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Regioselective ring-opening of epoxides with amines using $Zn(ClO_4)_2$–Al_2O_3 as a heterogeneous and recyclable catalyst

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Abstract

A simple and efficient method has been developed for the synthesis of β-amino alcohols by regioselective ring-opening of epoxides with amines in the presence of zinc perchlorate–neutral alumina as a heterogeneous recyclable catalyst at room temperature in high yields.

Keywords: Epoxides; Amines; Zinc perchlorate–neutral alumina; β-Amino alcohols

1. Introduction

Regioselective ring-opening of epoxides with amines is an important reaction for synthetic organic and medicinal chemists as the resultant β-amino alcohols represent a wide range of β-adrenergic blockers and used in the management of cardiovascular disorders.[1] The versatility of this transformation is recognized well as it constitutes the key step for the synthesis of β_2-adrenoceptor agonists,[2] anti HIV agents,[3] glycosidase inhibitor,[4] 4-demethoxydaunomycine,[5] antimalarial agents,[6] liposidomycin B class of antibiotics,[7] taxoid side chain,[8] protein kinase C inhibitor balanol[9] and naturally occurring brassinosteroids,[10] a vast range of biologically active natural and synthetic products,[11] unnatural amino acids[12] and chiral auxiliaries for asymmetric synthesis.[13] The classical synthesis of β-amino alcohols involves the heating of epoxide with an excess of amines at elevated temperature.[14] Recently, various methods have been reported using metal amides,[15] metal salts,[16] metal alkoxides,[17] metal triflates[18] and metal halides.[19] Some heterogeneous catalysts such as zirconium sulfophenyl phosphonate,[20] clays,[21] polymer supported copper sulfate,[22] ionic liquids[23] and rare earth metals[24] have been utilized. However, there are some limitations such as longer reaction times, and use of expensive reagents in stoichiometric quantities and hazardous organic solvents and poor regioselectivity. Zinc perchlorate $Zn(ClO_4)_2$ belongs to the class of Lewis acids. The catalyst using zinc perchlorate supported on neutral alumina and a related solid acid catalyzed reaction was the field of growing interest. The acidic or neutral solid substances like silica gel, alumina, ion exchange resin and active carbon are suitable supports and the more commonly being used one is neutral alumina for various organic transformations.[25]

2. Results and discussion

In this Letter, we have described a mild and efficient method for the nucleophilic ring-opening of epoxides with amines in the presence of heterogeneous catalyst zinc perchlorate–neutral alumina to afford the corresponding β-amino alcohols in excellent yields. It was observed in the absence of catalyst, the reaction did not proceed in dichloromethane even after prolonged reaction times (Scheme 1). In the presence of zinc perchlorate $Zn(ClO_4)_2$

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Scheme 1.

without using alumina only trace amount of product was obtained even after 2 h.

Using the optimized reaction condition, styrene oxide underwent reaction with aryl amines, in the presence of zinc perchlorate–neutral alumina, at room temperature to afford the corresponding β-amino alcohols in excellent yields with high regioselectivity. The epoxide opening takes place in a regioselective manner with preferential nucleophilic attack at the benzylic position. This success encouraged us to examine the generality of this reaction with various epoxides and amines and the results are summarized in Table 1. Interestingly, aliphatic amines on treatment with styrene oxide formed the product by cleavage at the terminal position. Thus, aryl amines, being less nucleophilic react preferentially at the benzylic carbon of styrene oxide, whereas in the case of aliphatic amines, the preferential attack of the amine occurs at the terminal carbon of styrene oxide, because of the increased nucleophilicity favouring the S_N2 process.[26] The cyclic aliphatic amines such as morpholine and pyrrolidine reacted with styrene oxide to afford the corresponding β-amino alcohols in excellent yields (Table 1, entries e and f). We have clearly observed the ^{1}H NMR spectra of crude products showing the formation of only one regioisomer in each case and no other product could be detected.

