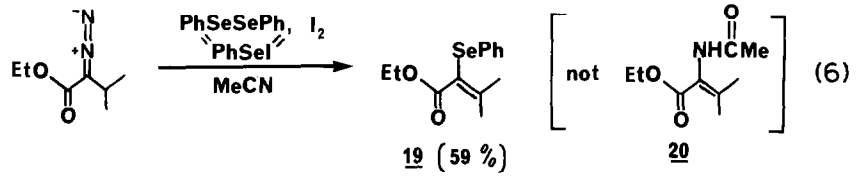
*N*-(Phenylseleno)phthalimide (*N*-PSP) was observed to react with diazo compounds by either of two different pathways, depending on the presence or absence of hydrogens $\beta$ to the diazo group. When such hydrogens were unavailable, an insertion reaction analogous to eq. 2 and 3 occurred, affording the corresponding products **16** and **17** in moderate yields (Table 2). Otherwise, vinyl selenides **18** and **19** were formed as the principal products, presumably via elimination effected by the relatively basic phthalimide anion as depicted in eq. 5.




(5)

*Benzeneselenenyl iodide*

Benzeneselenenyl iodide has recently been generated in situ from diphenyl diselenide and iodine in acetonitrile [16]. The reaction of this putative electrophile with ethyl 2-diazo-3-methylbutanoate produced the vinyl selenide **19** in 59% yield (eq. 6), indicating that dehydrohalogenation occurs readily under these conditions. Solvent incorporation, which was observed in the reaction of the selenenyl iodide with diolefins [16], was not observed *.



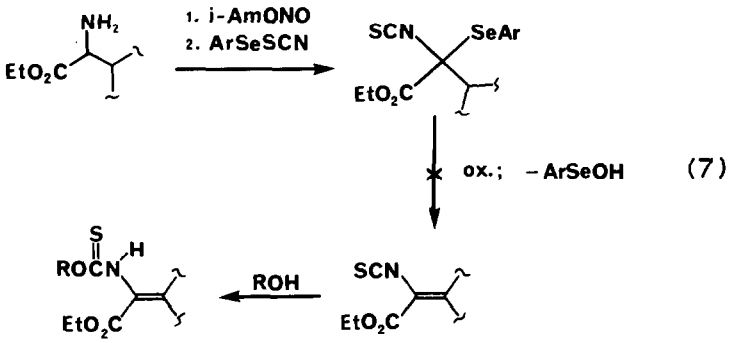

(6)

*Attempted preparation of dehydroamino acid derivatives*

The availability of $\alpha$-phenylseleno isothiocyanates **7a** and **8a** from the corresponding $\alpha$-diazo esters (Table 1) suggested a possible protocol for converting amino acids to biologically interesting dehydroamino acid derivatives [17]. The required diazo esters were themselves easily prepared from the diazotization of esters of amino

* Solvent incorporation followed by hydrolysis would be expected to afford the corresponding dehydroamino acid **20** (vide infra).

acids with isoamyl nitrite [18]. Their transformation to isothiocyanates such as **7a–10a** via eq. 3, followed by selenoxide elimination [19] was expected to afford $\alpha,\beta$-unsaturated isothiocyanates. Addition of an appropriate alcohol to the isothiocyanate moiety would then provide the corresponding dehydroamino acid in the form of its thionocarbamate derivative (eq. 7). Unfortunately, all attempts to effect the selenoxide eliminations of **7a–10a** with conventional procedures employing *m*-chloroperbenzoic acid, hydrogen peroxide, sodium *m*-periodate and t-butyl hydroperoxide under a variety of conditions failed. Low temperature ozonolysis, followed by rapid pyrolysis of the resulting selenoxide in refluxing carbon tetrachloride also proved unsuccessful. This latter method has been reported as the only successful procedure for the conversion of a series of related $\beta$-phenylseleno isothiocyanates to their $\alpha,\beta$-unsaturated derivatives [20].




