Silica Chloride Nano Particle Catalyzed Ring Opening of Epoxides by Aromatic Amines

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Silica chloride nano particle (nano SiO_2-Cl), has been found to be heterogeneous catalyst for facile, simple and mild ring opening of epoxides with aromatic amines to afford β-amino alcohols in dry CH_2Cl_2 at room temperature.

Keywords silica chloride, nano particle, epoxides, catalyzed, ring opening

Introduction

Epoxides are versatile intermediates in organic synthesis and a large variety of reagents are known for the ring opening of these compounds.[1,2] β-Amino alcohols are among the most important precursor for a wide range of biologically active natural and synthetic products,[3-5] unnatural amino acids[6,7] and chiral auxiliaries.[8] The practical route for synthesis of β-amino alcohols is direct aminolysis of epoxides in presence of surplus amine at elevated temperature. However, this methodology suffers from one or more disadvantages such as high toxicity and corrosiveness of the acids employed, moisture sensitivity of catalyst systems, high temperature, hazardous organic solvent, extended time and the use of catalyst in a stoichiometric amount or inconvenient handling procedures.[9-11] Therefore, continuous efforts have been made to develop catalyst-free metohd[12] and various catalysts such as sulfamic acid,[13] metal triflates,[14] metal alkoxides,[15] metal halides,[16] transition metal salts,[17] heteropolymolybdate or tungstate,[18] for the synthesis of β-amino alcohols. Other limitations such as low yields, failure of deactivated amines and sterically demanding aromatic amines are associated with most of the literature methods. Therefore, the introduction of new and efficient methods is still in demand. The use of heterogeneous catalysts provides a perfect solution to overcome the above limitations. In recent years, the use of reagents and catalysts on solid supports has made significant progress.[19] Nano silica gel is one of the extensively used surface material supports for different chemical transformations in organic chemistry. One of such modified nano silica is nano silica chloride (nano SiO_2-Cl), which at the first time we reported to be an efficient catalyst for the synthesis of many organic compounds such as the amorphous silica chloride.[20] Solid acid catalysts such as amberlyst-15,[21] monodispersed silica nanoparticles,[22] zeolites,[23] montmorillonite K10[24] and ionic liquids,[25] functionalized alumina or supported ferric chloride or copper sulfate, $Yb(OTf)_3$[26] and TS-1[27] have revealed great promise in this area.

We modified nano silica gel surface by using thionyl chloride, which acts as a mild and efficient catalyst, and can be a useful and cheap catalyst for the synthesis of β-amino alcohols. Our studies have shown that thionyl chloride is a satisfactory chlorinating agent for nano silica and amorphous silica, if used undiluted. The extent of reaction with thionyl chloride gives values for active silanols per unit area of silica surface, comparable to other method, for determining available activities. Nano silica chloride was prepared by the readily available material and can also be easily removed from the reaction mixture.

Results and discussion

In this paper, a simple and effective catalytic route for the synthesis of β-amino alcohols under aerobic conditions is described. 30 mg of amorphous silicon dioxide, nano silicon dioxide, amorphous silica chloride and nano silica chloride, catalyzed ring opening of epoxy glycidyl phenyl ether. In order to show the applicability and efficiency of this method, our results have been compared with some of the same catalysts on the aminolysis of epoxy glycidyl phenyl ether. As you can see in Table 1, nano silica chloride is superior to the other catalysts.

The reaction of an aromatic amine with an epoxide in the presence of nano silica chloride as catalyst, leads to the formation of the corresponding β-amino alcohols 2 (Eq. 1).

