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# Magnesium Oxide Nanoparticles for Catalytic Synthesis of 2-Substituted Alcohols from Regioselective Ring Opening of Epoxides in Water

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Epoxides undergo regioselective ring opening with various nucleophiles using catalytic amount of nano magnesium oxide and water as solvent under mild reaction conditions. The remarkable features of this method are improved yields, high regioselectivity, and green chemistry agreement.

**Keywords:** Nano MgO, Ring opening, Epoxides, 1,2-Diols, 2-Substituted diols

## INTRODUCTION

Organic transformations involving benign reaction media are of considerable interest in synthesis. The use of many toxic and volatile organic solvents, particularly chlorinated hydrocarbons, as reaction media contributes pollution to the environment, and it is highly desirable to develop environmentally benign processes that can be conducted in green solvents. The low cost of water, along with its non-toxic nature, renders it as an attractive media for chemical synthesis. Reactions in aqueous media offer many advantages such as simple operation and high efficiency in many organic reactions involving water soluble substrates and reagents [1]. These advantages become even more attractive if such reactions can be conducted using heterogeneous catalysts.

Heterogeneous catalysts have advantages over homogeneous ones as they can be easily recovered from the reaction mixture by simple filtration. Among the heterogeneous basic catalysts, MgO has found wide applications either in commercial form (CM-MgO) or in nanoscale. MgO is a unique metal oxide because it has high ionic nature and simple stoichiometry and can be produced in various particle sizes and shapes [2]. It has been used as a substrate for the epitaxial growth of thin films and is also a valuable crystal in optical transmitters [3,4]. In addition, magnesium oxide is an important adsorbent and there are many reports on the adsorption of $H_2$, CO, $NH_3$, pyridine, nitrobenzene, dimethyl methylphosphonate (DMMP), HCl, HBr, NO and $SO_3$ on commercial or nanoscale MgO [5-8]. Due to its minimum environmental impact and low solubility, MgO is one of the best materials to remove organic and inorganic pollutants from water [9]. Surface study shows that there are different reactive sites on MgO including $Mg^{2+}$ site, which is of Lewis-acid type, $O^{2-}$ site, which is of Lewis-base type, lattice-bound hydroxyls, isolated hydroxyls, and anionic and cationic vacancies [10]. As magnesium oxide turns into its nanoparticle form, surface area and defect sites are increased considerably and a more reactive surface is obtained [7]. Also, MgO has been used for several base-catalyzed organic transformations [11].

Epoxides are important intermediates in organic synthesis [12]. Although epoxides can be opened under various conditions, the most practical strategy for the synthesis of 1,2-bifunctional compounds is via nucleophilic ring opening using a Lewis acid or a strong base [13]. In most of the epoxide ring opening reactions under acidic conditions, the formation of a mixture of regio-isomers and polymerization is observed. On the other hand, some of the reported catalysts suffer from disadvantages such as high acidity, the non-catalytic nature of the reagents, long

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reaction times and inconvenient handling procedures [14]. Therefore, the introduction of new methods which work under mild conditions, are still in demand and are important in synthetic organic chemistry. A number of methods using Lewis acids and one-electron transfer catalysts have been also reported for the ring-opening reactions of epoxides with different nucleophiles [15].

Having all above in mind and in line with our previous works on bulky and nano sized metal oxides [16], herein we find that the synthesized nano MgO can act as an efficient catalyst for the azidolysis and nitrilolysis in water, acetolysis, and also for the conversion of epoxides to 1,2-diols in solvent-free conditions.

## EXPERIMENTAL

Chemicals were either prepared in our laboratory (epoxides 1f and 1g, Table 2, entries 6 and 7) or were purchased from Fluka and Merck Chemical Companies. To prepare epoxide 1f, α-naphthol was mixed with anhydrous $K_2CO_3$ and epibromohydrine. The same procedure was carried out with *m*-cresol to prepare epoxide 1g. The mole ratio of $K_2CO_3$ should be twice the alcohol and epibromohydrine should be more than triplicate of alcohol. The mixture was stirred for 48h in reflux condition and dry acetone was used as solvent. After 48 h, the mixture was filtered and desired epoxide was separated by a column chromatography. Hexane was used as the column eluent.

### Synthesis of Nano MgO

1.2 g Dextran (Mw 40000) and 2 ml of 3.9 M $Mg(NO_3)_2$ aqueous solution were mixed while stirring to form a paste in a crucible. The crucible was maintained at room temperature for 24 h and then heated to 600 °C for 2 h. After being naturally cooled to room temperature in the furnace, white products could be obtained [3,16g].

### General Procedure for Ring Opening of Epoxides with $NaN_3$ and NaCN

A mixture of epoxide (1 mmol), sodium azide or sodium cyanide (1 mmol), and nano MgO (5 mol%, 0.002 g) in water (1 ml) as solvent was stirred in an oil-bath at 80 °C (50 °C in the case of NaCN). When the reaction was completed (monitored by TLC or GC), the mixture was extracted with ethyl acetate (three times) and the products were separated by column chromatography. A mixture of *n*-hexane and ethyl acetate (ratio 4:1) was used as eluent.

**1-Azido-3-phenoxy-2-propanol (3a).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1040, 1250, 2105, 3420; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.85 (br, 1H, -O*H*), 3.31-3.41 (m, 2H, -C$H_2$-$N_3$), 3.81-3.92 (d, 2H, PhO-C$H_2$-, $J$ = 5.3 Hz), 3.94-3.99 (m, 1H, -C*H*(OH)-), 6.72-6.89 (m, 3H, Ar-*H*), 7.10-7.26 (m, 2H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 53.4, 69.00, 69.3, 114.6, 121.5, 129.653, 158.252; MS m/z (%): 57 (73.0), 77 (80.9), 94 (100.0), 133 (58.3), 150 (20.9), 193 ($M^+$, 35.7), 194 ($M^+$+1, 21.7).

**1-Azido-3-chloro-2-propanol (3b).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 760, 2163, 3425; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.88 (br, 1H, -O*H*), 3.38 (d, 2H, -C$H_2$-$N_3$, $J$ = 5.7 Hz), 3.65-3.78 (m, 1H, -C*H*(OH)-), 3.94-3.97 (m, 2H, -C$H_2$-Cl); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 53.9, 63.9, 69.5; MS m/z (%): 55 (100.0), 81 (54.4), 97 (52.9), 136 ($M^+$, 20.6).

