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A mild, rapid and highly regioselective ring-opening of epoxides and aziridines with acetic anhydride under solvent-free conditions using ammonium-12-molybdophosphate☆

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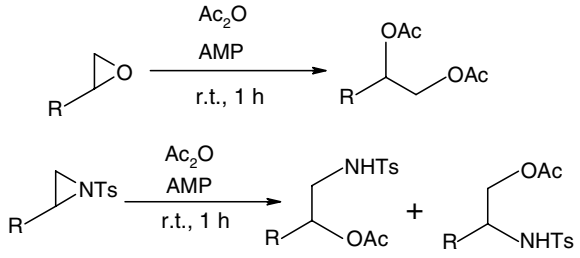
Abstract—A highly regioselective ring opening of epoxides and aziridines can be carried out efficiently with acetic anhydride to form the acetates of the corresponding 1,2-diols and 2-amino-alcohols, respectively, using ammonium-12-molybdophosphate (AMP) as a heterogeneous catalyst, at room temperature, in the absence of solvent.

Epoxides[1] and aziridines[2] are important precursors in organic syntheses. They are capable of reacting with various nucleophiles to afford 1,2-difunctional products.[3] Thus they can be utilized for the preparation of 1,2-diols and 2-amino-alcohols, which possess valuable synthetic utilities.[4] Earlier, di-*O*-acetyl-1,2-diols and *O*-acetyl-2-amino alcohols were prepared directly from epoxides and aziridines, respectively, by treatment with Ac_2O in the presence of tributylphosphine as a catalyst.[4] However, this reaction was conducted under reflux and reaction times were high (12–48 h). The regioselectivity of the ring opening of 2-phenyl-*N*-tosyl aziridines was also not impressive.[4] In continuation of our work[5] on the development of useful synthetic methodologies, we now report that ammonium-12-molybdophosphate (AMP), $(NH_4)_3[PMo_{12}O_{40}]$[6] can efficiently be applied for cleavage of epoxides and aziridines with Ac_2O to produce the acetate esters of 1,2-diols and 2-amino-alcohols, respectively (Scheme 1).



Scheme 1.

Several epoxides and *N*-tosyl aziridines underwent ring-opening easily with Ac_2O in the presence of AMP at room temperature (Table 1). No solvent was required for the reaction.The conversion was complete in 1 h and the products were formed in excellent yields. An epoxide derived from trisubstituted alkene, such as **1f**, also afforded the desired product, **2f** smoothly.[5d] This chiral epoxide furnished the product with inversion of configuration by ring cleavage in an *anti* manner involving an S_N2 process.[3c]

The ring opening of epoxides with Ac_2O by internal or external attack of the nucleophile afforded similar products. However, the conversion of aziridines took place with high regioselectivity. *N*-Tosyl-2-aryl aziridines yielded products formed by cleavage at the benzylic position while *N*-tosyl-2-alkyl aziridines afforded products formed by opening at the terminal position. The cleavage of symmetrical bicyclic epoxides and *N*-tosyl aziridines with Ac_2O formed trans products. The structures and stereochemistry of the acetates were established from their analytical and spectral (^1H NMR and MS) data.

Keywords: Epoxide; Aziridine; Acetic anhydride; Ammonium-12-molybdophosphate; Regioselectivity.

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Table 1. Ring-opening of epoxides and aziridines with acetic anhydride using AMP[a]

