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Organoselenium-mediated Reduction of α,β-Epoxy Esters to β-Hydroxy Esters

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α,β-Epoxy esters were reduced to β-hydroxy esters with an organoselenium reagent, $Na^+[PhSeB(OEt)_3]^-$, via α-substitution process.

β-Hydroxy esters are useful synthetic intermediates and frequently utilized as construction units in important class of natural products. Potential precursors for these compounds may be α,β-epoxy esters (glycidic esters) since a variety of glycidic esters are readily available by the Darzens reaction[1] or epoxidation of α,β-unsaturated esters (acids).[2] Although a number of efficient methods have been developed for the regioselective reduction of α,β-epoxy ketones to β-hydroxy ketones,[3] only few precedents for the reductive cleavage of α,β-epoxy esters to give β-hydroxy esters are known in literature.[4] Recently SmI_2 has been employed as an effective reagent for this particular transformation.[5]

We have recently reported that an organoselenium reagent, sodium phenylseleno(triethoxy)borate **1**, which is easily prepared by reducing $(PhSe)_2$ with $NaBH_4$ in ethanol[6] (Eq. 1), serves as an efficient reagent for the reduction of α,β-epoxy ketones to β-hydroxy ketones.[3] In this communication we describe the use of this selenium reagent **1** in the reduction of α,β-epoxy esters.

$$(PhSe)_2 + 2\ NaBH_4 + 6\ EtOH \longrightarrow 2\ \underset{\mathbf{1}}{Na^+[PhSeB(OEt)_3]^-} + 7\ H_2 \qquad (1)$$

The results are listed in Table 1. As in the reduction of epoxy ketones,[3] brief treatment of diethyl cis- or trans-epoxy succinate with the reagent **1** (3 equiv.) in ethanol produced the desired hydroxy succinate in high yield (entries 1 and 2). Similarly, epoxy ester **2** was reduced at 50 °C to give β-hydroxy ester **3** as the sole product in 91% yield (entry 3). Thus a variety of α-unsubstituted epoxy esters were efficiently and regioselectively reduced to β-hydroxy esters (entries 1-5). On the other hand, substrates bearing an α-alkyl substituent reacted sluggishly to give a mixture of β-hydroxy esters and a β-phenylseleno substitution product (entry 6), and an α-alkyl-β-unsubstituted epoxy ester produced only a β-substitution product (entry 7).

Since the present reduction proceeds via α-substitution process (Eq. 2) in contrast with the reductive cleavage by electron transfer reagents,[5] the intermediate β-hydroxy-α-phenylseleno esters **5** are also obtainable in high yields by using 1 equiv. of the reagent **1**.[7] These compounds as well as β-hydroxy esters will serve as useful synthetic intermediates.

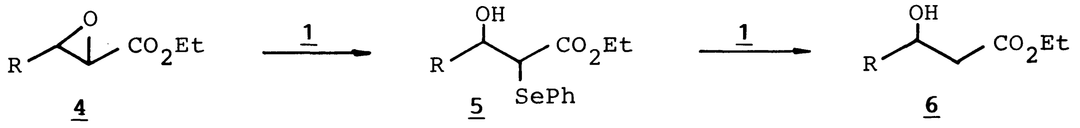
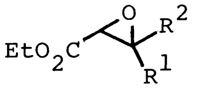
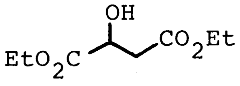
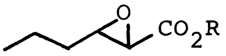
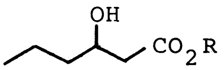
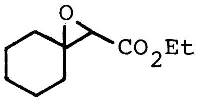
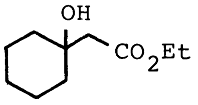
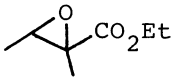
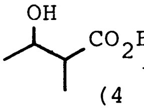
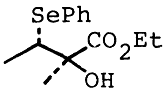
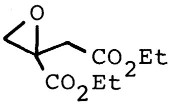
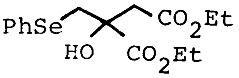

(2)

Table 1. Reduction of α,β-Epoxy Esters with $Na^+[PhSeB(OEt)_3]^-$ [a)]

Entry	Substrate	Temp/°C	Time/min	Product(s)	Yield/%
1	 $R^1 = CO_2Et$, $R^2 = H$	0	10		86
2	$R^1 = H$, $R^2 = CO_2Et$	0	10		83
3	 **2** R = Et	50	20	 **3** R = Et	91
4[b)]	R = Me	50	45	R = Me	80
5		50	45		97
6		50	90	 c) +  (4 : 5)	90
7		20	35		82

a) The reaction was carried out by using 3 equiv. of the reagent **1** in EtOH.
b) The reaction was performed using 3 equiv. of $Na^+[PhSeB(OMe)_3]^-$ in MeOH.[8)]
c) A mixture of the stereoisomers (5:3).

References

1) M. S. Newman and B. J. Magerlein, Org. React., 5, 413 (1949).
2) G. B. Payne and P. H. Williams, J. Org. Chem., 24, 54 (1959).
3) M. Miyashita, T. Suzuki, and A. Yoshikoshi, Tetrahedron Lett., 28, 4293 (1987) and references cited therein.
4) For the reductive cleavage of α,β-epoxy ester, only NaTeH and alkali metal have been reported as reagents : A. Osuka, K. Taka-oka, and H. Suzuki, Chem. Lett., 1984, 271; E. Bartmann, Angew. Chem., Int. Ed. Engl., 25, 653 (1986).
5) K. Otsubo, J. Inanaga, and M. Yamaguchi, Tetrahedron Lett., 28, 4437 (1987).
6) Very recently the structure of the selenium reagent **1** has been established by us: Tetrahedron Letters, in press.
7) Treatment of **2** with 1 equiv. of the reagent **1** resulted in the exclusive formation of β-hydroxy-α-phenylseleno ester **5** (R = C_3H_7), which was readily transformed into β-hydroxy ester **3** by further treatment with the reagent **1**.
8) This reagent was prepared in methanol according to Eq. 1.

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