**2-Azidocyclohexanol (3c).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 2096, 3361; $^1$HNMR ($CDCl_3$, 250 MHz) $\delta$ 1.28-1.38 (m, 4H, -C$H_2$-cyclohexyl), 1.71-1.85 (m, 2H, -C$H_2$-cyclohexyl), 2.00-2.24 (m, 2H, -C$H_2$-cyclohexyl), 2.40 (s, 1H, -O*H*), 3.15-3.37 (m, 1H, -C*H*($N_3$)-), 3.34-3.58 (m, 1H, -C*H*(OH)-); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 23.8, 24.1, 29.77, 33.0, 67.0, 73.5; MS m/z (%): 57 (100.0), 81 (63.1), 97 (43.1), 141 ($M^+$, 26.2).

**1-Azido-3-bromo-2-propanol (3d).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 633, 2165, 3415; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.61 (br, 1H, -O*H*), 3.38-3.48 (m, 2H, -C$H_2$-$N_3$), 3.62-3.76 (m, 1H, -C*H*(OH)-), 3.87-4.01 (m, 2H, -C$H_2$-Br); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 53.8, 69.5, 70.9; MS m/z (%): 57 (100.0), 83 (60.6), 111 (36.4), 133 (16.2), 180 ($M^+$, 16.2), 181 ($M^+$+1, 3.0).

**1-Azido-2-propanol (3e).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 2100, 3355; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.19-1.35 (m, 3H, -C$H_3$), 1.95 (s, 1H, -O*H*), 3.20-3.44 (m, 2H, -C$H_2$-), 3.93-4.12 (m, 1H, -C*H*(OH)-); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.2, 58.3, 66.9; MS m/z = 101, calc. 101.

**1-Azido-3-(naphthalen-1-yloxy)-2-propanol (3f).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1035, 1252, 2110, 3422; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.17 (br, 1H, -O*H*), 3.61-3.64 (m, 2H, -C$H_2$-$N_3$), 4.17-3.21 (m, 2H, ArO-C$H_2$-), 4.33.4.35

(m, 1H, -C*H*(OH)-), 6.82 (d, 1H, Ar-*H*, *J* = 7.4 Hz), 7.47-7.51 (m, 4H, Ar-*H*), 7.80-7.93 (m, 1H, Ar-*H*), 8.19-8.21 (m, 1H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 53.6, 69.2, 69.4, 105.0, 121.1, 121.5, 125.4, 125.7, 126.5, 127.4, 127.6, 134.5, 156.8; MS m/z (%): 57 (100.0), 82 (66.7), 124 (25.3), 149 (22.7), 221 (17.3), 242 (22.7), 243 ($M^+$, 4.0).

**1-Azido-3-(*m*-tolyloxy)-2-propanol (3g).** Light yellow liquid; IR (neat) *v* ($cm^{-1}$): 1038, 1250, 2100, 3420; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.33 (s, 3H, Ar-C$H_3$), 2.55 (br, 1H, -O*H*), 3.50-3.63 (m, 2H, -C$H_2$-$N_3$), 3.97-4.12 (m, 2H, ArO-C$H_2$-), 4.13-4.26 (m, 1H, -C*H*(OH)-), 6.75-6.87 (m, 3H, Ar-*H*), 7.17-7.39 (m, 1H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.4, 53.3, 68.9, 69.3, 111.4, 115.3, 122.2, 129.3, 139.7, 158.2; MS m/z (%): 55 (100.0), 73 (48.1), 97 (47.2), 123 (14.4), 149 (11.1), 207 ($M^+$, 12.0), 208 ($M^+$+1, 6.5).

**2-Azido-2-phenylethanol (4h).** Yellow liquid; IR (neat) *v* ($cm^{-1}$): 2096, 3405; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.64 (s, 1H, -O*H*), 3.70-3.85 (m, 2H, -C$H_2$-OH), 4.66 (t, 1H, -C*H*($N_3$)-, *J* = 6.7 Hz), 7.33-7.57 (m, 5H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 66.4, 67.8, 125.9, 127.1, 128.94, 136.3; MS m/z (%): 69 (100.0), 95 (43.5), 112 (16.9), 149 (42.7), 163 ($M^+$, 12.9).

**3-Hydroxy-4-phenoxybutanenitrile (3a).** Dark yellow liquid; IR (neat) *v* ($cm^{-1}$): 1040, 1230, 2260, 3450; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.61 (br, 1H, -O*H*), 2.71-2.84 (m, 2H, -C$H_2$-CN), 4.05-4.18 (m, 2H, PhO-C$H_2$-), 4.31-4.45 (m, 1H, -C*H*(OH)-), 6.95-7.12 (m, 3H, Ar-*H*), 7.29-7.43 (m, 2H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 22.5, 66.3, 69.7, 114.5, 117.7, 121.8, 129.6, 158.4; MS m/z (%): 69 (100.0), 95 (22.2), 112 (11.8), 129 (11.8), 149 (31.4), 177 ($M^+$, 7.2).

**4-Chloro-3-hydroxybutanenitrile (3b).** Dark yellow liquid; IR (neat) *v* ($cm^{-1}$): 2255, 3385; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.61 (br, 1H, -O*H*), 3.46 (d, 2H, -C$H_2$-CN, *J* = 5.6 Hz), 3.62-3.75 (m, 1H, -C*H*(OH)-), 3.71-3.84 (m, 2H, -C$H_2$-Cl); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.3, 47.8, 69.93, 117.0; MS m/z = 120, Calcd. 119.5.

**2-Hydroxycyclohexanecarbonitrile (3c).** Dark yellow liquid; IR (neat) *v* ($cm^{-1}$): 2230, 3420; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.76-1.84 (m, 4H, -C$H_2$-cyclohexyl), 1.91-2.05 (m, 2H, -C$H_2$-cyclohexyl), 2.03-2.16 (m, 2H, -C$H_2$-cyclohexyl), 2.44-2.67 (m, 1H, -C*H*(CN)-), 2.81 (s, 1H, -O*H*), 3.73-3.86 (m, 1H, -C*H*(OH)-); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 22.4, 23.0, 28.3, 32.9, 37.1, 66.8, 120.36; MS m/z = 125, Calcd. 125.

**4-Bromo-3-hydroxybutanenitrile (3d).** Dark yellow liquid; IR (neat) *v* ($cm^{-1}$): 2250, 3360; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.57 (br, 1H, -O*H*), 3.44 (d, 2H, -C$H_2$-CN, *J* = 5.6 Hz), 3.62-3.75 (m, 1H, -C*H*(OH)-), 3.68-3.80 (m, 2H, -C$H_2$-Br); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 22.4, 42.5, 69.91, 117.5; MS m/z = 164, Calcd. 164.

