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Short communication

A rapid and high-yielding synthesis of β-hydroxyselenides by regio- and stereoselective ring-opening of epoxides with benzeneselenol using ammonium-12-molybdophosphate☆

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Abstract

β-Hydroxyselenides have conveniently been synthesized within a short period of time and in excellent yields by regio- and stereoselective ring-opening of epoxides with benzeneselenol at room temperature in the presence of ammonium-12-molybdophosphate (AMP) as a heterogeneous catalyst.

Keywords: Epoxide; Benzeneselenol; Ammonium-12-molybdophosphate; β-Hydroxyselenide

β-Hydroxyselenides are highly useful intermediates in organic synthesis as they can be converted into allylic alcohols, olefins and various oxygenated heterocycles [1]. A common route for the synthesis of these selenide derivatives involves the ring-opening of epoxides with selenoate anions which are generally generated from diselenides [2]. A number of methods [3] are known for conversion of epoxides into β-hydroxyselenides following this route. However, most of these methods suffer from certain drawbacks such as high or low temperature, longer reaction times, unsatisfactory yields and weak regioselectivity.

In continuation of our work [3] on the development of useful synthetic methodologies we have recently discovered that epoxides can efficiently be cleaved with benzeneselenol at room temperature using ammonium-12-molybdophosphate [AMP], $(NH_4)_3$ $[PMo_{12}O_{40}]$ as a heterogeneous catalyst to form the corresponding β-hydroxyselenides (Scheme 1).

Various epoxides were treated with benzeneselenol in the presence of AMP to prepare a series of β-hydroxyselenides (Table 1). The products were formed in excellent yields within 20 min. The conversion occurred under very mild conditions. Different functionalities such as alkyl, halogen and ether remained intact.

β-Hydroxyselenides were produced by highly regio- and stereoselective ring-opening of epoxides with benzeneselenol. 2-Alkylepoxides furnished the products by opening at the terminal position while styrene oxide afforded the product by cleavage at the benzylic position. Bicyclic epoxides underwent ring-opening to form the corresponding β-hydroxyselenides with *trans* configuration. The structures and stereochemistry of the products were settled from their spectral (^{1}H NMR) and analytical data.

The catalyst, AMP works under heterogeneous conditions in the present conversion. It can conveniently be handled and removed from the reaction mixture by simple filtration. In recent years, heteropolyacids and their salts have gained much attention as catalysts due to their interesting activity and capability of conducting the organic transformations in cleaner manner [4]. However, the applications of these catalysts have not yet been fully explored. The ammonium salt of a heteropolyacid (AMP) was found to be highly effective for ring-opening of epoxides with benzeneselenol at room temperature. In absence of the catalyst only a trace amount of the products were obtained even after 2 h. The catalyst is commercially available.

In conclusion, we have developed a simple, mild and efficient method for conversion of epoxides into β-hydroxyselenides using AMP as a catalyst. The heterogeneous reaction condi-

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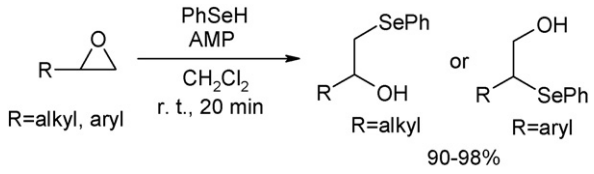


Scheme 1.

