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Synthesis of β-hydroxy selenides using benzeneselenol and oxiranes under supramolecular catalysis in the presence of β-cyclodextrin in water

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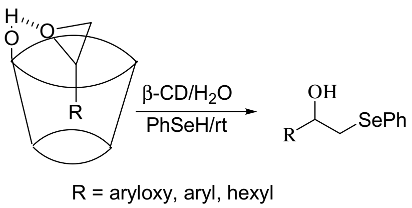
Abstract—A simple and efficient method for the synthesis of β-hydroxy selenides is reported at room temperature in impressive yields for the first time by the highly the regioselective ring-opening of oxiranes with benzeneselenol in water under supramolecular catalysis in the presence of β-cyclodextrin. This is a direct one-pot synthesis of β-hydroxy selenides under mild conditions using water as solvent and has many advantages over the existing methodologies. β-Cyclodextrin can also be recovered and reused.

β-Hydroxy selenides are highly valuable intermediates in organic synthesis[1] due to their potential for transformation into allylic alcohols, olefins, epoxides, halohydrins, oxygenated five- and six-membered hetreocycles, etc.[2–5] Consequently, a number of methodologies have been developed for the synthesis of β-hydroxy selenides.[6] Most of the syntheses of β-hydroxy selenides involve ring-opening of epoxides with diselenide by the in situ formation of selenolate anions in the presence of metal catalysts with poor yields and low regioselectivities in certain cases.[6a,b]

In view of these limitations, there is still a need for the development of clean procedures for the synthesis of β-hydroxy selenides via ring opening of oxiranes directly with benzeneselenol in water in the presence of a recyclable catalyst and without using any harmful organic solvents; water is safe, economical and environmentally benign.[7] To achieve these ideal conditions, the best choice appeared to be through supramolecular catalysis involving cyclodextrins.

Cyclodextrins (CDs) are cyclic oligosaccharides possessing hydrophobic cavities which bind substrates selectively and catalyze chemical reactions with high selectivity. They catalyze reactions by supramolecular catalysis involving reversible formation of host–guest complexes via non-covalent bonding as seen in enzymes. Complexation depends on the size, shape and hydrophobicity of the guest molecule. Thus, mimicking of biochemical selectivity through orientation of the substrate by complex formation positioning only certain regions for favorable attack will be superior to chemical selectivity, which typically involves random attack. Our earlier studies in the field of biomimetic modelling of organic chemical reactions involving cyclodextrins[8] prompted us to attempt the regioselective ring opening of oxiranes with benzeneselenol under biomimetic conditions using cyclodextrins in water as the solvent at room temperature (Scheme 1).

In general, the reaction was carried out by the in situ formation of the β-CD complex of the oxirane in water followed by the addition of benzeneselenol and stirring at room temperature to give the corresponding β-hydroxy



Scheme 1.

Keywords: Oxiranes; Benzeneselenol; β-Hydroxy selenides; β-Cyclodextrin; Supramolecular; Water.

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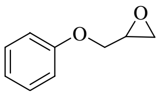
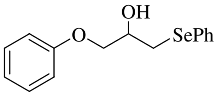
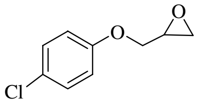
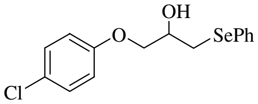
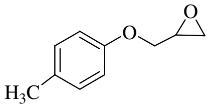
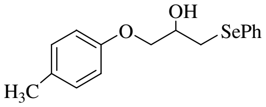
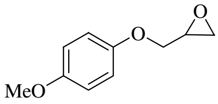
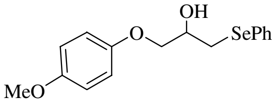
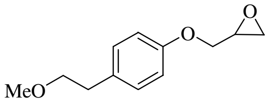
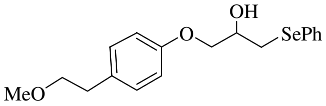
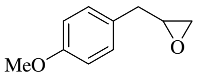
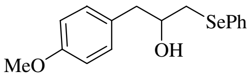
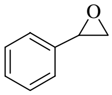
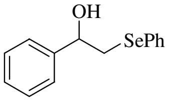
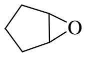
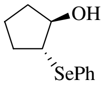
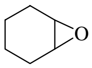
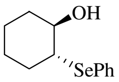
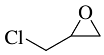
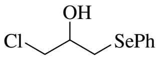
Table 1. Oxirane opening with benzeneselenol in the presence of β-CD in water

Entry	Epoxide	Product	Time (min)	Yield[a] (%)
1			30	86
2			30	86
3			30	84
4			35	82
5			35	82
6			35	80
7			25	78
8			40	80
9			40	80
10			40	75

[a] Isolated yields after purification.

selenides in a highly regioselective fashion with impressive yields (Table 1).[9] This methodology is also compatible with functionalities such as chloro, methyl, methoxy and methoxyethyl. High selectivity was also observed with styrene epoxide where the benzeneselenol attacks the terminal carbon. These cyclodextrin-mediated water-based reactions proceed under mild conditions without generation of any toxic waste. β-Cyclodextrin can also be easily recovered and reused. The compounds were characterized by spectroscopy, elemental analysis or otherwise compared with the known compounds.[6]

The reactions also take place with α-CD as well with the same regioselectivity and stereochemistry, however, β-CD was chosen as the catalyst since it is inexpensive and easily accessible. These reactions do not proceed in the absence of cyclodextrin. This is the first practical regioselective ring opening of oxiranes with benzeneselenol in water. The reaction proceeds efficiently at room temperature without the need of any acid, base and metal catalyst. The reactions are also complete in a short time (25–40 min).

The role of CD appears to be not only to activate the oxiranes but also to promote highly regioselective ring opening via inclusion complex formation. The complex of epoxide and cyclodextrin, though generated in situ, has been isolated and characterized by ^{1}H NMR.[10] There is an upfield shift of the H-3 (0.03 ppm) and H-5 (0.057 ppm) protons of cyclodextrin in the CD–epoxide complex as compared to CD indicating the formation of an inclusion complex of the epoxide with β-CD. In this type of complex, the α-position of the epoxide is more hindered and β-attack predominates to give a single regioisomer.

These CD mediated water solvent reactions are very useful both from economical and environmental points of view in contrast to existing methodologies using diphenyldiselenide and metal catalysts. Thus, it has been shown for the first time that β-hydroxy selenides of high synthetic potential can be made in a biomimetic fashion with high regioselectivity from easily accessible oxiranes and benzeneselenol in the presence of β-cyclodextrin in water. This methodology, which is simple and convenient, should be a useful addition to modern synthetic methodology with the ever-growing demand for eco-conscious chemical processes and increasing interest in green chemistry.

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9. *General procedure*: β-CD (1 mmol) was dissolved in water (15 mL) under nitrogen by warming to 60 °C until a clear solution was formed, then oxirane (1 mmol) dissolved in acetone (1 mL) was added dropwise and the mixture was allowed to reach room temperature. Benzeneselenol (1.1 mmol) was then added and the mixture stirred at room temperature until the reaction was complete (TLC) (Table 1). The organic material was extracted with ethyl acetate, dried and concentrated under reduced pressure. The resulting crude product was further purified by silica gel column chromatography with ethyl acetate–*n*-hexane (2:8) as eluent.
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