Alternatively, the base-catalyzed addition of methanol to the isothiocyanate group of **8a** was attempted prior to oxidation of the phenylseleno group. The addition was accompanied by transesterification and rapid reductive cleavage of the selenide moiety, producing the saturated thionocarbamate **22** as the chief product. This unwelcome result may transpire via the formation of the intermediate heterocycle **21** (eq. 8).

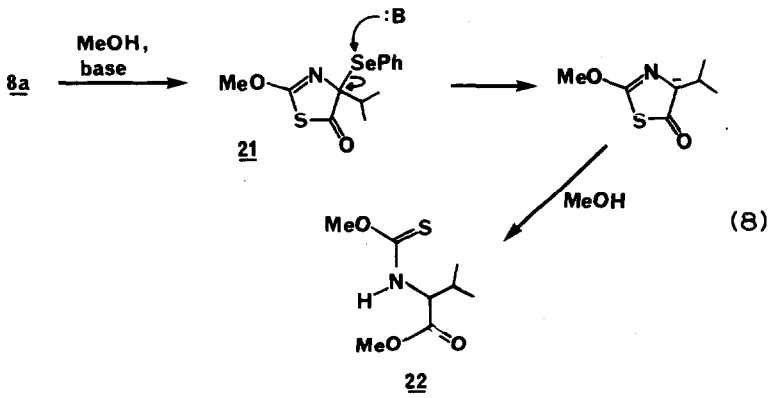
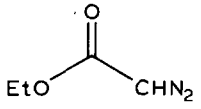
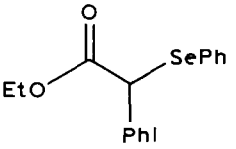
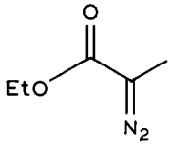
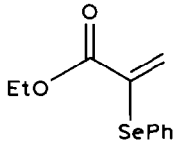
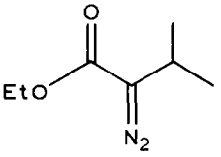
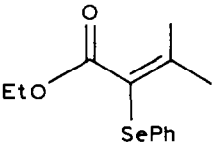


TABLE 2

REACTIONS OF *N*-(PHENYLSELENO)PHTHALIMIDE WITH DIAZO COMPOUNDS

| Diazo compound | Product [a] | Isolated yield (%) |
|---|---|---|
| $CH_2N_2$ | $PhSeCH_2Phl$ (16) | 70 |
|  |  (17) | 58 |
|  |  (18) | 43 |
|  |  (19) | 45 |

[a] Phl = phthalimido.

## Conclusion

It therefore appears that the insertion of diazo compounds into selenenyl pseudohalides RSeX is a general process which resembles their reaction with PhSeBr. Elimination to a vinyl selenide is possible in certain cases of $\alpha$-diazo esters containing $\beta$-hydrogens. Neither the use of $\alpha$-arylseleno isothiocyanates, nor the functionalization of diazo esters with *N*-PSP or PhSeI (due to elimination) provide satisfactory approaches to dehydroamino acids. The latter two processes may, however, prove of interest as a new route to synthetically useful vinyl selenides [21].

## Experimental section

Melting points were obtained on an A.H. Thomas hot stage apparatus and are uncorrected. IR Spectra were recorded on a Perkin–Elmer 467 spectrometer and NMR spectra were obtained on a Hitachi Perkin–Elmer R24B or a Varian XL200 spectrometer in $CDCl_3$ solution. Chemical shifts are reported in ppm downfield

from internal tetramethylsilane. Mass spectra were recorded on a Varian MAT CH5 or a Kratos MS 80 instrument. Preparative TLC was carried out on Analtech 20 × 20 cm glass plates coated with 1 mm of silica-gel GF. Ozonolyses were performed on a Welsbach T-23 apparatus. Elemental analyses were obtained by Dr. W.S. Lin.

