routes, see G. W. K. Cavill in "Cyclopentanoid Terpene Derivatives", W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, New York, N.Y., 1969, Chapter 3; and G. W. K. Cavill and D. V. Clark in "Naturally Occurring Insecticides", M. Jacobson and D. J. Grosby, Ed., Marcel Dekker, New York, N.Y., 1971, Chapter 7.
(4) Supplied by Chemical Samples Co., Columbus, Ohio 43221
(5) Proton and ^{13}C magnetic resonance, infrared, and low resolution mass spectral data as well as either elemental analytical or high resolution mass spectral data consistent with the proposed structures of all intermediates were obtained. All of the intermediates were obtained as oils.
(6) E. F. Knights and H. C. Brown, *J. Am. Chem. Soc.*, **90**, 5280 (1968).
(7) R. K. Crossland and K. L. Servis, *J. Org. Chem.*, **35**, 3195 (1970).
(8) No evidence is presently in hand which bears on the relative configuration at C-2, though one of the epimeric alcohols appears by ^{13}C spectral analysis to be favored to an extent greater than 90%.
(9) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Vol. 1, Wiley, New York, N.Y., 1967, p 142.
(10) R. D. Clark and C. H. Heathcock, *Tetrahedron Lett.*, 2027 (1974).
(11) F. Korte, J. Falbe, and A. Zschocke, *Tetrahedron*, **6**, 201 (1959); K. J. Clark, G. I. Fray, R. H. Jaeger, and R. Robinson, *ibid.*, **6**, 217 (1959).
(12) The infrared spectra of the synthetic iridomyrmecin and isoiridomyrmecin corresponded well with published spectra.[11]

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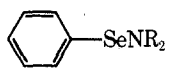
Organoselenium Chemistry. Preparation and Reactions of Benzeneselenenamides

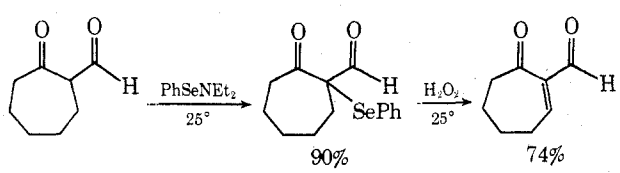
Summary: *N,N*-Dialkylbenzeneselenenamides react with β-dicarbonyl compounds to give β-dicarbonyl selenides, with acetic anhydride to give benzeneselenenyl acetate, and with some enones to give α-phenylseleno-β-dialkylamino ketones.

Sir: The chemistry of the amides of selenenic acids (selenenamides) has been little studied.[1] We have prepared several simple *N,N*-dialkylbenzeneselenenamides (**1a–c**) by reaction of secondary amines with PhSeCl, PhSeBr, or PhSeOH (generated in situ by selenoxide syn elimination) and examined their chemistry.[2] Compound **1a**[3a] is rather easily hydrolyzed and should be handled with appropriate care. The more hindered diethyl (**1b**)[3b] and diisopropyl (**1c**)[3b] derivatives are substantially more resistant to hydrolysis.

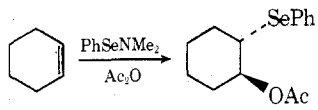


1a, R = CH_3
b, R = CH_2CH_3
c, R = $CH(CH_3)_2$

Selenenamides undergo a number of reactions similar to those of the analogous sulfenamides. For example, 2-formylcycloheptanone is selenenylated cleanly and rapidly by reaction with **1b** or **1c**.[3c,d] Careful oxidation of the selenide with hydrogen peroxide (2 equiv) then leads to β-dicarbonyl enone.[4,5a–c]

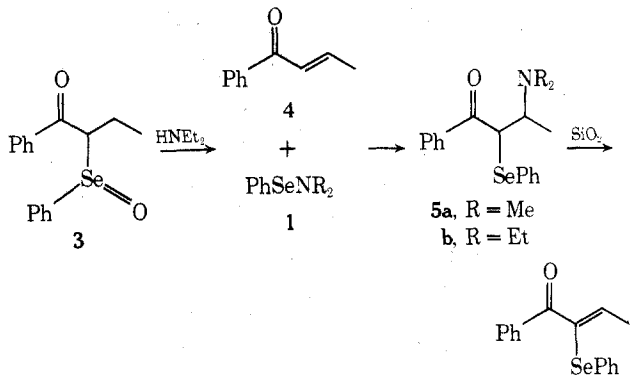


Compound **1a** reacts with acetic anhydride in the presence of cyclohexene to give the adduct **2**. Apparently benzeneselenenyl acetate ($PhSeO_2CCH_3$)[5d,6,7] is formed under these conditions.