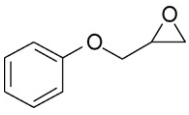
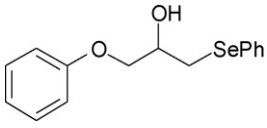
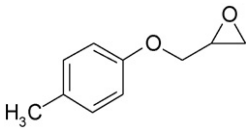
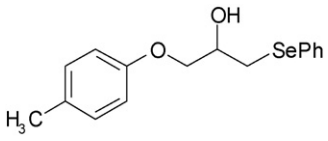
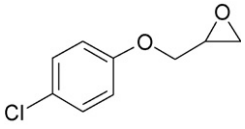
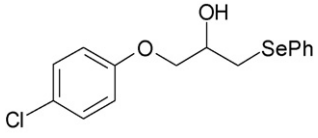
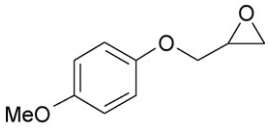
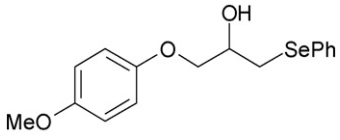
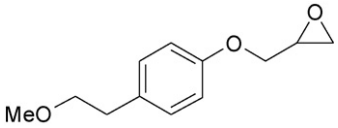
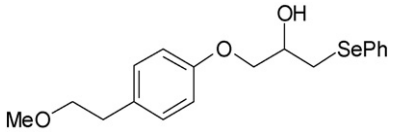
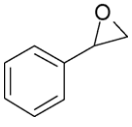
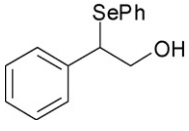
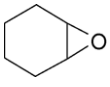
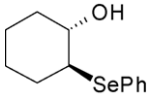
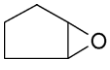
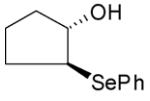
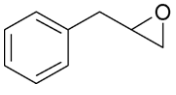
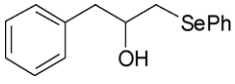
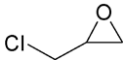
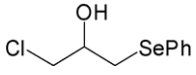
tions, short conversion times, high yields and excellent regio- and stereoselectivity are the notable advantages of the method.

1. Experimental

1.1. General experimental procedure

To a solution of an epoxide (1 mmol) in CH_2Cl_2 (5 ml) benzeneselenol (1.2 mmol) and AMP (10 mol%) were added. The mixture was stirred at room temperature for 20 min when

Table 1
Conversion of epoxides into β-hydroxyselenides using AMP[a]

Entry	Epoxide **1**	Product **2**	Isolated yield (%)
a			98
b			96
c			97
d			94
e			92
f			96
g			92
h			90
i			95
j			90

[a] The structures of the products were settled from their spectral (^{1}H NMR) and analytical data.

TLC indicated the completion of the reaction. The mixture was filtered and the filtrate was concentrated. Water (10 ml) was added to the concentrated mass followed by extraction of the organic material with EtOAc (2× 10 ml). The solvent was removed from the extract and the residue was subjected to column chromatography (silica gel, hexane–EtOAc) to obtain pure β-hydroxyselenide.

The spectral (^{1}H NMR) and analytical data of some representative products are given below.

2b: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.54–7.50 (2H, m), 7.29–7.21 (3H, m), 7.02 (2H, d, J = 8.0 Hz), 6.72 (2H, d, J = 8.0 Hz), 4.04 (1H, m) 3.96 (2H, d, J = 6.0 Hz), 3.18 (1H, dd, J = 12.0, 4.8 Hz), 3.21 (1H, dd, J = 12.0, 7.6 Hz), 2.29 (3H, s); Anal. Calcd. for $C_{16}H_{18}O_2Se$: C, 59.81%; H, 5.61%. Found: C, 59.88%; H, 5.56%.

2d: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.57–7.48 (2H, m), 7.28–7.21 (2H, m), 6.81–6.70 (5H, m), 4.03 (1H, m), 3.92 (2H, d, J = 6.0 Hz), 3.75 (3H, s), 3.20 (1H, dd, J = 12.0, 5.4 Hz), 3.09 (1H, dd, J = 12.0, 7.5 Hz), 2.82 (1H, brs); Anal. Calcd. for $C_{16}H_{18}O_3Se$: C, 56.97%; H, 5.34%. Found: C, 56.82%; H, 5.39%.

2f: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.62–7.45 (2H, m), 7.38–7.15 (8H, m), 4.43 (1H, t, J = 7.6 Hz), 4.05 (1H, dd, J = 12.0, 7.6 Hz), 3.82 (1H, dd, J = 12.0, 7.6 Hz), 2.12 (1H, brs); Anal. Calcd. for $C_{14}H_{14}OSe$: C, 60.65%; H, 5.05%. Found: C, 60.72%; H, 5.12%.

2h: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.57–7.49 (2H, m), 7.28–7.22 (3H, m), 4.13 (1H, ddd, J = 9.2, 9.0, 3.5 Hz), 3.35 (1H, ddd, J = 9.5, 9.0, 4.0 Hz), 2.25 (1H, m), 2.04 (1H, m), 1.82–1.53 (4H, m); Anal. Calcd. for $C_{12}H_{14}OSe$: C, 56.92%; H, 5.53%. Found: C, 56.81%; H, 5.61%.

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