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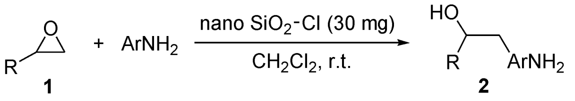
Table 1 Comparison of results for the aminolysis of epoxy glycidyl phenyl ether catalyzed by some of the silicon catalysts at the same conditions

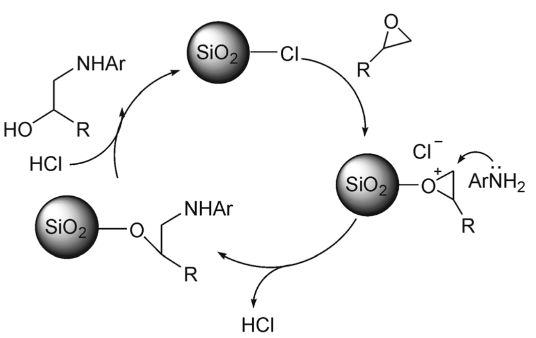
Entry	Catalyst	Time/h	Yield/%
1	Amorphous SiO_2	16	97
2	Nano SiO_2	4.15	95
3	Amorphous SiO_2-Cl	9.20	92
4	Nano SiO_2-Cl	1.55	95



(1)

The ring opening of epoxides can be explained by the mechanism presented in Scheme 1. Typically, 1.2 mmol of the amine were reacted with 1 mmol of the epoxide in dichloromethane at room temperature under the air. The nucleophilic addition is catalyzed by the presence of 30 mg of nano silica chloride which is very easy to handle. Several aromatic amines and epoxides were employed and the results are reported in Table 2. Eight aminolyses of styrene oxide even led to total conversions (Entries 1—9). At this point, it should be mentioned that no reaction was observed between aniline and styrene oxide in the absence of nano silica chloride. The reactions of aliphatic epoxides were slightly slower than those of styrene oxide. Furthermore, aliphatic epoxides such as glycidyl phenyl ether and glycidyl isopropyl ether and cyclohexene oxide (Table 2, Entries 10—36) reacted with aromatic amines to give the expected products in satisfactory yields. Sterically more hindered anilines such as *N*-methylaniline and 2,4,6-trimethylaniline led to the alcohols still in excellent yields. Electron deficient amines like 3-nitroaniline and 4-nitroaniline also led to the corresponding *β*-amino alcohol in high yields. An interesting feature of this method is that the aliphatic amines such as diethyl amine, benzylamine and cyclohexylamine failed to affect the ring opening under the same reaction conditions even after 1 d at reflux. Inspection of the TEM images of a sample catalyst from the ring opening of epoxides indicates the involvement of silica chloride nanoparticles with a size distribution of 15—35 nm (average≈20 nm) (Figure 1). A number of different solvents such as THF, Et_2O, *n*-hexane, toluene, CH_3CN and CH_2Cl_2 were also investigated and it turned out that CH_2Cl_2 was the best suited one as solvent for this purpose.

Scheme 1 Mechanism of the ring opening of epoxides



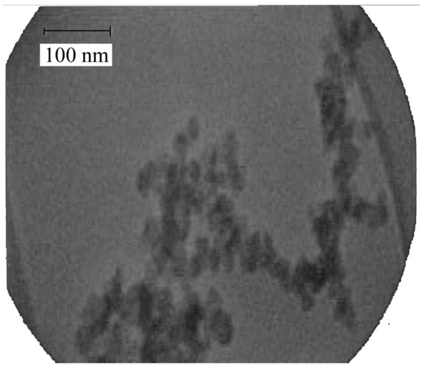


Figure 1 TEM image of silica chloride nano particle.

The nano silica chloride was recovered using simple centrifugation, filtration and readily used in subsequent reactions (1st=95%, 2nd=83%, 3rd=68% yield) and exhibited consistent catalytic activity for the ring opening of epoxides without further purification. However, owing to extensive agglomeration, the activity of the catalyst dramatically decreased after the second run. The chlorine content of the SiO_2Cl nanoparticle was also determined with the use of back-titration of the resulting HCl upon the treatment of the material with deionized water for 10 h. This value was 2.99 $mmol•g^{-1}$ for SiO_2Cl nanoparticle. SiO_2Cl nanoparticle was preheated at 180 ℃, before performing hydrolysis and titration experiments. These results clearly excluded any interference that might result from physically adsorbed HCl in the calculation of total chlorine content.