2 (80%)

A reaction of selenenamides which appears to have no parallel in sulfur chemistry[8] is the addition to electron-deficient olefins. This reaction was discovered when **3** was warmed in the presence of diethylamine. Selenoxide syn elimination gives a mixture of enone **4** and selenenamide[9] **1b**. These compounds then react with each other slowly at 25° to give a new product identified from its spectral data as **5b**.[10] Similar results were obtained when pure **1a** or **1b** and **4** were allowed to react. Attempted purification of **5** by chromatography on silica gel resulted in elimination of dialkylamine giving **6** (88% yield using **1a**).

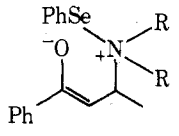


3 **1** **5a**, R = Me; **b**, R = Et

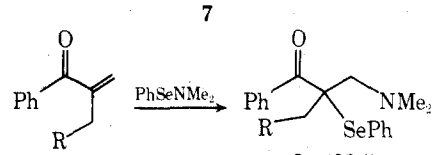
6

The formation of **5** probably occurs by a Michael addition leading to **7**, followed by an intramolecular selenenylation. Indirect evidence for a long-lived reversibly formed intermediate is provided by the observation that the cis isomer of **4** is isomerized to **4** in the presence of **1b**.[11]

The addition of selenenamides to α,β-unsaturated carbonyl compounds is successful only with some of the more reactive Michael acceptors,[12] and **1a** is significantly more reactive than **1b** or **1c**. Benzene and chloroform are the preferred solvents for the addition. Addition of **1a** in chloroform to compound **8a** is complete in 18 hr, **8b** requires 3 days, while 2-ethyl-1-phenyl-2-buten-1-one is incomplete after several weeks.



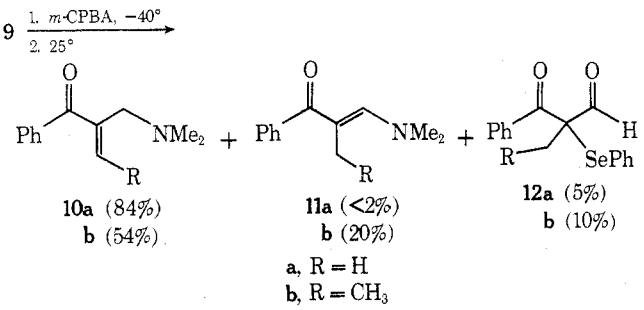
7



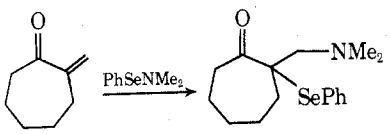
8a, R = H
b, R = CH_3

9a (93%)
b (94%)

Of several possible transformations of the adducts **9** we have examined oxidation and subsequent selenoxide elimination. Oxidation of **9a** with *m*-chloroperbenzoic acid at −40° followed by warming to room temperature leads to **10a** in good yield. Only trace amounts of the products **11a** and **12a** resulting from elimination toward the dimethylamino group are formed. The additional substituent in **9b** almost equalizes the ratio of elimination directions. The product **12b** is apparently formed by reaction of **11b** with an active selenenylating reagent (PhSeOH or a dispropor-



tionation product of it)[5b,13] produced in the course of the selenoxide elimination. Quite similar results are found for **13** where products analogous to **10**, **11**, and **12** are formed in 48, 6, and 22% yields, respectively.



Pronounced control of selenoxide eliminations away from hydroxy-, alkoxy-, and acetoxy-substituted carbons has been previously reported.[5e,6,7,14] The dimethylamino group, at least in these carbonyl substituted systems, appears to exert a much less pronounced control of the elimination. In fact, a methyl substituent apparently retards elimination toward a carbon almost as effectively as dimethylamino (compare **9a** and **9b**).

Preliminary attempts to add *N,N*-dimethylbenzenesulfenamide to enones have not been successful.

