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Short communication

Regioselective nucleophilic opening of epoxides and aziridines under neutral conditions in the presence of β-cyclodextrin in water

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Abstract

A variety of β-hydroxy nitriles and β-amino alcohols have been synthesized by the regioselective ring opening of epoxides and aziridines under neutral and aqueous conditions in the presence of β-cyclodextrin in good yields.

Keywords: Epoxide; Sodium cyanide; β-Hydroxy nitrile; *N*-Tosyl aziridines; β-Amino alcohols; β-Cyclodextrin; Supramolecular catalysis; Water

1. Introduction

β-Hydroxy nitriles and β-amino alcohols are versatile intermediates in a variety of organic transformations such as bioactive compounds, unnatural amino acids, β-blockers and chiral auxiliaries [1–7]. The nitrile group is a precursor to both amino alcohols and carbonyl compounds [8,9]. Direct synthesis of β-hydroxy nitriles consist of ring opening of epoxides with cyanide with various reagents such as acetone cyanohydrin under basic conditions [10], LiCN–acetone complex [11], LiCN [12], HCN-$AlEt_3$ [13], KCN/Bu_4NI, KCN/18-Crown-6 [14], KCN/methanol [15], KCN/$LiClO_4$, KCN/$MgClO_4$, KCN/NH_4Cl [16], NaCN/12-Crown-4 [17], NaCN/Ce $(OTf)_4$ [18], Ln $(O^iPr)_3$/acetone/cyanohydrin [19], trimethylsilylcyanide (TMSCN) catalyzed by titaniumalkoxide-Schiff-base complexes [20], TMSCN/Yb $(CN)_3$ [21], etc. Addition of TMSCN to epoxides leads either to β-hydroxy nitriles or isonitriles, depending on the type of catalyst and on the reaction conditions [22]. Even in the case of the reaction of NaCN, KCN or HCN with epoxides it usually requires protic solvents and additives and results in the formation of mixtures of regioisomers [16,18,23]. Thus various drawbacks associated with these methodologies are: severe reaction conditions in certain cases, commercial non-availability of some reagents, hygroscopic nature of catalysts, refluxing temperatures, anhydrous organic solvents, expensive and hazardous reagents, non-recyclable catalysts, volatile and toxic nature of HCN.

In the case of β-amino alcohols, hydrolysis of aziridines is the most straightforward synthetic procedure but only few methods were reported which involve lewis acids/strong bases [24–31], metal salts [32–38] and Bu_4NHSO_4 [39]. These reagents have various disadvantages such as hygroscopic nature of catalysts, anhydrous organic solvents, reflux temperatures, expensive and hazardous reagents, longer reaction times, formation of isomers, etc.

To over come these limitations we have developed new methodologies to synthesize β-hydroxy nitriles and β-amino alcohols in water under neutral conditions in the presence of a recyclable catalyst β-cyclodextrin.

The water-based reactions are mild, practically easy to handle, economic and environ friendly. β-Cyclodextrin was chosen, as a catalyst since it is inexpensive, easily accessible and can be recycled. Cyclodextrins are cyclic oligosaccharides possessing hydrophobic cavities, which bind substrates selectively and catalyze chemical reactions with high selectivity. They catalyze chemical reactions by supramolecular catalysis involving reversible formation of host–guest complexes by non-covalent bonding as seen in enzymes. Complexation depends on the size, shape and hydrophobicity of the guest molecule. Our earlier studies in the field of biomimetic modeling of organic chemical reactions involving cyclodextrins [40] prompted us to attempt the regioselective ring opening of oxiranes and aziridines, under biomimetic conditions using β-cyclodextrin in water (Scheme 1).

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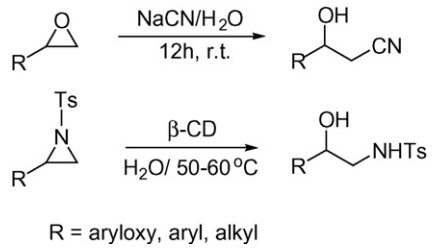


Scheme 1.

