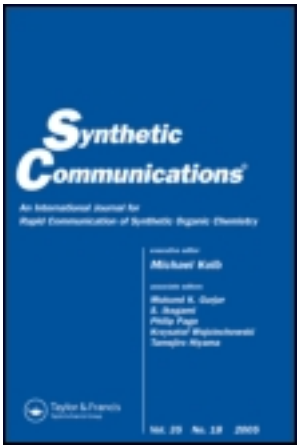

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B_2O_3/Al_2O_3 as an Efficient and Recyclable Catalyst for the Synthesis of β-Amino Alcohols under Solvent-Free Conditions

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Abstract: A convenient and efficient procedure for the solvent-free synthesis of β-amino alcohols has been achieved via B_2O_3/Al_2O_3-promoted highly regioselective ring opening of epoxides with aromatic amines in good to excellent yields at room temperature. Additionally, the catalyst can be recycled without affecting the catalytic property.

Keywords: β-Amino alcohols; Anilines; B_2O_3/Al_2O_3, Epoxides, Solvent-free conditions

INTRODUCTION

β-Amino alcohols are important intermediates in the synthesis of a large number of biologically active natural and synthetic products,[1] amino acids,[2] and chiral auxiliaries.[3] One of the most common and practical methods for the preparation of these compounds is the aminolysis of epoxides at elevated temperature with an excess of amines.[4] Subsequently, various activators/promoters have been developed to perform the epoxide ring-opening reaction under mild conditions such as metal amides (lithium, magnesium, lead, tin),[5] metal alkoxide [diisopropoxyaluminium

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trifluoroacetate (DIPAT), $Ti(OiPr)_4$],[6] metal triflates (lithium, Ph_4SbOTf, lanthanide, tin, scandium),[7] metal halides ($TaCl_5$, $ZrCl_4$, VCl_3, $ZnCl_2$, $CeCl_3$, $BiCl_3$),[8] silica under high pressure,[9] ionic liquids,[10] water,[11] clay,[12] and others.[13] However, there are some limitations with these methodologies such as longer reaction times, use of stoichiometric or moisture-sensitive catalysts, and hazardous organic solvents. More recently, Robinson and coworkers have reported the aminolysis of epoxides using a mesoporous aluminosilicate catalyst.[14] These reactions also require longer reaction times (6–12 h). Therefore, the development of convenient, efficient, and environmentally friendly catalytic systems for their preparation is highly attractive.

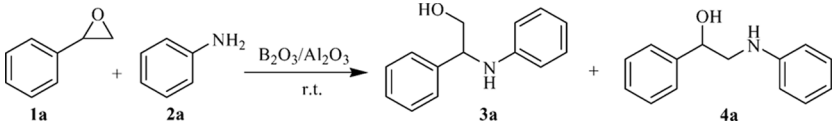
Recently, some organic reactions running on the surfaces of solids such as mesoporous aluminosilicate,[14] titanosilicate molecular sieves,[15] alumina,[16] and silica gel[17] have been reported, and these heterogeneous catalysts offer several intrinsic advantages such as the easy separation of product, the convenient recovery and reuse of catalyst, and the minimization of waste production. Herein we report that B_2O_3/Al_2O_3 efficiently promoted the ring-opening reactions with aromatic amines at room temperature under solvent-free conditions.

RESULTS AND DISCUSSION

First, to optimize the best reaction conditions, styrene oxide **1a** (1 mmol) was taken as a representative substituted epoxideand treated with aniline **2a** (1 mmol) under various conditions (Table 1). The results clearly revealed that the B_2O_3/Al_2O_3-promoted ring-opening reaction best proceeded for 2 h at room temperature under solvent-free conditions to give **3a** in excellent yield (yield 90%) with high regioselectivity (Table 1, entry 5). Prolonging the reaction time did not improve the yield of **3a** (Table 1, entries 5, 6). The yield was unsatisfactory when an organic solvent was used such as CH_3CH_2OH, CH_3CN, CH_2Cl_2, or H_2O (Table 1, entries 1–4). We found that the yield was affected by adding different amounts of B_2O_3/Al_2O_3; better conversions were achieved by using 0.03 g B_2O_3/Al_2O_3 (Table 1, entries 5, 7, 8). When only Al_2O_3 was used as the catalyst or no catalyst was used for the ring-opening reactions, **3a** was obtained in low yield (Table 1, entries 9 and 10).