The ring-opening of cyclohexene oxide was treated with various amines such as aromatic, benzylic and aliphatic amines to afford the corresponding amino alcohols in high yields. In the ^{1}H NMR spectra of the products, the coupling constants of the ring protons adjacent to the –NHR and –OH groups provided the evidence for this stereochemical assignment. For example, the *J* values of these two protons for **3g** are 3.5, 10.0 and 10.0 Hz and 4.0, 10.0 and 10.5 Hz, suggesting the trans-configuration of the compound (Scheme 2).

The glycidyl ethers also reacted smoothly with aromatic, benzylic and aliphatic amines to afford the corresponding β-amino alcohols in excellent yields with high regioselectivity. The reaction did not proceed under solvent-free conditions even after prolonged reaction times (Scheme 3).

In the glycidyl ethers reactions, the main product was β-amino alcohols, where the nucleophile strongly favoured attack at the less hindered carbon atom of the epoxide ring. Presumably, this is because the zinc perchlorate–neutral alumina formed a chelate structure with the oxygen atoms of the glycidyl ether. This is also probably due to the decreased Lewis acidic effect that the metal would usually have on the internal carbon atom, allowing steric effects to play a more dominant role. Therefore the nucleophile attacked at the less hindered carbon atom and the β-amino alcohols were formed.

However, simple acyclic aliphatic amines such as pentyl amine and hexyl amine did not give any satisfactory yields less than 20% in the reaction of aliphatic epoxide of propylene oxide (Scheme 4).

The regioselective outcome can be explained by the steric and electronic factors associated with the epoxide and the amine. In general, the alkyl amines are harder bases than the aromatic amines and therefore more efficiently compete with the epoxides for the catalyst. According to the Pearson theory (hard–soft acid–base theory), ethers are considered hard bases, as alkyl amines. In contrast, aryl amines are considered as borderline cases. This being the case, the harder amines will tend to retard the rate of the reaction, in line with our observations and concomitantly requires slightly elevated levels of catalyst to observe similar rates and conversions. The lack of reactivity of aliphatic amines towards aminolysis of epoxides has been reported due to the stronger complexation with the catalyst as a consequence of their higher basicity.

In general, the methodology worked well independently on the nature of the epoxide, furnishing the corresponding β-amino alcohols in high yields. The catalyst system of zinc perchlorate–neutral alumina was conveniently separated from the reaction mixture by simple filtration. The catalyst was recovered, activated and reused for two consecutive times with only slight variation in the yields of the corresponding products. It is clear from Table 2 that the activity and selectivity are retained during the two recycling steps.

3. Conclusion

We have demonstrated a mild and efficient method for the preparation of β-amino alcohols by the ring-opening of epoxides with amines using zinc perchlorate–neutral alumina at room temperature. The present method is associated with several advantages such as application of a heterogeneous catalyst, operational simplicity, short reaction times, reduction of by-products, high yields and excellent regioselectivity are the notable advantages of this protocol.

4. Experimental

4.1. The preparation of $Zn(ClO_4)_2$–Al_2O_3

Ten grams of neutral alumina (BIO-RAD, Brockman activity, grade I, 2–44 μm) was impregnated with 11.4 g of $Zn(ClO_4)_2{\cdot}6H_2O$ (Aldrich) dissolved in 10 g of distilled water, and the mixture was stirred at room temperature and the precatalyst was then dried for 16 h at 120 °C, and then calcined for 4 h at 250 °C under air. The resulting powdered catalyst was stored under argon for future use.