Ethereal diazomethane was prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide ("Diazald", Aldrich Chemical Co.) by a standard method [22]. Ethyl diazoacetate was obtained from the Aldrich Chemical Co. as a solution in dichloromethane, and its concentration was assayed prior to use by NMR integration. Ethyl 2-diazopropanoate and ethyl 2-diazo-3-methylbutanoate were obtained from the ethyl esters of alanine and valine by a literature procedure [18]. All experiments with diazo compounds were conducted behind a safety shield. Literature methods were employed for the preparation of benzenesulfenyl thiocyanate [23] (**3**) and *N*-(phenylseleno)phthalimide [24] (*N*-PSP). Benzeneselenenyl selenocyanate (**4**) was prepared in situ immediately prior to use by a modification of the procedure of Rheinboldt and Giesbrecht [25]. All other reagents were purchased from commercial sources.

*Benzeneselenenyl thiocyanate (**1**)*

Trimethylsilyl isothiocyanate (0.655 g, 5.0 mmol) and benzeneselenenyl chloride (0.96 g, 5.0 mmol) were stirred for 3.5 h in 50 ml of dichloromethane. The solution changed from red to yellow. The solvent was evaporated to afford 1.07 g (100%) of **1** as an orange oil with spectral properties as reported in the literature [14]. Crystallization from hexane gave 92% of **1** with m.p. 36–37°C.

*o-Nitrobenzeneselenenyl thiocyanate (**2**)*

Compound **2** was prepared from *o*-nitrobenzeneselenenyl chloride and sodium thiocyanate by a variation of the method of Foss [26].

*Phenylselenomethyl isothiocyanate (**5**)*

Benzeneselenenyl chloride (3.83 g, 20 mmol) and potassium thiocyanate (2.13 g, 22 mmol) were stirred 4 h in 50 ml of dichloromethane. Excess ethereal diazomethane was then added and after 2 h the mixture was filtered, evaporated and distilled (Kugelrohr) to afford 3.87 g (85%) of **5** as a pale yellow oil, b.p. 120°C (0.4 mmHg); IR (film) 2200 (sh), 2070, 1578 $cm^{-1}$; NMR 7.7–7.1 (complex, 5H) 4.56 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 229 ($M^+$, $^{80}Se$, 56), 227 ($M^+$, $^{78}Se$, 33), 72 ($M^+$ – PhSe, 100). Anal. Found: C, 42.45; H, 2.92; N, 5.85; S, 14.32. $C_8H_7NSSe$ calcd.: C, 42.11; H, 3.09; N, 6.14; S, 14.06%.

*Ethyl α-phenylseleno-α-isothiocyanoacetate (**6a**) and -thiocyanate (**6b**)*

*(a) Using KSCN.* Benzeneselenenyl chloride (192 mg, 1.00 mmol) and KSCN (107 mg, 1.10 mmol) were stirred 12 h in 5 ml of dichloromethane. Ethyl diazoacetate (1.00 mmol) was added and after 1 h the yellow solution was filtered, concentrated and separated by preparative TLC in benzene to afford 211 mg (70%) of **6a** as an oil, $R_f$ 0.85; IR (film) 2041, 1740, 1578 $cm^{-1}$; NMR 7.7–7.1 (complex, 5H), 5.04 (s, 1H), 4.03 (q, *J* 7 Hz, 2H), 1.20 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 301 ($M^+$, $^{80}Se$, 17), 299 ($M^+$, $^{78}Se$, 8), 144 ($M^+$ – PhSe, 100). High resolution mass spectrum. Found: 300.9662. $C_{11}H_{11}NO_2SSe$ calcd.: 300.9675. A more polar band gave 54 mg (18%) of **6b** as an oil, $R_f$ 0.72; IR (film) 2168, 1734,

1577 $cm^{-1}$; NMR 7.7–7.1 (complex, 5H), 4.91 (s, 1H), 4.09 (q, *J* 7 Hz, 2H), 1.23 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 301 ($M^+$, $^{80}Se$, 20), 299 ($M^+$, $^{78}Se$, 14), 243 ($M^+$ – SCN, 35). Anal. Found: C, 44.42; H, 3.78; N, 4.35. $C_{11}H_{11}NO_2SSe$ calcd.: C, 44.00; H, 3.70; N, 4.67%.

*(b) Using NaSCN.* The above reaction was repeated with NaSCN in place of KSCN to furnish 16% of **6a** and 71% of **6b**.

