

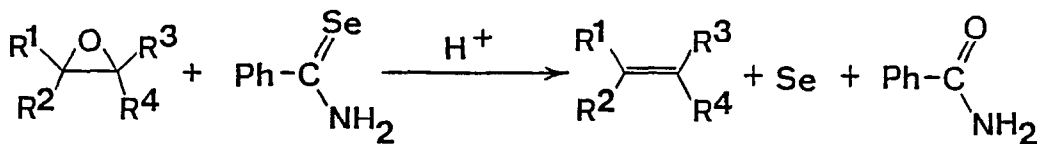
SELENOCARBOXAMIDES AS NEW REAGENTS FOR STEREOSPECIFIC
DEOXYGENATION OF EPOXIDES UNDER MILD CONDITIONS

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Summary: Selenocarboxamides have been found to be efficient reagents for converting epoxides into olefins stereospecifically in high yields under mild conditions.

Deoxygenation of epoxides is one of the important methodologies for control of olefin stereochemistry¹ and for synthesis² and structural analysis³ of natural products. For this purpose, high yields, mild conditions, and high stereospecificity are essential. A variety of methods⁴ have been devised to accomplish the transformation, and in some cases, the deoxygenation was found to proceed stereospecifically: for example, inversion with Me₃SiK,^{1g} Me₂PhSiLi,^{1f} Ph₂PLi,^{1h} and Co₂(CO)₈,^{1c} and retention with KSeCN,^{1m} 3-methyl-2-selenoxobenzothiazole,^{1l} Me(PhO)₃PI,¹ⁱ Ph₃P·HI/Ph₃PI₂,^{1j} and WCl₆/n-BuLi.^{1a,1b}

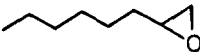

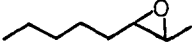

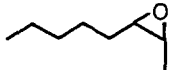
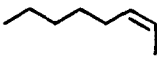
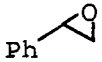







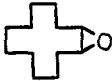

We have found that arylselenocarboxamides easily undergo deoxygenation of epoxides with high stereospecificity in the presence of catalytic amounts of a strong acid:



The present method offers several advantages: (i) high yields under mild conditions; (ii) facile olefin synthesis with simple operations; (iii) the reagents, selenoamides, can be prepared easily by the reaction of nitriles with elemental selenium, carbon monoxide, and water⁵; (iv) high stereospecificity; (v) versatile applicability to synthesis of mono-, di-, and trisubstituted olefins.

Representative results are shown in Table 1. 1- And 2-octene oxides, cyclohexene oxide, and 1-methylcyclohexene oxide underwent smooth deoxygenation at 0°C. Cyclopentene oxide and cyclododecene oxide were sluggish under the same conditions. But slightly higher temperatures and longer reaction times enabled these reactions to complete successfully. On the other hand sterically hindered epoxides such as norbornene oxide did not give any olefinic products. Reaction of cis- and trans-2-octene oxides and trans-dodecene oxide afforded olefins having the same geometry as the epoxides. All reactions in Table 1 were accompanied by the concomitant formation of metallic selenium and benzamide.

Table 1. Deoxygenation of Epoxides with Benzeneselenoamide^a

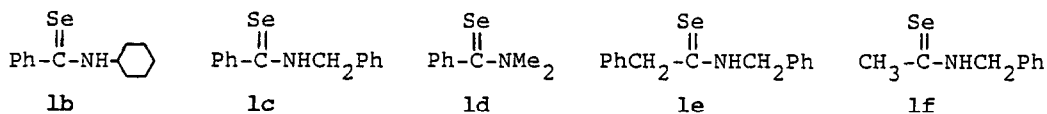
entry	epoxide	temp, °C	time	product	yield, % ^b
1		0	5 min		89
2		0	10 min		74 ^c
3		0	10 min		75 ^c
4		0	30 min		54
5		20	30 h		85
6		0	5 min		84
7		0	5 min		51
8		40	21 h		82 ^c

^aAll reactions were carried out in the similar manner to that described in the text. ^bDetermined by GLC. ^cSingle isomer was formed stereospecifically.

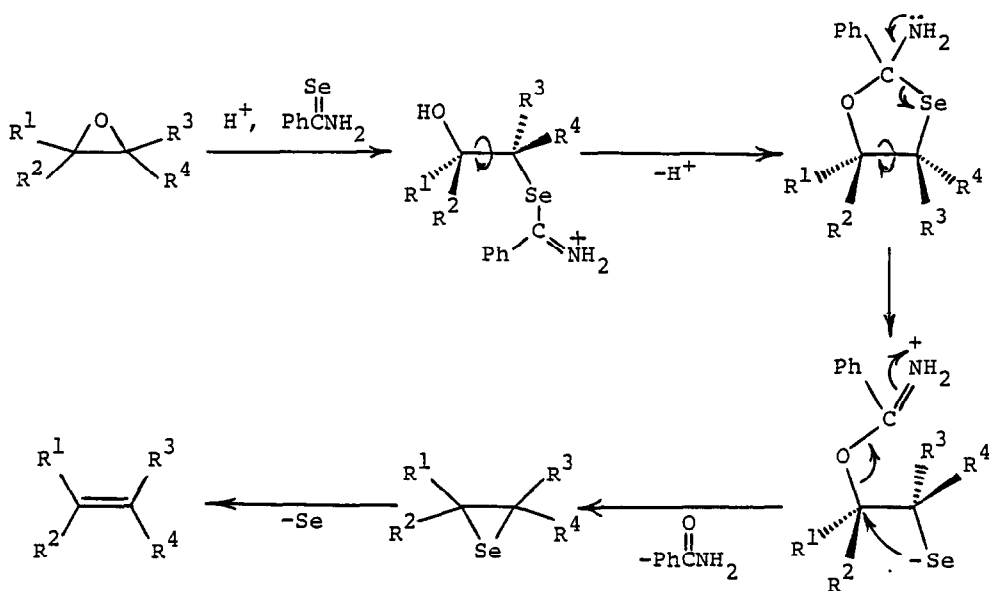
A typical procedure is as follows: to the stirred mixture of cyclohexene oxide (0.098 g, 1 mmol) and benzeneselenocarboxamide (1a) (0.276g, 1.5 mmol) in 7 mL of dry dichloromethane under nitrogen at 0°C was added dropwise trifluoroacetic acid (0.11 g, 1 mmol). Elemental selenium precipitated almost instantly. After stirring for 5 minutes, GLC analysis indicated the formation of cyclohexene in 84 % yield.

