Synthesis of β-Amino Alcohols from Aromatic Amines and Alkylene Carbonates Using Na-Y Zeolite Catalyst

Anandkumar B. Shivarkar, Sunil P. Gupte,*[a] Raghunath V. Chaudhari*[b]

Homogeneous Catalysis Division, National Chemical Laboratory, Pune-411008, India
Fax +91(20)25902621; E-mail: sp.gupte@ncl.res.in; E-mail: rv.chaudhari@ncl.res.in

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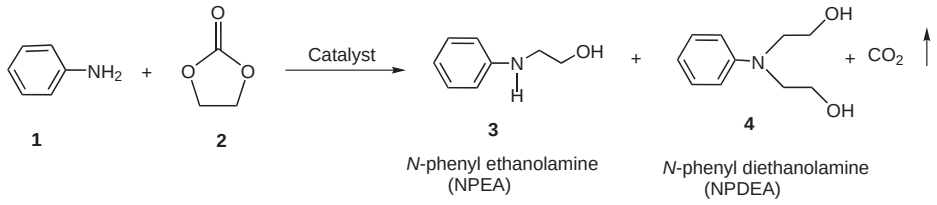
Abstract: A simple, efficient, and environmentally benign methodology for the synthesis of β-amino alcohols from aromatic amines and alkylene carbonates in the presence of the highly active and reusable solid base catalyst Na-Y zeolite is demonstrated.

Key words: alkylation, amine, amino alcohols, alkylene carbonate, zeolite

The synthesis of β-amino alcohols by N-alkylation of aromatic amines using alkylene carbonates is attractive due to the non-hazardous nature of alkylene carbonates. The major drawback of conventional methodology is that it involves handling of potentially hazardous epoxides[1] and the reaction is usually non-facile when poorly nucleophilic amines, such as anilines, are used.[2] In order to overcome the problem of the poor reactivity of anilines, catalysts are necessary;[2] however, these catalysts are often corrosive and costly.[3] In contrast, the alkylation employing an alkylene carbonate is easy to handle and does not require the high-pressure equipment often necessary when working with highly volatile epoxides (especially when working with ethylene oxide).[4] β-Amino alcohols are extensively used in medicinal chemistry in the preparation of biologically active natural and synthetic products, as artificial amino acids, and as chiral auxiliaries for asymmetric synthesis.[5] They are also useful as intermediates in the synthesis of perfumes,[6] hair dyes, and photo developers,[4a] while oxazolidones[7] are useful in the field of biology.

Although, N-alkylation and alkoxy carbonylation of amines by dimethyl carbonate to an *N*-alkyl amine and carbamate, respectively, is well known;[8,9] the extension of this methodology to the preparation of β-amino alcohols is not well investigated.[10] Aromatic amines are reported to react with alkylene carbonate in the presence of LiCl as a catalyst to give oxazolidones as the major product, along with β-amino alcohols.[11] Kaye et al. reported the synthesis of *N*-methyl-*N*-phenylethanolamine from *N*-methylaniline and ethylene carbonate using a corrosive and flammable homogeneous lithium amide catalyst.[12] It has been reported that reaction between an amine and alkylene carbonate gives polymeric products possessing carbamate and carbonate functionality.[13–15] The patent literature on this reaction revealed that the use of solid base catalysts such as mixed metal oxides and hydrotalcite could be effective.[16] However, these catalysts show poor activity and are not attractive from a synthetic viewpoint. Thus, there is scope to develop an efficient method for the synthesis of β-amino alcohols. To the best of our knowledge, the detailed information on this simple but useful reaction to give β-amino alcohols is not available in the literature. As a part of our ongoing program to develop green chemistry processes, we are exploring new protocols to replace toxic and hazardous reagents e.g. epoxides with alkylene carbonates, a benign reagent, to generate versatile organic molecules using heterogeneous catalysts. Interest in the use of solid base catalysts for organic synthesis is increasing because these catalysts are safe to handle, non-corrosive, low cost, have a long shelf life, and are commercially available. In this context zeolites are promising due to their microporous, aluminosilicate structure with a highly ordered crystalline nature. The combination of acid and base properties and shape selectivity in the zeolite catalyst is an important factor for the synthesis of fine chemicals; faujasites are often the preferred catalysts for various types of reactions like alkylation, isomerization, polymerization, cyclization, nitrile hydrolysis, photo-reduction, nitration of aromatic compounds etc.[17]



