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Mild and Efficient Ring Opening of Epoxides Catalyzed by Potassium Dodecatungstocobaltate(III)

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Summary. Efficient ring opening of epoxides under mild conditions is reported. Potassium dodecatungstocobaltate(III) trihydrate was used as an efficient catalyst for the alcoholysis and acetolysis of epoxides. Conversion of epoxides to thiiranes was also performed efficiently in the presence of this catalyst.

Keywords. Epoxides; Polyoxometalate; Alcoholysis; Acetolysis; Thiirane.

Introduction

Epoxides have become very popular in organic synthesis not only as building blocks but also as synthesis intermediates [1–4]. They can be easily prepared from a variety of substrates and are easily opened under a broad range of conditions giving a wide spectrum of regio- and stereoselective ring-opened products. Epoxide ring-opening reactions to give β-substituted alcohols with carbon- and heteroaromatic nucleophiles are useful tools in organic synthesis, and most of these reactions generally proceed under basic or acidic conditions [5]. In most of the epoxides' ring-opening reactions under acidic conditions, the formation of a mixture of regio isomers and polymerization is observed. Some of the reported catalysts suffer from disadvantages such as high acidity, the non-catalytic nature of the reagents, long reaction times, and inconvenient handling [6–8]. Therefore, the introduction of new methods for the nucleophilic ring-opening of epoxides, which work under mild conditions, is still in demand and is important in synthetic organic

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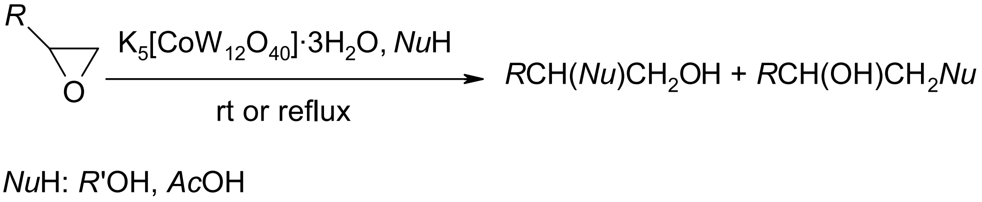
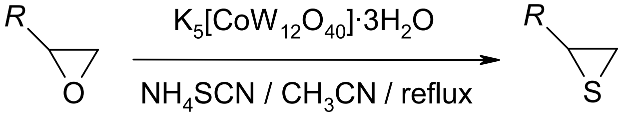


Scheme 1



Scheme 2

chemistry. A number of methods using *Lewis* acids and one-electron transfer catalysts have been also reported for the ring-opening reactions of epoxides with different nucleophiles [9–25]. Recently, we have reported the ability of electron deficient metalloporphryins in epoxides ring opening [26–29].

Heteropolyoxometalates as stable inorganic porphyrins have attracted much attention in the last two decades [30, 31]. The versatility of these catalysts has been demonstrated in various oxidation reactions, but there has been very little exploitation of their catalytic activity in nucleophilic ring-opening of epoxides [32, 33]. The high catalytic activity of potassium dodecatungstocobaltate(III) trihydrate, $K_5[CoW_{12}O_{40}] \cdot 3H_2O$, in various organic syntheses [34–38] and our interest in the application of polyoxometalates in nucleophilic ring opening of epoxides [39–41] prompted us to explore the potential of this catalyst for the nucleophilic ring-opening of epoxides. We found that $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ can be used as a mild and highly efficient catalyst for alcoholysis, acetolysis, and preparation of thiiranes with ammonium thiocyanate (Schemes 1 and 2).

Results and Discussion

Ring-Opening of Epoxides by Various Heteropolyanions

At first, in order to show the ability of various heteropolyanions in the ring-opening of epoxides, the methanolysis of styrene oxide was investigated. The summarized results in Table 1 show that $K_5[CoW_{12}O_{40}] \cdot 3H_2O$, $Na_4[W_{10}O_{32}] \cdot 4H_2O$, and $[(C_4H_9)_4N][W_{10}O_{32}]$ are more reactive than other catalysts and among these $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ is the best catalyst for the methanolysis of styrene oxide. Therefore, $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ was chosen as the catalyst for the ring-opening of epoxides.