Because of the good results obtained, we applied the optimal protocol to a variety of amines (Table 2). Most of the reactions proceeded smoothly at room temperature in good to excellent yields affording **3** as major products by amine attack at the benzylic carbon. Further studies indicated that strong electron-drawing groups ($-NO_2$) on the aromatic ring affected the product yields. The high regioselectivity obtained is

Table 1. Ring-opening of styrene oxide with aniline under various conditions



1a 2a 3a 4a

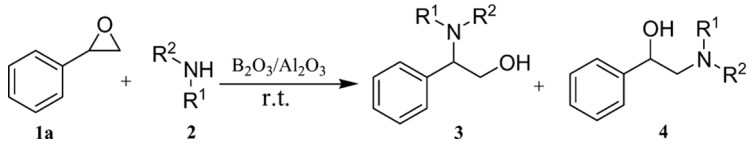
Entry	Solvent	Time (h)	Yield (%)[a]	Ratio **3a:4a**[b]
1	CH_3CH_2OH	2	35	>99:1
2	CH_3CN	2	30	>99:1
3	CH_2Cl_2	2	32	>99:1
4	H_2O	2	40	>99:1
5	Solvent-free	2	90	>99:1
6	Solvent-free	5	91	>99:1
7[c]	Solvent-free	2	85	>99:1
8[d]	Solvent-free	2	90	>99:1
9[e]	Solvent-free	2	25	>99:1
10[f]	Solvent-free	5	30	>99:1

[a]Isolated yield.
[b]Regioisomers were determined using ^{1}H NMR.
[c]0.01 g of B_2O_3/Al_2O_3 was used as a catalyst.
[d]0.05 g of B_2O_3/Al_2O_3 was used as a catalyst.
[e]In the absence of catalyst.
[f]0.03 g of Al_2O_3 was used as a catalyst.

noticeable (Table 2, entry 5). The steric effect also affected the reaction significantly in the yield of product (Table 2, entry 7). Furthermore, the hindered amines quite influenced the ring-opening reaction, and elevated temperature was needed (Table 2, entries 8, 9).

Various epoxides were treated with aniline in the presence of B_2O_3/Al_2O_3 (Table 3). Interestingly, aliphatic and aromatic epoxides gave the major products with the opposite regiochemistry (Table 3, entry 1). We suggest that the attack position of the nucleophile is governed by the nature of epoxides and the stability of carbonium ion. In the case of aryl epoxides, the positive charge on oxygen appears to be localized on the more highly substituted benzylic carbon leading to the major product **5**. For aliphatic epoxides, possibly steric factors predominate over electronic factors and the absolutely selective nucleophilic attack at the less hindered carbon of epoxide to afford the product **6** (Table 3, entries 2–6). Furthermore, we investigated cyclohexene oxide with aniline (Table 3, entry 7); the resultant racemic β-amino cyclohexanol was identified as the *trans*-diastereoisomer on the basis of ^{1}H NMR spectral data.

Table 2. Ring opening of styrene oxide with various amines under solvent-free conditions at room temperature catalyzed by B_2O_3/Al_2O_3



1a 2 3 4

Entry	R_1	R_2	Products	Time (h)	Yield (%)[a]	Ratio **3:4**[b]
1	Ph	H	**3a**	2	90	>99:1
2	4-Me(C_6H_4)	H	**3b**	2	85	98:2
3	4-Cl(C_6H_4)	H	**3c**	2	89	94:6
4	3-Cl(C_6H_4)	H	**3d**	2	93	95:5
5	2-NO_2(C_6H_4)	H	**3e**	3	62	>99:1
6	2-OMe(C_6H_4)	H	**3f**	2	94	93:7
7		H	**3g**	3	75	95:5
8[c]	Ph	CH_3	**3h**	4	98	94:6
9[c]	Ph	Ph	**3i**	3.5	55	90:10

[a]Isolated yields.
[b]Regioisomers were determined using ^{1}H NMR.
[c]At 60 °C.

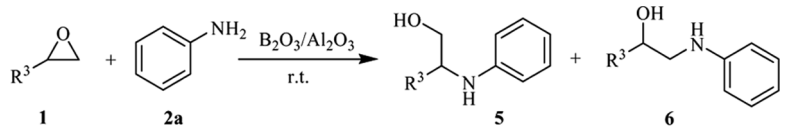
Finally, the reusability of B_2O_3/Al_2O_3 was further investigated in subsequent aminolysis reactions, taking the aminolysis of styrene oxide as an example (Scheme 1). The catalyst was easily recovered by simple filtration after diluting the reaction mixture with ethyl acetate and was reused after drying under vacuum. The catalyst (B_2O_3/Al_2O_3) was reused for four runs without any appreciable loss of activity.

