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# $SO_3H$-Carbon derived from glycerol: An efficient and recyclable catalyst for smooth and regioselective azidolysis of oxiranes in water

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ABSTRACT

A series of *β*-hydroxyazides were effectively synthesized from the regioselective ring opening of oxiranes by azide anion in presence of glycerol-based sulfonic acid functionalized carbon as a novel reusable heterogeneous catalyst in $H_2O$ achieving good yields (80-98%). The workup procedure was simple, and the catalyst could be reused over five times without losing its catalytic activity and selectivity.

## 1. Introduction

The 1,2-epoxide functionality is largely present in nature, having biologically important and a powerful building block in organic synthesis [1]. Their inherent polarity and strain, makes susceptible to react with a large number of organic compounds [2-5]. Ring opening reactions of epoxide with nucleophiles are considered as an interesting approach in organic synthesis of many functionalized oxygenated compounds. The reaction with nucleophiles such as oxygen compounds (Water, alcohols and phenols) [6-10], nitrogen compounds (Amine, amine derivatives, azide, nitrate, and isocyanate) [11-13], halides [14], and various carbon nucleophiles [15] have been performed in both organic and aqueous solvents. Among the numerous products from nucleophilic reactions of epoxide, vicinal azidohydrins [16] exhibit key role in organic synthesis as potential precursors for 1,2-aminoalcohols which are well known as β-blockers and a common structural component in vast group of natural products [11,17-20], and often used in carbohydrate chemistry or in the chemistry of carbocyclic nucleosides [11,16] can be obtained through the nucleophilic ring opening of epoxides with azide nucleophile [21-24]. Even though the classic protocol [11,16] uses sodium azide and ammonium chloride, the azidolysis reaction requires long reaction time (12-48 h) and the azidohydrin is often accompanied by isomerization, epimerization and rearrangement of products. However, the azide opening is promoted by traditional homogeneous systems as metal chlorides [25,26], salts [27] and alkyl metal azides [28-32]. Some heterogeneous catalysts, relying on the use of traditional solid acids such as amberlite IRA-400 supported azide [33]. Dowex resin grafted by poly ethylene glycol [34], oxone [35], sodium azide supported on Zeolite CaY [36], ammonium salt of a hetero poly acids [37], quaternized ammonium salt [38] and quaternized amino functionalized cross linked polyacrylamide [39] have been reported. Recently, hot water promoted azidolysis also reported [40]. Most of the reactions suffer from long reaction times, involving organic solvents and elevated temperatures; hence there is a need to develop green, mild, economically viable and eco-friendly method for the azidolysis of epoxide.

In recent years, carbon-based solid acid catalysts have gained significant attraction over homogeneous catalysts as they are highly efficient, sustainable, and eco-friendly [41-45]. In this connection, Prabhavathi *et al.*, reported sustainable method for the preparation of sulfonic acid functionalized carbon ($SO_3H$-carbon) catalyst having 1.6 mmol/g acid density with surface area of 0.21 $m^2/g$ from bioglycerol (Biodiesel by-product) and also from the glycerol-pitch (Waste from fat splitting industry) by the *in situ* partial carbonization in a single step [46,47]. This catalyst exhibited excellent catalytic properties by demonstrating its effectiveness for various transformations [46-53] due to its high thermal stability,


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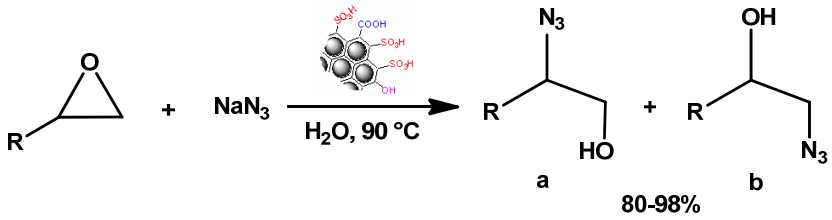


**Scheme 1**

reusability and strong acid sites of sulfonic acid functional groups. In continuation of our ongoing research in the applications of the glycerol-based catalyst, we herein report a simple and highly efficient method for the regioselective ring opening of oxirane by azide anion in water (Scheme 1).