General procedure for the synthesis of β-amino alcohols: To a solution of an epoxide (1 mmol) in dichloromethane (5 mL), amine (1 mmol) and zinc perchlorate–neutral

Table 1
Zinc perchlorate–Al_2O_3 catalyzed ring-opening of epoxides with amines

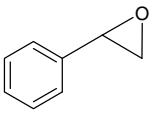
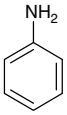
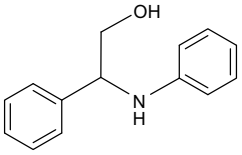
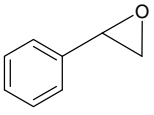
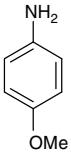
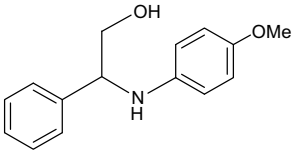
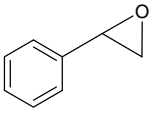
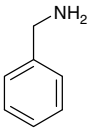
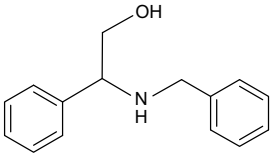
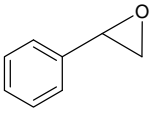
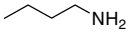
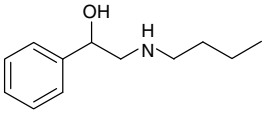
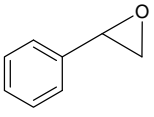
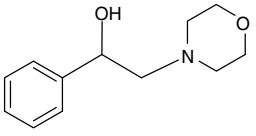
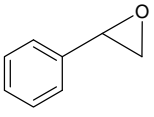
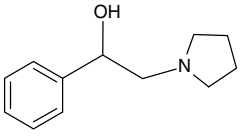
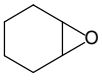
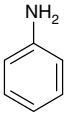
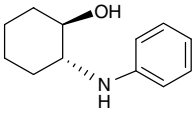
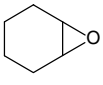
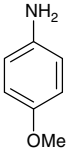
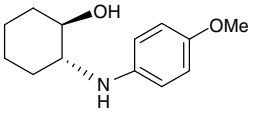
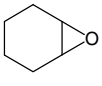
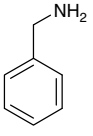
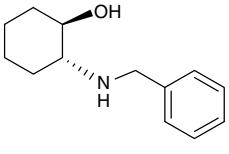
Entry	Epoxide **1**	Amine **2**	Product **3**	Time (h)	Yield (%)
a				1.0	95
b				1.5	92
c				2.0	90
d				2.5	89
e				3.5	94
f				3.5	91
g				1.5	93
h				2.0	91
i				2.5	89

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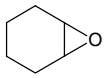
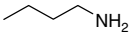
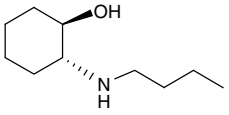
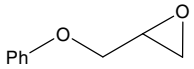
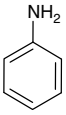
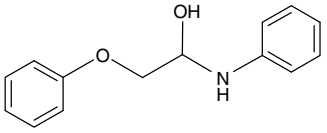
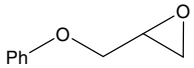
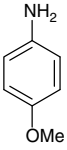
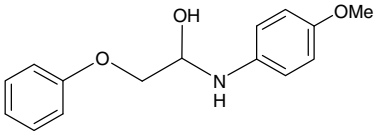
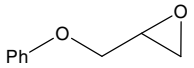
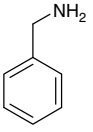
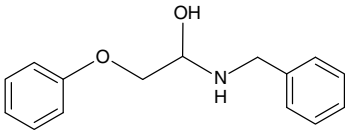
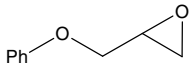
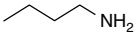
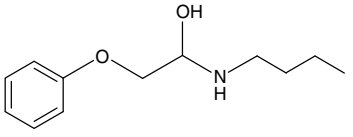
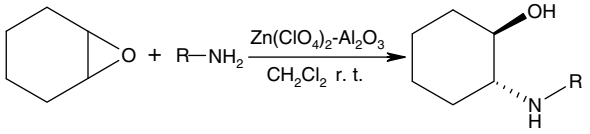
Table 1 (*continued*)

Entry	Epoxide **1**	Amine **2**	Product **3**	Time (h)	Yield (%)
j				3.0	87
k				1.5	90
l				2.0	91
m				2.5	88
n				3.0	85

The structures of the products were established from their spectral (^{1}H NMR and MS) data.