Scheme 1

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In the present work, we wish to report a simple methodology for the synthesis of β-amino alcohols in high yields from aromatic amines and alkylene carbonate in the presence of highly active, selective and recyclable Na-Y zeolite as a solid base catalyst (Scheme 1).

Before attempting detailed catalytic screening, a non-catalytic reaction between aniline and ethylene carbonate was examined and it was observed that under the experimental conditions, *N*-phenylethanolamine (NPEA) was produced in less than 5% yield, indicating that the reaction is quite slow and has no practical utility in the absence of a catalyst (Table 1, entry1). Soluble catalyst, tetraethyl ammonium bromide (TEAB) was examined for catalytic activity; however, NPEA was not formed selectively due to further N-alkylation of NPEA leading to the formation of appreciable quantities of *N*-phenyldiethanolamine (Table 1, entry 2). Several solid base catalysts, such as metal oxides (MgO, PbO, ZnO) and hydrotalcite reported earlier in the patent literature, were examined for their activity.[16] Some other solid base catalysts like carbonates ($PbCO_3$, $CsCO_3$, $PbZrCO_3$) were also tested. These catalysts gave poor yields of β-amino alcohols indicating that they are inefficient from a practical point of view (Table 1, entry 3–9). Solid base zeolites were also examined and it was noticed that with the exception of alkali cation exchange zeolites X and Y, other zeolite-based materials showed very poor yields (Table 1, entry 11–14). Since zeolites X and Y, resulted in a significant enhancement in yields (Table 1, entries 15 and 16, yield >95%) over other catalysts for N-alkylation of aniline by ethylene carbonate due to their benign nature and excellent reusability. Further exploitation of the substrate effects was carried out using Na-Y zeolite as catalyst. Na-Y zeolite is usually considered as amphoteric[18] in nature and its intrinsic pore structure containing framework oxygen is responsible for the basic active sites, which effectively activate polar reactant molecules.[19]

The mild acidic and basic nature of Na-Y zeolite facilitates nucleophilic attack of the amine onto the methylene carbon of alkylene carbonate liberating CO_2 to give a β-amino alcohol. In order to increase the range of applicable substrates the protocol was extended to a range of amines with different functional groups. It was noticed that aliphatic amines gave predominantly carbamates (Table 2, entry 10) while aromatic amines gave β-amino alcohols, selectively. This is expected, since the carbonate has two types of electrophilic carbons, a hard carbonyl carbon and a soft methylene carbon. On the basis of HSAB theory[20] soft nucleophiles such as aromatic amines would attack the methylene carbon giving rise to alcohol derivatives, while aliphatic amines (hard nucleophiles) should prefer to attack the hard electrophilic carbonyl carbon of ethylene carbonate giving rise to carbamate products. Recently, this type of selectivity pattern has been demonstrated for the dimethyl carbonate aminolysis reaction.[21] The results are generally in agreement with the reactivity pattern expected for substituted anilines. Electron-donating substituents such as -Me, $-NH_2$ and -OMe enhance the nucleophilicity of aniline thus increasing the reactivity as well as the yield of β-amino alcohols (Table 2, entry 3–5), while electron-withdrawing substituents such as -Cl or $-NO_2$ on the aniline ring decrease the reactivity as well as the yield (Table 2, entries 7 and 8). It was observed that mono-amino alcohol reacted further to give bis-amino alcohol decreasing the yield of the mono-derivative, the formation of bis-derivative depends on concentrations of cyclic carbonate (Table 2, entry 2), mono-amino alcohol,[22] and temperature. It was also observed in the case of *p*-phenylenediamine and 3-aminophenol, the selectivity of mono-amino alcohol decreased a little due to further N- or O-alkylation of the $-NH_2$ and -OH groups present on the aromatic amines (Table 2, entries 5 and 6). It should be noted that, since the reaction is taking place within the three-dimensional space of the zeolite, which consists of channels and cages, the shape of reactants could also play a role in determining the reactivity.