In summary, B_2O_3/Al_2O_3 is a highly efficient, mild, and reusable catalyst for ring-opening reaction of epoxides with amines with excellent regio- and stereoselectivity. The low cost and apparently nontoxic nature of B_2O_3/Al_2O_3 and the solvent-free reaction conditions make it environmentally friendly and potentially useful for industrial applications.

EXPERIMENTAL

All the melting points were uncorrected. Chemicals and solvents were either purchased or purified by standard techniques. IR spectra were

Table 3. Ring opening of various epoxides with aniline in the presence of B_2O_3/Al_2O_3 at room temperature under solvent-free conditions

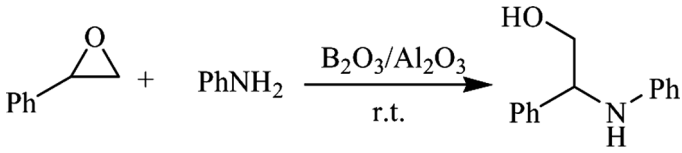


1 2a 5 6

Entry	Epoxide	Products	Time (h)	Yield (%)[a]
1		**5a**	3	98
2		**6b**	3	75
3		**6c**	3.5	72
4		**6d**	3	97
5		**6e**	3	78
6		**6f**	4	60
7		**6g**	3.5	76

[a]Isolated yields.

recorded on a Bruker Equinox 55 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC 300 instrument using $CDCl_3$ as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts are given in δ relative to TMS; the coupling constants J are given in hertz. Compounds were properly characterized by elemental analysis carried out using a Carlo-Erba EA1112 instrument. Silica gel 60 GF254 was used for analytical and preparative thin-layer chromatography (TLC).



Scheme 1. Reusing of the catalyst in subsequent aminolysis reactions. Run 1: 90%; run 2: 90%; run 3: 88%; run 4: 87%.

General Procedure for the Synthesis of β-Amino Alcohols

B_2O_3/Al_2O_3 (0.03 g, 15% w/w) was added to a magnetically stirred mixture of epoxide (1 mmol) and amine (1 mmol), and the reaction mixture was stirred at room temperature for the appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was diluted with ethyl acetate. The catalyst was separated by filtration, and then the solution was washed (ethyl acetate) and dried (Na_2SO_4). After evaporation of the solvent under reduced pressure, the crude product was obtained. The corresponding purified form was obtained by flash-column chromatography.

Characterization Data of All the Products

2-Phenyl-2-(phenylamino)ethanol (**3a**)[13l]

Oil. IR ν (cm^{-1}): 3397, 2932, 2873, 1600, 1502, 1451. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.26$–7.38 (m, 5H), 7.12 (m, 2H), 6.70 (m, 1H), 6.58 (m, 2H), 4.52 (m, 2H), 3.76–3.97 (m, 2H), 1.84 (s, 1H, OH). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 147.17$, 140.05, 129.12, 128.80, 127.58, 126.68, 117.83, 113.79, 67.33, 9.79.

2-(p-Toluidino)-2-phenylethanol (**3b**)[8b]

Solid, mp: 59–61 °C. IR ν (cm^{-1}): 3446, 3026, 2923, 2853, 1572, 1491, 1445, 1373. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.96$–7.39 (m, 5H), 6.95 (m, 2H), 6.54 (m, 2H), 4.48 (m, 2H), 3.68–3.94 (m, 2H), 2.53 (d, $J = 2.82$ Hz, 1H), 2.24 (s, 3H). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 144.85$, 140.24, 129.58, 128.67, 128.39, 127.42, 126.65, 113.97, 67.20, 60.07, 20.30.

2-(4-Chlorophenylamino)-2-phenylethanol (**3c**)[8b]

Solid, mp: 63–65 °C. IR ν (cm^{-1}): 3400, 3028, 2927, 2853, 1598, 1498, 1454. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.24$–7.39 (m, 5H), 7.04 (m,

2H), 6.47 (m, 2H), 4.65 (d, $J = 6.12$ Hz, 1H), 4.43 (dd, $J = 4.07$, 6.91 Hz, 1H), 3.92 (m, 1H), 3.70 (m, 1H), 2.41 (br s, 1H, OH). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 145.68$, 139.51, 128.83, 128.73, 127.60, 126.54, 122.20, 114.78, 67.05, 59.76.

