Oxidative Conversion of β-Hydroxyselenides to Epoxides and Ketones with *meta*-Chloroperbenzoic Acid

Sakae Uemura,* Kouichi Ohe, and Nobuyuki Sugita
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan

Treatment of β-hydroxy-primary-alkyl and β-hydroxy-β-phenyl-primary-alkyl phenyl selenides with 3—5 equiv. of *meta*-chloroperbenzoic acid in methanol or tetrahydrofuran gives the corresponding epoxides and phenyl migrated ketones, respectively, in high yields.

In sharp contrast to the well known selenoxide elimination leading to alkenes, treatment of alkyl phenyl selenides with an excess of *meta*-chloroperbenzoic acid (MCPBA) in alcohols results in a substitution of a PhSe moiety with an alkoxy group to afford the corresponding dialkyl ethers.[1] We now report that the application of this reaction to some β-hydroxyselenides leads to a selective and high yield formation of epoxides and ketones; treatment of some β-hydroxyalkylselenonium salts with alkali[2a] and that β-hydroxyselenides with a dichlorocarbene[2b] produces di- and tri-substituted epoxides.[2]

Treatment of 2-ethyl-2-hydroxypentadecyl phenyl selenide (**1**),† prepared by the addition of phenylselenomethyl-lithium to hexadecan-3-one in tetrahydrofuran (THF),[3] with MCPBA (5 equiv.) in methanol at 25 °C for 0.5 h afforded the oxirane (**3**) in 96% isolated yield. Prolonged reaction led to ring opening of the initially produced oxirane, affording monomethyl ethers of the corresponding diol. The use of THF as solvent was a convenient means of avoiding the formation of such ethers. Oxidation of 2-hydroxydecyl phenyl selenide (**2**), similarly prepared from nonanal, in THF (25 °C; 1 h), gave octyloxirane (**4**) in 73% isolated yield together with decan-2-one (8%). A similar procedure using 4-t-butylcyclohexanone in THF afforded the spiro compound (**5**)‡ stereospecifically in 73% yield (g.l.c.). This indicates that the addition of the phenylselenomethyl anion occurred stereoselectively to give the β-hydroxyselenide (**6**) having the OH group axial. On the other hand, from the selenides (**7**) and (**8**), prepared from benzophenone and acetophenone, the corresponding epoxide was not formed and instead the ketones (**9**) and (**10**) were produced in 50 and 60% overall isolated yields from the starting ketones, respectively. The reactions seem to proceed as shown in Scheme 1; intramolecular hydroxy participation (path a) or phenyl migration (path b) occurs in the selenone–MCPBA adduct intermediate (A).[1]

When the reaction was applied to the benzene-ring fused cyclic ketones indan-1-one (n = 2), 1-tetralone (n = 3), and benzosuber-1-one (n = 4) (Scheme 2), ring expansion occurred to afford the one-carbon homologated ketones (**14**)—(**16**) in 74, 84, and 97% yields, respectively, from (**11**), (**12**), and (**13**) by treatment with MCPBA (3 equiv.) in

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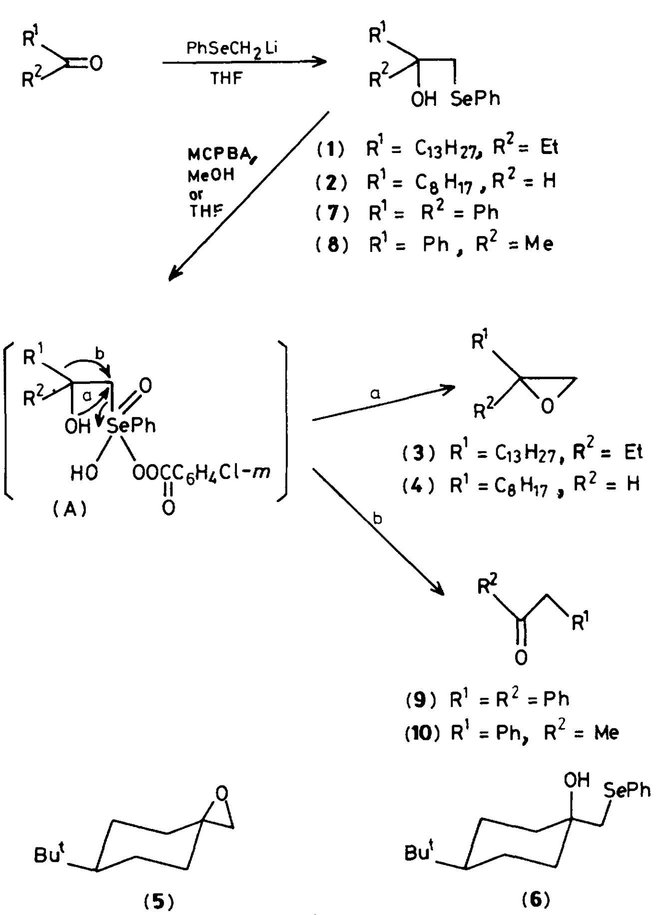
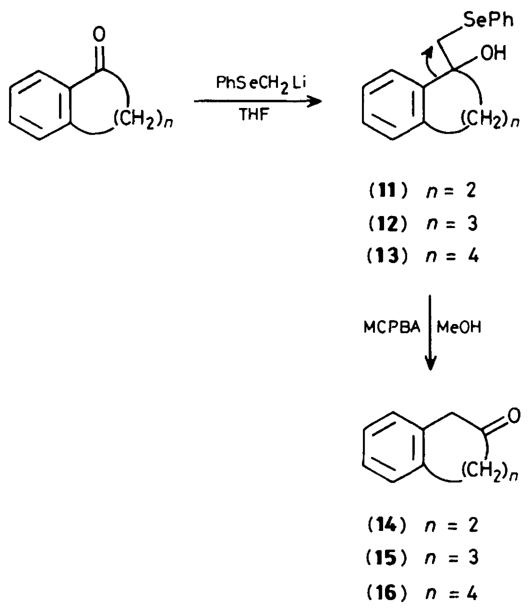
† Satisfactory i.r., ^{1}H n.m.r., and ^{13}C n.m.r. data as well as combustion analytical data were obtained for all new compounds.

‡ An authentic sample of (**5**) was prepared by the reported method[4] from 4-t-butylcyclohexanone and dimethyloxosulphonium methylide.



Scheme 1



Scheme 2

methanol (25 °C; 0.5—1 h). A similar ring expansion using β-hydroxysulphones and diethylaluminium chloride has recently been reported.[5]

Thus, the combination of the addition of a phenylselenomethyl moiety to a ketone or an aldehyde and the MCPBA oxidation of the resulting β-hydroxyselenides provides a simple method for the preparation of one-carbon homologated epoxides and ketones. The reaction is likely to be sensitive to the structure of the starting selenides§ and we are now studying the scope and limitation of this oxidation.

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§ Oxidation of 2-phenylselenodecanol, a regioisomer of (**2**), with MCPBA (5 equiv.) in methanol at 25 °C for 1 h afforded decanal (18%) and decane-1,2-diol monomethyl ethers (43%), no (**4**) being obtained. Similar oxidation at 70 °C for 5 h unexpectedly gave only methyl decanoate in 57% isolated yield.