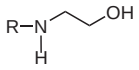
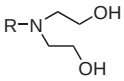
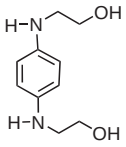
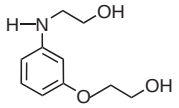
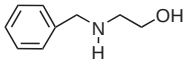
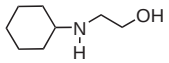
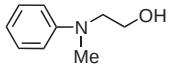
To further test the activity of the Na-Y catalyst and applicability of the method, various alkylene carbonates were subjected to N-alkylation with aniline to furnish β-amino alcohols (Table 3). Quantitative yields of the corresponding amino alcohols were obtained in the reaction of 1,2-

Table 1 Screening of Catalysts for N-Alkylation of Aniline Using Ethylene Carbonate[a]

Entry	Catalyst	Time (h)	Conversion aniline (%)[b]	Yield NP-EA (%)[b]	Yield NP-DEA (%)[b]
1	None	2	3.8	3.8	–
2	TEAB	2	82.5	68	14.5
3	PbO	2	10.7	10.7	–
4	ZnO	2	18.7	18.7	–
5	MgO	2	12.6	12.6	–
6	Mg-Al HTLC	2	10	10	–
7	$CsCO_3$	2	15.7	2	–
8	$PbZrCO_3$	2	10.8	10.8	–
9	$PbCO_3$	2	13.3	11.2	–
10	K^+ on silica	2	19.3	7.9	–
11	Na-ZSM5	2	4.3	4.3	–
12	KNO_3 on KL	2	19.2	7.8	–
13	4 Å MS	2	4.8	4.8	–
14	H-Y	2	28	28	–
15	Na-Y	0.5	100	100	–
16	Na-X	0.5	89.9	89.9	–
		2	100	95.7	4.3

[a] All reactions were carried out with aniline (0.0107 mol), ethylene carbonate (0.013 mol), triglyme (0.0155 mol), and catalyst [0.018 mol (entries 2–9) or 0.250 g (entries 10–16)] under an N_2 atmosphere.
[b] Conversion and yields were determined by GLC analysis.

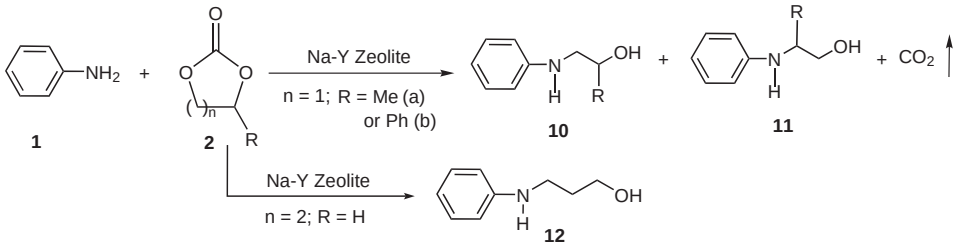
Table 2 Synthesis of β-Amino Alcohols Using Ethylene Carbonate[2,3]

Entry	Amine	Time (h)	Aniline conversion (%)	Products				Side-products (yield, %)[a,b]
					Yield (%)[a]		Yield (%)[a]	
1	aniline	0.5	100	**3a**[24]	100 (94)			
2[c]	aniline	0.5 2	100 100	**3a**	93 72 (63)	**4a**	7 28 (19)	
3	*p*-toluidine	1.5	100	**3b**	91 (86)	**4b**	9	
4	*p*-anisidine	1	100	**3c**	93 (88)	**4c**	7	
5	*p*-phenylenediamine	2	87	**3d**	80 (70)			 **8** (7)
6	*m*-aminophenol	2	100	**3e**	93 (84)			 **9** (8)
7	*p*-chloroaniline	12	100	**3f**	98 (91)	**4d**	2	
8	*p*-nitroaniline	12	61	**3g**	40 (30)			21
9	benzylamine	2	100	 **5**	40			60
10[d]	cyclohexylamine	2	100	 **6**	2			98
11	*N*-methylaniline	6	100	 **7**	100 (93)			