*(c) Using $Me_3SiNCS$.* The above reaction was repeated with pure PhSeSCN obtained via eq. 4 to provide 82% of **6a** and 12% of **6b**.

*Ethyl α-phenylseleno-α-isothiocyanopropanoate (7a) and -thiocyanate (7b)*

Compounds **7a,b** were prepared via procedure (c) described for **6a,b** above. Preparative TLC in 10% ethyl acetate/hexane provided: (i) 19% of diphenyl diselenide, $R_f$ 0.84, identical to an authentic sample in all respects. (ii) 60% of **7a** as an oil, $R_f$ 0.78, IR (film) 2041, 1732, 1570 $cm^{-1}$; NMR 7.7–7.0 (complex, 5H), 3.98 (q, *J* 7 Hz, 2H), 1.76 (s, 3H), 1.19 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 315 ($M^+$, $^{80}Se$, 4), 313 ($M^+$, $^{78}Se$, 3), 158 ($M^+$ – PhSe, 41). Anal. Found: C, 46.20; H, 4.24; N, 4.12; S, 10.68. $C_{12}H_{13}NO_2SSe$ calcd.: C, 45.86; H, 4.18; N, 4.46; S, 10.20%. (iii) 4% of **7b** as an oil, $R_f$ 0.40, IR (film) 2162, 1733, 1570 $cm^{-1}$; NMR 7.7–7.2 (complex, 5H), 4.16 (m, 2H), 2.05 (s, 3H), 1.23 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 315 ($M^+$, $^{80}Se$, 9), 313 ($M^+$, $^{78}Se$, 4), 257 ($M^+$ – SCN, 19). Anal. Found: C, 45.97; H, 4.09; N, 4.28; S, 10.64. $C_{12}H_{13}NO_2SSe$ calcd.: C, 45.86; H, 4.18; N, 4.46; S, 10.20%.

*Ethyl 2-phenylseleno-2-isothiocyano-3-methylbutanoate (8a) and -thiocyanate (8b)*

Compounds **8a,b** were prepared via procedure (c) for **6a,b**, above. Preparative TLC in 15% ethyl acetate/hexane provided: (i) 19% of diphenyl diselenide, $R_f$ 0.89, identical to an authentic sample in all respects. (ii) 65% of **8a** as an oil, $R_f$ 0.74, IR (film) 2060, 1733, 1578 $cm^{-1}$; NMR 7.6–7.0 (complex, 5H), 3.84 (q, *J* 7.0 Hz, 2H), 2.43 (m, 1H), superimposed signals at 1.26 (d, *J* 6.6 Hz, 3H), 1.10 (t, *J* 7.0 Hz, 3H) and 0.95 (d, *J* 6.6 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 343 ($M^+$, $^{80}Se$, 4), 341 ($M^+$, $^{78}Se$, 2), 186 ($M^+$ – PhSe, 100). Anal. Found: C, 49.39; H, 5.01; N, 4.18; S, 9.39. $C_{14}H_{17}NO_2SSe$ calcd.: C, 49.11; H, 5.02; N, 4.09; S, 9.36%. (iii) 7% of **8b** as an oil, $R_f$ 0.48, IR (film) 2161, 1720, 1574 $cm^{-1}$; NMR 7.7–7.25 (complex, 5H), 3.98 (m, 2H), 2.95 (m, 1H), 1.30 (d, *J* 6.7 Hz, 3H), 1.20 (d, *J* 6.7 Hz, 3H), 1.15 (t, *J* 7.1 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 343 ($M^+$, $^{80}Se$, 1), 341 ($M^+$, $^{78}Se$, 0.5), 186 ($M^+$ – PhSe, 61). Anal. Found: C, 49.27; H, 4.89; N, 3.88, S, 9.20. $C_{14}H_{17}NO_2SSe$ calcd.: C, 49.11; H, 5.02; N, 4.09; S, 9.36%.

