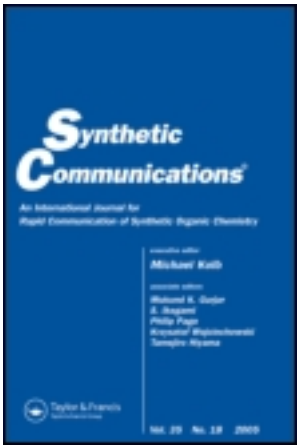

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Potassium Dodecatungstocobaltate Trihydrate ($K_5CoW_{12}O_{40} \cdot 3H_2O$) as an Efficient Catalyst for Aminolysis of Epoxides

E. Rafiee [a], Shahram Tangestaninejad [a], M. H. Habibi [a] & V. Mirkhani [a]
[a] Department of Chemistry, University of Isfahan, Isfahan, 81746-73441, Iran
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Potassium Dodecatungstocobaltate Trihydrate ($K_5CoW_{12}O_{40} \cdot 3H_2O$) as an Efficient Catalyst for Aminolysis of Epoxides

E. Rafiee,* Shahram Tangestaninejad, M. H. Habibi, and V. Mirkhani

Department of Chemistry, University of Isfahan, Isfahan, 81746-73441, Iran

ABSTRACT

Aminolysis of epoxides using various amines was catalyzed with potassium dodecatungstocobaltate trihydrate in a convenient and efficient method with good selectivities.

Key Words: Aminolysis; Epoxides; Potassium dodecatungstocobaltate trihydrate.

Aminolysis of epoxides is an excellent synthetic tool for construction of β-amino alcohols and has been well exploited for the synthesis of

*Correspondence: E. Rafiee, Department of Chemistry, University of Isfahan, Isfahan, 81746-73441, Iran; Tel.: +98-311-7932705; Fax: +98-311-6689732; E-mail: e.rafiee@sci.ui.ac.ir.

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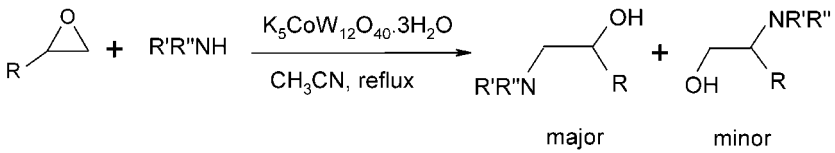
pharmacologically interesting compounds.[1] A wide variety of catalysts have already been applied to the aminolysis of epoxides, including $CoCl_2$,[2] Ti (*O*-i-Pr)$_4$,[3] SmI_2,[4] metal triflates,[3,5–8] basic metal amides,[9] diisopropoxyaluminum trifluoroacetate,[10] $TaCl_5$,[11] $CeCl_3$,[12] and montmorillonite.[13] However, some of the drawbacks of these methods are the long reaction times, the use of large amounts of expensive catalysts, and low chemo- regio- and stereoselectivity. Hence, the development of new catalysts with more efficiency and better selectivity is of interest.

Potassium dodecatungstocobaltate ($K_5CoW_{12}O_{40} \cdot 3H_2O$) is apparently a perfect outer-sphere one-electron oxidant,[14] due to the presence of a sheath of chemically inert oxygen atoms, which protect the central ion from undesired inner-sphere substitution reactions. For this reason, electron transfer with ($K_5CoW_{12}O_{40} \cdot 3H_2O$) typically leads to selective reactions and clean chemistry. This advantage has encouraged us to continue our investigation of applications of ($K_5CoW_{12}O_{40} \cdot 3H_2O$) in organic synthesis.[15,16] We wish to describe here that aminolysis of epoxides can be effectively catalyzed by a cheap and easily prepared cobalt heteropoly compound ($K_5CoW_{12}O_{40} \cdot 3H_2O$) (Sch. 1).