[a] Yields were determined by GLC based on amine conversion and isolated yields are indicated in brackets.
[b] Side products include 3-(4-nitrophenyl)oxazolidin-2-one (entry 8), 2-hydroxyethyl benzyl carbamate and 3-benzyloxazolidin-2-one (entry 9, 46% and 14% yields, respectively), and 2-hydroxyethyl cyclohexyl carbamate (entry 10). All side products were confirmed by GC-MS analysis but were not isolated.
[c] Ethylene carbonate was used as the solvent.
[d] Reaction carried out at 134 °C.

propylene carbonate, styrene carbonate and 1,3-propylene carbonate with aniline. Regioselective ring-opening reactions of unsymmetrical cyclic carbonates with amine by Na-Y catalyst were also evaluated. The corresponding amino alcohols from unsymmetrical cyclic carbonates were obtained in high yields but in the case of 1,2-propylene carbonate, the regioisomers could not be separated by column chromatography, hence the regioselectivity was determined by GC and GC-MS analysis (Table 3, entries 1 and 2). As expected, excellent regioselectivity in favor of nucleophilic attack at the sterically less hindered methylene carbon of carbonate was observed affording 1-(phenylamino)propan-2-ol (**10a**) from 1,2-propylene carbonate in 92% yield (Table 3, entry 1; **10a**/**11a**, 92:8) It was also observed that the regioselectivity was slightly improved by lowering the reaction temperature (Table 3, entry 2). The two regioisomers **10a** and **11a** show their characteristic ion peaks at $M^+ - 45$ due to loss of CH_3CHOH and $M^+ - 31$ due to loss of CH_2OH.[3] While, in the case of styrene carbonate, the reverse regioselectivity was observed, **10b** and **11b** were formed in a 9:91 ratio (Table 3, entry 3). The regioisomers in this case were isolated in pure form by flash chromatography. Selective formation of the regioisomeric product 2-phenylamino-2-phenylethanol (**11b**) was observed due to the preferred attack of the aniline nucleophile on the benzylic carbon of styrene carbonate.

Table 3 Synthesis of β-Amino Alcohols Using Various Alkylene Carbonates[a]



Entry	Cyclic carbonate	Time (h)	Conversion (%)[b]	**10**/**11**[c]	Isolated yield (%)
1	1,2-propylene carbonate	7	100	92:8	90 (**10a**/**11a**)
2[d]	1,2-propylene carbonate	72	100	96:4	91 (**10a**/**11a**)
3	styrene carbonate	8	100	9:91	3 (**10b**), 85 (**11b**)[25]
4	1,3-propylene carbonate	8	82		71 (**12**)

[a] Experimental conditions are the same as Table 1.
[b] Yields were determined by GLC based on amine conversion.
[c] Ratio of regioisomers was determined by GLC.
[d] Reaction was carried out at 95 °C in toluene.

An excellent yield of 3-(phenylamino)propan-1-ol was realized from 1,3-propylene carbonate (Table 3, entry 4). We also found that ethylene carbonate showed the highest reactivity among the alkylene carbonates screened and the order of reactivity obtained was R = H > Me > Ph which is consistent with that reported earlier.[10]

In summary, a simple but efficient and environmentally benign methodology for the synthesis of β-amino alcohols from aromatic amines and cyclic carbonates using highly active and reusable solid base Na-Y catalyst has been demonstrated. It has also been shown that alkylene carbonates have excellent reactivity and at the same time they are non-toxic and safer to work with and can effectively replace the use of epoxides in the synthesis β-amino alcohols.

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(22) The reaction of *p*-toluidine ethylene carbonate and triglyme (solvent) using Na-Y catalyst was carried out at 140 °C for 12 h. The product distribution and progress of the reaction were monitored by withdrawing samples. It was observed that even at lower temperature bis-amino alcohol formation

was seen after 70% formation of mono-amino alcohol. It shows that bis-amino alcohol formation is also dependant on the concentration of mono-amino alcohol.