2. Results and discussion

2.1. β-Hydroxy nitriles

These reactions were carried out by dissolving β-cyclodextrin in water at 60 °C followed by the addition of epoxide. The reaction mixture was cooled to room temperature and then NaCN was added. The mixture was stirred until the reaction was complete (TLC). This reaction has led to the formation of single regioisomer as could be seen from the ^{1}H NMR of the crude product. This is an improvement over the earlier methodologies, which report mixtures of regioisomers. These compounds were characterized by ^{1}H NMR, IR, mass or otherwise compared with the known compounds [10,11,41]. This methodology is also compatible with other substituted phenoxy epoxides and styrene oxide (Table 1).

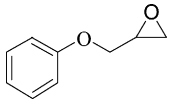
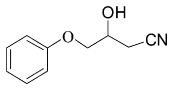
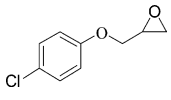
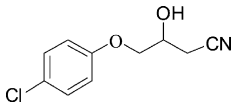
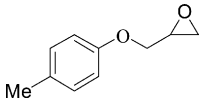
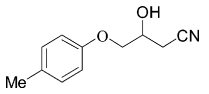
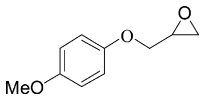
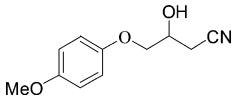
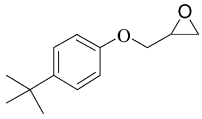
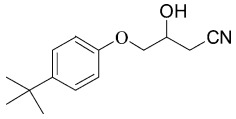
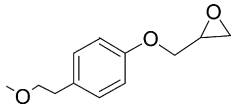
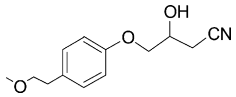
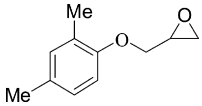
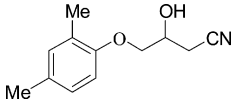
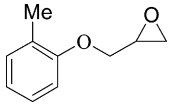
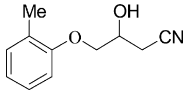
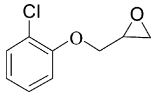
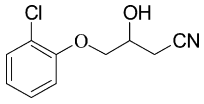
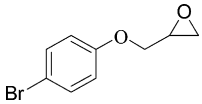
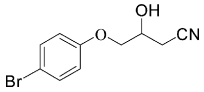
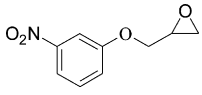
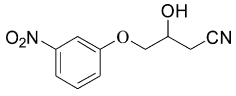
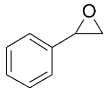
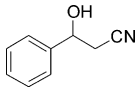
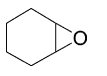
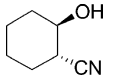
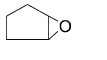
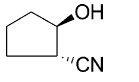
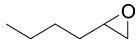
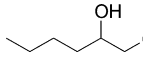
Though some optical induction was observed in certain compounds, enantiomeric excess (ee) was very low [42]. Maximum ee observed was 16.7% in the case of 3-hydroxy-4-(2-chlorophenoxy) butanenitrile (Table 1, entry 9) and 14.6% in the case of 3-hydroxy-4-(4-chloro phenoxy) butanenitrile (Table 1, entry 2). These compounds have been shown to have 'S' configuration by comparison of the sign of rotation with those of the known compounds. These epoxide-opening reactions were also carried out with TMSCN but the yields are not encouraging (20–30%).

The role of CD appears to be not only to activate the oxiranes but also to promote highly regioselective ring opening via inclusion complex formation with cyclodextrin. The complex of epoxide and cyclodextrin, though generated *in situ*, have been isolated and characterized by ^{1}H NMR [43]. There is an up field shift of H-3 (0.03 ppm) and H-5 (0.057 ppm) protons of cyclodextrin in the CD-epoxide complex as compared to CD indicating the formation supramolecular entity with the epoxide. In this type of complex, the α-position of the epoxide is more hindered and β-attack predominates to give a single regioisomer. These reactions did not proceed in the absence of β-cyclodextrin.

