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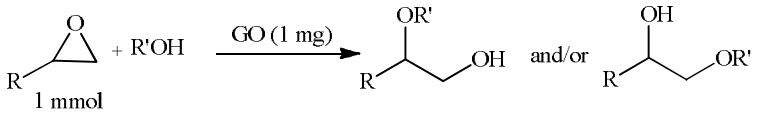
A simple, efficient and general procedure for the ring-opening of epoxides with various alcohols to give the corresponding β-alkoxy alcohols using graphite oxide (GO) as the catalyst under very mild reaction conditions is described.



R= Ph, Alkyl, Alkoxy

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.

Keywords: Epoxide; Ring-opening; Graphite oxide; 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 and co-workers 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]

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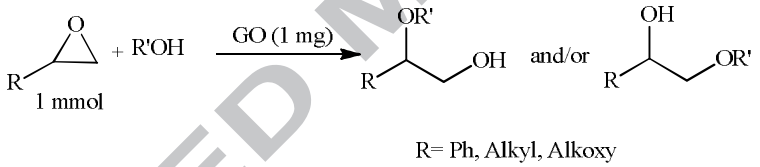
Heterogeneous catalysts such as metal-organic frameworks,[4a] mesoporous aluminosilicate,[4b] mesoporous activated carbon,[4c] propylsulfonic acid functionalized SBA-15 (SBA-15-pr-SO_3H)[4d] and mesoporous AlKIT-5[4e] have also been investigated for the ring-opening of epoxides.

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 the 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 and conditions (Scheme 1).

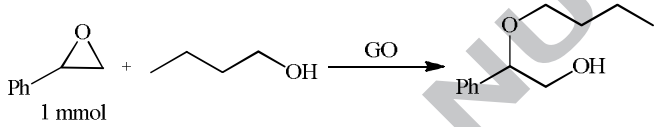


Scheme 1. Alcoholysis of epoxides using GO.

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 recovery of the starting materials, even after stirring at room temperature for 24 hours (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 after 5 minutes, 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 minutes and 105 minutes, 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 minutes (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 minutes for the alcoholysis of styrene oxide using GO (1 mg) under solvent-free conditions (entry 7, Table 1).

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] The reaction was performed in CH_2Cl_2 as the solvent.

Under the 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 of styrene oxide in the presence of GO afforded 2-methoxy-2-phenylethanol in 94% yield after 30 minutes (entry 1, Table 2). Similarly, the alcoholysis of styrene oxide with ethanol, *n*-propanol, allyl alcohol, *n*-butanol and *n*-pentanol gave 2-ethoxy-2-

phenylethanol, 2-propoxy-2-phenylethanol, 2-(allyloxy)-2-phenylethanol, 2-butoxy-2-phenylethanol and 2-(pentyloxy)-2-phenylethanol in 56-94% yields after 30-120 minutes (entries 2, 3, 5, 6 and 9, Table 2). We also investigated the alcoholysis of styrene oxide with acyclic and cyclic secondary alcohols such as *i*-propanol, 2-butanol and cyclohexanol. The results obtained indicated that a long reaction time was required for epoxide ring-opening with secondary alcohols. Indeed, 2-*iso*-propoxy-2-phenylethanol, 2-(*sec*-butoxy)-2-phenylethanol and 2-(cyclohexyloxy)-2-phenylethanol were obtained in 86%, 84% and 94% yields after 5, 6 and 4.5 hours, respectively (entries 4, 7 and 10, Table 2). The efficiency of this procedure was also demonstrated for the alcoholysis of styrene oxide with the tertiary alcohol, *t*-butanol, and 2-(*tert*-butoxy)-2-phenylethanol was isolated in 91% yield after 7 hours (entry 8, Table 2). The reaction of benzyl alcohol with styrene oxide afforded 2-(benzyloxy)-2-phenylethanol in 70% yield after two hours at room temperature (entry 11, Table 2).

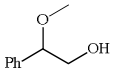
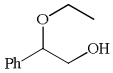
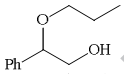
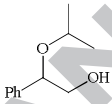
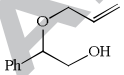
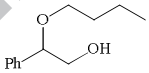
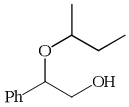
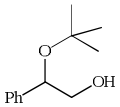
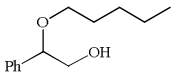
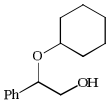
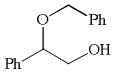
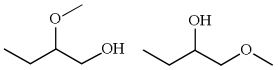
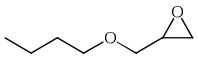
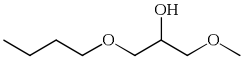
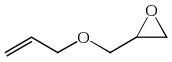
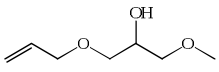
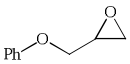
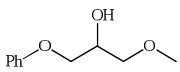
It should be noted that the alcoholysis of styrene oxide was remarkably regioselective and occurred at the more highly substituted carbon atom of the epoxide ring.[2d, 3b-c] The nucleophilic attack on the sterically more hindered position of the epoxide suggests that the reaction is controlled by electronic effects. In this case, electronic effects dominate over steric effects; the transition state carbocation at the secondary carbon atom is stabilized through resonance with the phenyl ring, thereby promoting nucleophilic attack at this position. Indeed, the regioselectivity of this reaction can be proved by analysis of the MS spectra. We observed a mass ion $[M\text{-}CH_2OH]^+$ due to the Marknikov-type products in the mass spectrum, which would not be observed for anti-Marknikov-type products.