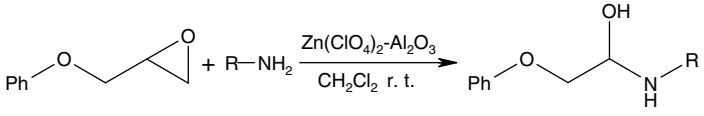
Scheme 2.

alumina [10 mol % (37 mg)] were added. The reaction mixture was stirred at room temperature and reaction was monitored by TLC. The resulting mixture was filtered and then washed with dichloromethane (2 × 5 mL). The filtrate was concentrated under vacuo and the products were purified by silica gel column chromatography eluted by an EtOAc and hexane to afford the corresponding pure β-amino alcohols in excellent yields.

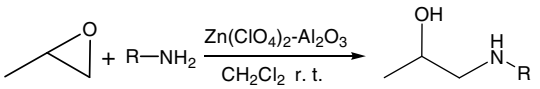
The spectral (IR, ^{1}H NMR and MS) data of the β-amino alcohols (Table 1) are given below.

Compound **3a**: IR (KBr): ν_{max} 3341, 3267, 3047, 3051, 2972, 2847, 1605, 1543, 1438, 1361, 1232, 1128, 1045, 878, 746 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.78 (dd, 1H, $J = 5.0$, 10.5 Hz), 3.90 (dd, 1H, $J = 4.0$, 10.5 Hz), 4.55 (dd, 1H, $J = 6.5$, 10.8 Hz), 6.40 (d, 2H, $J = 7.5$ Hz), 6.80 (t, 1H, $J = 7.8$ Hz), 6.95 (d, 2H, $J = 8.0$ Hz), 7.30–7.45 (m, 5H); EIMS: m/z (%): 213 (M^+), 195 (18), 185 (10), 107 (100), 91 (35), 77 (28), 57 (40).

Compound **3b**: IR (KBr): ν_{max} 3385, 3271, 3049, 2937, 2851, 1614, 1546, 1438, 1361, 1293, 1202, 1138, 1045, 1065, 878, 741 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.76 (dd, 1H, $J = 4.5$, 10.0 Hz), 3.90 (dd, 1H, $J = 4.0$, 10.0 Hz), 3.93 (s, 3H), 4.50 (dd, 1H, $J = 6.0$, 10.5 Hz), 6.45 (d, 2H, $J = 8.1$ Hz), 6.90 (d, 2H, $J = 8.0$ Hz),



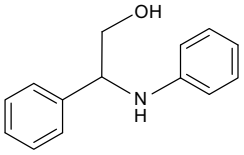
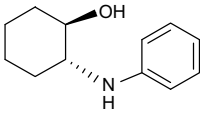
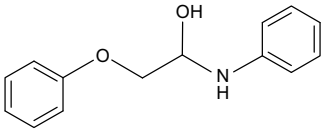
Scheme 3.



Amine	Yield (%)
Pentyl amine	18
HExyl amine	15

Scheme 4.

Table 2
Yields (%) of catalyst recycling reactions

Product	Yields (%)		
	Initial reaction	1st recycle	2nd recycle
	95	91	86
	93	89	84
	90	87	80

7.35–7.45 (m, 5H); EIMS: *m*/*z* (%): 243 (M^+), 195 (18), 185 (10), 107 (100), 91 (35), 77 (28), 57 (40).

Compound **3c**: IR (KBr): ν_{max} 3293, 3057, 2941, 2858, 1606, 1580, 1452, 1373, 1256, 1208, 1182, 1106, 1025, 859, 736 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 2.70–2.85 (m, 2H), 3.30 (br s, 2H), 3.75–3.85 (m, 2H), 4.75–4.82 (m, 1H), 7.35–7.48 (m, 10H); EIMS: *m*/*z* (%): 227 (M^+), 209 (10), 185 (10), 136 (65), 118 (25), 91 (100), 77 (22), 57 (35), 51 (18).