Alcoholysis and Acetolysis of Epoxides Catalyzed by $K_5[CoW_{12}O_{40}] \cdot 3H_2O$

Alcoholysis of various epoxides such as cyclohexene and styrene oxides, (chloromethyl)oxirane, allyl oxiranylmethyl ether, isopropyl oxiranylmethyl ether, and

Table 1. Methanolysis of styrene oxide by different heteropolyanions[a]

Entry	Heteropolyanion	Yield/%[b]
1	$K_5[CoW_{12}O_{40}] \cdot 3H_2O$	100
2	$Na_4[W_{10}O_{32}] \cdot 4H_2O$	22
3	$[(C_4H_9)_4N][W_{10}O_{32}]$	15
4	$Na_4[NiMo_9H_6O_{24}] \cdot 9H_2O$	0
5	$(NH_4)_6[NiMo_9O_{32}] \cdot 6H_2O$	0
6	$K_6[MnMo_9O_{32}] \cdot 6H_2O$	0
7	$K_3[FeW_{12}O_{40}] \cdot 10H_2O$	0
8	$(NH_4)_8[Co^{II}Co^{II}W_{12}O_{42}]$	0
9	$(NH_4)_7[Co^{II}Co^{III}W_{12}O_{42}]$	0

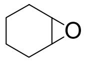
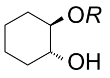
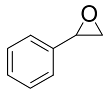
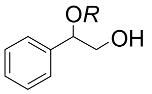
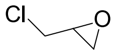
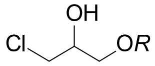
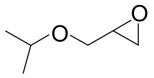
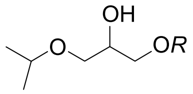
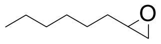
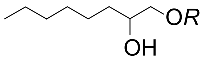
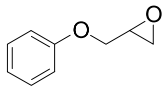
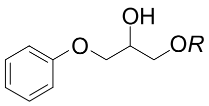
[a] Reaction conditions: styrene oxide (1 mmol), catalyst (0.05 mmol), methanol (4 cm^3); [b] GC yields based on the starting styrene oxide and determined after 15 min at room temperature

1,2-epoxyoctane as examples of aliphatic, alicyclic, activated, and deactivated epoxides, were performed with primary, secondary, and tertiary alcohols affording the corresponding β-alkoxy alcohols in high to excellent yields in the presence of 0.05 molar equivalents of $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ as catalyst (Table 2). The reactions in the case of cyclohexene oxide were stereospecific, and only *trans* products were obtained (Entries 1–5). In the case of unsymmetrical epoxides, the reactions are regioselective with an attack of the nucleophile (alcohol) on the less substituted oxirane carbon to yield the anti-*Markovnikov* type products (Entries 11–35). The only exception is given by styrene oxide, in which the reactions occur on the more substituted carbon; *Markovnikov* type products were obtained (Entries 6–10). The $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ was used for acetolysis of epoxides and the results (Table 3) show that this catalyst is an efficient catalyst for conversion of epoxides to β-acetoxy alcohols. In the case of allyl oxiranylmethyl ether, isopropyl oxiranylmethyl ether, phenyl oxiranylmethyl ether, and 1,2-epoxyoctane, 20–27% of the minor isomers were produced.

Conversion of Epoxides to Thiiranes Catalyzed by $K_5[CoW_{12}O_{40}] \cdot 3H_2O$

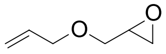
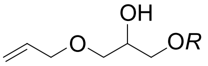
Many methods have been already reported for the preparation of thiiranes. The most general one is based on conversion of oxiranes to thiiranes by an oxygen-sulfur exchange reaction. Among other reagents NH_4SCN was already used for this purpose. Conversion of epoxides to thiiranes with NH_4SCN in the presence of a suitable catalyst [42–53] under nonaqueous conditions different from classical methods, which are generally carried out in homogeneous or heterogeneous aqueous media, is important in organic chemistry. Reaction of different aliphatic and cyclic epoxides including those with electron-withdrawing substituents with NH_4SCN were performed in refluxing acetonitrile in the presence of 0.05 molar equivalent of $K_5[CoW_{12}O_{40}] \cdot 3H_2O$. Table 4 summarizes the results obtained for conversion of different epoxides to their corresponding thiiranes. The effects of other solvents such as acetone, dichloromethane, chloroform, and carbontetrachloride were also investigated. Compared to acetonitrile as the solvent, the reaction times were longer and the yields of thiiranes were lower in all of the other solvents.

