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Graphite oxide: a simple and efficient solid acid catalyst for the ring-opening of epoxides by alcohols

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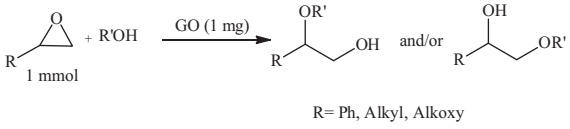
ABSTRACT

A simple, efficient, and general procedure for the ring-opening of epoxides with various alcohols to give the corresponding β-alkoxy alcohols using graphite oxide (GO) as the catalyst, under very mild reaction conditions is described. The method proceeds in good to excellent yields and in short reaction times at room temperature under metal-free conditions.

Epoxides are useful and valuable intermediates because of their versatility and reactivity with a large range of nucleophiles such as alcohols, amines, and thiols.[1] The ring-opening of epoxides by the addition of alcohols leads to synthetically important β-alkoxy alcohols.[2] This reaction can be catalyzed under basic or acidic conditions. Several Lewis[2a–c,3a–d] and Brønsted acids,[2e,3e] porphyrin complexes,[3f] perchlorates,[3g] and triflates[3h] have been used as catalysts for the activation of epoxides to nucleophilic attack. For example, bis(cyclopentadienyl)zirconium dichloride catalyzed ring-opening reactions of epoxides to give β-alkoxy alcohols occur in good to excellent yields.[2b] Bradley et al., found that $Al(OTf)_3$ (at ppm levels) was an effective catalyst for the ring-opening of epoxides using a wide range of alcohols.[2d] Heterogeneous catalysts such as metal-organic frameworks,[4a] mesoporous aluminosilicate,[4b] mesoporous activated carbon,[4c] propylsulfonic acid functionalized SBA-15 (SBA-15-pr-SO_3H),[4d] and mesoporous AlKIT-5[4e] have also been investigated for the ring-opening of epoxides.

Graphite oxide (GO), prepared by exhaustive oxidation of graphite, has been used as a heterogeneous catalyst for several organic transformations.[5] We have reported on the use of GO as a highly efficient reagent for the oxidation of 1,4-dihydropyridines into pyridine derivatives.[6] More recently, GO and oxone have been successfully applied for direct oxidative ester formation from aldehydes and alcohols under ultrasonication.[7] The surface of GO comprises different oxygen-containing groups such as hydroxyl, epoxy, and carbonyl, which confer an acidic character to the material. This property has recently been applied for the esterification of organic acids with alcohols under mild conditions.[8] In continuation of our investigations on the use of GO for organic transformations,[6–10] we report herein a new and simple method for the ring-opening of epoxides by various alcohols using GO as a solid acid catalyst under very mild metal-free reaction conditions (Scheme 1).



Scheme 1. Alcoholysis of epoxides using GO.

The experimental procedure is quite simple and straightforward. Initially, we tested the efficacy of GO, a readily available and inexpensive material, for this chemical transformation by screening the reaction of styrene oxide (1 mmol) with *n*-butanol (3 mmol) under different conditions. The resulting mixture was stirred for the time indicated in Table 1 prior to GC/MS analysis. The reaction of styrene oxide (1 mmol) with *n*-butanol (3 mmol) in the absence of GO led to the recovery of the starting materials, even after stirring at room temperature for 24 h (entry 1, Table 1). When the reaction of styrene oxide (1 mmol) with *n*-butanol (3 mmol) was performed in the presence of 50 mg or 25 mg of GO, an exothermic reaction took place and the corresponding alcohol, 2-butoxy-2-phenylethanol, was obtained in 59% and 66% yield

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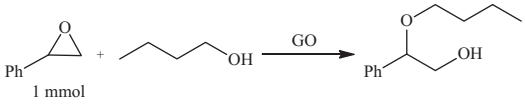
Table 1
Optimization of the reaction conditions for the ring-opening of styrene oxide with *n*-butanol[a]



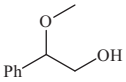
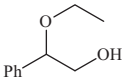
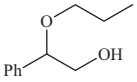
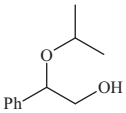
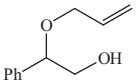
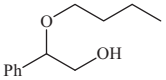
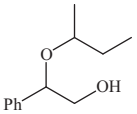
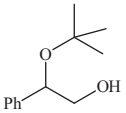
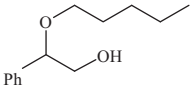
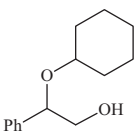
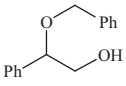
Entry	GO (mg)	*n*-Butanol (mmol)	Time (min)	Yield (%)
1	—	3	24	—
2	50	3	5	59
3	25	3	5	66
4	12	3	30	79
5	1	3	105	90
6	1	3	195	64[b]
7	1	5	60	94

[a] Conditions: a mixture of styrene oxide (1 mmol), *n*-butanol, and GO was stirred at room temperature for the time indicated.
[b] Reaction was performed in CH_2Cl_2 as the solvent.

after 5 min, respectively, (entries 2 and 3, Table 1). It should be noted that several unknown compounds were observed in the GC/MS spectra. Decreasing the amount of GO to 12 mg and 1 mg gave 2-butoxy-2-phenylethanol in 79% and 90% yields after 30 min and 105 min, respectively, (entries 4 and 5, Table 1). Thus 1 mg of GO was found to be sufficient for this reaction. We also investigated this reaction in dichloromethane as the solvent and the obtained results indicated a decrease in the yield to 64% and an increase of the reaction time to 195 min (entry 6, Table 1). Using 5 mmol of *n*-butanol (instead of 3 mmol) led to an increase of the reaction yield to 94% and a decrease of the reaction time to 90 min for the alcoholysis of styrene oxide using GO (1 mg) under solvent-free conditions (entry 7, Table 1).

Under optimized conditions, a wide range of epoxides (1 mmol) was converted into the corresponding alcohols in good to excellent yields by treatment with various alcohols (5 mmol) in the presence of GO (1 mg) at room temperature for the time indicated in Table 2.[11] Under these experimental conditions, the methanolysis

Table 2
Alcoholysis of epoxides catalyzed by GO[a]

Entry	Epoxide	Alcohol	Product	Time (h)	Yield[b] (%)
1		Methanol		0.5	94[3e]
2		Ethanol		0.5	72[4b]
3		*n*-Propanol		0.5	90[4b]
4		*i*-Propanol		5	86[4b]
5		Allyl alcohol		0.5	56[12]
6		*n*-Butanol		1	94[2d]
7		2-Butanol		6	84[3e]
8		*t*-Butanol		7	91[2d]
9		*n*-Pentanol		2	84
10		Cyclohexanol		4.5	94[3h]
11		Benzyl alcohol		2	70[13]

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