**3-Hydroxybutanenitrile (3e).** Dark yellow liquid; IR (neat) *v* ($cm^{-1}$): 2195, 3325; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.25 (m, 3H, -C$H_3$), 1.88 (s, 1H, -O*H*), 3.15-3.32 (m, 2H, -C$H_2$-), 3.95-4.09 (m, 1H, -C*H*(OH)-); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.3, 26.2, 67.5, 117.4; MS m/z = 85, Calcd. 85.

**3-Hydroxy-4-(naphthalen-1-yloxy)butanenitrile (3f).** Yellow liquid; IR (neat) *v* ($cm^{-1}$): 1037, 1256, 2240, 3365; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.63 (br, 1H, -O*H*), 2.66-2.72 (m, 2H, -C$H_2$-CN), 3.95-4.11 (m, 2H, ArO-C$H_2$-), 4.30-4.45 (m, 1H, -C*H*(OH)-), 6.81 (d, 1H, Ar-*H*, *J* = 7.4 Hz), 7.48-7.68 (m, 4H, Ar-*H*), 7.83-7.95 (m, 1H, Ar-*H*), 8.20-8.41 (m, 1H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 22.3, 66.3, 69.7, 105.0, 117.2, 121.1, 121.5, 125.4, 125.7, 126.5, 127.4, 127.6, 134.5, 156.8; MS m/z = 227, Calcd. 227.

**3-Hydroxy-4-(*m*-tolyloxy)butanenitrile (3g).** Yellow liquid; IR (neat) *v* ($cm^{-1}$): 1035, 1252, 2240, 3360; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 1.61 (br, 1H, -O*H*), 2.31 (s, 3H, Ar-C$H_3$), 2.73-2.86 (m, 2H, -C$H_2$-CN), 4.05-4.31 (m, 2H, ArO-C$H_2$-), 4.32-4.48 (m, 1H, -C*H*(OH)-), 6.71-6.85 (m, 3H, Ar-*H*), 7.16-7.37 (m, 1H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.5, 22.5, 66.3, 69.7, 111.4, 115.3, 117.6, 122.2, 129.3, 139.7, 158.2; MS m/z = 191, Calcd. 191.

**3-Hydroxy-2-phenylpropanenitrile (4h).** Yellow liquid; IR (neat) *v* ($cm^{-1}$): 2165, 3405; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.95-2.98 (m, 2H, -C$H_2$-OH), 3.12 (br, 1H, -O*H*), 4.17 (t, 1H, -C*H*(CN)-, *J* = 6.6 Hz), 7.44-7.58 (m, 5H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 51.9, 76.3, 117.2, 127.0, 128.0, 128.6, 144.9; MS m/z = 147, Calcd. 147.

## General Procedure for Ring Opening of Epoxides with AcOH and $Ac_2O$

A mixture of epoxide (1 mmol), glacial acetic acid or acetic anhydride (1 mmol), and nano MgO (5 mol%, 0.002 g) was stirred without any solvent under reflux condition. Finally, after extraction with ethyl acetate and saturated

solution of sodium bicarbonate (three times), the products were separated by column chromatography. A mixture of *n*-hexane and ethyl acetate (ratio 4:1) was used as eluent.

**2-Hydroxy-3-phenoxypropyl acetate (5a).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1040, 1150, 1255, 1740, 3355; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 2.10-2.25 (m, 3H, -(CO)-C$H_3$), 2.35-2.49 (br, 1H, -O*H*), 4.01-4.30 (m, 5H, -C$H_2$-OAc, -C*H*(OH)-, PhO-C$H_2$-), 6.90-7.12 (m, 3H, Ar-*H*), 7.25-7.43 (m, 2H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.8, 65.4, 66.1, 68.4, 114.5, 121.2, 129.5, 158.3, 170.9; MS m/z (%): 57 (100.0), 83 (42.8), 111 (24.3), 129 (13.2), 207 (8.2), 210 ($M^+$, 4.5).

**3-Chloro-2-hydroxypropyl acetate (5b).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1745, 3465; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 2.07 (s, 3H, -(CO)-C$H_3$), 3.27 (br, 1H, -O*H*), 3.61 (d, 2H, -C$H_2$-Cl, $J$ = 5.4 Hz), 4.22 (d, 2H, -C$H_2$-OAc, $J$ = 5.4 Hz), 4.95-5.18 (m, 1H, -C*H*(OH)-); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.6, 44.1, 67.9, 68.8, 170.2; MS m/z = 153, Calcd. 152.5.

**2-Hydroxycyclohexyl acetate (5c).** Colorless liquid; IR (neat) $\nu$ ($cm^{-1}$): 1723, 3410; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.21-1.27 (m, 4H, -C$H_2$-cyclohexyl), 1.67-1.73 (m, 2H, -C$H_2$-cyclohexyl), 1.98-2.07 (m, 2H, -C$H_2$-cyclohexyl), 2.08-2.14 (s, 3H, -(CO)-C$H_3$), 3.67 (s, 1H, -O*H*), 4.11-4.20 (m, 1H, -C*H*(OH)-), 4.31-4.45 (m, 1H, -C*H*(OAc)-); $^{13}C$NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.0, 21.5, 23.4, 26.9, 31.1, 76.1, 79.4, 171.0; MS m/z = 158, Calcd. 158.

**3-Bromo-2-hydroxypropyl acetate (5d).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1744, 3463; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 2.07 (s, 3H, -(CO)-C$H_3$), 3.21 (br, 1H, -O*H*), 3.56 (d, 2H, -C$H_2$-Br, $J$ = 5.4 Hz), 4.21 (d, 2H, -C$H_2$-OAc, $J$ = 5.4 Hz), 4.84-4.95 (m, 1H, -C*H*(OH)-); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.5, 39.1, 68.9, 72.5, 170.2; MS m/z = 197, Calcd. 197.

**2-Hydroxypropyl acetate (5e).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1738, 3460; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.23-1.37 (m, 3H, -C$H_3$), 2.07 (s, 3H, -(CO)-C$H_3$), 3.12 (br, 1H, -O*H*), 3.95-4.08 (m, 1H, -C*H*(OH)-), 4.10-4.26 (d, 2H, -C$H_2$-OAc, $J$ = 5.4 Hz); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.5, 22.0, 67.9, 72.4, 170.1; MS m/z = 118, Calcd. 118.

