

Aluminumdodecatungstophosphate (AIPW₁₂O₄₀) as a reusable Lewis acid catalyst

Facile regioselective ring opening of epoxides with alcohols, acetic acid and thiols

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Abstract

AIPW₁₂O₄₀ as a recyclable Lewis acid and stable solid compound was introduced for efficient ring opening of different epoxides with thiols, acetic acid, and primary, secondary, and tertiary alcohols. These processes were carried out at room temperature with high regio- and stereoselectivity. © 2006 Published by Elsevier B.V.

Keywords: Aluminumdodecatungstophosphate; AIPW₁₂O₄₀; Epoxide; Alcohol; Acetic acid; Thiol; Ring opening

1. Introduction

Alcohols and acetic acid behave as poor nucleophilic reagents in substitution processes. Nevertheless, under strongly acidic or basic conditions [1] their use for ring-opening reactions of epoxides [2] is well established and provides a powerful entry to β -alkoxyalcohols or β -acetoxyalcohols [3]. Meanwhile, the regioselective ring opening of epoxides by *ter*-butanol or acetic acid is a useful method to produce selective protected diols. The harsh conditions associated with the procedures have spurred a search for new and mild methodologies. The Lewis acids employed recently for this purpose includes BF₃·OEt₂ [4a], SnCl₄ [4b], FeCl₃ [4c], FeCl₃·6H₂O/SiO₂ [4d], Fe(O₂CCF₃)₃ [4e], Fe(III)-montmorillonite [4f], Ce(OTf)₄ [4g], (NH₄)₂Ce(NO₃)₃ [4h], Ce[(PVP)₂(NO₃)₃] [4i], (NH₄)₈[CeW₁₂O₃₆] [4j], Cp₂ZrCl₂ [4k]. Most of the reactions conducted in the presence of these catalysts were proceeded under reflux conditions, especially in the case of using secondary and tertiary alcohols. Introduction of heterogeneous, easy accessible and efficient catalyst is of high demands for ring opening of epoxides. There is ongoing

activity aimed to establish a more general, simple, eco-friendly, recyclable and efficient catalytic protocol to accomplish this transformation.

In continuation of our interest in the applications of aluminumdodecatungstophosphate (AIPW₁₂O₄₀) in organic synthesis [5], we here report a new application of AIPW₁₂O₄₀ as an effective catalyst for the ring opening of epoxides with thiols, acetic acid and primary, secondary and tertiary alcohols at room temperature. AIPW₁₂O₄₀ is easily prepared quantitatively by the reaction of H₃PW₁₂O₄₀ (a cheap and commercially available compound) with Al(NO₃)₃ in water. In comparison with AlCl₃ which is water sensitive and corrosive, AIPW₁₂O₄₀ is highly water tolerant and a stable solid compound with high Lewis acid activity.

2. Results and discussion

Our study on the ring opening of styrene oxide by methanol at room temperature showed that 1 mol% of AIPW₁₂O₄₀ was an adequate amount of the catalyst to conduct the ring-opening reaction quantitatively to give a mixture of 2-methoxy-2-phenyl ethanol and 2-methoxy-1-phenyl ethanol with the ratio of 94/6 in 92% total yield (Table 1, entry 1). When similar reaction was conducted at 0 °C, the reaction proceeded well with very high regioselectivity and 2-methoxy-2-phenyl

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Table 1
Solvvolysis of epoxides catalyzed by AIPW₁₂O₄₀ at room temperature