Table 2. Alcoholysis of various epoxides catalyzed by $K_5[CoW_{12}O_{40}]\cdot 3H_2O$[a]

Entry	Epoxide	R–OH/Condition	Time/min	Product/Yield/%[b,c]
				
1		$R=CH_3$/rt	30	100
2		$R=C_2H_5$/rt	30	100
3		$R=n\text{-}Pr$/rt	30	99
4		$R=i\text{-}Pr$/rt	30	97
5		$R=t\text{-}Bu$/rt	30	70
				
6		$R=CH_3$/rt	15	100
7		$R=C_2H_5$/rt	30	100
8		$R=n\text{-}Pr$/rt	30	100
9		$R=i\text{-}Pr$/rt	30	92
10		$R=t\text{-}Bu$/rt	30	88
				
11		$R=CH_3$/reflux	30	94
12		$R=C_2H_5$/reflux	30	88
13		$R=n\text{-}Pr$/reflux	30	86
14		$R=i\text{-}Pr$/reflux	30	80
15		$R=t\text{-}Bu$/reflux	30	67
				
16		$R=CH_3$/reflux	15	99
17		$R=C_2H_5$/reflux	30	98
18		$R=n\text{-}Pr$/reflux	30	97
19		$R=i\text{-}Pr$/reflux	30	96
20		$R=t\text{-}Bu$/reflux	30	63
				
21		$R=CH_3$/rt	30	96
22		$R=C_2H_5$/reflux	30	100
23		$R=n\text{-}Pr$/reflux	30	95
24		$R=i\text{-}Pr$/reflux	30	70
25		$R=t\text{-}Bu$/reflux	30	42
				
26		$R=CH_3$/rt	15	100
27		$R=C_2H_5$/reflux	30	100
28		$R=n\text{-}Pr$/reflux	30	95

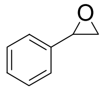
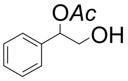
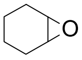
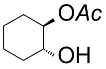
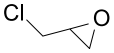
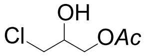
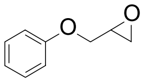
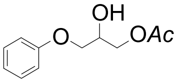
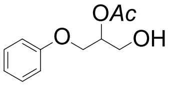
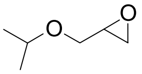
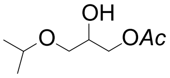
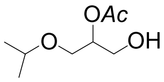
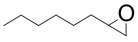
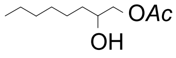
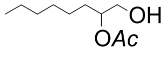
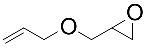
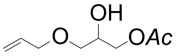
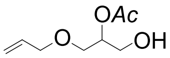
(*continued*)

Table 2 (*continued*)

Entry	Epoxide	*R*–OH/Condition	Time/min	Product/Yield/%[b,c]
29		*R* = *i-Pr*/reflux	30	90
30		*R* = *t-Bu*/reflux	30	60
				
31		*R* = CH_3/rt	15	99
32		*R* = C_2H_5/reflux	30	99
33		*R* = *n-Pr*/reflux	30	96
34		*R* = *i-Pr*/reflux	30	89
35		*R* = *t-Bu*/reflux	30	61

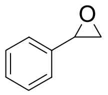
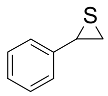
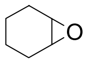
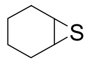
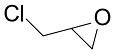
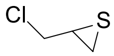
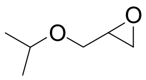
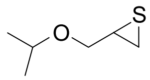
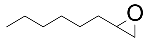
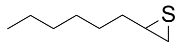
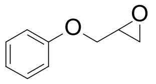
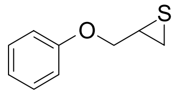
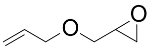
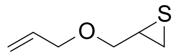
[a] Catalyst 0.05 molar amount; [b] all products were identified by comparison of their physical and spectral data with those of authentic samples; [c] yields refer to GLC yields