*Ethyl α-(o-nitrophenyl)seleno-α-isothiocyanopropanoate (9)*

Ethyl α-diazopropanoate (99 mg, 0.77 mmol) and selenenyl thiocyanate **2** (200 mg, 0.77 mmol) were stirred 2 h in dichloromethane. Preparative TLC in benzene afforded 187 mg (52%) of **9**, a yellow solid, $R_f$ 0.58, m.p. 52–54°C (from chloroform/hexane); IR ($CHCl_3$) 2039, 1737, 1592, 1570, 1517 $cm^{-1}$; NMR 8.3–7.25 (complex, 4H), 4.23 (q, *J* 7 Hz, 2H), 2.04 (s, 3H), 1.24 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 360 ($M^+$, $^{80}Se$, 0.6), 358 ($M^+$, $^{78}Se$, 0.4), 158 ($M^+$ – ArSe, 100). Anal. Found: C, 40.24; H, 3.18; N, 8.05; S, 8.56. $C_{12}H_{12}N_2O_4SSe$ calcd.: C, 40.11; H, 3.37; N, 7.80; S, 8.93%.

*Ethyl 2-(o-nitrophenyl)seleno-2-isothiocyano-3-methylbutanoate (10)*

Ethyl 2-diazo-3-methylbutanoate (156 mg, 1.00 mmol) and selenenyl thiocyanate **2** (259 mg, 1.00 mmol) were stirred 2 h in 10 ml of chloroform. Preparative TLC in benzene afforded 224 mg (58%) of **10**, a yellow solid, $R_f$ 0.65, m.p. 161–163°C (from chloroform/hexane); IR (Nujol) 2028, 1728, 1588, 1568 $cm^{-1}$; NMR 8.2–7.3 (complex, 4H), 4.01 (q, *J* 7 Hz, 2H), 2.59 (m, 1H), superimposed signals at 1.28 (d, *J* 7 Hz, 3H), 1.12 (t, *J* 7 Hz, 3H), 0.96 (d, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 388 ($M^+$, $^{80}Se$, 0.3), 386 ($M^+$, $^{78}Se$, 0.2), 186 ($M^+$ – ArSe, 95). Anal. Found: C, 43.62; H, 4.08; N, 7.06; S, 8.56. $C_{14}H_{16}N_2O_4SSe$ calcd.: C, 43.41; H, 4.17; N, 7.23; S, 8.28%.

*Phenylthiomethyl isothiocyanate (11) [27]*

Excess ethereal diazomethane was added to sulfenyl thiocyanate **3** (105 mg, 0.63 mmol) in 5 ml of ether. After 2 h, concentration and preparative TLC in 40% benzene/hexane afforded 15 mg (23%) of diphenyl disulfide, $R_f$ 0.72, identical to an authentic sample, and 82 mg (72%) of compound **11** as an oil, $R_f$ 0.57; IR (film) 2180 (sh), 2070, 1580 $cm^{-1}$; NMR 7.5–7.0 (complex, 5H), 4.40 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 181 ($M^+$, 23), 123 ($M^+$ – SCN, 100). High resolution mass spectrum, found: 181.0044. $C_8H_7NS_2$ calcd.: 181.0020.

*Ethyl α-phenylthio-α-isothiocyanoacetate (12)*

Sulfenyl thiocyanate **3** (178 mg, 1.07 mmol) and ethyl diazoacetate (1.04 mmol) were allowed to react for 1 h in 2 ml of dichloromethane. Preparative TLC in 10% ethyl acetate/hexane provided 162 mg (61%) of **12** as an oil, $R_f$ 0.33; IR (film) 2010, 1741, 1577 $cm^{-1}$; NMR 7.5–6.9 (complex, 5H), 4.89 (s, 1H), 3.96 (q, *J* 7 Hz, 2H), 1.12 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 253 ($M^+$, 30), 180 ($M^+ - CO_2Et$, 100). High resolution mass spectrum. Found: 253.0209. $C_{11}H_{11}NO_2S_2$ calcd.: 253.0231.

