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OXIDATION OF SELENIDES TO SELENOXIDES USING 2-SULFONYLOXAZIRIDINES

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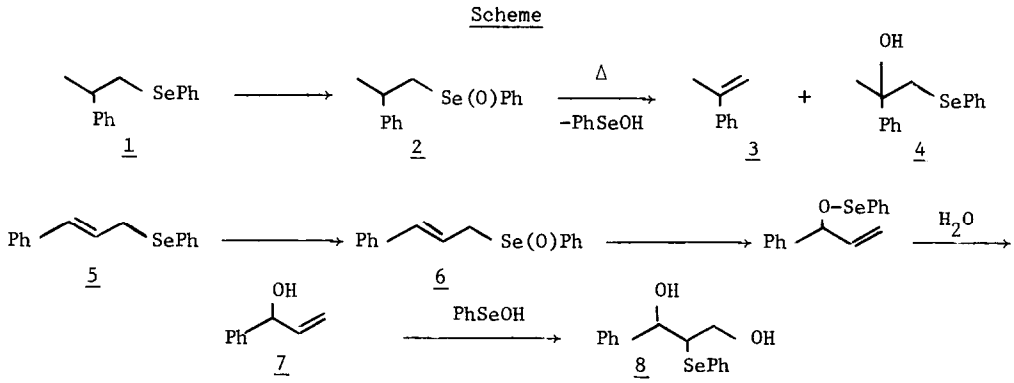
Abstract: Application of 2-sulfonyloxaziridine, 9, for the "one pot" transformation of selenides to alkenes and the rearrangement of allylic selenides to allylic alcohols are described.

The synthetic utility of selenoxides in the preparation of complex organic molecules is well documented.[1] Most important of these transformations are the syn-elimination of selenoxides to provide alkenes (2 to 3) and the rearrangement of allylic selenoxides to allylic alcohols (6 to 7) illustrated in the Scheme.

Scheme

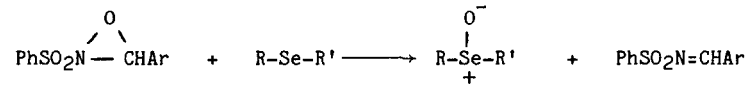


Although many oxidizing reagents can be used to oxidize selenides to selenoxides (1 to 2 and 5 to 6) nearly all have some disadvantages because of side reactions (Scheme).[1] These side reactions, discussed by Reich[2] and by Sharpless[3], include inhibition of selenoxide syn-elimination by protic oxidizing agents and those that require protic media, and the catalytic destruction of oxidizing reagents such as H_2O_2 by selenoxides. The most serious of these side reactions, however, results from addition of the by-product, benzeneselenenic acid (PhSeOH), to the alkene affording β-hydroxy selenides, 4 and 8. Excess oxidant is generally used to control this reaction, but over-oxidation (epoxidation, Baeyer-Villiger oxidations, etc.) of sensitive functionalities in the substrate is problematical. Addition of alkyl amines, after the oxidation, but before elimination[2] and the use

of tert-butyl hydroperoxide (TBHP)[3] have in certain cases been used to circumvent this problem.

2-Sulfonyl oxaziridines, 9, are a new class of aprotic and neutral oxidizing reagents of considerable synthetic and mechanistic versatility.[4] These reagents selectively oxidize sulfides to sulfoxides[5], epoxidize alkenes slowly at 60 °C[6] and are approximately four orders of magnitude more reactive than TBHP.[7]

Addition of 2-benzenesulfonyl-3-(p-nitrophenyl)oxaziridine (9)[4] to methyl phenyl selenide in chloroform at 25 °C quantitatively gives methyl phenyl selenoxide (PhSe(O)Me) in less than a minute as indicated by PMR. None of the selenone ($PhSeO_2Me$) could be detected even in the presence of excess 9. The fact that 9 is also stable in the presence of the selenoxide means that only stoichiometric quantities of 9 need be used for the oxidation of selenides to selenoxides. An additional advantage of using 9 is the fact that the sulfonimine, 10, precipitates from $CHCl_3$ in 70-80 percent yield.[8] Methyl phenyl selenoxide was isolated in 97 percent yield by preparative TLC on silica gel (Table).



9 10

Ar= p-nitrophenyl

These properties and the fact that 9 is stable in the presence of pyridine suggested that these reagents would be useful oxidants for the "one pot" transformations outlined in the Scheme.

Selenoxide Syn-Elimination

One equivalent of solid 9 (typically 1.0 mmol) was added portionwise to phenyl 2-phenylpropyl selenide (1)[2] in 1.5 mL of $CHCl_3$. The reaction was immediate, and after a few minutes sulfonimine, 10, precipitated from solution and was collected by filtration (>70 %). After heating the reaction mixture at 60 °C for 1 h a 1:1 mixture of α-methylstyrene (3) and 2-phenyl-1-phenylseleno-2-propanol (4)[2] was obtained as indicated by PMR (Table, entry 3).