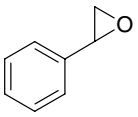
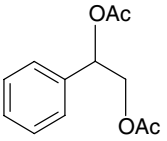
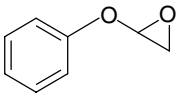
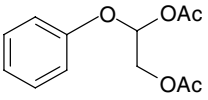
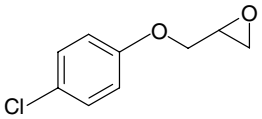
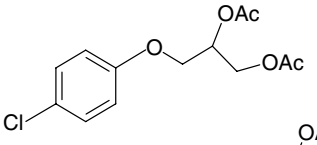
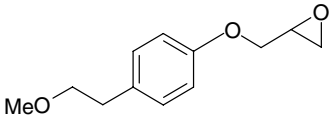
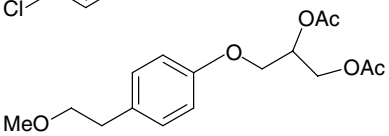
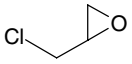
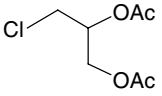
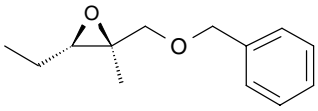
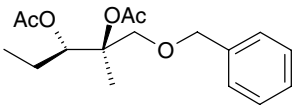
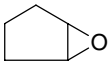
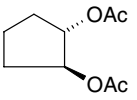
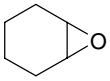
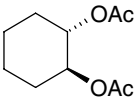
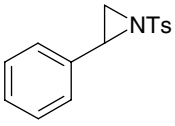
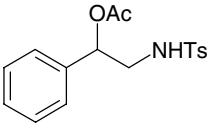
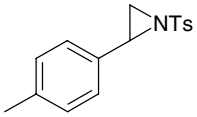
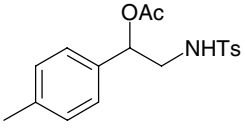
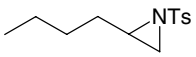
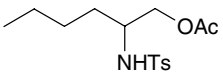
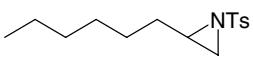
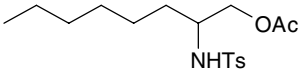
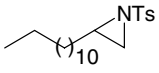
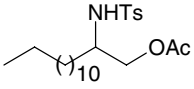
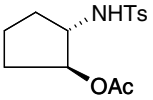
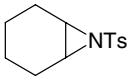
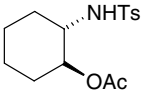
Entry	Epoxide/aziridine **1**	Product **2**	Isolated yield (%)
a			98
b			96
c			94
d			96
e			92
f			91
g			93
h			93
i			98
j			96
k			92[b]
l			93[b]
m			92[b]

Table 1 (*continued*)

Entry	Epoxide/aziridine **1**	Product **2**	Isolated yield (%)
n			94
o			93

[a] The structures of the products were established from their spectral (^{1}H NMR and MS) and analytical data.
[b] The other regioisomer (~5%) was also obtained.

In recent years, heteropoly acids and their salts have gained much importance due to their interesting catalytic activity and ability to carry out reactions in a clean manner.[7] The synthetic utilities of these catalysts has not yet been fully discovered. The present catalyst, AMP (the ammonium salt of a heteropoly acid), has been found to be highly efficient for the ring opening of both epoxides and aziridines with Ac_2O at room temperature. In the absence of this catalyst, only trace amounts of products were obtained even after 2 h. The catalyst operates under heterogeneous conditions and can conveniently be handled and separated from the reaction mixture by simple filtration.

In conclusion, we have developed a mild and efficient method for the preparation of acetate esters of 1,2-diols and 2-amino-alcohols by ring opening of epoxides and aziridines, respectively, with Ac_2O using AMP as a heterogeneous catalyst. The high yields, short reaction times and excellent regio- and stereoselectivities are advantages of the present protocol.

General experimental procedure: To a mixture of epoxide (or *N*-tosyl aziridine) (1 mmol) and Ac_2O (1.2 mmol), AMP (10 mol %) was added. The mixture was stirred at room temperature for 1 h. TLC indicated the completion of the reaction. Water–EtOAc (1:1) (10 ml) was added and the mixture was shaken and filtered. The organic portion was separated from the filtrate and the aqueous portion was extracted twice with EtOAc (2×5 ml). The combined organic portions were concentrated and subjected to column chromatography (silica gel, hexane–EtOAc) to afford the ester.