Table 3. Acetolysis of various epoxides catalyzed by $K_5[CoW_{12}O_{40}] \cdot 3H_2O$[a]

Entry	Epoxide	Time/min/Condition	Product[b]	Yield[c]
1		30/rt		100
2		15/reflux		100
3		30/reflux		100
4		30/reflux		72
				22
5		30/reflux		74
				24
6		30/rt		66
				27
7		30/reflux		64
				21

[a] Catalyst 0.05 molar amount; [b] all products were identified by comparison of their physical and spectral data with those of authentic samples; [c] yields refer to GC yields

Table 4. Conversion of epoxides to thiiranes catalyzed by $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ in refluxing acetonitrile[a]

Entry	Epoxide	Time/min	Yield/%[b]	Product[c]
1		30	100	
2		60	100	
3		60	100	
4		60	100	
5		60	100	
6		60	100	
7		60	100	

[a] Catalyst 0.05 molar amount; [b] yields refer to GC yields; [c] all products were identified by comparison of their physical and spectral data with those of authentic samples

In conclusion, we suggest that selective ring opening of different epoxides with alcohols and acetic acid is potentially performed through an electron transfer mechanism. The possibility of an electron transfer mechanism was strongly supported by the following experiment: when small amounts of acrylonitrile were added to the reaction mixture as radical scavenger, a large decrease in the reaction rates was noticed.

Experimental

All chemicals used were of reagent grade. The heteropolyanions were prepared according to Refs. [54–60]. Products were characterised by comparison of their physical, IR, and NMR data with those of known samples. ^{1}H NMR spectra were obtained with a Brucker AW 80 (80 MHz) spectrometer. GLC analyses were performed on a Shimadzu GC-16A instrument with a flame ionization detector using a Silicon DC-200 or Carbowax 20 M column. Infrared spectra were recorded on Philips PU-9716 or Shimadzu IR-4350 spectrophotometers.

Alcoholysis of Epoxides by $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ (General Procedure)

To a solution of 1 mmol epoxide in 4 cm^3 of the appropriate alcohol was added 157 mg $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ (0.05 mmol). The mixture was stirred for the specified time and at the appropriate temperature according to Table 2. The progress of the reaction was monitored by GLC. The solvent was evaporated and 20 cm^3 H_2O were added and extracted with Et_2O ($3 \times 10\,cm^3$). The organic layer was separated and dried (Na_2SO_4). The etheral solution was concentrated under reduced pressure and chromatographed on a silica gel column to give the pure product.

Acetolysis of Epoxides by $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ (General Procedure)

$K_5[CoW_{12}O_{40}] \cdot 3H_2O$ (0.05 mmol) was added to a solution of 1 mmol epoxide in 4 cm^3 acetic acid. The progress of reaction was monitored by GLC. The solvent was evaporated and 20 cm^3 H_2O were added. The product was extracted with ether ($3 \times 10\,cm^3$). The organic layer was washed with a 5% solution of $NaHCO_3$ and dried (Na_2SO_4). Evaporation of the solvent followed by TLC gave the product.

Conversion of Oxiranes to Thiiranes by $K_5[CoW_{12}O_{40}] \cdot 3H_2O$ (General Procedure)

To a mixture of 1 mmol oxirane and 2 mmol ammonium thiocyanate in 4 cm^3 acetonitrile, was added 0.05 mmol $K_5[CoW_{12}O_{40}] \cdot 3H_2O$. The reaction mixture was refluxed for 0.5–1 h, the reaction progress was monitored by GLC. After completion of the reaction, the solvent was evaporated, the product was extracted with CCl_4 ($3 \times 10\,cm^3$), and the solid residue was filtered off. Concentration of the solution led to the desired product in quantitative yield.

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