In contrast, the methanolysis of 2-ethyloxirane provided two isomers: 2-methoxybutan-1-ol and 1-methoxybutan-2-ol in 38% and 58% yield (1:1.5 mole ratio), respectively. In this case, the reaction is not regioselective and two isomers resulting from attack at either end of the epoxide ring were observed.

Furthermore, we investigated the methanolysis of 2-(butoxymethyl)oxirane, 2-[(allyloxy)methyl]oxirane and 2-(phenoxy)methyloxirane under similar conditions. 1-Butoxy-3-methoxypropan-2-ol, 1-(allyloxy)-3-methoxypropan-2-ol and 1-methoxy-3-phenoxypropan-2-ol were isolated in 81%, 25% and 38% yields after 5, 2 and 2 hours, respectively (entries 13-15, Table 2). The results obtained suggest that

alcoholysis of the epoxide is regioselective and that nucleophilic attack occurs at the less hindered carbon atom of the epoxide ring. In these cases, steric effects dominate over electronic effects. Increasing the amount of GO to 10 mg led to higher yields of the expected products (entries 14 and 15, Table 2).

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]
12		methanol		1	38/58[2d]
13		methanol		5	81[14]
14		methanol		2 2	25[15] 67[c]
15		methanol		2 2	38[4b] 72[c]

[a] Conditions: a mixture of epoxide (1 mmol), alcohol (5 mmol) and GO (1 mg) was reacted at room temperature for the time indicated in Table 2.

[b] Isolated yield.
[c] 10 mg of GO was used.

In summary, the described procedure using graphite oxide as a solid acid catalyst provides a very simple and efficient method for the ring-opening of a wide range of epoxides by a variety of alcohols at room temperature. The alcoholysis of epoxides in the presence of GO afforded the corresponding alcohols in good to very high yields and in short reaction times, under metal-free and mild conditions with excellent regioselectivity.

References

1. (a) Robinson, M. W. C.; Buckle, R.; Mabbett, I.; Grant, G. M.; Graham, A. E. *Tetrahedron Lett.* **2007**, *48*, 4723; (b) Yarapathi, R. V.; Reddy, S. M.; Tammishetti, S. *React. Funct. Polym.* **2005**, *64*, 157; (c) Huang, J.; Akita, T.; Faye, J.; Fujitani, T.; Takei, T.; Haruta, M. *Angew. Chem. Int. Ed.* **2009**, *48*, 7862; (d) Ollevier, T.; Lavie-Compin, G. *Tetrahedron Lett.* **2004**, *45*, 49.
2. (a) Chandrasekhar, S.; Reddy, Ch. R.; Babu, B. N.; Chandrashekar, G. *Tetrahedron Lett.* **2002**, *43*, 3801; (b) Kantam, M. L.; Aziz, K.; Jeyalakshmi, K.; Likhar, P. R. *Catal. Lett.* **2003**, *89*, 95; (c) Prestat, G.; Baylon, C.; Heck, M.-P.; Mioskowski, C. *Tetrahedron Lett.* **2000**, *41*, 3829; (d) Bradley, G.; Williams, D.; Lawton, M. *Org. Biomol. Chem.* **2005**, *3*, 3269; (e) Gallo, J. M. R.; Teixeira, S.; Schuchardt, U. *Appl. Catal. A* **2006**, *311*, 199; (f) Solodenko, W.; Jas, G.; Kunz, U.; Kirschning, A. *Synthesis* **2007**, 583; (g) Iranpoor, N.; Baltork, I. M. *Tetrahedron Lett.* **1990**, *31*, 735;
3. (a) Barluenga, J.; Vázquez-Villa, H.; Ballesteros, A.; González, J. M. *Org. Lett.* **2002**, *4*, 2817; (b) Kim, B. H.; Piao, F.; Lee, E. J.; Kim, J. S.; Jun, Y. M.; Lee, B. M. *Bull. Korean Chem. Soc.* **2004**, *25*, 881; (c) Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Shaibani, R. *Tetrahedron* **2004**, *60*, 6105; (d) Firouzabadi, H.; Iranpoor, N.; Jafari, A. A.; Makarem, S. *J. Mol. Catal. A: Chem.* **2006**, *250*, 237; (e) Weil, T.; Kotke, M.; Kleiner, C. M.; Schreiner, P. R. *Org. Lett.* **2008**, *10*, 1513; (f) Zakavi, S.; Karimipour, G. R.; Gharab, N. G. *Catal. Commun.* **2009**, *10*, 388; (g) Salehi, P.; Seddighi, B.; Irandoost, M.; Behbahani, F. K. *Synth. Commun.* **2000**, *30*, 2967; (h) Likhar, P.; Kumar, M.; Bandyopadhyay, A. *Synlett* **2001**, 1196.