We first examined the reaction of some representative epoxides with aniline and ($K_5CoW_{12}O_{40} \cdot 3H_2O$) (5 mole%) in acetonitrile to give the corresponding amino alcohols in 93–98% yields (Table 1). Ring opening of epoxides occurs with very high regioselectivity, and only one product was obtained in these cases (except for 1,2-octeneoxide) (Table 1).

This success encouraged us to exploit the generality of the reaction to a few other amines. Treatment of epoxides with sterically hindered aromatic amines, such as 2-chloroaniline or 2-methoxyaniline and other amines, affords the corresponding amino alcohols in good yields.

The reaction rates depend on the structures of the amines and the epoxides. With nonaromatic epoxides, the primary carbon is much more reactive toward amines than the secondary one. Interesting to note is that aliphatic secondary amines also responded well, with excellent yields. We believe that due to the protection of the central cobalt ion with inert oxygen atoms, aliphatic amines, even those with strong complexation ability, could not attach the



Scheme 1.

Table 1. Aminolysis of epoxides in the presence of potassium dodecatungstocobaltate trihydrate.

St. no.	Epoxide	Amine	Time (h)	%Yield[a]
1	Cyclohexeneoxide	Aniline	3	93
2		2-Chloroaniline	3	93
3		4-Ethylaniline	3	94
4		4-Methylaniline	2.5	92
5		2-Methoxyaniline	3.5	95
6		3-Methoxyaniline	2.5	94
7		4-Methoxyaniline	3.75	91
8		4-Bromoaniline	3.25	93
9		3-Methylpiperidine	7	60
10		4-Methylpiperidine	7	80
11	Styreneoxide	Aniline	3.5	98
12		2-Chloroaniline	3.5	93
13		4-Ethylaniline	1.5	96
14		4-Methylaniline	2	98
15		2-Methoxyaniline	1.75	97
16		3-Methoxyaniline	2.5	97
17		4-Methoxyaniline	4	98
18		4-Bromoaniline	1	98
19		3-Methylpiperidine	6	64
20		4-Methylpiperidine	6	74
21	1-Allyloxy-2,3-	Aniline	4	93
22	epoxypropane	2-Chloroaniline	4	98
23		4-Ethylaniline	2	93
24		4-Methylaniline	2.5	99
25		2-Methoxyaniline	3.75	97
26		3-Methoxyaniline	4	93
27		4-Methoxyaniline	4	98
28		4-Bromoaniline	3.5	98
29		3-Methylpiperidine	6	85
30		4-Methylpiperidine	6	76
31	2,3-Epoxypropyl-	Aniline	4	98
32	isopropyl ether	2-Chloroaniline	2	93
33		4-Ethylaniline	2.5	93
34		4-Methylaniline	2	96
35		2-Methoxyaniline	4	94
36		3-Methoxyaniline	3.75	99
37		4-Methoxyaniline	4.75	90
38		4-Bromoaniline	2.25	93
39		3-Methylpiperidine	7	74

(*continued*)

Table 1. Continued.

