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CHEMOSELECTIVE REDUCTION OF AN α,β-EPOXY KETONE MOIETY COEXISTING WITH AN ENONE FUNCTION

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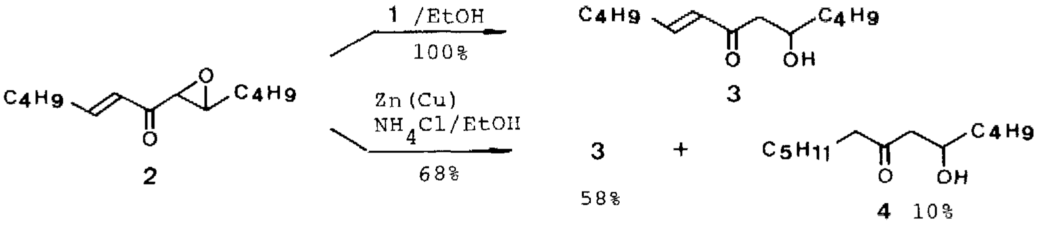
Summary: The chemoselective reduction of an α,β-epoxy ketone moiety coexisting with an enone function has been efficiently achieved with an organoselenium reagent $Na^+[PhSeB(OEt)_3]^-$.

We have recently reported an efficient method for the reduction of α,β-epoxy ketones[1] and α,β-epoxy esters[2] to the corresponding β-hydroxy carbonyl compounds using an organoselenium reagent $Na^+[PhSeB(OEt)_3]^-$ (1),[3] which is readily prepared by reduction of diphenyl diselenide $(PhSe)_2$ with $NaBH_4$ in ethanol.[3,4]

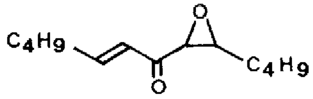
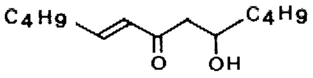
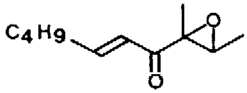
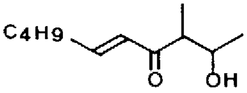
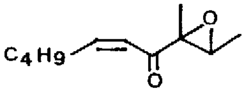
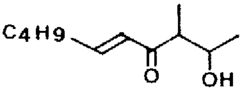
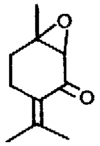
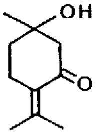
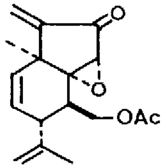
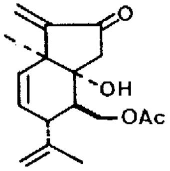
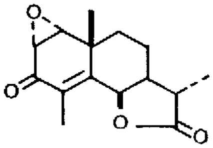
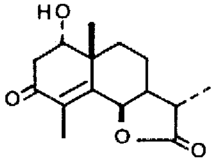
We report herein the chemoselective reduction of an α,β-epoxy ketone moiety coexisting with an enone function with the reagent **1**, which may be inaccessible with the common electron transfer reducing agents such as chromium(II) salts,[5] zinc,[6] SmI_2,[7] etc.

To probe the chemical behavior of such a system, epoxy enone **2** was treated with 3 equiv of $Na^+[PhSeB(OEt)_3]^-$ (**1**) in EtOH (room temp., 10 min) to form β-hydroxy enone **3** exclusively in quantitative yield, while reduction of **2** with Zn(Cu)/aq NH_4Cl in ethanol (80 °C, 15 min) afforded a mixture of **3** (58%) and a saturated compound **4** (10%) along with other by-products. Similarly, treatment of **5** (Table 1, entry 5) with the reagent **1** produced hydroxy enone **6** in excellent yield whereas reduction of 5 with Zn(Cu) gave **6** in poor yield (5%). These results imply that the common electron transfer reducing agents are not effective for the selective reduction of epoxy ketone function in such systems.



In order to illustrate the potential of the present method, reductions of various α,β-epoxy enones were examined and the results are listed in Table 1.[8] As seen, the regioselective reduction of an epoxy ketone moiety occurred, regardless of the stereochemistry of the epoxide, smoothly to give the corresponding β-hydroxy enones in high yields. Neither selenenylated compounds nor dehydration products were isolated. It should be noted that the double bond of an enone remained intact under the reaction conditions, although isomerization of a Z-enone to an E-congener was observed (entry 3). The present method is mild enough to use on complex systems containing polyfunctional groups.

Table 1. Reduction of Epoxy Enones with Na^{+}[PhSeB(OEt)$_3$]$^{-}$ in EtOH[a]

entry	substrate	time (min)	product(s)	yield (%)[b]
1		10		89[c]
2		25		83[d]
3		25		82[d]
4		10		97[e]
5	 **5**	10	 **6**	90[e]
6		10		81[e]

[a] Reaction was carried out with 3 equiv of the reagent **1** at room temperature.
[b] Purified by silica gel chromatography.
[c] A trace of α-hydroxy-β-phenylseleno ketone was detected.
[d] A diastereomeric mixture.
[e] Reaction was carried out in the presence of 0.2 equiv of AcOH.[1]

References and Notes

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8. A typical experiment is as follows: To a solution of **2** (53 mg, 0.25 mmol) in EtOH (1 mL) was added an ethanolic solution of Na^{+}[PhSeB(OEt)$_3$]$^{-}$ (**1**), prepared by reduction of (PhSe)$_2$ (118 mg, 0.38 mmol) with NaBH$_4$ (29 mg, 0.76 mmol) in EtOH (1 mL), under argon at room temperature. After 10 min, the reaction mixture was diluted with AcOEt (5 mL) and a stream of oxygen was bubbled through the mixture for 5 min, and then washed with half-saturated brine. Removal of the solvents left an oil which was purified by preparative TLC (AcOEt/hexane (1:6)) to give the pure product **3** (54 mg, 100%).

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