*Phenylselenomethyl isoselenocyanate (13)*

Benzeneselenenyl chloride (192 mg, 1.0 mmol) and potassium selenocyanate (159 mg, 1.1 mmol) were stirred 1 h in 5 ml of dichloromethane. Excess ethereal diazomethane was added and stirring continued for an additional 2 h. Preparative TLC in 50% benzene/hexane afforded 186 mg (68%) of compound **13** as a reddish oil which darkened after several hours, $R_f$ 0.58; IR (film) 2135, 1577 $cm^{-1}$; NMR 7.8–7.1 (complex, 5H), 4.67 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 277 ($M^+$, $^{80}Se_2$, 14), 275 ($M^+$, $^{80}Se$–$^{78}Se$, 12), 273 ($M^+$, $^{78}Se_2$, 7), 171 ($M^+$ – SeCN, $^{80}Se$, 100), 169 ($M^+$ – SeCN, $^{78}Se$, 58). High resolution mass spectrum, found: 276.8996. $C_8H_7NSe_2$ calcd.: 276.8909.

*Ethyl α-phenylseleno-α-isoselenocyanoacetate (14)*

Compound **14** was prepared using the same procedure as for **13**. The crude product was isolated in 98% yield by filtration and evaporation of the reaction mixture. It contained ca. 5% of impurities (NMR) and decomposed during further attempts at purification; IR (film) 2070, 1734, 1572 $cm^{-1}$; NMR 7.7–7.0 (complex, 5H), 5.16 (s, 1H), 4.05 (q, *J* 7 Hz, 2H), 1.21 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 349 ($M^+$, $^{80}Se_2$, 16) 347 ($M^+$, $^{80}Se$–$^{78}Se$, 13), 345 ($M^+$, $^{78}Se_2$, 7), 243 ($M^+$ – SeCN, $^{80}Se$, 100), 241 ($M^+$ – SeCN, $^{78}Se$, 67). High resolution mass spectrum, found: 348.9124. $C_{11}H_{11}NO_2Se_2$ calcd.: 348.9120.

*N-(Phenylselenomethyl)phthalimide (16)* *

*N*-(Phenylseleno)phthalimide (302 mg, 1.0 mmol) and excess ethereal diazomethane were stirred in 12 ml of dry THF. After 1 h, the mixture was evaporated to dryness, triturated with 10 ml of hexane and filtered. The residue was washed with $3 \times 10$ ml of benzene, the combined filtrate was evaporated in vacuo and crystallized from chloroform/hexane to afford 220 mg (70%) of **16** as a pale yellow solid, m.p. 193–195°C; IR (Nujol) 1722, 1620 $cm^{-1}$; NMR 7.6–6.9 (complex, 9H), 5.90 (s, 2H); mass spectrum, *m/e* (relative intensity, %) 317 ($M^+$, $^{80}Se$, 3), 315 ($M^+$, $^{78}Se$, 2), 160 ($M^+ -$ PhSe, 100). High resolution mass spectrum, found: 316.9990. $C_{15}H_{11}NO_2Se$ calcd.: 316.9955.

*Ethyl α-phenylseleno-α-phthalimidoacetate (17)* *

*N*-(Phenylseleno)phthalimide (3.02 g, 10 mmol) ethyl diazoacetate (10 mmol) and triethylamine (1.01 g, 10 mmol) were allowed to react for 0.5 h in 50 ml of dichloromethane. The solution was reduced to 15 ml, 5 ml of hexane were added and the mixture was filtered. The filtrate was concentrated further and chromatographed over 30 g of silica-gel to provide 2.25 g (58%) of product **17**, eluted with 10–50% ethyl acetate/hexane, m.p. 120–121°C (from chloroform/hexane); IR ($CHCl_3$) 1777, 1726 $cm^{-1}$; NMR 7.68 (s, 1H) superimposed on 7.75–7.2 (m, 9H), 3.83 (q, *J* 7 Hz, 2H), 1.05 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 389 ($M^+$, $^{80}Se$, 53), 387 ($M^+$, $^{78}Se$, 27), 232 ($M^+ -$ PhSe, 39). High resolution mass spectrum, found: 389.0120. $C_{18}H_{15}NO_4Se$ calcd.: 389.0166.

