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Hydroxyselenation of Allylic Alcohols

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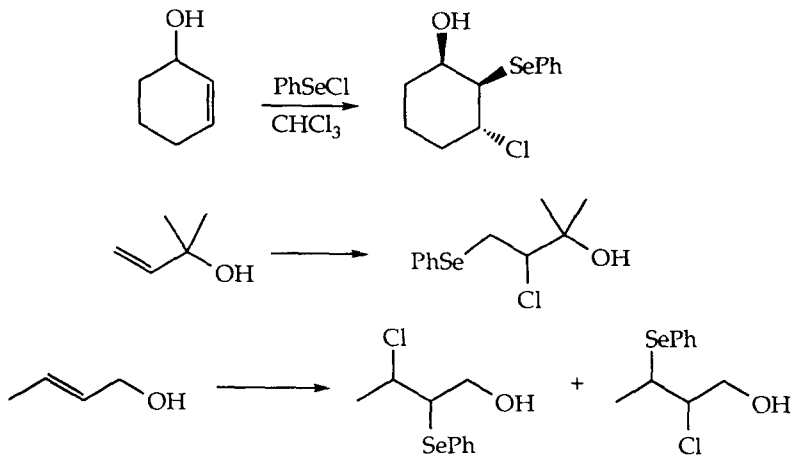
Abstract: *Hydroxyselenation of terminal or cyclic allylic alcohols occurs with high regio- and stereoselectivity to give β,β'-dihydroxyphenylselenated adducts in high yields. A mechanism for this selectivity is proposed. The utility of these adducts is illustrated by the conversion of the hydroxyselenide (9a) to the epoxide (11) via the intermediacy of a selenone.*

β-Hydroxyselenides are valuable intermediates in organic synthesis[1-4] and are readily formed by the reaction of an alkene with phenylselenenyl phthalimide[5,6] or phenylselenenyl chloride[7] in the presence of water. This hydroxyselenation procedure has not been applied to allylic alcohols. Liotta and co-workers have reported[8,9] that addition of phenylselenenyl chloride to cyclic or terminal allylic alcohols occurs in a highly regio- and stereoselective manner, whereas reaction with non-terminal allylic alcohols usually results in the formation of a mixture of regioisomers (scheme 1).

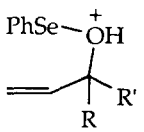


Scheme 1

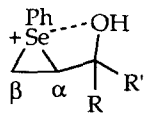
We have found that hydroxyselenation of allylic alcohols also proceeds with a high degree of regio- and stereoselectivity (table 1). Reaction of 2-methylbut-3-ene-2-ol or 3-methylbut-2-en-1-ol with phenylselenenyl chloride in aqueous acetonitrile gave only (**2**) (entries 2,3). Similar reaction with methallyl alcohol gave only the anti-Markovnikov adduct (**4**) (entry 4). The latter two regioselective additions are in contrast to the exclusive formation of Markovnikov adducts upon

addition of phenylselenenyl halides to terminal allylic alcohols in polar solvents.[9] The formation of anti-Markovnikov "PhSeOH" adducts suggests that the allylic hydroxy group is directing attack of water to the β-position of a reactive episelenonium ion intermediate (**3b**). These results also imply that the addition of "PhSeOH" to these allylic alcohols is irreversible as the adducts do not isomerise[10,11] to the thermodynamically more stable Markovnikov adducts. The ^2J couplings observed for the hydroxyl protons in the ^1H n.m.r. spectra of the isolated adducts suggest that they may be stabilised by intramolecular hydrogen bonding. Hydroxyselenation of the non-terminal allylic alcohol, crotyl alcohol, gave a mixture of regioisomers (entry 1), which reflects the similar steric environments of the α and β carbons of this substrate. The stereochemical course of the addition was determined to be *trans*-specific as hydroxyselenation of *cis*- and *trans*-hex-2-ene-1-ols gave only *threo* and *erythro* adducts respectively (entries 5,6).

In order to determine if selenium was being delivered to the double bond from an oxonium ion intermediate (**3a**),[9,12] we subjected the alcohols linalool and geraniol to the conditions described above (entries 7,8). In both cases no preference for selective addition to the allylic double bond over the isolated double bond was observed, suggesting that no prior complexation of selenium to the hydroxyl group occurs.

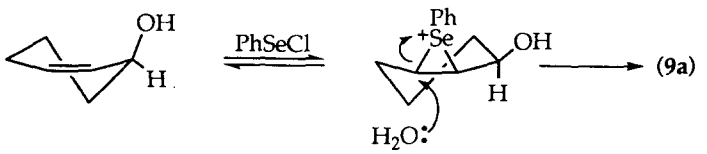


(**3a**)



(**3b**)

Hydroxyselenation of 2-cyclohexene-1-ol gave a 10:1 mixture of the diastereomers (**9a**) and (**9b**)[13] (entry 9). The major diastereomer (**9a**) arises from axial attack of water on a *syn*-episelenonium ion intermediate in the more stable pseudoequatorial conformation (scheme 2).