Conclusion

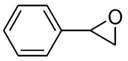
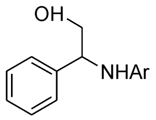
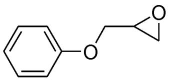
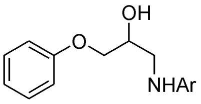
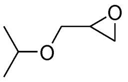
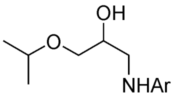
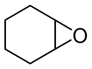
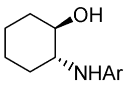
A mild, efficient and simple method for the synthesis of *β*-amino alcohols has been described using nano silica chloride as a heterogeneous catalyst. The main advantage of this method is that it requires mild reaction conditions, short reaction times, takes place at room temperature with operational simplicity and with excellent yields.

Experimental

Preparation of nano silica chloride

To an oven-dried (120 ℃) nano silica gel (5 g) in a round bottomed flask (250 mL) equipped with a condenser and a drying tube, was added thionyl chloride

Table 2 Silica chloride nano particle catalyzed ring opening of epoxides with aromatic amines produced via Eq. 1

Entry	Epoxide	ArNH$_2$	Time	Conversion (Selectivity)^{b,c}/%	Product
1		PhNH$_2$	68 min	100 (93)^{a,b,c}	
2		PhNHMe	60 min	100 (97)^{b,c}	
3		3-NO$_2$PhNH$_2$	75 min	100 (91)^{b,c}	
4		4-NO$_2$PhNH$_2$	150 min	100 (91)^{b,c}	
5		4-FPhNH$_2$	45 min	100 (86)^{b,c}	
6		4-BrPhNH$_2$	40 min	100 (93)^{b,c}	
7		4-MePhNH$_2$	20 min	100 (95)^{b,c}	
8		4-MeOPhNH$_2$	20 min	100 (93)^{b,c}	
9		2,4,6-tri-MePhNH$_2$	120 min	100 (99)^{b,c}	
10		PhNH$_2$	1.50 h	95 (90)^{a,b,c}	
11		PhNHMe	2 h	100 (93)^{b,c}	
12		3-NO$_2$PhNH$_2$	6 h	85 (79)^{b,c}	
13		4-NO$_2$PhNH$_2$	6 h	85 (90)^{b,c}	
14		4-FPhNH$_2$	5 h	100 (90)^{b,c}	
15		4-BrPhNH$_2$	5 h	95 (93)^{b,c}	
16		4-MePhNH$_2$	1 h	97 (90)^{b,c}	
17		4-MeOPhNH$_2$	1 h	98 (85)^{b,c}	
18		2,4,6-tri-MePhNH$_2$	6 h	92 (95)^{b,c}	
19		PhNH$_2$	3 h	90 (72)^{a,b,c}	
20		PhNHMe	3.10 h	80 (82)^{b,c}	
21		3-NO$_2$PhNH$_2$	9 h	53 (68)^{b,c}	
22		4-NO$_2$PhNH$_2$	9 h	68 (71)^{b,c}	
23		4-FPhNH$_2$	9 h	80 (71)^{b,c}	
24		4-BrPhNH$_2$	6.25 h	75 (71)^{b,c}	
25		4-MePhNH$_2$	2.40 h	88 (86)^{b,c}	
26		4-MeOPhNH$_2$	1.45 h	70 (65)^{b,c}	
27		2,4,6-tri-MePhNH$_2$	12 h	87 (89)^{b,c}	
28		PhNH$_2$	1.30 h	95^{a,b,d}	
29		PhNHMe	1.30 h	100^{b,d}	
30		3-NO$_2$PhNH$_2$	7 h	71^{b,d}	
31		4-NO$_2$PhNH$_2$	9 h	75^{b,d}	
32		4-FPhNH$_2$	3.50 h	85^{b,d}	
33		4-BrPhNH$_2$	4.50 h	100^{b,d}	
34		4-MePhNH$_2$	1 h	97^{b,d}	
35		4-MeOPhNH$_2$	0.50 h	98^{b}	
36		2,4,6-tri-MePhNH$_2$	2.50 h	95^{b}	

[a] Yields refer to crude product (isolated product). [b] All products were identified by comparison of their physical and spectral data with those of authentic samples. [c] Sectivity. [d] Only yield.