*Ethyl α-(phenylseleno)propenoate (18) [28]*

Ethyl α-diazopropanoate (64 mg, 0.50 mmol) was added to *N*-PSP (151 mg, 0.50 mmol) in 5 ml of dichloromethane. After 3 h, preparative TLC in 10% ethyl acetate/hexane provided 55 mg (43%) of vinyl selenide **18** as an oil, $R_f$ 0.51; IR (film) 1720, 1704 (sh), 1585, 1575 $cm^{-1}$; NMR 7.5–6.95 (complex, 5 H), 6.40 (s, 1H), 5.09 (s, 1H), 4.04 (q, *J* 7 Hz, 2H), 1.18 (t, $J = 7$ Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 256 ($M^+$, $^{80}Se$, 35), 254 ($M^+$, $^{78}Se$, 17), 183 ($PhSeCH{=}CH_2$, $^{80}Se$, 100), 181 ($PhSeCH{=}CH_2$, $^{78}Se$, 52). High resolution mass spectrum, found: 256.0011. $C_{11}H_{12}O_2Se$ calcd.: 256.0002.

*Ethyl 2-phenylseleno-3-methyl-2-butenoate (19)*

*(a) From N-PSP.* Product **19** was prepared from the corresponding diazo ester and *N*-PSP in the same manner as **18**, in 45% yield, isolated as an oil, $R_f$ 0.53 in 10% ethyl acetate/hexane, IR (film) 1713, 1610, 1577 $cm^{-1}$; NMR 7.5–7.2 (complex, 5H), 4.01 (q, *J* 7 Hz, 2H), 2.08 (s, 3H), 2.06 (s, 3H), 1.08 (t, *J* 7 Hz, 3H); mass spectrum, *m/e* (relative intensity, %) 284 ($M^+$, $^{80}Se$, 80), 282 ($M^+$, $^{78}Se$, 38). High resolution mass spectrum, found: 284.0320. $C_{13}H_{16}O_2Se$ calcd.: 284.0315.

*(b) From PhSeI.* The diazo compound (156 mg, 1.00 mmol) in 1 ml of acetonitrile was added to a solution of iodine (254 mg, 1.00 mmol) and diphenyl diselenide (312

* Products **16** and **17** were found to contain traces of phthalimide (IR) which were not removed by further recrystallization. Satisfactory elemental analyses could not be obtained. The products also partially decomposed when subjected to chromatography on silica-gel.

mg, 1.00 mmol) in 5 ml of acetonitrile. After 2 h, the concentrated reaction mixture was separated by preparative TLC to afford 166 mg (59%) of **19** with the same properties as the product from the previous procedure.

*Reaction of isothiocyanate **8a** with methanol*

Isothiocyanate **8a** (125 mg, 0.364 mmol) was refluxed for 48 h in 5 ml of methanol and 1 ml of triethylamine. The mixture was evaporated in vacuo and separated by preparative TLC in benzene to afford 55 mg (97%) of diphenyl diselenide, $R_f$ 0.90, identical to an authentic sample. A more polar band provided 50 mg (67%) of thionocarbamate **22** as an oil, $R_f$ 0.50; IR (film) 3326, 1741 $cm^{-1}$; NMR 6.68 (br s, exchanged $D_2O$, 1H), 4.82 (dd, $J$ 8.7, 4.8 Hz, collapsed to d, $J$ 4.8 Hz upon $D_2O$ exchange, 1H), 3.92 (s, 3H), 3.69 (s, 3H), 2.21 (m, 1H), 0.91 (d, $J$ 7 Hz, 3H), 0.90 (d, $J$ 7 Hz, 3H), signals from an unidentified impurity were observed at $\delta$ 3.97. 3.68 and 0.87; mass spectrum, $m/e$ (relative intensity, %) 205 ($M^+$, 14), 173 ($M^+ - MeOH$, 24), 146 ($M^+ - CO_2Me$, 38). High resolution mass spectrum. found: 205.0759. $C_8H_{15}NO_3S$ calcd.: 205.0773.

The same product was obtained in comparable yield when **8a** was treated with 1 $N$ sodium methoxide in methanol at room temperature for 4 h.

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