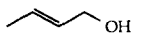
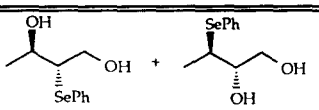
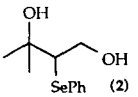
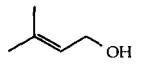
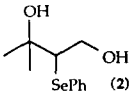
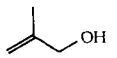
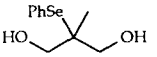
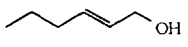
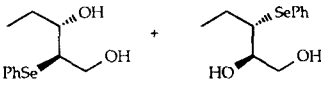
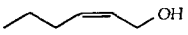
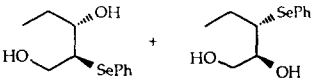
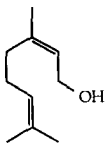
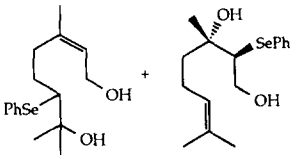
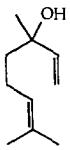
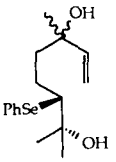
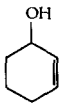
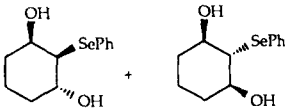
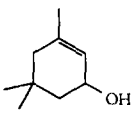
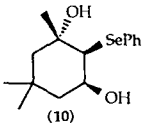


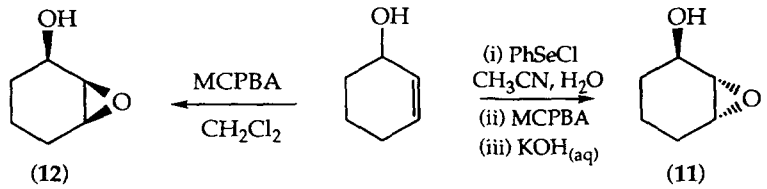
Scheme 2

More substituted cyclic allylic alcohols such as myrtenol and pulegol gave complex product mixtures, however with isophorol (entry 10) the major diastereomer (**10**) crystallized from such a mixture.

The selenide (**9a**) was converted to the trans epoxide (**11**) in good yield *via* oxidation[4,14] to the corresponding selenone with *m*-chloroperbenzoic acid (MCPBA) followed by treatment with aqueous potassium hydroxide. This reaction of a β,β'-dihydroxyselenone with base to form a *trans* α-hydroxyepoxide complements established methodologies[15-17] which give *cis* hydroxyepoxides (**12**) (scheme 3).

Table 1: Hydroxyselenation of allylic alcohols

Entry	Alkene	Addition Product	%Yield
1		 (1a) 64 : 36 (1b)	100
2		 (2)	100
3		 (2)	86
4		 (4)	85
5		 (5a) 98 : 2 (5b)	91
6		 (6a) 92 : 8 (6b)	72
7		 (7a) 42 : 58 (7b)	62
8		 (8)	42
9		 (9a) 91 : 9 (9b)	91
10		 (10)	60



(12) (11)

Scheme 3

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13. Typical procedure: To a stirred mixture of cyclohex-2-en-1-ol (98mg, 1mmol) in acetonitrile (20 ml) and water (4 ml) was added phenylselenenyl chloride (192mg, 1mmol). The mixture was stirred at room temperature for 2 h, diluted with 10% sodium bicarbonate (10 ml) and extracted with chloroform (2x15 ml). The combined organic extracts were dried, the solvent removed under reduced pressure and the residue chromatographed (ethyl acetate/hexane) to give a 10:1 mixture of the selenides **9a** and **9b** as a yellow oil (248mg, 91%). b.p. 165°C/0.03mm (block). Found: C 53.38%, H 6.06% $C_{12}H_{16}O_2Se$ requires C 53.14% H 5.95%. ^1H n.m.r. (**9a**): 7.62, m, 2H ; 7.27, m, 3H ; 4.11, m, H_1 ; 3.94, dt (J 4.2, 9.7Hz), H_3 ; 3.22, dd (J 2.7, 9.7Hz), H_2 ; 2.67, s, 2OH ; 1.80, m, 2H ; 1.60, m, 2H ; 1.40, m, 2H. (**9b**): 7.62, m, 2H ; 7.27, m, 3H ; 3.28, dt (J 4.2, 10.1Hz), H_1H_3 ; 3.03, s, 2OH ; 2.77, t (J 10.1Hz), H_2 ; 1.6-1.2, m, 6H. υ_{max} : 3400, 1600, 1500, 1095 cm^{-1}. Mass spectrum: 272 (M^+), 158 (M-Ph -2OH), 97 (M-SePh -OH).
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