(23) **Typical Procedure** The reaction was conducted in a 50-mL round-bottom flask under a nitrogen atmosphere. Aniline (0.0107 mol), cyclic carbonate (0.013 mol), triglyme (0.0155 mol), and Na-Y zeolite (0.250 g, activated at 500 °C for 6 h) were added. The reaction mixture was stirred at 160 °C for 0.5 h. After cooling to r.t., the reaction mixture was filtered to separate the catalyst and the reaction mass (filtrate) was quantitatively analyzed by GC. Then H_2O (15–20 mL) was added and extracted with Et_2O (3 × 20 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (4 g RediSep column normal phase silica, hexane–EtOAc). Liquid chromatography was performed using CombiFlash Companion, supplied by Teledyne ISCO, USA. *N*-Phenylethanolamine was thus isolated in pure form in 94% yield.

After completion of the reaction, the reaction mixture was filtered (sartorius-393 grade filter paper) to separate the catalyst, which was washed with acetone to remove organic impurities. Then the catalyst was calcined at 500 °C for 6 h in air. This catalyst was re-used affording **3a** in 100% yield. The catalyst was recycled five times retaining up to 99% of its original activity and selectivity.

***N*-Phenylethanolamine (3a)**[24]

IR (film): 3392 (OH, NH), 2943 (CH), 1602 (Ar-C=C), 1506 (Ar-C=C), 1323 (Ar-CN), 1058, 752 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.86 (br s, 2 H, NH, OH), 3.27 (t, *J* = 5.4 Hz, 2 H, NCH_2), 3.80 (t, *J* = 5.4 Hz, 2 H, OCH_2), 6.63–6.77 (m, 3 H, Ar-CH), 7.14–7.22 (m, 2 H, Ar-CH). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 45.99 (NCH_2), 60.97 (OCH_2), 113.20 (Ar-CH), 117.84 (Ar-CH), 129.21 (Ar-CH), 148.00 (Ar-C). GC-MS (EI, 70 eV): *m*/*z* (%) = 137 (23) $[M]^+$, 106 (100) $[C_6H_5NH{=}CH_2]^+$, 91 (2), 77 (23), 65 (3), 51 (8).

***N*-Phenyldiethanolamine (4a)**

IR (film): 3382 (OH, NH), 2952 (CH), 1598 (Ar-C=C), 1504 (Ar-C=C), 1355 (Ar-CN), 1062, 750 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 3.49 (t, *J* = 4.9 Hz, 4 H, NCH_2), 3.75 (t, *J* = 4.9 Hz, 4 H, OCH_2), 6.63–6.75 (m, 3 H, Ar), 7.17–7.25 (m, 2 H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 55.21 (NCH_2), 60.48 (OCH_2), 112.41 (Ar-CH), 116.75 (Ar-CH), 129.20 (Ar-CH), 147.62 (Ar-C). GC-MS (EI, 70 eV): *m*/*z* (%) = 181 (16) $[M]^+$, 150 (100) $[C_6H_5N(C_2H_4OH){=}CH_2]^+$, 106 (56), 91 (7), 77 (16), 65 (1), 52 (4), 45 (7).

2-[Methyl(phenyl)amino]ethanol (7)

IR (film): 3344 (OH, NH), 2906 (CH), 1596 (Ar-C=C), 1505 (Ar-C=C), 1340 (Ar-CN), 1056, 746 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.74 (br s, 1 H, OH), 2.96 (s, 3 H, NCH_3), 3.47 (t, *J* = 5.6 Hz, 2 H, NCH_2), 3.81 (t, *J* = 5.6 Hz, 2 H, OCH_2), 6.72–6.83 (m, 3 H, Ar), 7.21–7.29 (m, 2 H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 38.68 (NCH_3), 55.32 (NCH_2), 59.90 (OCH_2), 112.93 (Ar-CH), 117.07 (Ar-CH), 129.11 (Ar-CH), 149.94 (Ar-C). GC-MS (EI, 70 eV): *m*/*z* (%) = 151 (17) $[M]^+$, 120 (100) $[C_6H_5N(CH_3){=}CH_2]^+$, 105(11), 91 (5), 77 (15), 65(1), 51 (5).