2-(3-Chlorophenylamino)-2-phenylethanol (**3d**)[13o]

Solid, mp: 53–54 °C. IR ν (cm^{-1}): 3404, 3028, 2930, 2877, 1596, 1493. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$–7.38 (m, 5H), 7.03 (m, 1H), 6.70 (m, 1H), 6.58 (t, $J = 2.08$, 4.16 Hz, 1H), 6.46 (m, 1H), 4.72 (d, $J = 5.12$ Hz, 1H), 4.46 (m, 1H), 3.89 (m, 1H), 3.72 (m, 1H), 2.42 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.32$, 139.39, 134.66, 130.06, 128.77, 127.65, 126.54, 117.55, 113.43, 111.82, 66.98, 59.45.

2-(2-Nitrophenylamino)-2-phenylethanol (**3e**)[7f]

Oil. IR ν (cm^{-1}): 3372, 3030, 2930, 2826, 1616, 1507, 1448. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.20$ (m, 1H), 6.62–6.67 (m, 2H), 4.74 (dd, $J = 6.15$, 10.53 Hz, 1H), 3.92–4.15 (m, 2H). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 144.57$, 138.64, 136.02, 132.48, 129.03, 128.67, 128.03, 126.55, 115.88, 115.08, 66.99, 59.18.

2-(2-Methoxyphenylamino)-2-phenylethanol (**3f**)[8b]

Oil. IR ν (cm^{-1}): 3396, 3053, 2926, 1598, 1502, 1450. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.26$–7.40 (m, 5H), 6.69–6.83 (m, 3H), 6.43 (d, $J = 7.48$ Hz, 1H), 5.07 (d, $J = 5.47$ Hz, 1H), 4.53 (d, $J = 4.41$ Hz, 1H), 3.74–3.98 (m, 5H). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 147.00$, 140.14, 136.87, 128.63, 126.60, 120.98, 116.97, 111.36, 109.27, 67.31, 59.65, 55.31.

2-(Naphthalen-1-ylamino)-2-phenylethanol (**3g**)[13m]

Solid, mp: 130–132 °C. IR ν (cm^{-1}): 3421, 3305, 3055, 2924, 2863, 1580, 1525, 1477. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.22$–8.11 (m, 11H), 6.41 (dd, $J = 1.02$, 1.05 Hz, 1H), 5.38 (br s, 1H, NH), 4.66 (dd, $J = 4.06$, 7.03 Hz, 1H), 4.05 (dd, $J = 4.05$, 11.14 Hz, 1H), 3.87 (dd, $J = 7.09$, 12.13 Hz, 1H), δ 2.09 (br s, 1H, OH). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 142.10$, 139.75, 134.19, 128.71, 128.40, 128.16, 127.86, 126.60, 125.71, 124.83, 123.72, 120.00, 117.77, 106.49, 67.43, 59.78.

2-(Methyl(phenyl)amino)-2-phenylethanol (**3h**)[13n]

Oil. IR ν (cm^{-1}): 3404, 3028, 2884, 2816, 1598, 1500, 1452, 1378. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.26$–7.45 (m, 7H), 6.48 (m, 3H), 5.01 (dd, $J = 4.62$, 8.31 Hz, 1H), 3.48 (m, 2H), 2.95 (s, 3H), 2.56 (s, 1H). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 149.92$, 141.89, 129.25, 128.53, 127.83, 125.89, 117.49, 113.21, 71.69, 62.03, 39.37.

2-(Diphenylamino)-2-phenylethanol (**3i**)

Oil. IR ν (cm^{-1}): 3400, 3052, 2932, 2873, 1600, 1507, 1456. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.21$–7.31 (m, 9H), 6.95–7.02 (m, 6H), 5.39 (dd, $J = 6.00$, 2.25 Hz, 1H), 4.03–4.10 (m, 2H), 1.71 (dd, $J = 5.25$, 2.13 Hz, 1H). ^{13}C MNR (75 MHz, $CDCl_3$): $\delta = 146.71$, 139.14, 129.22, 129.12, 128.56, 127.56, 127.50, 123.08, 122.27, 64.38, 62.73. Anal. Calcd. for $C_{20}H_{19}NO$: C, 83.01; H, 6.62. Found: C, 82.81; H, 6.47.

2-(4-Chlorophenyl)-2-(phenylamino)ethanol (**5a**)[8g]

Oil. IR ν (cm^{-1}): 3400, 3052, 2931, 2874, 1601, 1498. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.31$ (m, 4H), 7.12 (dd, $J = 7.44$, 8.43 Hz, 2H), 6.71 (m,1H), 6.54 (d, $J = 7.68$ Hz, 2H), 4.53 (s, 1H), 4.46 (m, 1H), 3.89 (d, $J = 2.64$ Hz, 1H), 3.71 (m, 1H), 1.91 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 146.88$, 138.67, 133.23, 129.16, 128.94, 128.08, 118.07, 113.80, 67.11, 59.26.