**2-Hydroxy-3-(naphthalen-1-yloxy)propyl acetate (5f).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1038, 1160, 1250, 1738, 3360; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 2.12-2.28 (m, 3H, -(CO)-C$H_3$), 2.37 (br, 1H, -O*H*), 4.05-4.14 (m, 5H, -C$H_2$-OAc, -C*H*(OH)-, ArO-C$H_2$-), 6.84 (d, 1H, Ar-*H*, $J$ = 7.4 Hz), 7.50-7.64 (m, 4H, Ar-*H*), 7.82-7.97 (m, 1H, Ar-*H*), 8.20-8.35 (m, 1H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.8, 65.4, 66.1, 68.4, 105.0, 121.1, 121.5, 125.4, 125.7, 126.5, 127.4, 127.6, 134.5, 156.8, 171.2; MS m/z = 260, Calcd. 260.

**2-Hydroxy-3-(*m*-tolyloxy)propyl acetate (5g).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1035, 1130, 1255, 1740, 3375; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 2.08-2.16 (m, 3H, -(CO)-C$H_3$), 2.33 (s, 3H, Ar-C$H_3$), 2.39 (br, 1H, -O*H*), 4.08-4.30 (m, 5H, -C$H_2$-OAc, -C*H*(OH)-, ArO-C$H_2$-), 6.75-6.86 (m, 3H, Ar-*H*), 7.17-7.30 (m, 1H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.8, 21.4, 65.4, 66.1, 68.4, 111.4, 115.3, 122.3, 129.3, 139.7, 158.2, 170.9; MS m/z = 224, Calcd. 224.

**2-Hydroxy-1-phenylethyl acetate (6h).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1250, 1733, 3360; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.93 (s, 3H, -(CO)-C$H_3$), 3.45 (s, 1H, -O*H*), 4.58-4.67 (m, 2H, -C$H_2$-OH), 5.62 (t, 1H, -C*H*(OAc)-, $J$ = 5.2), 7.13-7.27 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.1, 65.4, 73.1, 127.4, 128.1, 129.2, 141.3, 170.9; MS m/z = 180, Calcd. 180.

**3-Phenoxypropane-di-*O*-acetyl-1,2-diol (7a).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1049, 1174, 1226, 1747; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.85-1.93 (m, 6H, -(CO)-C$H_3$), 3.94-4.03 (m, 2H, PhO-C$H_2$-), 4.17-4.21 (m, 2H, -C$H_2$-OAc), 5.17-5.28 (m, 1H, -C*H*(OAc)-), 6.72-6.84 (m, 3H, Ar-*H*), 7.10-7.23 (m, 2H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.7, 20.9, 62.5, 65.9, 69.7, 115.0, 121.1, 129.5, 158.2, 170.3, 170.6; MS m/z (%): 57 (100.0), 83 (45.2), 110 (22.3), 149 (10.9), 167 (7.2), 194 (6.8), 210 (4.2), 236 (7.6), 252 ($M^+$, 2.3).

**3-Chloropropane-di-*O*-acetyl-1,2-diol (7b).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1160, 1748; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 2.12 (s, 6H, -(CO)-C$H_3$), 3.75-7.89 (m, 2H, -C$H_2$-Cl), 3.85-3.91 (m, 2H, -C$H_2$-OAc), 4.30-4.38 (m, 1H, -C*H*(OAc)-); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.7, 21.0, 41.3, 61.9, 75.1, 171.3, 171.4; MS m/z = 195, Calcd. 194.5.

**Cyclohexane-di-*O*-acetyl-1,2-diol (7c).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1160, 1744; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.42-1.63 (m, 4H, -C$H_2$-cyclohexyl), 1.84-1.96 (m, 2H, -C$H_2$-cyclohexyl), 2.10-2.35 (m, 2H, -C$H_2$-cyclohexyl), 2.25 (s, 6H, -(CO)-C$H_3$), 4.62-4.79 (m, 2H, -C*H*(OAc)-); $^{13}C$NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.2, 21.4, 24.3, 36.8, 77.6, 170.2, 170.3; MS m/z = 200, Calcd. 200.

**3-Bromopropane-di-*O*-acetyl-1,2-diol (7d).** Yellow

liquid; IR (neat) $\nu$ ($cm^{-1}$): 1146, 1745; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 2.11 (s, 6H, -(CO)-C*H*$_3$), 3.40-3.58 (m, 2H, -C*H*$_2$-Br), 3.82-3.97 (m, 2H, -C*H*$_2$-OAc), 4.30-4.46 (m, 1H, -C*H*(OAc)-); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.7, 21.0, 38.1, 59.2, 71.3, 171.3, 171.3; MS m/z = 239, Calcd. 239.

**Propane-di-*O*-acetyl-1,2-diol (7e).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1120, 1736; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.61-1.77 (m, 3H, -C*H*$_3$); 2.11 (s, 6H, -(CO)-C*H*$_3$), 3.80-3.94 (m, 2H, -C*H*$_2$-OAc), 4.18-4.26 (m, 1H, -C*H*(OAc)-); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 17.9, 20.0, 20.3, 66.3, 66.7, 170.2, 170.3; MS m/z (%): 69 (100.0), 95 (33.3), 121 (18.5), 160 ($M^+$, 5.8).

**3-(Naphthalen-1-yloxy)propane-di-*O*-acetyl-1,2-diol (7f).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1045, 1170, 1230, 1746; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.91-2.06 (m, 6H, -(CO)-C*H*$_3$), 3.91-4.12 (m, 2H, ArO-C*H*$_2$-), 4.21-4.36 (m, 2H, -C*H*$_2$-OAc), 5.21-5.35 (m, 1H, -C*H*(OAc)-), 6.84 (d, 1H, Ar-*H*, *J* = 7.4 Hz), 7.50-7.71 (m, 4H, Ar-*H*), 7.81-7.98 (m, 1H, Ar-*H*), 8.23-8.32 (m, 1H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.7, 20.9, 62.5, 65.9, 69.7, 105.0, 121.1, 121.5, 125.4, 125.7, 126.5, 127.4, 127.6, 134.5, 156.8, 170.3, 170.6; MS m/z = 302, Calcd. 302.

**3-(*m*-Tolyloxy)propane-di-*O*-acetyl-1,2-diol (7g).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1048, 1180, 1229, 1740; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.85-2.04 (m, 6H, -(CO)-C*H*$_3$), 2.33 (s, 3H, Ar-C*H*$_3$), 3.92-4.15 (m, 2H, ArO-C*H*$_2$-), 4.19-4.27 (m, 2H, -C*H*$_2$-OAc), 5.17-5.27 (m, 1H, -C*H*(OAc)-), 6.74-6.88 (m, 3H, Ar-*H*), 7.17-7.35 (m, 1H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.7, 20.9, 21.4, 62.5, 65.9, 69.7, 111.4, 115.3, 122.2, 129.3, 139.7, 158.2, 170.3, 170.6; MS m/z = 266, Calcd. 266.