(toxic and should be used with caution) (100 mL) and refluxed for one week. The excess thionyl chloride was distilled off. The resulting white-grayish powder was flame-dried and stored in a tightly capped bottle.

Typical experimental procedure

To a mixture of epoxide (1 mmol) and aromatic amine (1.2 mmol) in CH_2Cl_2 (5 mL) was added nano silica chloride (30 mg) at room temperature. The mixture was stirred for a specified period (Table 2). The progress of the reaction was monitored by TLC. After complete conversion of the starting material as indicated by TLC, the reaction mixture was filtered and diluted with methylenedichloride (25 mL) and washed with water followed by brine solution. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to obtain the crude product, which was purified by column chromatography (silica gel 60—120 mesh) using ether and petroleum ether ($V:V=3:7$) to afford pure β-amino alcohol. β-Amino alcohols were characterized according to their data of ^{1}H NMR, ^{13}C NMR and mass spectra.

2-Phenylamino-2-phenyl ethanol Liquid; ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 3.75 (dd, $J=6.9$, 10.9 Hz, 1H), 3.95 (dd, $J=3.9$, 10.9 Hz, 1H), 4.45 (brs, 2H, OH, NH), 4.50 (dd, $J=6.9$, 3.9 Hz, 1H), 6.50 (d, $J=8.0$ Hz, 2H), 6.70 (t, $J=7.8$ Hz, 1H), 7.10 (t, $J=7.9$ Hz, 2H), 7.30—7.50 (m, 7H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ: 149.3, 145.5, 128.7, 128.2, 126.5, 125.8, 120.1, 114, 60.3, 57.4.

1-(Phenylamino)-3-phenoxy-2-propanol Liquid; ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 3.10 (dd, $J=7.0$, 12.5 Hz, 1H), 3.25 (dd, $J=4.0$, 12.5 Hz, 1H), 3.40—3.55 (m, 2H), 3.95—4.2 (brs, 2H, OH, NH), 6.50—6.70 (m, 4H), 7.10—7.40 (m, 6H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ: 158.2, 139.0, 129.0, 128.0, 127.8, 126.7, 120.5, 114.1, 70.1, 67.8, 51.0.

1-Isopropoxy-3-(phenylamino)-2-propanol Liquid; ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 140 (d, $J=6.5$ Hz, 6H), 3.00 (m, 1H), 3.22 (dd, $J=7.0$, 11.5 Hz, 1H), 3.25 (dd, $J=4.0$, 11.5 Hz, 1H), 3.40—3.55 (m, 2H), 3.95 (brs, 2H, OH, NH), 3.95—4.0 (m, 1H), 6.70—7.30 (m, 5H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ: 144.3, 131.5, 121.1, 113.7, 72.2, 71.5, 70.3, 53.4, 25.7.

***trans*-2-(Phenylamino)cyclohexanol** Solid; m.p. 60—62 ℃; ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 1.25—1.45 (m, 4H), 1.70—1.90 (m, 2H), 2.10—2.20 (m, 2H), 3.15 (ddd, $J=10.5$, 9.5, 4.5 Hz, 1H), 3.30 (ddd, $J=9.8$, 9.8, 4.5 Hz, 1H), 3.80 (brs, 2H, OH, NH), 6.70—6.80 (m, 2H), 7.15—7.25 (m, 3H); ^{13}C NMR ($CDCl_3$, 63 MHz) δ: 148.3, 129.8, 118.6, 114.7, 74.9, 60.5, 33.6, 32.0, 25.4, 24.7.

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