2.2. β-Amino alcohols

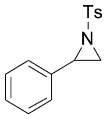
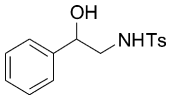
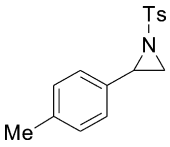
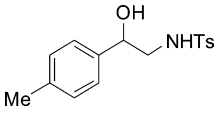
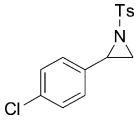
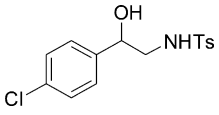
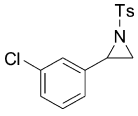
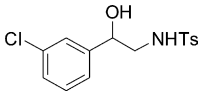
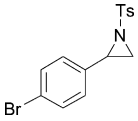
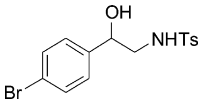
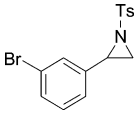
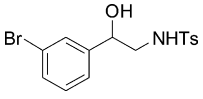
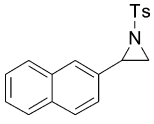
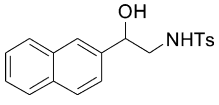
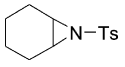
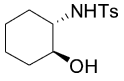
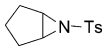
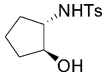
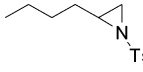
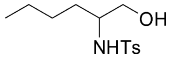
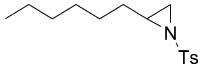
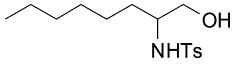
In general, the reaction was carried out by dissolving β-cyclodextrin in water, followed by the addition of aziridine. The reaction mixture was stirred at 50 °C for 6 h to get the corresponding β-amino alcohols in impressive yield. This methodology is also compatible with other functionalities such as chloro, bromo and methyl (Table 2). All the products were identified by

Table 1
Synthesis of β-hydroxy nitriles from epoxides and NaCN in the presence of β-CD

Entry	Substrate	Product[a]	Yield (%)[b]
1			87
2			85
3			84
4			81
5			80
6			83
7			86
8			84
9			90
10			88
11			85
12			83
13			79
14			81
15			77

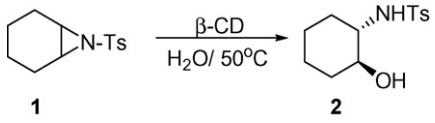
[a] All the products were characterized by ^{1}H NMR, IR spectroscopy and mass spectrometry.
[b] Isolated yield obtained after column chromatography.

Table 2
Synthesis of β-amino alcohols in the presence of β-CD in water

Entry	Substrate	Product[a]	Time (h)	Yield (%)[b]
1			5.1	92
2			5.4	90
3			5.3	93
4			5.4	91
5			5.2	95
6			5.5	92
7			5.3	94
8			6.1	89
9			6.0	86
10			6.5	85
11			7.1	85

[a] All the products were identified by IR, NMR, and mass spectroscopy.
[b] Yields of products isolated after column chromatography.

^{1}H NMR, IR, mass spectroscopy or otherwise compared with the known compounds [39,44,45]. In the case of cycloalkyl-*N*-tosyl aziridines (Table 2, entries 8 and 9) *trans* isomer (**2**) was obtained as the only product (Scheme 2).



Scheme 2.

The reaction proceeds smoothly without the formation of any by-products. The catalyst can also be recovered and reused. The reaction also takes place in the presence of catalytic amounts of β-cyclodextrin at longer hours (∼36 h, yields are up to 60%), but the reaction did not proceed in the absence of β-cyclodextrin.

3. Conclusions

In conclusion, these methodologies provide an easy access to highly regioselective synthesis of β-hydroxy nitriles and β-amino alcohols. Moreover, the reaction proceeds under neutral and mild conditions with recycling of the catalyst β-cyclodextrin. These water-based reactions are mild, easy to handle, economic and eco-friendly.