Deoxygenation using 0.03 equivalent of trifluoroacetic acid relative to cyclohexene oxide also proceeded at 25°C for 24 h to give the corresponding olefin in 87 % yield.

Some other selenoamides (1b-1f) were examined and found to be effective for the deoxygenation. For example, cyclohexene oxide was converted into cyclohexene in ca. 80 % yield in every case.



A suggested reaction path⁶ for the present deoxygenation of acyclic epoxides is illustrated in the following scheme from an analogy of the deoxygenation using KSeCN .^{1m}

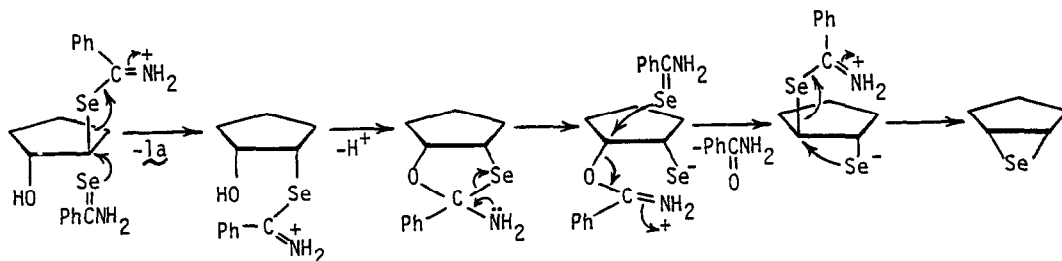


Scheme 1. A plausible reaction path.

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References and notes

- (1) (a) K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, *J. Am. Chem. Soc.*, **94**, 6538 (1972). (b) M. A. Umbreit and K. B. Sharpless, *Org. Syn.*, **60**, 29 (1981). (c) P. Dowd and K. Kang, *J. C. S., Chem. Commun.*, 384 (1974). (d) P. F. Hudrlik, D. Peterson, and R. J. Rona, *J. Org. Chem.*, **40**, 2263 (1975). (e) M. Rosenblum, M. R. Saidi, and M. Madhavarao, *Tetrahedron Lett.*, 4009 (1975). (f) M. T. Reetz and M. Plackky, *Synthesis*, 199 (1976). (g) P. B. Dervan and M. A. Shippey, *J. Am. Chem. Soc.*, **98**, 1265 (1976). (h) E. Vedejs and P. L. Fuchs, *J. Am. Chem. Soc.*, **95**, 822 (1973). (i) K. Yamada, S. Goto, H. Nagase, Y. Kyotani, and Y. Hirata, *J. Org. Chem.*, **43**, 2076 (1978). (j) P. E. Sonnet, *Synthesis*, 828 (1980). (k) D. L. J. Clive and C. V. Denyer, *J. C. S., Chem. Commun.*, 253 (1973). (l) V. Calo, L. Lopez, A. Mincuzzi, and G. Pesce, *Synthesis*, 200 (1976). (m) J. M. Behan, R. A. W. Johnstone, and M. J. Wright, *J. C. S., Perkin Trans I*, 1216 (1975). (n) H. Suzuki, T. Fuchita, A. Iwasa, and T. Mishina, *Synthesis*, 905 (1978).
- (2) (a) K. B. Sharpless, *J. C. S., Chem. Commun.*, 1450 (1970). (b) D. R. James, R. W. Rees, and C. W. Shoppee, *J. Chem. Soc.*, 1370 (1955). (c) T. van Es, *Carbohydrate Res.*, **5**, 282 (1967). (d) A. Guzman, P. Ortiz de Montellano, and P. Crabbe, *J. C. S., Perkin Trans I*, 91 (1973). (e) S. M. Kupchan and M. Maruyama, *J. Org. Chem.*, **36**, 1187 (1973). (f) M. P. Cook, Jr., *Tetrahedron Lett.*, 1983 (1973).
- (3) For example, C. W. Shoppee, S. Sternhell, and W. C. Taylor, *Aust. J. Chem.*, **19**, 1265 (1966).
- (4) For a list of methods, see: (a) I. T. Harrison and S. Harrison, "Compendium of Organic Synthetic Methods", Wiley Interscience, New York, pp 501-504 (1971). (b) Idem, *ibid.*, Vol. 2, pp 200-201 (1974). (c) L. S. Hegedus and L. Wade, *ibid.*, Vol. 3, pp 317-319 (1977). (d) L. G. Wade, Jr., *ibid.*, Vol. 4, pp 324-327 (1980). (e) Idem, *ibid.*, Vol. 5, pp 380-382 (1983).
- (5) A. Ogawa, J. Miyake, Y. Karasaki, S. Murai, and N. Sonoda, *J. Org. Chem.*, **50**, xxxx (1985).
- (6) In the case of cyclic epoxides, absence of C-C free rotation indicates that the mechanism of Scheme 1 is unlikely. The deoxygenation of cyclic epoxides may be explained by the following scheme:



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