

Oxidation of 1,2-Bis(phenylseleno)-1-alkenes. A Novel Example of Selenoxide *anti*-Elimination

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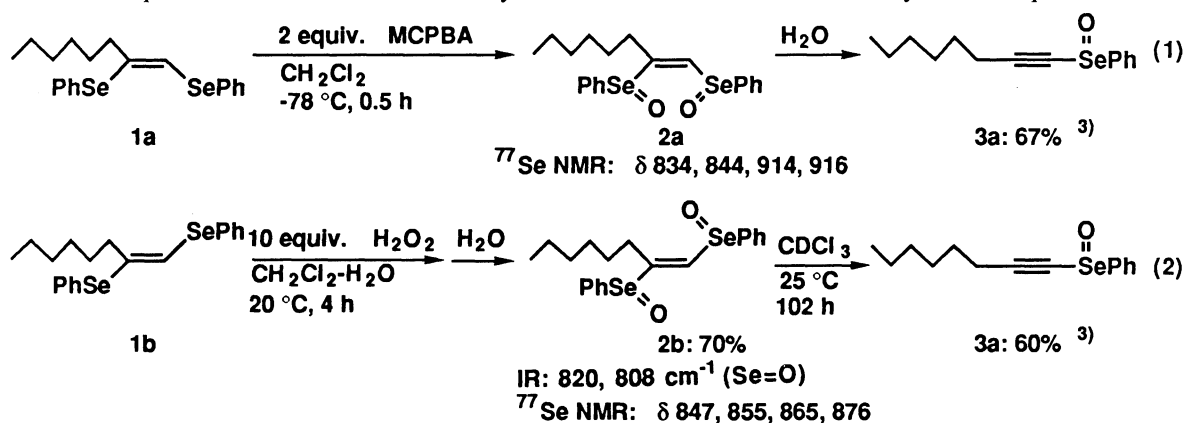
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The oxidation of 1,2-bis(phenylseleno)-1-alkenes and the reactivity of thus formed selenoxides have been investigated. When (Z)-1,2-bis(phenylseleno)-1-octene was oxidized with two equivalents of MCPBA, a novel selenoxide *anti*-elimination has been found to take place at or below room temperature.

The selenoxide *syn*-elimination is widely accepted as one of the most expedient methods for olefin formation from a saturated substrate.¹⁾ The elimination is believed to take place *via* a cyclic transition state, where all five participating centers are located on the same plane, and so is highly stereoselective (*syn*). During the course of our studies on the synthesis and reactions of 1,2-bis(phenylseleno)-1-alkenes,²⁾ we have found a novel example of selenoxide *anti*-elimination on oxidation of (Z)-1,2-bis(phenylseleno)-1-alkenes. In this paper, we wish to report a preliminary result of the oxidation of some 1,2-bis(phenylseleno)-1-alkenes.

The oxidation of (Z)-1,2-bis(phenylseleno)-1-octene (**1a**, 1 mmol) was carried out by using two equivalents of *m*-chloroperbenzoic acid in CH₂Cl₂ at -78 °C for 0.5 h. The measurement of ⁷⁷Se NMR at this stage indicated the formation of corresponding selenoxide (**2a**) as a mixture of diastereomers. It is well-known that vinylic selenoxides are stable enough to be isolated in pure form.^{1a)} So the isolation of **2a** by aqueous workup was examined at room temperature. However, the desired selenoxide **2a** was not obtained, and instead acetylenic selenoxide **3a** was formed. This means that the elimination of selenenic acid took place at or below room temperature, and more interestingly, *anti*-nature of the elimination was observed (Eq. 1).

Next, the oxidation of (E)-1,2-bis(phenylseleno)-1-octene (**1b**) was attempted (Eq. 2). The E-isomer was much more subject to oxidation than the Z-isomer: the oxidation of **1b** with excess 30% H₂O₂ (10 equiv.) at 20 °C for 4 h provided selenoxide **2b** in 70% yield, whereas the oxidation of **1a** by the same procedure



resulted in the recovery of 75% of **1a**. Selenoxide **2b** is isolable, but was gradually converted into acetylenic selenoxide **3a** at room temperature *via* selenoxide *syn*-elimination.⁴⁾

Although the precise mechanism of the *anti*-elimination observed in the oxidation of (*Z*)-1,2-bis(phenylseleno)-1-alkenes requires further investigations, the participation by the neighboring seleninyl group may conceivably cause this novel selenoxide *anti*-elimination (Fig. 1). Interestingly, the elimination of PhSeOH from the *Z*-isomer **2a** is much faster than that from the *E*-isomer **2b** (the elimination from **2a** took place even below 0 °C).