Addition of 5 equivalents of pyridine to the reaction mixture prior to addition of 9 resulted in a 96:4 ratio of 3:4 after 18 h (Table, entry 5). When the reaction was carried out at 60 °C in the presence of 5 and 10 equivalents of pyridine 80:20 and 84:16 ratios of 3:4 were obtained, respectively (Table, entries 6 and 7). The alkene, 3, was isolated in greater than 85 percent yield, after removal of solvent, by selective solubilization into n-pentane. Compound 4 was isolated by prep. TLC, silica gel G (Table, entries 3-6).

Selenoxide Allylic Rearrangement

To phenyl cinnamyl selenide (5)[9], in 1.5 mL of THF cooled to -5 to -8 °C in an ice-methanol bath was added one equivalent of 9 (typically 1 mmol). After stirring for 5 min., 1.0 mL of water or 1.0 mL of water and 0.5 mL of pyridine were added and the reaction allowed to stir for 1 to 7 h (Table, entries 7-8). The reaction mixture was diluted with 20 mL of water and extracted with ether. 1-α-Phenyl allyl alcohol (7) and 1-phenyl-2-phenylseleno-1,3-propanediol (8)[10] were isolated by prep. TLC. Note that in the absence of added pyridine, 8, the addition product of benzeneselenenic acid and 7, is

Table: Oxidation of Selenides to Selenoxides Using 2-Benzenesulfonyl-3-(p-nitrophenyl)oxaziridine (9)

entry	Selenide	Temp. °C	Conditions	Products[a] (% NMR Yield)[% Isolated Yield]
1	PhSeMe	0-5	$CHCl_3$	PhSe(O)Me, (100), [97]
2		0-5	$CHCl_3$ 8 h	PhSe(O)Me (100)
3	1	60	1 h	3(50)[43], 4(50)[39]
4		60	$CHCl_3$/1.1 eq pyridine, 1 h	3(85)[80], 4(15)[10]
5		25	$CHCl_3$/5.0 eq pyridine, 18 h	3(96)[85], 4(4)
6		60	$CHCl_3$/5.0 eq pyridine, 1 h	3(80)[76], 4(20)[13]
7		60	$CHCl_3$/10 eq pyridine, 1 h	3(84)[76], 4(16)[10]
8	5	25	THF/H_2O, 8 h	7[25], 8[49]
9		25	THF/H_2O, pyridine, 1 h	7[88]

a) Products were identified by comparison with authentic samples. b) Two equivalents of 9 used.

he principal product (Table, entry 8).

In summary, these studies demonstrate the application of 2-sulfonyloxaziridines, 9, as oxidizing reagents for the syn-elimination of selenoxides to alkenes and the rearrangement of allylic selenoxides to allylic alcohols (Scheme). When a highly selective oxidizing reagent is required for the oxidation of selenides to selenoxides in the synthesis of complex, polyfunctionalized molecules, 2-sulfonyloxaziridines are indicated.

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1. For discussions of synthetic organoselenium chemistry see:
   a. Reich, H. J., in "Oxidation in Organic Chemistry, Part C", Trahanovsky, W., Ed., Academic Press, New York, 1978, p 1.

   b. Clive, D. K. J., Tetrahedron, 1978, 34, 1049.

2. Reich, H. J., Wollowita, S., Trend, J. E., Chow, F., Wendelborn, D. F., J. Org. Chem., 1978, 43, 1697.

3. Hori, T., Sharpless, K. B., ibid., 1978, 43, 1689

4. Davis, F. A., Stringer, O. D., ibid., 1982, 47, 1774.

5. Davis, F. A., Jenkins, R. H., Jr., Yocklovich, S. G., Tetrahedron Lett., 1978, 5171.

6. Davis, F. A., Abdul-Malik, N. F., Awad, S. B., Harakal, M. E., ibid., 1981, 917

7. Unpublished results of Joanne M. Billmers from our laboratories.

8. In the absence of solvent selenoxides slowly react with sulfonimines to give selenium imides ($PhSO_2N{=}Se(Me)Ph$) and will be described in detail elsewhere.

9. Gunther, W. H. H., Mautner, H. G., J. Med. Chem., 1962, 7, 229.

10. Compound 8 was prepared independently, in greater than 60% yield, from phenyl allyl alcohol, diphenyl diselenide, phenylseleninic acid and water.[3] This diol had the following properties: mp 92-94 °C (cyclohexane-benzene); NMR ($CDCl_3$)δ 2.5 (s, 1H, OH, exchanges with D_2O), 3.2 (s, 1 H, OH, exchanges with D_2O), 3.3-3.6 (m, 1H, Se-CH, J=3Hz), 3.72 (d, 2H, CH_2OH, J=4Hz), 4.95 (d, 1H, benzylic CH, J=4Hz) and 7.1-7.6 (quintet, 10H); IR (KBr) 3100-3500 cm^{-1} OH stretching; Mass spectrum (E.I): 308 (M^+). Anal. Calcd. for $C_{15}H_{16}O_2Se$: C, 58.44; H, 5.19. Found: C, 58.38; H, 5.02.

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