Compound **3d**: IR (KBr): ν_{max} 3379, 3246, 3051, 2943, 2862, 1634, 1589, 1512, 1473, 1410, 1396, 1318, 1295, 1169, 1086, 1015, 868, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.95 (t, 3H, $J = 6.5$ Hz), 1.30–1.40 (m, 2H), 1.45–1.55 (m, 2H), 2.35 (br s, 2H), 2.55–2.65 (m, 2H), 3.80–3.90 (m, 2H), 4.25 (d, 1H, $J = 6.0$ Hz), 7.30–7.45 (m, 5H); EIMS: *m*/*z* (%): 193 (M^+), 175 (28), 164 (20), 146 (42), 136 (10), 107 (15), 103 (100), 91 (35), 78 (22), 53 (35).

Compound **3g**: IR (KBr): ν_{max} 3352, 3295, 3068, 2935, 2857, 1604, 1543, 1502, 1498, 1450, 1430, 1321, 1243, 1156, 1102, 1031, 1008, 976, 891, 743 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.02–1.43 (m, 4H), 1.50 (br s, 1H), 1.70–1.75 (m, 2H), 2.12–2.18 (m, 2H), 3.05 (br s, 1H), 3.15 (ddd, 1H, $J = 3.5$, 10.0, 10.0 Hz), 3.40 (ddd, 1H, $J = 4.0$, 10.0, 10.5 Hz), 6.65–7.10 (m, 5H); EIMS: *m*/*z* (%): 191 (M^+), 173 (10), 147 (10), 131 (15), 117 (20), 105 (12), 92 (20), 81 (100), 77 (31), 52 (41), 41 (18).

Compound **3h**: IR (KBr): ν_{max} 3361, 3274, 3052, 2943, 2851, 1608, 1569, 1506, 1452, 1315, 1243, 1205, 1122, 1062, 1015, 987, 857, 743 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.08–1.30 (m, 1H), 1.38–1.48 (m, 4H), 1.75–1.83 (m, 2H), 2.20–2.30 (m, 2H), 3.20 (ddd, 1H, $J = 3.5$, 10.0, 10.0 Hz), 3.40 (ddd, 1H, $J = 4.0$, 10.0, 10.0 Hz), 3.80 (br s, 1H), 3.90 (s, 3H), 6.85 (d, 2H, $J = 7.0$ Hz), 7.30 (d, 2H, $J = 7.0$ Hz); EIMS: *m*/*z* (%): 221 (M^+), 206 (18), 190 (56), 174 (10), 114 (100), 99 (10), 92 (25), 82 (15), 77 (68), 63 (18), 51 (24), 43 (20).

Compound **3i**: IR (KBr): ν_{max} 3487, 3261, 3124, 2963, 2847, 1605, 1581, 1508, 1462, 1325, 1246, 1215, 1120, 1059, 1005, 981, 853, 736 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.06–1.28 (m, 1H), 1.35–1.45 (m, 2H), 1.73–1.82 (m, 2H), 2.21–2.30 (m, 1H), 3.24 (ddd, 1H, $J = 3.5$, 10.0, 10.0 Hz), 3.41 (ddd, 1H, $J = 4.0$, 10.0, 10.0 Hz), 3.85 (br s, 1H), 3.91 (s, 2H), 4.10 (br s 1H), 4.80 (s, 2H), 7.20–7.50 (m, 5H); EIMS: *m*/*z* (%): 205 (M^+), 187 (12), 174 (10), 114 (100), 107 (25), 99 (10), 92 (25), 82 (15), 77 (60), 63 (18), 51 (28), 43 (20).