St. no.	Epoxide	Amine	Time (h)	%Yield[a]
40		4-Methylpiperidine	7	76
41	1,2-Octeneoxide	Aniline	3.5	96(96/4)[b]
42		2-Chloroaniline	4	95(61/39)[b]
43		4-Ethylaniline	2.5	92(74/26)[b]
44		4-Methylaniline	4	97(78/22)[b]
45		2-Methoxyaniline	1.5	98(64/36)[b]
46		3-Methoxyaniline	4	98(67/33)[b]
47		4-Methoxyaniline	6	86(81/19)[b]
48		4-Bromoaniline	5	98(92/8)[b]
49		3-Methylpiperidine	7	45(89/11)[b]
50		4-Methylpiperidine	7	54(89/11)[b]
51	2,3-Epoxypropyl-	Aniline	4.5	93
52	phenyl ether	2-Chloroaniline	4	98
53		4-Ethylaniline	1	98
54		4-Methylaniline	1.75	97
55		2-Methoxyaniline	3.5	98
56		3-Methoxyaniline	3	98
57		4-Methoxyaniline	4	98
58		4-Bromoaniline	0.75	98
59		3-Methylpiperidine	7	75
60		4-Methylpiperidine	6	78
61	Epichlorohydrine	Aniline	4	95
62		2-Chloroaniline	3.5	92
63		4-Ethylaniline	2	89
64		4-Methylaniline	2.5	97
65		2-Methoxyaniline	3	96
66		3-Methoxyaniline	4.5	96
67		4-Methoxyaniline	6	92
68		4-Bromoaniline	5.5	99
69		3-Methylpiperidine	7	98
70		4-Methylpiperidine	6	98
71	Buthyl glycidyl ether	Aniline	3.5	98
72		2-Chloroaniline	3.25	98
73		4-Ethylaniline	1.75	98
74		4-Methylaniline	1.5	99
75		2-Methoxyaniline	4.25	98
76		3-Methoxyaniline	3.5	94
77		4-Methoxyaniline	5.5	98
78		4-Bromoaniline	2.5	98
79		3-Methylpiperidine	7	94

(*continued*)

Table 1. Continued.

St. no.	Epoxide	Amine	Time (h)	%Yield[a]
80		4-Methylpiperidine	7	98
81	Epibromohydrine	Aniline	1	96
82		2-Chloroaniline	1.5	96
83		4-Ethylaniline	1	97
84		4-Methylaniline	2.5	98
85		2-Methoxyaniline	3	99
86		3-Methoxyaniline	3	99
87		4-Methoxyaniline	2.5	99
88		4-Bromoaniline	2.5	98
89		3-Methylpiperidine	6	98
90		4-Methylpiperidine	6	97

[a]Determined by GLC analysis of crude product.
[b]Ratio of (major/minor) product.

cobalt ion and deactivate it. However, such deactivation has been previously reported for metal triflate, $TaCl_5$ and $CeCl_3$ as catalysts. With 1,2-octeneoxide, the regioselectivity is lower, but the attack on the less-hindered side of the epoxide remains preponderant.

In conclusion, ($K_5CoW_{12}O_{40} \cdot 3H_2O$) can be regarded as an efficient catalyst for ring opening of epoxide with amines of low nucleophilicity. All β-amino alcohols are obtained in good yields with high regioselectivity.

EXPERIMENTAL

The ($K_5CoW_{12}O_{40} \cdot 3H_2O$) was prepared according to the previously reported procedures.[15,16] All products were identified by comparison of their physical and spectroscopic data with authentic samples prepared in accordance with the procedures in the literature.[2,5,10,13,17]

General Procedure for the Preparation of β-Amino Alcohols

A solution of the epoxide (1.0 mmol) in acetonitrile (2.5 ml) was treated with ($K_5CoW_{12}O_{40} \cdot 3H_2O$) (0.02 mmol) and the amine (2 mmol). The mixture was stirred at reflux until completion [monitored by gas chromatography (GC) or thin-layer chromatography (TLO)]. The catalyst was filtered, and the reaction mixture was washed with water. Diethyl ether was added, and after

separation of phases, the organic layer was dried over Na_2SO_4 and purified on silica-gel plates or silica-gel column.

SPECTROSCOPIC DATA OF SOME OF THE β-AMINOALCOHOLES

***trans*-2-(4-Ethylanilino)cyclohexan-1-ol (Entry 3):** viscous liquid, IR (KBr, cm^{-1}): 3487–3299 (NH and OH), 1587, 1516, 1069, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.9–1.0 (m, 1H), 1.2 (t, $J = 4.65$, 3H), 1.25–1.5 (m, 3H), 1.7–1.8 (m, 2H), 2.16–2.20 (m, 2H), 2.9 (s, 1H), 3.21–3.47 (m, 3H), 3.55–3.8 (m, 1H), 6.79 (t, $J = 4.5$ Hz, 1H), 6.90 (d, $J = 9$ Hz, 2H), 7.25 (t, $J = 4.5$ Hz, 2H). Analysis calculated for $C_{14}H_{21}NO$; C, 76.67; H, 9.65; N, 6.39. Found: C, 76.75; H, 9.70; N, 6.45.