Entry	Epoxide	Catalyst (mol%)	Alcohol	R	Ratio of ^a (a/b)	Time (h)	Yield ^b (%)	Reference for known compound
1		1	Methanol	Me	94/6	0.1	92	[4d]
2		1	Methanol	Me	100/0	0.15	94 ^c	[4d]
3		2	2-Propanol	2-Propyl	100/0	0.2	90	[4d]
4		2	<i>t</i> -Butanol	<i>t</i> -Butyl	100/0	0.7	77	[4d]
5		2	CH ₃ CO ₂ H	CH ₃ CO	90/10	0.5	88	[4d]
6		1	Methanol	Me		0.1	90	[4d]
7		2	2-Propanol	2-Propyl		0.15	89	[4d]
8		2	<i>t</i> -Butanol	<i>t</i> -Butyl		0.5	71	[4d]
9		2	CH ₃ CO ₂ H	CH ₃ CO		0.1	91	[4d]
10		1	Methanol	Me	60/40	0.3	91	[4i,j]
11		2	2-Propanol	2-Propyl	72/28	2.2	87	[4i,j]
12		2	<i>t</i> -Butanol	<i>t</i> -Butyl	82/18	3.5	76	[4i,j]
13		2	CH ₃ CO ₂ H	CH ₃ CO	70/30	0.3	90	[4i,j]
14		3	Methanol	Me		0.4	94	[4c]
15		3	2-Propanol	2-Propyl		1.5	90	[4c]

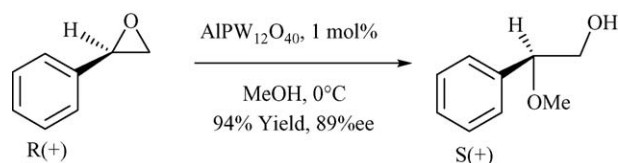
Table 1 (Continued)

Entry	Epoxide	Catalyst (mol%)	Alcohol	R	Ratio of ^a (a/b)	Time (h)	Yield ^b (%)	Reference for known compound
16		3	<i>t</i> -Butanol	<i>t</i> -Butyl		16.5	89	[4c,d]
17		2	CH ₃ CO ₂ H	CH ₃ CO		70/30	92	[4i]
18		3	Methanol	Me		0.4	93	[4c]
19		3	2-Propanol	2-Propyl		2	95	[4c]
20		3	<i>t</i> -Butanol	<i>t</i> -Butyl		18	85	[4c]
21		3	CH ₃ CO ₂ H	CH ₃ CO		1.5	91	[4j]
22		3	Methanol	Me		0.25	94	[4c]
23		3	2-Propanol	2-Propyl		1.5	96	[4d]
24		5	<i>t</i> -Butanol	<i>t</i> -Butyl		48	90	[4d]
25		3	CH ₃ CO ₂ H	CH ₃ CO		2	95	[4d]
26		3	Methanol	Me		8	87	[4d]
27		3	2-Propanol	2-Propyl		20	92	[4d]
28		5	<i>t</i> -Butanol	<i>t</i> -Butyl		40	85	[4d]
29		3	CH ₃ CO ₂ H	CH ₃ CO		3	78	[4d]
30		13	Methanol	Me		33	98	[4i]
31		13	2-Propanol	2-Propyl		48	89	[4i]

^a Regioselectivity was determined by GC, NMR.

^b All the compounds were characterized by IR, NMR and MS and compared with authentic samples [4].

^c The reaction was occurred at 0 °C.



Scheme 1.

ethanol was isolated as the sole product in 94% yield (Table 1, entry 2). We have also studied the reaction of *R*(+)-styrene oxide in methanol in the presence of 1 mol% of the catalyst at 0 °C. The reaction proceeded with high stereospecificity of the ring opening of optically active styrene oxide. The optical rotation of the isolated product was determined and compared with the reported data in the literature [4a]. The optical rotation of the isolated product; shows that the ring opening has been proceeded with 89% enantiomeric excess (Scheme 1).

In order to show the general applicability of the method for the ring opening of epoxides with structurally different alcohols and acetic acid, we studied the reaction of styrene oxide with primary, secondary and tertiary alcohols as the reaction models. We found that the amount of the catalyst required for the completion of the reaction is depended on the bulkiness of the alcohols. For the reactions conducted in the presence of isopropyl and *tert*-butyl alcohols, 2 mol% of the catalyst was required (Table 1, entries 3 and 4). However, we applied similar reaction conditions for the solvolysis of different epoxides with different alcohols and acetic acid in the presence of this catalyst. As it is shown in Table 1, solvolysis of alkyl substituted epoxides occurs much faster than those epoxides carrying electron-withdrawing substituents.