Compound **3j**: IR (KBr): ν_{max} 3386, 3271, 2845, 1684, 1610, 1573, 1508, 1491, 1426, 1395, 1321, 1276, 1208, 1169, 1124, 1081, 1012, 993, 915, 874, 831, 786, 734 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 0.95 (t, 3H, $J = 7.0$ Hz), 0.98–1.05 (m, 2H), 1.25–1.45 (m, 8H), 1.72–1.76 (m, 2H), 2.20–2.40 (m, 1H), 2.50–2.60 (m, 1H), 2.80 (ddd, 1H, $J = 11.5$, 9.0, 3.0 Hz), 3.20 (ddd, 1H, $J = 11.5$, 9.0, 3.0 Hz), 4.05 (br s, 2H); EIMS: *m*/*z* (%): 171 (M^+), 153 (10), 142 (15), 114 (10), 99 (100), 69 (12), 56 (45), 43 (20).

Compound **3k**: IR (KBr): ν_{max} 3392, 3261, 3057, 2926, 2871, 1612, 1542, 1505, 1495, 1456, 1356, 1312, 1296, 1245, 1110, 1079, 1015, 972, 841, 743 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 3.22–3.26 (m, 1H), 3.38–3.42 (m, 1H), 3.60–3.65 (m, 2H), 3.98–4.05 (m, 2H), 4.25 (br s, 1H), 6.64–6.68 (m, 2H), 6.70–6.75 (m, 2H), 6.88–6.91 (m, 2H), 7.05–7.25 (m, 2H); EIMS: *m*/*z* (%): 229 (M^+), 195 (10), 166 (42), 133 (28), 106 (61), 94 (100), 77 (30), 65 (20), 57 (40), 51 (15).

Compound **3l**: IR (KBr): ν_{max} 3260, 3054, 2939, 2865, 1638, 1605, 1596, 1508, 1495, 1446, 1352, 1302, 1269, 1235, 1170, 1079, 1016, 982, 823, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 3.20–3.28 (m, 1H), 3.35–3.45 (m, 1H), 3.63 (br s, 2H), 3.79 (s, 3H), 4.05–4.10 (m, 2H), 4.28 (br s, 1H), 6.70 (d, 2H, $J = 8.5$ Hz), 6.85 (d, 2H, $J = 8.5$ Hz), 6.90–7.10 (m, 3H); EIMS: *m*/*z* (%): 259 (M^+), 258 (10), 242 (35), 195 (10), 166 (23), 137 (36), 107 (41), 93 (40), 91 (68), 77 (22), 65 (20), 57 (40), 51 (25).

Compound **3m**: IR (KBr): ν_{max} 3305, 3272, 3061, 2953, 2846, 1632, 1598, 1583, 1510, 1490, 1453, 1368, 1305, 1246, 1215, 1126, 1078, 1012, 983, 869, 751 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 2.75–2.85 (m, 1H), 2.95 (br s, 1H), 3.80 (d, 2H, $J = 2.0$ Hz), 3.95 (d, 2H, $J = 5.0$ Hz), 4.05–4.15 (m, 1H), 6.85–6.95 (m, 3H), 7.30–7.40 (m, 7H);

EIMS: *m/z* (%): 243 (M^+), 180 (100), 160 (34), 142 (20), 117 (56), 91 (42), 88 (10), 77 (62), 65 (20), 57 (28), 51 (10).

Compound **3n**: IR (KBr): ν_{max} 3312, 3256, 3072, 2967, 2853, 1605, 1586, 1508, 1492, 1446, 1358, 1315, 1296, 1241, 1173, 1109, 1085, 1035, 1026, 986, 873, 749 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz): δ 1.05 (t, 3H, $J = 6.0$ Hz), 1.85–1.95 (m, 4H), 2.70–2.90 (m, 4H), 3.90 (s, 2H), 4.01–4.05 (m, 1H), 6.80–6.90 (m, 3H), 7.25–7.35 (m, 2H); EIMS: *m/z* (%): 209 (M^+), 194 (10), 166 (15), 146 (20), 137 (18), 130 (100), 93 (42), 91 (42), 88 (10), 77 (25), 74 (10), 65 (20), 57 (28), 51 (18).

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