**1-Phenylethane-di-*O*-acetyl-1,2-diol (7h).** Dark yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 1160, 1738; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.94-2.13 (m, 6H, -(CO)-C*H*$_3$), 3.85-3.97 (m, 2H, -C*H*$_2$-OAc), 4.23-4.40 (m, 1H, -C*H*(OAc)-), 7.46-7.60 (m, 5H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 20.7, 20.9, 64.6, 74.3, 127.4, 128.1, 129.2, 141.3, 170.3, 170.6; MS m/z = 222, Calcd. 222.

## General Procedure for Hydrolysis of Epoxides

A mixture of epoxide (1 mmol) and nano MgO (0.5 mmol, 0.02 g) was stirred in an oil bath at 80 °C without any additive. The progress of the reaction was monitored by TLC or GC. Then, the mixture was extracted with ethyl acetate (three times) and the diol was purified by column chromatography. A mixture of *n*-hexane and ethyl acetate (ratio 5:1) was used as eluent.

**3-Phenoxypropane-1,2-diol (8a).** White solid; M.p.: 105-107 °C (lit. 105-106 °C) [17]; IR (KBr) $\nu$ ($cm^{-1}$): 1040, 1230, 3320; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 3.42 (s, 2H, -O*H*), 3.73-3.85 (m, 2H, -C*H*$_2$-OH), 3.98-4.12 (d, 2H, PhO-C*H*$_2$-, *J* = 5.0 Hz), 4.08-4.22 (m, 1H, -C*H*(OH)-), 6.90-7.14 (m, 3H, Ar-*H*), 7.26-7.40 (m, 2H, Ar-*H*); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 63.6, 68.9, 70.5, 114.5, 121.2, 129.5, 158.3; MS m/z (%): 57 (100.0), 73 (36.2), 94 (98.7), 113 (15.9), 129 (15.3), 149 (33.6), 168 ($M^+$, 22.3).

**3-Chloropropane-1,2-diol (8b).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 3340; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 3.00 (s, 2H, -O*H*), 3.59-3.65 (m, 2H, -C*H*$_2$-Cl), 3.69-3.79 (m, 1H, -C*H*(OH)-), 4.12-4.34 (m, 2H, -C*H*$_2$-OH); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 45.7, 63.7, 71.9; MS m/z (%): 69 (74.8), 95 (16.8), 110 ($M^+$, 10.1).

**Cyclohexane-1,2-diol (8c).** White solid; M.p.: 103-105 °C (lit. 104-105 °C) [17]; IR (KBr) $\nu$ ($cm^{-1}$): 3250, 3420; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.23 (s, 4H, -C*H*$_2$-cyclohexyl), 1.67 (s, 2H, -C*H*$_2$-cyclohexyl), 1.93 (s, 2H, -C*H*$_2$-cyclohexyl), 3.32 (s, 2H, -O*H*), 3.60 (s, 2H, -C*H*(OH)-); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 24.3, 32.8, 75.6; MS m/z (%): 57 (100.0), 73 (40.6), 97 (29.7), 116 ($M^+$, 7.4).

**3-Bromopropane-1,2-diol (8d).** Yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 3338; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 3.02 (s, 2H, -O*H*), 3.52-3.66 (m, 2H, -C*H*$_2$-Br), 3.64-3.81 (m, 1H, -C*H*(OH)-), 4.10-4.26 (m, 2H, -C*H*$_2$-OH); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 41.2, 62.3, 71.8; MS m/z (%): 57 (100.0), 96 (45.3), 112 (37.3), 149 (24.0), 155 ($M^+$, 16.0), 156 ($M^+$+1, 9.3).

**Propane-1,2-diol (8e).** Light yellow liquid; IR (neat) $\nu$ ($cm^{-1}$): 3310; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 1.17-1.31 (m, 3H, -C*H*$_3$); 3.41-3.60 (m, 2H, -O*H*), 3.87-3.94 (m, 1H, -C*H*(OH)-), 4.38-4.52 (m, 2H, -C*H*$_2$-OH); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz) $\delta$ 18.2, 66.3, 68.1; MS m/z = 76, Calcd. 76.

**3-(Naphthalen-1-yloxy)propane-1,2-diol (8f).** White solid; M.p.: 98-101 °C (lit. 99-100 °C) [18]; IR (KBr) $\nu$ ($cm^{-1}$): 1038, 1253, 3325; $^1H$ NMR ($CDCl_3$, 250 MHz) $\delta$ 3.41 (s, 2H, -O*H*), 3.73-3.86 (m, 2H, -C*H*$_2$-OH), 3.96-4.12 (d, 2H, ArO-C*H*$_2$-, *J* = 5.0 Hz), 4.08-4.25 (m, 1H, -C*H*(OH)-), 6.82 (d, 1H, Ar-*H*, *J* = 7.4 Hz), 7.49-7.67 (m, 4H, Ar-*H*), 7.82-7.96 (m, 1H, Ar-*H*), 8.20-8.36 (m, 1H, Ar-*H*);

$^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 63.6, 68.9, 70.5, 105.0, 121.1, 121.5, 125.4, 125.7, 126.5, 127.4, 127.6, 134.5, 156.8; MS m/z = 218, Calcd. 218.

**3-(*m*-Tolyloxy)propane-1,2-diol (8g).** White solid; M.p.: 70-73 °C (lit. 71.5-73 °C) [19]; IR (KBr) $\nu$ ($cm^{-1}$): 1040, 1252, 3325; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 2.33 (s, 3H, Ar-C*H*$_3$), 3.42 (s, 2H, -O*H*), 3.73-3.91 (m, 2H, -C*H*$_2$-OH), 3.98-4.23 (d, 2H, ArO-C*H*$_2$-, *J* = 5.0 Hz), 4.08-4.30 (m, 1H, -C*H*(OH)-), 6.76-6.98 (m, 3H, Ar-*H*), 7.18-7.42 (m, 1H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 21.4, 63.6, 68.9, 70.5, 111.4, 115.3, 122.2, 129.3, 139.7, 158.2; MS m/z = 182, Calcd. 182.

**1-Phenylethane-1,2-diol (8h).** White solid; M.p.: 66-68 °C (lit. 65-67 °C) [17]; IR (KBr) $\nu$ ($cm^{-1}$): 3055, 3060, 3260; $^1$H NMR ($CDCl_3$, 250 MHz) $\delta$ 3.59-3.69 (m, 2H, -O*H*), 4.15-4.32 (m, 2H, -C*H*$_2$-OH), 4.73-4.92 (m, 1H, -C*H*(OH)-), 7.26-7.42 (m, 5H, Ar-*H*); $^{13}$C NMR ($CDCl_3$, 62.9 MHz) $\delta$ 64.4, 74.1, 127.4, 128.1, 129.2, 141.3; MS m/z (%): 57 (100.0), 77 (41.2), 97 (34.1), 125 (14.7), 138 ($M^+$, 12.3), 139 ($M^+$+1, 7.1).