2-Phenylamino-1-phenylethanol (10b)

IR ($CHCl_3$): 3610 (OH), 3433 (NH), 2927 (CH), 1604 (Ar-C=C), 1505 (Ar-C=C), 1316 (Ar-CN), 1060, 790 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.61 (br s, 2 H, NH, OH), 3.32 (dd, *J* = 8.5, 13.1 Hz, 1 H, NCH_2), 3.48 (dd, *J* = 4.0, 13.1 Hz, 1 H, NCH_2), 4.96 (dd, *J* = 4.0, 8.5 Hz, 1 H, OCH), 6.68 (d, *J* = 7.6 Hz, 2 H, Ar), 6.76 (t, *J* = 7.3 Hz, 1 H, Ar), 7.20 (t, *J* = 7.5 Hz, 2 H, Ar), 7.30–7.42 (m, 5 H, Ar). GC-MS (EI, 70 eV): *m*/*z* (%) = 213 (8) $[M]^+$, 194 (13), 182 (10), 165 (2), 106 (100) $[C_6H_5NH{=}CH_2]^+$, 91 (7), 77 (33), 65 (3), 51 (9).

2-Phenylamino-2-phenylethanol (11b)[3,25]

IR (film): 3396 (OH, NH), 2927 (CH), 1602 (Ar-C=C), 1504 (Ar-C=C), 1317 (Ar-CN), 1066, 750 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 2.71 (br s, 2 H, NH, OH), 3.76 (dd, *J* = 7.0, 11.1 Hz, 1 H, OCH_2), 3.96 (dd, *J* = 4.2, 11.1 Hz, 1 H, OCH_2), 4.50 (dd, *J* = 4.2, 7.0 Hz, 1 H, NCH) 6.55 (d, *J* = 7.5 Hz, 2 H, Ar), 6.88 (t, *J* = 7.3 Hz, 1 H, Ar), 7.11 (t, *J* = 7.4 Hz, 2 H, Ar), 7.30–7.36 (m, 5 H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 59.83 (NCH), 67.33 (OCH_2), 113.82 (Ar-CH), 117.86 (Ar-CH), 126.70 (Ar-CH), 127.58 (Ar-CH), 128.80 (Ar-CH), 129.13 (Ar-CH), 140.10 (Ar-C), 147.20 (Ar-C). GC-MS (EI, 70 eV): *m*/*z* (%) = 213 (7) $[M]^+$, 182 (100) $[C_6H_5NH{=}CHPh]^+$, 104 (17), 91 (4), 77 (23), 65 (2), 51(5).

3-(Phenylamino)propan-1-ol (12)

IR (film): 3381 (OH, NH), 2935 (CH), 1602 (Ar-C=C), 1506 (Ar-C=C), 1321 (Ar-CN), 1064, 752 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ = 1.87 (quin, *J* = 5.9, 6.4 Hz, 2 H, CH_2), 2.79 (br s, 2 H, NH, OH), 3.27 (t, *J* = 6.4 Hz, 2 H, NCH_2), 3.80 (t, *J* = 5.9 Hz, 2 H, OCH_2), 6.62–6.76 (m, 3 H, Ar), 7.14–7.22 (m, 2 H, Ar). ^{13}C NMR (50 MHz, $CDCl_3$): δ = 31.85 (CH_2), 41.89 (NCH_2), 61.55 (OCH_2), 113.10 (Ar-CH), 117.63 (Ar-CH), 129.22 (Ar-CH), 148.28 (Ar-C). GC-MS (EI, 70 eV): *m*/*z* (%) = 151 (27) $[M]^+$, 132 (1), 118 (2), 106 (100) $[C_6H_5NH{=}CH_2]^+$, 93 (5), 77 (15), 65 (4), 51 (4).

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