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References and Notes

(1) (a) H. Rheinboldt in "Houben Weyl. Methoden der Organischen Chemie, Schwefel-, Selen-, Tellurverbindungen", Vol. IX, 1955, p 1178; (b) D. L. Klayman and W. H. H. Gunther, Ed., "Organic Selenium Compounds: Their Chemistry and Biology", Wiley, New York, N.Y., 1973, p 108; (c) Von O. J. Scherer and J. Wokulat, *Z. Anorg. Allg. Chem.*, **357**, 92 (1968).

(2) All new compounds (except **5** and the selenoxides, which were unstable) gave satisfactory elemental analyses or elemental compositions.

(3) (a) **1a** was prepared in 62% yield by addition of PhSeCl to 2 equiv of dry dimethylamine in hexane at 0°, filtration, and distillation: pale yellow liquid; bp 39–40° (0.1 mm); ^{1}H NMR δ (CCl_4) 2.81 (s, 6 H), 7.28 (m, 3 H), 7.56 (m, 2 H); ^{13}C NMR δ^{TMS} ($CDCl_3$) 51.0 (*N*-CH_3), 128.9 (C-1), 134.5 (C-2), 128.5 (C-3), 128.2 (C-4) (J_{C_2Se} = 9.7 Hz). (b) **1b** and **1c** were prepared as above (59% yield of **1b** and 24% yield of **1c**) except that reaction was performed at 50°. (c) 2-Carbomethoxybutyrophenone (92%), 2-formylbutyrophenone (80%), and 2-acetylcyclohexanone (92%) have similarly been converted to selenides. Use of **1a** results in cleavage (reverse Claisen) of some selenides. (d) Sulfenamides also react with β-dicarbonyl compounds: T. Mukaiyama, S. Kobayashi, and T. Kumamoto, *Tetrahedron Lett.*, 5115 (1970).

(4) The crude enone was a 56:44 mixture of keto to enol forms; almost complete enolization occurred during distillation. In less readily enolized systems, this method usually gives only traces of the enol form.[5b,c]

(5) (a) H. J. Reich, I. L. Reich, and J. M. Renga, *J. Am. Chem. Soc.*, **95**, 5813 (1973); (b) H. J. Reich, J. M. Renga, and I. L. Reich, *ibid.*, **97**, 5434 (1975); (c) H. J. Reich, J. M. Renga, and I. L. Reich, *J. Org. Chem.*, **39**, 2133 (1974); (d) H. J. Reich, ibid., **39**, 428 (1974); (e) H. J. Reich and S. K. Shah, *J. Am. Chem. Soc.*, **97**, 3250 (1975).

(6) K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **39**, 429 (1974).

(7) D. L. J. Clive, *Chem. Commun.*, 100 (1974).

(8) N. E. Heimer and L. Field [*J. Org. Chem.*, **35**, 3012 (1970)] have studied the reaction of *N*-ethylthiopiperidine with N-substituted maleimides and ethyl acrylate. They obtained the amine adducts.

(9) The selenenamides (**1b** and **1c**) survive aqueous work-up under mildly basic conditions.

(10) **5b**: NMR δ ($CDCl_3$) 0.72 (t, $J \simeq 7$ Hz, 3H), 1.24 (d, $J \simeq 6.5$ Hz, 3 H), 2.38 (m, 2 H), 3.56 (dq, $J \simeq 11$,6.5 Hz, 1 H), 4.46 (d, $J \simeq 11$ Hz, 1 H, 7.0–7.7 (m, 8 H), 7.80 (m, 2 H); ir ($CDCl_3$) 1672, 1599, 1581 cm^{-1}. A second stereoisomer was formed in 4–5% yield.

(11) Support for a mechanism involving intramolecular selenenylation is provided by the observation of cis addition to dimethyl acetylenedicarboxylate (H. J. Reich, J. M. Renga, and J. E. Trend, unpublished results).

(12) Methyl acrylate, phenylacetylene, cyclohexene, and ethyl 2-phenylcrotonate did not react with **1a**. Cyclohexenone, cyclopentenone, 2-*p*-tolylidenecyclohexanone, and *N*-methylmaleimide react with **1a** to give mixtures of products.

(13) Thermolysis of **3** in the presence of **11b** results in partial conversion (~66%) to **12b**.

(14) K. B. Sharpless and R. F. Lauer, *J. Am. Chem. Soc.*, **95**, 2697 (1973).

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