1-(Phenylamino)propan-2-ol (**6b**)[13l]

Oil. IR ν (cm^{-1}): 3396, 2926, 2854, 1602, 1500, 1453. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.17$–7.26 (m, 2H), 6.74 (t, $J = 7.32$ Hz, 1H), 6.66 (m, 3H), 3.96–4.06 (m, 1H), 3.22 (dd, $J = 3.33$, 12.93 Hz, 1H), 2.98 (dd, $J = 8.55$, 12.93 Hz, 1H), 2.35 (br s, 1H), 1.25 (d, $J = 6.27$ Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.12$, 129.30, 117.89, 113.77, 66.29, 50.57, 20.73.

2-Azido-2-(4-bromophenyl)ethanol (**6c**)[8b]

Oil. IR ν (cm^{-1}): 3407, 3026, 2923, 2853, 1572, 1496. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.12$–7.27 (m, 2H), 6.78 (m, 1H), 6.69 (m, 2H), 4.06 (dd, $J = 5.99$, 7.22 Hz, 1H), 3.59–3.70 (m, 2H), 3.38 (dd, $J = 4.37$, 13.27 Hz, 1H), 3.23 (dd, $J = 7.27$, 13.30 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.64$, 129.40, 117.98, 113.24, 69.35, 57.94, 47.53.

1-(Benzyloxy)-3-(phenylamino)propan-2-ol (**6d**)[13n]

Oil. IR ν (cm^{-1}): 3396, 3027, 2861, 1603, 1504, 1456, 1095. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.33–7.43$ (m, 5H), 7.21 (m, 2H), 6.76 (m, 1H), 6.65 (d, $J = 8.25$ Hz, 2H), 4.60 (s, 2H), 4.08 (d, $J = 3.09$ Hz, 2H), 3.54–3.66 (m, 2H), 3.32 (dd, $J = 4.32$, 12.78 Hz, 1H), 3.19 (dd, $J = 7.14$, 12.78 Hz, 1H), 2.64 (br s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.14$, 137.69, 129.23, 128.50, 127.90, 127.80, 117.74, 113.12, 73.49, 72.33, 69.04, 46.58.

1-Azido-3-phenoxypropan-2-ol (**6e**)[8b]

Solid, mp: 58–60 °C. IR ν (cm^{-1}): 3398, 3050, 2925, 1598, 1498, 1241. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.68–7.36$ (m, 10H), 4.25 (dd, $J = 10.56$, 17.01 Hz, 1H), 4.06 (m, 2H), 3.44 (dd, $J = 4.29$, 12.96 Hz, 1H), 3.29 (dd, $J = 7.17$, 12.96 Hz, 1H), 2.79 (s, 1H, OH). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.28$, 147.97, 129.53, 129.28, 121.24, 117.97, 114.43, 113.21, 69.88, 68.68, 46.48.

1-(Phenylamino)octan-2-ol (**6f**)[13m]

Solid, mp: 46–47 °C. IR ν (cm^{-1}): 3268, 2926, 2854, 1604, 1502, 1457. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.16–7.28$ (m, 2H), 6.74 (m, 1H), 6.69 (m, 2H), 4.02 (s, 1H), 3.85 (s, 1H), 3.29 (dd, $J = 3.12$, 12.84 Hz, 1H), 3.02 (m, 1H), 1.33–1.56 (m, 10H), 2.00 (s, 1H), 0.92 (t, $J = 6.51$, 6.90 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 148.25$, 129.27, 117.84, 113.22, 70.35, 50.26, 35.07, 31.76, 29.31, 25.58, 22.59, 14.08.

Anti-2-(phenylamino)cyclohexanol (**6g**)[13l]

Solid, mp: 57–59 °C. IR ν (cm^{-1}): 3392, 3025, 2925, 2852, 1601, 1500, 1446. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.18–7.24$ (m, 2H), 6.72–6.80 (m, 3H), 3.25 (m, 2H), 3.18 (m, 1H), 3.11 (br s, 1H, OH), 2.13 (d, $J = 12.04$ Hz, 2H), 1.71–1.81 (m, 2H), 1.29–1.44 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 147.73$, 129.21, 118.13, 114.93, 74.30, 59.90, 33.06, 31.44, 24.86, 24.16.

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