## 2. Experimental

### *2.1. Materials and methods*

Chemicals were purchased from S. D. Fine or Sigma Aldrich Chemical Companies. All other reagents and solvents used were of analytical grade. TLC was monitored by using silica gel ($SiO_2$) $60F_{254}$ plates (Merck, India). Conversion percentages were studied on Agilent 6850 series Gas Chromatography (GC). Column chromatography was performed by using $SiO_2$, 100-200 mesh, Qualigens, India. IR Spectra was recorded on Perkin Elmer, Model: Spectrum BX, FT-IR using $CHCl_3$; in $cm^{-1}$. $^1H$ and $^{13}C$ NMR Spectra were recorded on Varian 300, Palo Alto, USA spectrometer at 300 and 75 MHz respectively at 25 °C in $CDCl_3$, δ in ppm relative to $Me_4Si$ as internal standard and coupling constant (*J*) in Hz. Mass spectra was recorded on Waters, Micromass-Quatromicro electron spray ionization.

### *2.2. Glycerol-based sulfonic acid functionalized carbon catalyst* [46]

A mixture of glycerol (10 g) and concentrated sulphuric acid (30 g) was heated from ambient temperature to 220 °C for 20 min, to facilitate *in situ* partial carbonization and sulfonation. The reaction mixture was allowed to remain at that temperature for about 20 min (until foaming ceased) to obtain solid carbon material and was cooled to ambient temperature and washed with hot water until the wash water becomes neutral to pH. The partially crystalline product was filtered and dried in an oven at 120 °C for 2 h until it was moisture free to obtain the carbon acid catalyst in ~56% yield (5.60 g).

### *2.3. General procedure for the synthesis of β-hydroxyazides*

Sodium azide (1.2 mmol) was added to the mixture of oxirane (1 mmol), carbon catalyst (2 wt.% of oxirane) in water (1 mL). The suspension was stirred at 90 °C (TLC (hexane:ethyl acetate, *v*:*v*, 4:1)). After completion of the reaction, the catalyst was recovered for reuse by simple filtration, and the product was extracted with ethyl acetate (3×5 mL). The extract was dried over anhydrous $Na_2SO_4$, and concentrated under vacuum to obtain *β*-hydroxyazide. The product mixture was analyzed by GC for the determination of conversion % and the pure product was isolated (80-98%) by silica gel column chromatographic separation.

*2-Azido-2-phenylethanol* (**1a**): FT-IR (Neat, *v*, $cm^{-1}$): 3369 (OH), 2103 ($N_3$). $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm): 7.28-7.38 (m, 5H, Ar-H), 4.61 (t, *J* = 6.7 Hz, 1H, CH), 3.67 (d, *J* = 6.0 Hz, 2H, $CH_2$), 2.33 (s, 1H, OH). ESI-MS (*m/z*): 186 $(M + Na)^+$.

*Trans-2-azidocyclohexanol* (**2b**): FT-IR (Neat, *v*, $cm^{-1}$): 3345 (OH), 2102 ($N_3$). $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm): 3.25-3.33 (m, 1H, C*H*OH), 3.05-3.14 (m, 1H, $CHN_3$), 2.25 (s, 1H, OH), 1.93-2.02 (m, 2H, CH(OH)C$H_2$), 1.65-1.74 (m, 2H, CH($N_3$)C$H_2$), 1.15-1.24 (m, 4H, C$H_2$-C$H_2$). ESI-MS (*m/z*): 164 $(M + Na)^+$.

*1-Azido-3-phenoxypropan-2-ol* (**3b**): FT-IR (Neat, *v*, $cm^{-1}$): 3391(OH), 2104 ($N_3$). $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm): 7.23-7.30 (m, 2H, Ar-H), 6.86-6.98 (m, 3H, Ar-H), 4.10-4.18 (m, 1H, CH), 3.98 (d, *J* = 5.2 Hz, 2H, $OCH_2$), 3.46-3.52 (m, 2H, $CH_2N_3$), 2.68 (s, 1H, OH). ESI-MS (*m/z*): 216 $(M + Na)^+$.