## RESULTS AND DISCUSSION

### Ring Opening of Epoxides with Sodium Azide ($NaN_3$) and Sodium Cyanide (NaCN) Catalyzed by Nano MgO in $H_2O$

2-Azido alcohols are precursors of vicinal amino alcohols, which are well known as $\beta$-blockers and present in different bioactive molecules, and in the structure of carbohydrates, nucleosides, lactames, and oxazolines [21, 22]. Azido alcohols are often prepared via the ring opening of epoxides by different azide reagents [22]. The disadvantages of the conventional method with $NaN_3$ and $NH_4Cl$ are long reaction times (12-48 h) and side products [23]. Another method in which $NaN_3$ is used in the presence of a Lewis acid or a transition metal complex, has been also reported [24]. On the other hand, $\beta$-hydroxy nitriles are also versatile intermediates in some organic transformations such as bioactive compounds, unnatural amino acids, $\beta$-blockers and chiral auxiliaries [25]. Direct synthesis of $\beta$-hydroxy nitriles consist of ring opening of epoxides with various reagents of cyanide such as acetone cyanohydrin under basic conditions [26a], LiCN-acetone complex [26b], LiCN [26c], HCN-$AlEt_3$ [26d], KCN/$Bu_4NI$, KCN/18-Crown-6 [26e], KCN/methanol [26f], KCN/$LiClO_4$, KCN/$MgClO_4$, KCN/$NH_4Cl$ [26g], NaCN/12-Crown-4 [26h], NaCN/$Ce(OTf)_4$ [26i], Ln(O*i*-Pr)$_3$/acetone/cyanohydrin [26j], trimethylsilylcyanide (TMSCN) catalyzed by titanium alkoxide Schiff base complexes [26k] and TMSCN/$Yb(CN)_3$ [26l]. Various drawbacks of 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.

Herein using a catalytic amount of nano MgO solves these problems for the synthesis of 2-azido alcohols and $\beta$-hydroxy nitriles. Another advantage of our method is using water as solvent. Water treatment enhances the basicity of MgO and its catalytic performance [27].

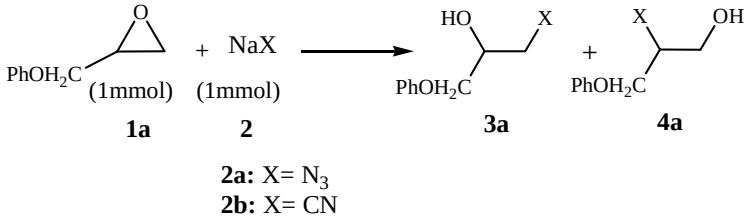
At first, solvents, temperatures, and the amount of catalyst were optimized to obtain the best reaction conditions in the reaction between epoxides (1a) and sodium salts (2) as model compounds (Scheme 1, Table 1).

Isolated yields, b) a mixture of substitution and hydrolysis products were observed, c) a mixture of substitution and elimination products were observed. As shown in Table 1, water is the best solvent for this reaction.

Beside its uniqueness as a green solvent, water treatment enhances the basicity of nano MgO [27]. Temperature is an important parameter in the reaction of epoxides with sodium cyanide (entries 13-16). As temperature increases, elimination will compete with nucleophilic substitution. On the other hand, at room temperature, epoxide hydrolysis on the surface of nano MgO may occur. Therefore, the temperature should be optimized to accelerate nucleophilic substitution reaction and prevent side reactions. So, temperature of 50 °C is the best in which, elimination and hydrolysis are the least (entry 14).

According to the optimized reaction conditions, the ring opening of various epoxides was carried out with azide and cyanide nucleophiles to show the generality and originality of this protocol (Table 2).

As expected, the major product is the result of nucleophile attack to the less hindered side of epoxide except in the case of styrene oxide which prefers benzylic position attack (entry 8). This table illustrates the efficiency of nano MgO to catalyze the azidolysis and nitrilolysis of various epoxides including aliphatic, aromatic, and alicyclic



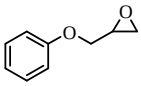
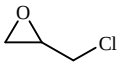
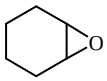
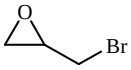
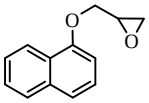
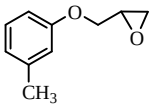
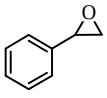

*Scheme 1*

**Table 1.** Examination of Different Parameters in Ring Opening of Phenyl Glycidyl Ether (1a) by $NaN_3$ and NaCN in the Presence of Nano MgO as Catalyst

| Entry | Na salt | mol% of nano MgO | Solvent | T (°C) | Time (h) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | $NaN_3$ 2a | 100 | $H_2O$ | r.t | 7 | 90 |
| 2 | 2a | 50 | $H_2O$ | r.t | 7 | 90 |
| 3 | 2a | 5 | $H_2O$ | r.t | 7 | 95 |
| 4 | 2a | 5 | PEG-300 | r.t | 7 | 95 |
| 5 | 2a | 5 | PEG-400 | r.t | 7 | 90 |
| 6 | 2a | 5 | $CH_3CN$ | r.t | 24 | 0 |
| 7 | 2a | 5 | $CHCl_3$ | r.t | 24 | 0 |
| 8 | 2a | 5 | AcOEt | r.t | 24 | 0 |
| 9 | 2a | 5 | - | r.t | 48 | 10 |
| 10 | 2a | 5 | $H_2O$ | 80 | 4.5 | 95 |
| 11 | 2a | 5 | - | 80 | 8 | 30 |
| 12 | 2a | - | $H_2O$ | 80 | 10 | 50 |
| 13 | NaCN 2b | 5 | $H_2O$ | r.t | 8 | 70[b] |
| 14 | 2b | 5 | $H_2O$ | 50 | 4 | 95 |
| 15 | 2b | 5 | $H_2O$ | 70 | 3.5 | 75[c] |
| 16 | 2b | 5 | $H_2O$ | 80 | 3 | 70[c] |
| 17 | 2b | - | $H_2O$ | r.t | 8 | 60 |

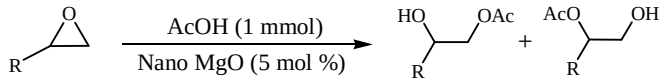
[a]Isolated yields. [b]) A mixture of substitution and hydrolysis products were observed. [c]A mixture of substitution and elimination products were observed.