The spectral and analytical data of some representative acetates are given below:

Compound **2a**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.42–7.28 (5H, m), 6.01 (1H, dd, $J = 7.8$, 4.3 Hz), 4.33 (1H, dd, $J = 12.0$, 4.3 Hz), 4.21 (1H, dd, $J = 12.0$, 7.8 Hz), 2.02 (3H, s), 2.05 (3H, s); FABMS: m/z 223 $[M+H]^{+\cdot}$. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.86; H, 6.31. Found: C, 64.72; H, 6.38.

Compound **2d**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.08 (2H, d, $J = 8.0$ Hz) 6.79 (2H, d, $J = 8.0$ Hz), 5.30 (1H, m), 4.41 (1H, dd, $J = 12.0$, 3.8 Hz), 4.25 (1H, dd, $J = 12.0$, 6.0 Hz), 4.06 (2H, d, $J = 5.3$ Hz), 3.51 (2H, t, $J = 7.0$ Hz), 3.30 (3H, s), 2.76 (2H, t, $J = 7.0$ Hz), 2.08 (3H, s), 2.03 (3H, s); FABMS: m/z 311 $[M+H]^{+\cdot}$. Anal. Calcd for $C_{16}H_{22}O_6$: C, 61.94; H, 7.10. Found: C, 61.83; H, 7.17.

Compound **2h**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.38 (2H, dd, $J = 7.3$, 2.9 Hz), 2.02 (6H, s), 1.39–1.34 (2H, m), 1.22–1.14 (6H, m); FABMS: m/z 201 $[M+H]^{+\cdot}$. Anal. Calcd for $C_{10}H_{16}O_4$: C, 60.00; H, 8.00. Found: C, 60.24; H, 8.17.

Compound **2j**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.72 (2H, d, $J = 8.0$ Hz), 7.28 (2H, d, $J = 8.0$ Hz), 7.20–7.03 (4H, m), 5.65 (1H, t, $J = 6.0$ Hz), 5.32 (1H, t, $J = 6.0$ Hz), 3.27 (2H, t, $J = 6.0$ Hz), 2.47 (3H, s), 2.32 (3H, s), 2.01 (3H, s); FABMS: m/z 348 $[M+H]^{+\cdot}$. Anal. Calcd for $C_{18}H_{21}NO_4S$: C, 62.25; H, 6.05; N, 4.03. Found: C, 62.38; H, 6.12; N, 4.11.

Compound **2k**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.75 (2H, d, $J = 8.0$ Hz), 7.30 (2H, d, $J = 8.0$ Hz), 5.11 (1H, d, $J = 6.0$ Hz), 4.28–4.20 (2H, m), 3.22 (1H, m), 2.41 (3H, m), 1.96 (3H, s), 1.59–1.42 (2H, m), 1.31–1.11 (4H, m), 0.82 (3H, t, $J = 8.0$ Hz); FABMS: m/z 314 $[M+H]^{+\cdot}$. Anal. Calcd for $C_{15}H_{23}NO_4S$: C, 57.51; H, 7.35; N, 4.47. Found: C, 57.65; H, 7.42; N, 4.52.

Compound **2o**: ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.76 (2H, d, $J = 8.0$ Hz), 7.28 (2H, d, $J = 8.0$ Hz), 5.79 (1H, d, $J = 6.8$ Hz), 4.83 (1H, ddd, $J = 9.0$, 7.6, 4.0 Hz), 3.42 (1H, m), 2.41 (3H, s), 2.10–1.88 (2H, m), 1.85 (3H, s), 1.72–1.38 (6H, m); FABMS: m/z 312 $[M+H]^{+\cdot}$. Anal. Calcd for $C_{15}H_{21}NO_4S$: C, 57.88; H, 6.75; N, 4.50. Found: C, 57.96; H, 6.82; N, 4.58.

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