***trans*-2-(4-Bromoanilino)cyclohexan-1-ol (Entry 8):** yellow solid, m.p. 126–128°C (lit. 125–127°C), IR (KBr, cm^{-1}): 3497–3286 (NH and OH), 1580, 1506, 1063, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.09 (m, 1H), 1.38 (m, 3H), 1.72 (m, 2H), 1.92–2.23 (m, 2H), 2.94–3.2 (ddd, $J = 10.9$, 9.4, 3.8 Hz, 1H), 3.22–3.42 (ddd, $J = 10.1$, 10.1, 4.3 Hz, 1H), 3.51–4.07 (bs, 2H), 6.49 (d, $J = 10.3$ Hz, 2H), 7.22 (d, $J = 10.3$ Hz, 2H). ^{13}C-NMR ($CDCl_3$, 200 MHz) δ 24.6, 25.3, 31.8, 33.7, 60.9, 74.8, 110.6, 116.5, 132.5, 146.9.

2-(4-Ethylanilino)-1-phenylethanol (Entry 11): viscous yellow liquid, IR (KBr, cm^{-1}): 3500–3140 (NH and OH), 1557, 1510, 1089, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 1.90 (br s., 1H, OH, D_2O exch.), 3.80 (dd, $J = 6.9$, 10.7 Hz, 1H), 3.85 (dd, $J = 4.1$, 10.7 Hz, 1H), 4.60 (dd, $J = 6.9$, $J = 10.7$ Hz, 1H), 6.50 (d, $J = 8.3$ Hz, 2H), 6.80 (t, $J = 8.0$ Hz, 1H), 7.25 (t, $J = 8.1$ Hz, 2H), 7.30–7.45 (m, 5H). Analysis calculated for $C_{14}H_{15}NO$; C, 78.87; H, 7.04; N, 6.57. Found: C, 77.75; H, 7.10; N, 6.45.

1-Anilino-2-octanol (Entry 41): viscous liquid; IR (NaCl, cm^{-1}): 3598–3100 (NH and OH), 1592, 1495, ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 0.92 (t, $J = 7$ Hz, 3H), 1.24–1.86 (m, 10H), 3.21 (dd, $J = 10$, 10 Hz, 2H), 3.32 (dd, $J = 8$, 4 Hz, 1H), 3.91 (m, 1H), 6.68–7.35 (m, 5H), ^{13}C-NMR ($CDCl_3$, 200 MHz) δ 14.5, 23.0, 26.0, 29.8, 32.2, 35.5, 51.0, 70.7, 114.0, 118.7, 129.7, 151.6, Analysis calculated for $C_{14}H_{23}NO$; C, 75.97; H, 10.47; N, 6.33. Found: C, 75.71; H, 10.66; N, 6.48.

1-Anilino-3-chloro-2-propanol (Entry 61): viscous liquid; IR (NaCl, cm^{-1}): 3504–3100 (NH and OH), 1594, 1497, 1090, ^{1}H-NMR

($CDCl_3$, 200 MHz) δ 3.24 (m, 2H), 3.45 (dd, $J = 10.1$, 4.8 Hz, 1H), 3.72 (d, $J = 8$ Hz, 2H), 4.12 (m, 1H), 6.74 (m, 3H), 7.19 (m, 2H), ^{13}C-NMR ($CDCl_3$, 200 MHz) δ 47.7, 48.1, 70.2, 113.9, 118.9, 129.9, 148.0, Analysis calculated for $C_9H_{12}ClNO$; C, 58.23; H, 6.51; N, 7.54. Found: C, 58.02; H, 6.68; N, 7.69.

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