**Table 2.** Reaction of Epoxides with $NaN_3$[a] and NaCN[b] Using 5 mol% Nano MgO as Catalyst in Water as Solvent

| Entry | Epoxide | Salt | Time (h) | Yield (%)[c] | Ratio of 3:4[d] |
|---|---|---|---|---|---|
| 1 |  **1a** | $NaN_3$ (2a) | 4.5 | 95 | 93:7 |
| | | NaCN (2b) | 4 | 95 | 93:7 |
| 2 |  **1b** | 2a | 4 | 95 | 90:10 |
| | | 2b | 1 | 95 | 90:10 |
| 3 |  **1c** | 2a | 4 | 95 | 100:0 |
| | | 2b | 2 | 95 | 100:0 |
| 4 |  **1d** | 2a | 4 | 90 | 89:11 |
| | | 2b | 1 | 90 | 90:10 |
| 5[e] |  **1e** | 2a | 3 | 95 | 95:5 |
| | | 2b | 2 | 95 | 95:5 |
| 6 |  **1f** | 2a | 10 | 95 | 90:10 |
| | | 2b | 5 | 95 | 90:10 |
| 7 |  **1g** | 2a | 9 | 95 | 90:10 |
| | | 2b | 5 | 95 | 90:10 |
| 8 |  **1h** | 2a | 4 | 95 | 5:95 |
| | | 2b | 3 | 95 | 5:95 |

[a]Reaction temperature was 80 °C; [b]Reaction temperature was 50 °C; [c]Isolated yields; [d]The ratio was determined by GC or $^1$H NMR, [e]Due to its low boiling point, excess amount of 2-methyloxirane was used at room temperature.

**Table 3.** Reaction of Various Epoxides with AcOH Using Nano MgO (5 mol%)

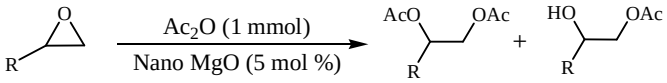



(1 mmol) **1** **5** **6**

| Entry | Epoxide | Time (h) | Yield (%)[a] | Ratio of 5:6[b] |
|---|---|---|---|---|
| 1 | 1a | 10 | 90 | 90:10 |
| 2 | 1b | 10 | 85 | 90:10 |
| 3 | 1c | 8 | 90 | 100:0 |
| 4 | 1d | 9 | 85 | 88:12 |
| 5[c] | 1e | 14 | 90 | 95:5 |
| 6 | 1f | 12 | 90 | 90:10 |
| 7 | 1g | 12 | 90 | 90:10 |
| 8 | 1h | 8 | 90 | 5:95 |

[a]Isolated yields. [b]The ratio was determined by GC or $^1$H NMR. [c]Excess amount of epoxide was used.

**Table 4.** Reaction of Epoxides with $Ac_2O$ Using Nano MgO (5 mol%)

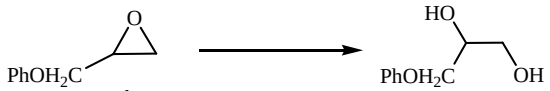



(1 mmol) **1** **7** **5**

| Entry | Epoxide | Time (h) | Yield (%)[a] | Ratio of 7:5[b] |
|---|---|---|---|---|
| 1 | 1a | 8 | 95 | 90:10 |
| 2 | 1b | 7 | 90 | 90:10 |
| 3 | 1c | 7 | 90 | 100:0 |
| 4 | 1d | 8 | 90 | 85:15 |
| 5[c] | 1e | 12 | 90 | 90:10 |
| 6 | 1f | 10 | 90 | 85:15 |
| 7 | 1g | 12 | 90 | 90:10 |
| 8 | 1h | 7 | 95 | 95:5 |

[a]Isolated yields. [b]The ratio was determined by GC or $^1$H NMR. [c]Excess amount of epoxide was used.

**Table 5.** Conversion of Phenyl Glycidyl Ether (1a) to the Corresponding 1,2-Diol 8a




**1a** (1 mmol) → **8a**

| Entry | Catalyst (mol%) | Solvent | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | Nano MgO (5) | $H_2O$ | 24 | 35 |
| 2 | Nano MgO (50) | - | 18 | 80 |
| 3 | Nano MgO (100) | - | 20 | 60 |
| 4 | CM-MgO[b] (5) | - | 24 | 20 |
| 5 | - | $H_2O$ | 24 | 25 |
| 6 | - | - | 24 | 10 |

[a]Isolated yields. [b]CM means commercially.

ones and also some with deactivating groups. Our method shows good results in the case of all epoxides especially epibromohydrine (1d) which is seldom observed in the previous papers as the reactant in nucleophilic ring opening of epoxides.

## Ring Opening of Epoxides with Acetic Acid and Acetic Anhydride (AcOH, $Ac_2O$) Catalyzed by Nano MgO

Acetic acid and acetic anhydride are poor nucleophilic reagents in substitution reactions. However, their use in ring opening of epoxides is a powerful way to *β*-acetoxy alcohols and di-*O*-acetyl-1,2-diols, respectively. Up to now, a variety of Lewis acids have been employed for ring opening of epoxides with acetic acid such as $K_5[CoW_{12}O_{40}].3H_2O$ [28a], $Sn(tpp)(OTf)_2$ [17], $Sn(tpp)(BF_4)_2$ [28b], $AlPW_{12}O_{40}$ [28c], $BF_3.OEt_2$ [28d], $SnCl_4$ [28e], $FeCl_3$ [28f], $FeCl_3.6H_2O/SiO_2$ [28g], $Fe(O_2CCF_3)_3$ [28h], $Ce(OTf)_4$ [28i], $(NH_4)_2Ce(NO_3)_3$ [28j], $Ce[(PVP)_2(NO_3)_3]$ [28k] and $ZrCl_2Cp_2$ [28l]. In comparison with acetic acid, there are much less reports on ring opening of epoxides with acetic anhydride. Direct transformation of epoxides into 1,2-diacetates is a very important reaction, however, it has not been studied extensively. In fact, if a plethora of methods are reported for the synthesis of β-hydroxy ethers and β-amino alcohols, only few methods lead to 1,2-diacetates from epoxides involving the use of acetic anhydride [29]. In these reactions, only two reports have a general value, and the others are limited in scope.