4. Experimental

All the reactions were carried out without any special precautions in an atmosphere of air. Chemicals were purchased from Aldrich and S.D. Fine Chemicals and used as received. The ^{1}H NMR spectra were recorded on VARIAN-200 or BRUCKER-300 MHz spectrometer. IR spectra were recorded on a NICOLET FT-IR spectrometer. Mass spectra were observed on V.G. auto spectrometer.

Oxiranes and aziridines were either purchased commercially or synthesized as reported in the literature [46,47].

4.1. Synthesis of β-hydroxy nitriles

β-CD (1 mmol) was dissolved in water (15 ml) by warming to 60 °C until a clear solution was formed; then oxirane (1 mmol) dissolved in acetone (2 ml) was added dropwise and the mixture was allowed to reach room temperature. Sodium cyanide (1.5 mmol) was added and the mixture was stirred at room temperature until the reaction was complete (TLC) (Scheme 1). The organic material was extracted with ethyl acetate. The filtrate was cooled to 5 °C to recover CD by filtration (>90%). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. The resulting crude product was further purified by silica-gel column chromatography with ethyl acetate:*n*-hexane (2:8) as eluent.

4.1.1. 4-(4-Tert-butylphenoxy)-3-hydroxybutanenitrile (Table 1, entry 5)

IR (KBr) 3432, 2925, 2254 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ: 1.30 (s, 9H), 2.60–2.80 (m, 2H), 4.0 (d, 2H, J = 5.2 Hz), 4.22–4.39 (m, 1H), 6.80 (d, 2H, J = 8.3 Hz), 7.28 (d, 2H, J = 8.3 Hz). Mass (EI) 233 *m/z*. Anal. Calcd for $C_{14}H_{19}NO_2$: C 72.07, H 8.21, N 6.00; found C 72.01, H 8.20, N 6.07.

4.1.2. 4-(4-(2-Methoxyethyl) phenoxy)-3-hydroxybutanenitrile (Table 1, entry 6)

IR (KBr) 3435, 2926, 2252 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 2.61–2.82 (m, 4H), 3.32 (s, 3H), 3.52 (t, 2H, J = 6.7 Hz), 3.98 (d, 2H, J = 5.2 Hz), 4.2–4.29 (m, 1H), 6.79 (d, 2H, J = 8.3 Hz), 7.10 (d, 2H, J = 8.3 Hz). Mass (EI) 235 *m/z*.

Anal. Calcd for $C_{13}H_{17}NO_3$: C 66.36, H 7.28, N 5.95; found C 66.05, H 7.54, N 5.96.

4.1.3. 4-(2,4-Dimethylphenoxy)-3-hydroxybutanenitrile (Table 1, entry 7)

IR (KBr) 3437, 2926, 2255 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.48 (bs, 1H), 2.18 (s, 3H), 2.25 (s, 3H), 2.66 (dd, 1H, J = 16.6, 6.1 Hz), 2.75 (dd, 1H, J = 16.6, 6.1 Hz), 4.02 (d, 2H, J = 5.2 Hz), 4.25–4.34 (m, 1H), 6.66 (d, 1H, J = 8.3), 6.8 (m, 2H); Mass (EI) 205 *m/z*. Anal. Calcd for $C_{12}H_{15}NO_2$: C 70.22, H 7.37, N 6.82; found C 70.12, H 7.52, N 6.15.

4.1.4. 4-(2-Chlorophenoxy)-3-hydroxybutanenitrile (Table 1, entry 9)

IR (KBr) 3444, 2950, 2257 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ: 2.66 (dd, 1H, J = 16.06, 4.5 Hz), 2.75 (dd, 1H, J = 11.65, 3.52 Hz), 4.0 (d, 2H, J = 5.2 Hz), 4.25–4.34 (m, 1H), 6.70–6.90 (m, 2H), 7.05–7.15 (m, 2H); Mass (EI) 211 *m/z*. Anal. Calcd for $C_{10}H_{10}ClNO_2$: C 56.75, H 4.76, N 6.62; found C 56.70, H 4.71, N 6.74.

