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Selenoxides as Leaving Groups: Synthesis of Epoxides

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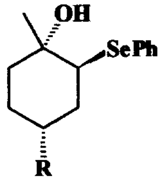
Abstract: β-Hydroxyselenoxides, prepared from substituted cyclohexenes, have been selectively transformed into chiral epoxides by treatment with alkali.

The oxidation of selenides with a variety of oxidizing agents generates the corresponding selenoxides whose overoxidation with selected reagents allows the preparation of selenones.[1] The former usually eliminate arylseleninic acid (ArSeOH) when a β-hydrogen is present, resulting in a well-known carbon-carbon double bond forming procedure.[2] Selenones undergo replacement of the phenylselenium moiety by a concerted attack of a nucleophile or through a predictable carbocationic intermediate, whose fate depends on the structure of the starting selenide.[3] We have been interested in the reactivity of β-hydroxyselenides and have described reactions of olefines with an excess of phenylselenenyl chloride in water[4] or methanol.[5] Further examination of the reactivity of β-hydroxyselenides has led to the new findings that β-hydroxyselenoxides may serve as a versatile building unit for the selective preparation of oxirane ring. This paper describes their utility as precursors of epoxycyclohexanes.

It is worth noting that the selenoxides *syn*-elimination process is usually performed in polar aprotic solvents;[1] in methanol a dramatic decrease in the olefine formation rate is observed. We discovered that in the presence of strong alkali the methanolic solution of β-hydroxyselenoxides leads to epoxides instead of allylic alcohols. Thus, treatment of 1-hydroxy-2-phenylselenyl-cyclohexane [6] with an excess of hydrogen peroxide in methanol, followed by addition of a 10% methanolic solution of KOH and gentle warming (40° C) for 2 hours, affords epoxy-cyclohexane in 74% yield.[7] Similarly, the reaction was performed using selenides **1a**,[4] **1b**,[4] **1c**[8] and **1d**[9] to test the usefulness of this procedure, and the corresponding epoxides **2a**,[10] **2b**,[4] **2c**[8] and **2d**[11] were obtained in excellent yields (85%, 90%, 73% and 81%, respectively). Under the same reaction conditions, linear β-hydroxyselenides afford allyl alcohols. Thus the tendency of the selenoxide group to behave as a leaving group in the presence of alkali, seems to be restricted to cylic compounds in which the hydroxy and the selenoxide groups achieve the *anti*-periplanar relationship. Investigations are in progress to use this unprecedented reactivity of β-hydroxyselenoxides in the stereospecific synthesis of epoxy containing pheromones.



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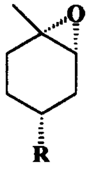

2

a R = H

b R = $(CH_3)_2CH$

c R = CH_3CO

d R = CH_3CCH_2

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