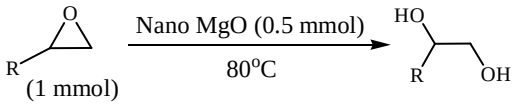
Because of some superiorities over these catalysts such as availability, safety, and cost, introduction of nano MgO as a heterogeneous catalyst with good efficacy can be a new way to improve reaction conditions. Therefore, the acetolysis of various aliphatic, alicyclic, activated, and deactivated epoxides was performed with acetic acid and acetic anhydride using 5 mol% nano MgO as catalyst at reflux condition affording the corresponding *β*-acetoxy alcohols and di-*O*-acetyl-1,2-diols in high yields, respectively. These results are shown in Tables 3 and 4. It is important to note that in these reactions, about 30-50% of epoxide remains un-reacted within heating. Therefore, reflux condition was used to improve the yield [30].

According to Table 4, although di-*O*-acetyl-1,2-diols (**7**) are the main products in this reactions, based on $^1$H NMR spectrum , a little amount (5-15%) of *β*-acetoxy alcohols (5) is generated as the side products.

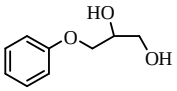
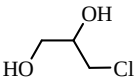
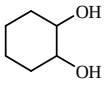
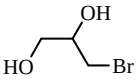
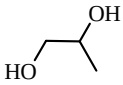
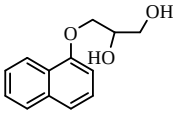
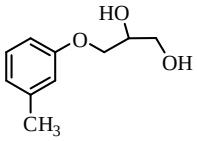
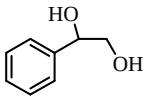
## Hydrolysis of Epoxides Catalyzed by Nano MgO

1,2-Diols and their derivatives are present in many natural and biological compounds [31]. Recently, they have

**Table 6.** Ring Opening of Various Epoxides to 1,2-Diols Using Nano MgO




(1 mmol) **1** **8**

| Entry | Epoxide | Product | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 1a |  **8a** | 18 | 80 |
| 2 | 1b |  **8b** | 10 | 70 |
| 3 | 1c |  **8c** | 12 | 80 |
| 4 | 1d |  **8d** | 10 | 70 |
| 5[b] | 1e |  **8e** | 14 | 60 |
| 6 | 1f |  **8f** | 20 | 80 |
| 7 | 1g |  **8g** | 20 | 75 |
| 8 | 1h |  **8h** | 10 | 85 |

[a]Isolated yields. [b]Due to its low boiling point, excess amount of 2-methyloxirane was used at room temperature.

**Table 7.** Reaction of 1a with some Nucleophiles in the Presence of Nano MgO (5 mol%) and Water

| Entry | Nucleophile | T (°C) | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | $CH_3COONa$ | 80 | 18 | 95 |
| 2 | KF | 80 | 21 | 95 |
| 3 | KBr | 80 | 24 | 50 |
| 4 | KBr (wet) | 80 | 24 | 40 |
| 5 | KBr | 100 | 24 | 60 |
| 6 | NaI | 80 | 24 | 50 |
| 7 | NaI | 100 | 24 | 70 |

[a]Isolated yields.

been used as building blocks for surface engineering to provide a stable binding of organic ligands onto the surface of $Fe_2O_3$ nanoparticles [32]. Since then, several methods have been reported to produce 1,2-diols such as aldol condensation of α-hydroxy- and α-alkoxy acetones with aldehydes [33], treatment of primary ozonides derived from alkenyl stannanes with dimethyl sulfide and borane-methyl sulfide complex [34], oxidation of olefins by t-butyl hydrogen peroxide over metal oxide catalysts [35], using hypervalent iodine(III) reagent [36], and homologation of boronic esters with lithiated epoxides [37]. The last one is one of the newest methods in which epoxides are used as reactant for preparation of 1,2-diols. Despite of their efficacy, some of these methods use toxic materials as reagents. To eliminate this problem, herein we developed a new method in which nano MgO (18 nm) as a green material is used to convert epoxides into corresponding 1,2-diols without using any reagents or solvents.

Under our optimized conditions for the ring opening of epoxides with sodium azide (Table 1, entry 10), the ring opening of 1a to the corresponding 1,2-diol, very poor results were obtained (24 h, 35%). Therefore, we were screening this reaction to find the best conditions. The results are shown in Table 5.

From the results shown in Table 5, the noticeable difference between nano MgO and CM-MgO arises from their surface area. CM-MgO has a surface area in the range of 10-30 $m^2\ g^{-1}$ [2,10] while synthesized nano MgO exhibits a surface area of 119 $m^2\ g^{-1}$. Proportional to this increase, morphological defect sites such as steps and corners [38] are increased. In this manner, nano MgO will have higher concentration of hydroxyl and other active groups per unit area. As a result, in the absence of a strong nucleophile, surface hydroxyl groups of nano MgO attack the epoxide ring and 1,2-diols are obtained. Also, nano magnesium oxide even acts more effectively than water (entry 5). Using optimized conditions (entry 2), various epoxides turned into corresponding 1,2-diols.

Diol generation is a competitor reaction in the case of ring opening of epoxides by some nucleophiles. For example, we tested the reaction of phenyl glycidyl ether (1a) with sodium acetate in the presence of catalytic amount of nano MgO (5 mol%) and water as solvent (Table 7, entry 1). It is interesting that no β-acetoxy alcohol product was observed. $^1$H NMR, $^{13}$C NMR, and mass spectra proved that the pure product produced with high yield, was a 1,2-diol. The reactions of 1a with KF, KBr, and NaI in the same conditions had similar results. We conclude that nano MgO cannot be the catalyst of epoxide opening reaction by halides in these conditions.

To explain the result achieved in the case of sodium acetate, we should study the surface of nano MgO again. As reported, MgO may adsorb oxygen containing species [39]. For instance, it can be hydroxylated upon exposure to water and $MgOH^+$ or $Mg(OH)_2$ are formed [40]. Probably, some surface hydroxyl groups are released during the adsorption of oxygen containing species. Since the number of these hydroxyl groups is greater in nano MgO per unit area, it performs more effectively than its commercial analogue. Undoubtedly, other factors such as the nature of nucleophile and even hydrogen bonding (in the case of KF), are efficacious too.

In conclusion, epoxides regioselectively react with some nucleophiles in the presence of nano MgO as a heterogeneous catalyst. Water plays an important role in this method not only as a safe solvent but also to activate the catalyst and improve its basicity. Using this new method, a range of epoxides was converted to the corresponding 2-substituted alcohols. Also, unusual surface activity of nano MgO makes it suitable as a catalyst for many processes. Its numerous surface hydroxyl groups can act as nucleophile and cause ring opening of epoxides to convert to the corresponding 1,2-diols. In this method, without using any toxic reagent or harsh reaction conditions, epoxides turn into 1,2-diols with good to high yields.

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