4.1.5. 4-(3-Nitrophenoxy)-3-hydroxybutanenitrile (Table 1, entry 11)

IR (KBr) 3426, 2937, 2261 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ: 3.90–4.30 (m, 4H), 5.64–5.74 (m, 1H), 7.21–7.31 (m, 1H), 7.47 (t, 1H, J = 7.4 Hz), 7.70–7.89 (m, 2H). Mass (EI) 222 *m/z*. Anal. Calcd for $C_{10}H_{10}N_2O_4$: C 54.05, H 4.54, N 12.61; found C 54.07, H 4.56, N 12.57.

4.2. Synthesis of β-amino alcohols

β-Cyclodextrin (1 mmol) was dissolved in water (15 ml) at 60 °C, then the substrate aziridine (1 mmol) dissolved in acetone (1 ml) was added slowly and stirring at 50–60 °C was continued until the reaction was complete (Table 1). The mixture was cooled to room temperature and extracted with ethyl acetate. The filtrate was cooled to 5 °C to recover CD by filtration (>90%). The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum to get the products as single compounds which were further purified by flash column chromatography with ethyl acetate:*n*-hexane as eluent.

4.2.1. 1-(3-Chlorophenyl)-2-(tosylamino)ethanol (Table 2, entry 4)

IR (KBr) 3428, 3314, 2942 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.42 (s, 3H), 2.86–2.97 (m, 1H), 3.14–3.26 (m, 1H), 4.96 (t, 1H, J = 6 Hz), 7.05 (d, 1H, J = 2 Hz), 7.11 (m, 1H), 7.38 (d, 1H, J = 3 Hz), 7.45 (s, 1H). Mass (EI) 325 *m/z*. Anal. Calcd for $C_{15}H_{16}ClNO_3S$: C 55.3, H 4.95, N 4.30; found C 55.1, H 4.97, N 4.28.

4.2.2. 1-(3-Bromophenyl)-2-(tosylamino)ethanol (Table 2, entry 6)

IR (KBr) 3435, 3309, 2931 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.41 (s, 3H), 2.82–2.93 (m, 1H), 3.10–3.19 (m, 1H), 5.11 (t, 1H, J = 6 Hz), 7.08 (m, 2H), 7.37 (d, 1H, J = 3 Hz), 7.85 (s, 1H). Mass (EI) 368, 370 *m/z*. Anal. Calcd for $C_{15}H_{16}BrNO_3S$: C 48.66, H 4.36, N 3.78; found C 48.63, H 4.39, N 3.76.

4.2.3. 1-(Naphthalene-6-yl)-2-(tosylamino)ethanol (Table 2, entry 7)

IR (KBr) 3465, 3313, 2951 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ: 2.46 (s, 3H), 3.01–3.10 (m, 1H), 3.24–3.34 (m, 1H), 5.14 (t, 1H, J = 9 Hz), 7.25–7.32 (m, 2H), 7.49–7.52 (m, 2H), 7.70 (d, 1H, J = 4 Hz), 7.88 (s, 1H), 8.01 (d, 1H, J = 4 Hz). Mass (EI) 341 *m/z*. Anal. Calcd for $C_{19}H_{19}NO_3S$: C 66.84, H 5.61, N 4.10; found C 66.86, H 5.59, N 4.11.

4.2.4. 2-(Tosylamino)octan-1-ol (Table 2, entry 11)

IR (KBr) 3412, 3306, 2986 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ: 0.86 (t, 3H, J = 7 Hz), 1.10–1.56 (m, 10H), 2.46 (s, 3H), 3.44–3.55 (m, 1H), 4.52 (t, 2H, J = 7 Hz), 7.30 (d, 2H, J = 8.2 Hz), 7.75 (d, 2H, J = 8.2 Hz). Mass (EI) 299 *m/z*. Anal. Calcd for $C_{15}H_{25}NO_3S$: C 60.17, H 8.42, N 4.68; found C 60.15, H 8.44, N 4.65.

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