In order to show the merit of the presented protocol for the ring opening of epoxides with alcohols, we have compared the results obtained using AIPW₁₂O₄₀ with some of those reported in the literature for the reaction of 2,3-epoxypropylphenyl ether with methanol as tabulated in Table 2.

β -Hydroxysulfide moiety is present in compounds of biological and pharmacological interest [6] and is a versatile group for synthesizing allylic alcohols [7], benzoxathiepinines [8], benzotiazepines [9], α -thioketones [10], α -substituted α -unsaturated enones [11], and β -hydroxysulfoxides used in the synthesis of naturally occurring compounds [12]. The easiest access to β -

hydroxysulfides is the reaction of epoxides with thiols catalyzed by bases [13] or acids [14].

Generation of β -hydroxysulfide moiety from epoxides in the presence of AIPW₁₂O₄₀ with thiols has been studied. For this purpose, cyclohexene oxide reacted smoothly with thiols to afford the corresponding 2-hydroxysulfides in high yields in the presence of 2 mol% of AIPW₁₂O₄₀ (Table 2, entries 1 and 2). Styrene oxide was also reacted efficiently with thiophenol in the presence of 2 mol% of the catalyst. A mixture of two structural isomers with the ratio *ab* = 85/15 in 90% total yield (Table 3, entry 3). The reaction of epoxides with electron-withdrawing groups with thiophenol was also performed in the presence of 7 mol% of AIPW₁₂O₄₀ at room temperature (Table 3, entries 4–6).

In order to show the merit of AIPW₁₂O₄₀ as a Lewis acid catalyst we have shown the results of the reaction of cyclohexene oxide with thiophenol using AIPW₁₂O₄₀ with the results obtained using other Lewis acid catalysts for the similar reaction (Table 4).

In conclusion, AIPW₁₂O₄₀ was found to be an efficient Lewis acid catalyst for the reaction of various epoxides carrying electron-donating and electron-withdrawing groups with thiols, acetic acid and alcohols at room temperature. In addition, AIPW₁₂O₄₀ can be quantitatively recovered and reused after being dried under reduced pressure at 150 °C.

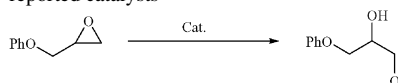
3. Experimental

Chemicals were either prepared in our laboratories or were purchased from Fluka and Merck Chemical Companies. The purity determination of the products was accomplished by GC on a Shimadzu model GC-14A instrument or by TLC on silica gel polygram SIL G/UV 254 plates. Mass spectra were run on a Shimadzu GC-Mass-QP 1000 EX at 20 eV. The IR spectra were recorded on a Shimadzu FT-IR-8300 spectrophotometer. The NMR spectra were recorded on a Bruker avance DPX 250 MHz spectrometer.

3.1. General procedure for the solvolysis of epoxides

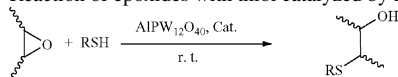
To a solution of epoxide (1.0 mmol) in alcohol (3 ml), the appropriate amounts of AIPW₁₂O₄₀ (Table 1) was added. The

Table 2
Comparison of the results obtained for the reaction of 2,3-epoxypropylphenyl ether with methanol catalyzed with AIPW₁₂O₄₀ with those obtained by the recently reported catalysts



Entry	Catalyst	Catalyst (mol%)	Temperature	Time (min)	Yield (%)	Reference
1	AIPW ₁₂ O ₄₀	3	r.t.	15	94	–
2	(NH ₄) ₈ [CeW ₁₂ O ₃₆]	4	Reflux	10	95	[4j]
3	Fe(III)-montmorillonite	0.2 g	r.t.	120	85	[4f]
4	FeCl ₃	15	65 °C	180	95	[4c]
5	Ce(OTf) ₄	5	Reflux	20	93	[4g]

Table 3

Reaction of epoxides with thiol catalyzed by AIPW₁₂O₄₀ at room temperature

Entry	Epoxide	Catalyst (mol%)	Thiol	Product	Time (min)	Yield ^a (%)	Reference for known compound
1		2	PhSH		20	93	[14f]
2		2	PhCH ₂ SH	PhCH ₂	20	90	[4f]
3		2	PhSH		10	90 ^b	[14f]
4		7	PhSH		90	93	[13d]
5		7	PhSH		90	89	–
6		7	PhSH		120	96	[14f]

^a All the compounds were characterized by IR, NMR & MS and compared with those of authentic samples.