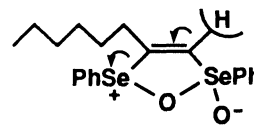
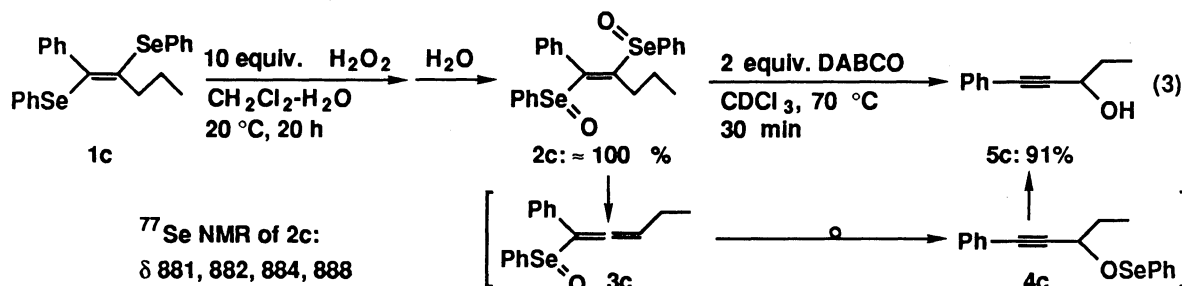


Fig. 1.

Finally, the oxidation of inner 1,2-bis(phenylseleno)-1-alkenes like **1c** was examined. When **1c** was oxidized by H₂O₂ (30%, 10 equiv.) at 20 °C, the corresponding selenoxide **2c** was isolated in almost quantitative yield after aqueous workup. Selenoxide elimination of **2c** in the presence of DABCO (2 equiv.)⁵⁾ at 70 °C led to the formation of propargylic alcohol **5c** in 91% yield (Eq. 3). The formation of **5c** can be explained by the mechanism that involves *syn*-elimination of PhSeOH from **2c** to give allenic selenoxide **3c**, followed by [2,3]-sigmatropic rearrangement.⁶⁾ Since such bis(phenylseleno)alkenes as **1c** can be easily synthesized by the addition of (PhSe)₂ to acetylenes,^{2,7)} the overall reaction path constitutes a useful method for propargylic oxidation of acetylenes.



Further extensions of this studies and elucidation of precise mechanism are underway.

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References

- 1) For reviews, see: a) H. J. Reich, "Oxidation in Organic Chemistry. Part C," ed by W. Trahanovsky, Academic Press, New York (1978) Chap. 1; b) C. Paulmier, "Selenium Reagents and Intermediates in Organic Synthesis," Pergamon Press, Oxford (1986), Chap. 5; c) T. G. Back, "The Chemistry of Organic Selenium and Tellurium Compounds," ed by S. Patai, John Wiley & Sons, New York (1987), Vol.2, Chap.3.
- 2) A. Ogawa, H. Yokoyama, K. Yokoyama, T. Masawaki, N. Kambe, and N. Sonoda, *J. Org.Chem.*, in press; H. Kuniyasu, A. Ogawa, S. Miyazaki, I. Ryu, N. Kambe, and N. Sonoda, *J. Am. Chem. Soc.*, in press.
- 3) The yield of **3a** was determined by converting into the acetylenic selenide (*n*-C₆H₁₃C≡CSePh).
- 4) For the *syn*-elimination of β-(phenylsulfonyl)vinyl selenoxides, see: T. G. Back, S. Collins, and R. G. Kerr, *J. Org. Chem.*, **48**, 3077 (1983); T. Miura and M. Kobayashi, *J. Chem. Soc., Chem. Commun.*, **1982**, 438.
- 5) Reich et al. reported that heating (95 °C) in the presence of base such as DABCO caused *syn*-elimination of vinylic selenoxides, see: H. J. Reich and W. W. Willis, Jr., *J. Am.Chem. Soc.*, **102**, 5967 (1980).
- 6) H. J. Reich, S. K. Shah, P. M. Gold, and R. E. Olson, *J. Am. Chem. Soc.*, **103**, 3112 (1981).
- 7) T. G. Back and M. V. Krishna, *J. Org. Chem.*, **53**, 2533 (1988).

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