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

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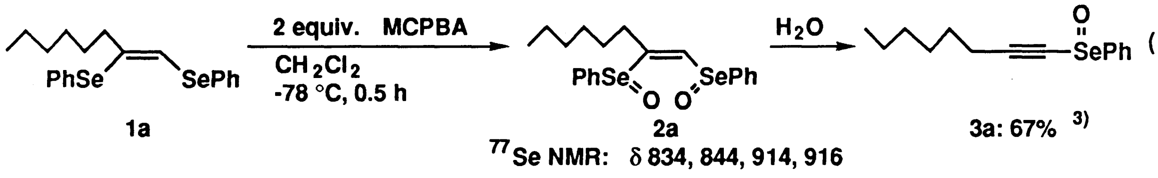
The oxidation of 1,2-bis(phenylseleno)-1-alkenes and the reactivity of thus formed selenoxides have been investigated. When (Z)-1,2-bis(phenylseleno)-1-octene was oxidized with two equivalents of MCPBA, a novel selenoxide *anti*-elimination has been found to take place at or below room temperature.

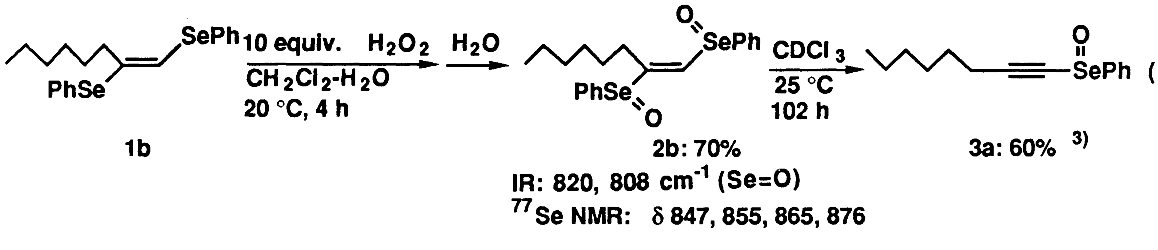
The selenoxide *syn*-elimination is widely accepted as one of the most expedient methods for olefin-formation from a saturated substrate.[1)] The elimination is believed to take place *via* a cyclic transition state, where all five participating centers are located on the same plane, and so is highly 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 CH_2Cl_2 at -78 °C for 0.5 h. The measurement of ^{77}Se 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% H_2O_2 (10 equiv.) at 20 °C for 4 h provided selenoxide **2b** in 70% yield, whereas the oxidation of **1a** by the same procedure



(1)



(2)

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).

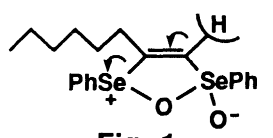
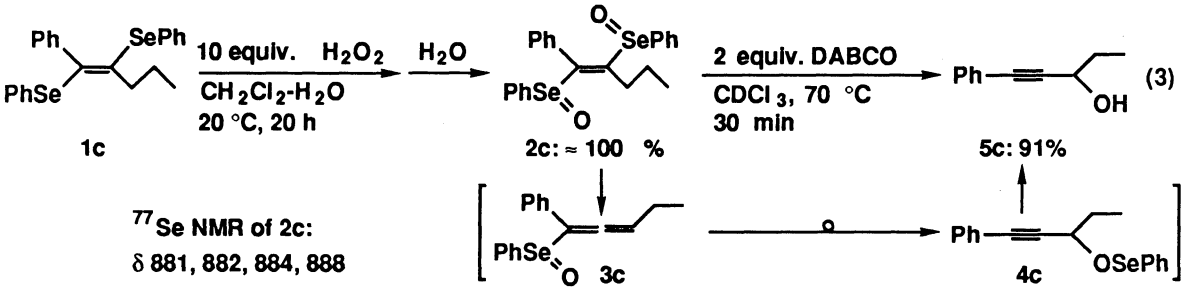


Fig. 1.

Finally, the oxidation of inner 1,2-bis(phenylseleno)-1-alkenes like **1c** was examined. When **1c** was oxidized by H_2O_2 (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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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-$C_6H_{13}C{\equiv}CSePh$).

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