*1-Azido-3-(benzyloxy)propan-2-ol* (**4b**): FT-IR (Neat, *v*, $cm^{-1}$): 3414 (OH), 2102 ($N_3$). $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm): 7.24-7.34 (m, 5H, Ar-H), 4.51 (s, 2H, Ar-$CH_2$), 3.87 (m, 1H, CH), 3.43-3.47 (m, 2H, $OCH_2$), 3.28-3.32 (m, 2H, $CH_2N_3$), 2.72 (bs, 1H, OH). ESI-MS (*m/z*): 230 $(M + Na)^+$.

*1-Azido-3-(cinnamyloxy)propan-2-ol* (**5b**): FT-IR (Neat, *v*, $cm^{-1}$): 3359 (OH), 2101 ($N_3$). $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm): 7.22-7.40 (m, 5H, Ar-H), 6.53 (d, *J* = 15.8 Hz, 1H, Ar-C*H*=CH), 6.22-6.28 (m, 1H, Ar-CH=C*H*), 4.17 (d, 2H, CH=CH-C$H_2$), 3.94-4.01 (m, 1H, CH), 3.45-3.56 (m, 2H, $OCH_2$), 3.34-3.40 (m, 2H, $CH_2N_3$), 2.49 (bs, 1H, OH). ESI-MS (*m/z*): 256 $(M + Na)^+$.

*1-Azido-3-(p-tolyloxy)propan-2-ol* (**6b**): FT-IR (Neat, *v*, $cm^{-1}$): 3396 (OH), 2103 ($N_3$). $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm): 7.06 (d, *J* = 8.3 Hz, 2H, Ar-H), 6.78 (d, *J* = 8.3 Hz, 2H, Ar-H), 4.09-4.17 (m, 1H, CH), 3.97 (d, *J* = 5.2 Hz, 2H, $OCH_2$), 3.47-3.52 (m, 2H, $CH_2$ $N_3$), 2.61 (bs, 1H, OH), 2.28 (s, 3H, Ar-$CH_3$). ESI-MS (*m/z*): 230 $(M + Na)^+$.

*1-Azido-3-(hexyloxy)propan-2-ol* (**7b**): FT-IR (Neat, *v*, $cm^{-1}$): 3422 (OH), 2102 ($N_3$). $^1H$ NMR (300 MHz, $CDCl_3$, δ, ppm): 3.86 (m, 1H, CH), 3.41-3.47 (m, 4H, 2 $OCH_2$), 3.31-3.33(m, 2H, $CH_2$ $N_3$), 2.56 (bs, 1H, OH), 1.56 (quin, 2H, $CH_2$), 1.25-1.38 (m, 6H, 3 $CH_2$), 0.90 (t, *J* = 6.4 Hz, 3H, $CH_3$). ESI-MS (*m/z*): 224 $(M + Na)^+$.

## 3. Results and discussion

Initially, different solvents like $CH_3COCH_3$, $CH_2Cl_2$, THF, $CH_3CN$, DMF and $H_2O$ were screened for the azidolysis of styrene oxide by treating with 1.2 mmol of sodium azide in presence of 10 wt% of catalyst at reflux temperatures. Among these, only $H_2O$ and DMF are found to be suitable for this reaction (Table 1). However, because of DMF's toxicity, cost, difficulty in removing and possible environmental problems, $H_2O$ was preferred as the most suitable solvent. It was investigated to optimize the reaction conditions like $H_2O$ content (0.5 to 2 mL), amount of the catalyst (2 to 10 wt% of oxirane) and sodium azide (1 to 2 mmol) for complete azidolysis of styrene oxide (1 mmol) to the corresponding azidohydrin at 90 °C. From this study, the optimum conditions were found to be 1.2 mmol of $NaN_3$ and 2 wt% of catalyst in 1 mL of water at 90 °C for 0.5 h.