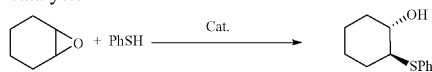
^b The ratio of two structural isomers *a/b* was 85/15 that were separated by simple plate chromatography (¹H NMR compound *a* (250 MHz, CDCl₃) δ (ppm) 7.36–7.23 (m, 10H), 4.32 (t, 1H, *J* = 6.9 Hz), 3.92 (d, 2H, *J* = 6.9 Hz, +1H, OH)). *b*: 7.44–7.25 (m, 10H), 4.74–4.71 (dd, 1H), 3.37–3.30 (dd, 1H), 3.14–3.05 (dd, 1H), 2.04 (1H, OH).

reaction mixture was stirred at room temperature for the time reported in Table 1. The progress of reaction was monitored by GC or TLC. After completion of the reaction, solvent was evaporated and dichloromethane (20 ml) was added to the resulting residue and stirred for 5 min. The resulting mixture was filtered and the filter cake was washed with dichloromethane (5 ml) to recover the catalyst. The dichloromethane solution was washed with water (10 ml). The organic layer was separated and dried over anhydrous Na₂SO₄. Evaporation of the solvent followed by column chromatography (where needed) on a short column of silica gel gave the desired pure product.

3.2. General procedure for the reaction of epoxides with thiol

To a mixture of epoxide (1.0 mmol) and thiol (1.1 mmol) in CH₃CN (3 ml), the appropriate amounts of AIPW₁₂O₄₀ (Table 2) were added. The reaction mixture was stirred at room temperature for 10–120 min (Table 3). Progress of the reaction was monitored by GC or TLC. After completion of the reaction, the catalyst was filtered and the filter cake was washed with CH₃CN (10 ml). Evaporation of the solvent followed by column chromatography on silica gel gave the desired pure product in high yield.

Table 4

Comparison of the results obtained for the reaction of cyclohexene oxide with thiophenol catalyzed with AIPW₁₂O₄₀ with those obtained by the recently reported catalysts

Entry	Catalyst	Catalyst (mol%)	Temperature	Time (min)	Yield (%)	Reference
1	AIPW ₁₂ O ₄₀	2	r.t.	5	93	–
2	TBAF	5	r.t.	30	100	[13d]
3	LiClO ₄	100	80	48h	95	[14c]
4	InCl ₃	10	r.t.	270	90	[14f]
5	B(C ₆ F ₅) ₃	5	r.t.	240	88	[14g]

The selected spectral data for 1-Isopropoxy-3-phenylsulfanyl-propan-2-ol (Table 3, entry 5): ^1H NMR (250 MHz, CDCl_3) δ (ppm) 7.39–7.35 (m, 2H), 7.30–7.23 (m, 2H), 7.20–7.19 (m, 1H), 3.90–3.81 (m, 1H), 3.61–3.41 (m, 3H), 3.08–3.04 (m, 2H), 2.6 (b, 1H, OH), 1.14 (d, 6H, $J=6.1\text{Hz}$); ^{13}C (63 MHz, CDCl_3) δ (ppm) 135.8, 129.4, 128.9, 126.2, 72.2, 70.3, 69.3, 37.3, 22.0; IR (neat) 3420, 3080, 2890, 2870, 2830, 1580, 1470, 1450, 1380, 1130, 1090, 710 cm^{-1} ; MS (70 eV) $m/z = 226 [M]^+$.

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