In order to generalize the validity of the protocol, we extended our study towards different oxiranes having activating and deactivating groups (Table 2). Excellent yields of the desired β-azido alcohols are obtained with a reversal of regioselectivity indicating attack at the less substituted carbon of the aliphatic oxiranes (Entries 2-7, Table 2), while styrene oxide (Entry 1, Table 2), as an aryl oxirane formed the major product as 2-azido-2-phenylethanol, by the attack of azide nucleophile at the benzylic position, this is due to the formation

**Table 1.** Effect of solvent on azidolysis of styrene oxide with $NaN_3$ (1.2 mmol) in presence of glycerol-based $SO_3H$-carbon catalyst.

| Solvent | Time (min) | Temperature | Result |
|---|---|---|---|
| $CH_2Cl_2$ | 60 | reflux | No reaction |
| $CH_3COCH_3$ | 60 | reflux | No reaction |
| $CH_3CN$ | 60 | reflux | No reaction |
| THF | 60 | reflux | No reaction |
| DMF | 60 | reflux | Completed |
| $H_2O$ | 60 | 90 °C | Completed |

**Table 2.** Glycerol-based $SO_3H$-carbon catalysed ring opening of epoxides with $NaN_3$ (1.2 mmol) in water at 90 °C.

| Entry | R | Product [a] | Time (h) | Yield (%) [b] |
|---|---|---|---|---|
| 1 | $C_6H_5$ | 1a | 0.5 | 94 |
| 2 | $C_6H_{10}$ | 2b | 0.5 | 92 |
| 3 | $C_6H_5OCH_2$ | 3b | 1.0 | 98 |
| 4 | $C_6H_5CH_2OCH_2$ | 4b | 1.25 | 90 |
| 5 | $C_6H_5CH{=}CHCH_2OCH_2$ | 5b | 4.0 | 90 |
| 6 | *p*-$CH_3$-$C_6H_4OCH_2$ | 6b | 5.0 | 89 |
| 7 | $C_6H_{13}OCH_2$ | 7b | 5.0 | 80 |

[a] Products were identified by comparison of their physical and spectral data with those of authentic samples.
[b] Isolated yields.

of a stable benzyl carbocation during mechanism, is evidenced by electronic factors [25-40], whereas in the case of aliphatic oxiranes (Entries 2-7, Table 2), steric factors predominate over electronic factors, thereby facilitating attack at the less hindered carbon atom of the oxirane ring. Furthermore, oxiranes derived from cycloalkenes, such as 7-oxabicyclo [4.1.0]heptanes (Entry 2, Table 2), reacted smoothly in $SN_2$ fashion to afford the corresponding azidohydrine; and the reaction was completely anti-sterioselective, thus resulting in trans isomer only. It was further evidenced by coupling constants of the ring H-atoms in $^1H$ NMR spectrum. All the purified products were characterized by ESI-MS, IR, $^1H$ NMR data and are in comparison with authentic samples.

The admirable quality of the carbon acid catalyst could be the recovery and reusability. After the reaction, the product was extracted into ethyl acetate, catalyst from aqueous layer was separated by simple filtration, washed with MeOH, dried and reused. The reusability study of the catalyst for the azidolysis of of 2-(phenoxymethyl) oxirane under optimized conditions for five catalytic runs was observed to be no considerable loss of activity of the catalyst and resulted in complete reaction within 1 h in 94-92% conversions against 99% of fresh catalyst as depicted in Figure 1.

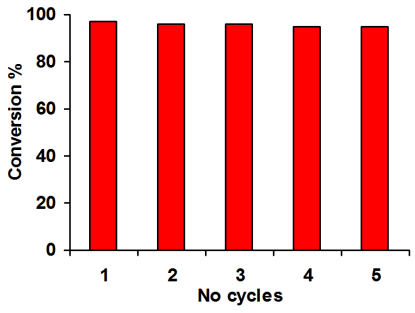


**Figure 1**. Catalyst reusability study.

## 4. Conclusion

In conclusion, a simple, efficient and environmental benign protocol for the synthesis of vicinal azidohydrins from oxiranes employing a novel highly efficient and reusable glycerol-based sulfonic acid functionalized carbon as a heterogeneous green catalyst was established. This catalyst displayed a remarkable efficiency in ring opening of oxiranes with azide ion in $H_2O$ at 90 °C. After isolating the products into the organic phase, the catalyst from the aqueous phase is recovered by simple filtration for reuse without any pre-treatment. Environmental acceptability, high yields, easy work-up, cleaner reaction profiles and recyclability of the catalyst are the important features of this protocol.

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