4. (a) Dhakshinamoorthy, A.; Alvaro, M.; Garcia, H. *Chem. Eur. J.* **2010**, *16*, 8530; (b) Robinson, M. W. C.; Davies, A. M.; Buckle, R.; Mabbett, I.; Taylor, S. H.; Graham, A. E. *Org. Biomol. Chem.* **2009**, *7*, 2559; (c) Matos, I.; Neves, P. D.; Castanheiro, J. E.; Perez-Mayoral, E.; Martin-Aranda, R.; Duran-Valle, C.; Vital, J.; Botelho do Rego, A. M.; Fonseca, I. M. *Appl. Catal., A* **2012**, *439–440*, 24; (d) Saikia, L.; Satyarthi, J. K.; Srinivas, D.; Ratnasamy, P. *J. Catal.* **2007**, *252*, 148; (e) Chakravarti, R.; Oveisi, H.; Kalita, P.; Pal, R. R.; Halligudi, S. B.; Kantam, M. L.; Vinu, A. *Microporous Mesoporous Mater.* **2009**, *123*, 338.
5. (a) Vijay Kumar, A.; Rama Rao, K. *Tetrahedron Lett.* **2011**, *52*, 5188; (b) Dreyer, D. R.; Bielawski, C. W. *Chem. Sci.* **2011**, *2*, 1233; (c) Dreyer, D. R.; Jia, H.-P.; Bielawski, C. W. *Angew. Chem. Int. Ed.* **2010**, *49*, 6686; (d) Jia, H.-P.; Dreyer, D. R.; Bielawski, C. W. *Tetrahedron* **2011**, *67*, 4431; (e) Jia, H.-P.; Dreyer, D. R.; Bielawski, C. W. *Adv. Synth. Catal.* **2011**, *353*, 528; (f) Dreyer, D. R.; Jia, H.-P.; Todd, A. D.; Geng, J.; Bielawski, C. W. *Org. Biomol. Chem.* **2011**, *9*, 7292; (g) Dreyer, D. R.; Jarvis, K. A.; Ferreira, P. J.; Bielawski, C. W. *Polym. Chem.* **2012**, *3*, 757; (h) Dreyer, D. R.; Jarvis, K. A.; Ferreira, P. J.; Bielawski, C. W. *Macromolecules* **2011**, *44*, 7659.
6. Mirza-Aghayan, M.; Boukherroub, R.; Nemati, M.; Rahimifard, M. *Tetrahedron Lett.* **2012**, *53*, 2473.
7. Mirza-Aghayan, M.; Zonoubi, S.; Molaee Tavana, M.; Boukherroub, R. *Ultrason. Sonochem.* **2014**, *22*, 359.
8. Mirza-Aghayan, M.; Rahimifard, M.; Boukherroub, R. *Turk. J. Chem.* **2014**, *38*, 859.
9. Mirza-Aghayan, M.; Kashef-Azar, E.; Boukherroub, R. *Tetrahedron Lett.* **2012**, *53*, 4962.
10. Mirza-Aghayan, M.; Molaee Tavana, M.; Boukherroub, R. *Tetrahedron Lett.* **2014**, *55*, 342.
11. General procedure for the alcoholysis of epoxides: To a solution of epoxide (1 mmol) and alcohol (5 mmol) was added 1 mg of graphite oxide (GO) at room temperature and the mixture stirred for the time indicated in Table 2 prior to GC/MS analysis. CH_2Cl_2 was added and the mixture was filtered and evaporated under reduced pressure. Pure products were isolated by flash column chromatography using hexane/EtOAc (6/1) as eluent. The products were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy and mass spectrometry.

Spectroscopic data for 2-(pentyloxy)-2-phenylethanol (entry 9, Table 2): Colorless oil, ^{1}H NMR (80 MHz, $CDCl_3$): δ = 0.8 (m, 3H, CH_3), 1.4 (m, 6H, $CH_2CH_2CH_2$), 3.3 (m, 3H, OCH_2, OH), 3.5 (m, 1H, CH_2OH), 4.25 (dd, *J*=1.6 Hz, 0.8 Hz, 1H, CH_2OH), 4.7 (dd, *J*=1.6 Hz, 0.8 Hz, 1H, CH), 7.3 (m, 5H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.43, 22.93, 28.76, 29.97, 67.91, 69.70, 83.28, 127.22, 128.42, 128.91, 139.44; MS (EI) (70 eV), *m*/*z* (%): 177 (32) $[M\text{-}CH_2OH]^+$, 121 (100), 107 (53), 91 (5), 71 (5); IR (KBr): ν = 3440, 2931, 2866, 1455, 1103, 1042, 913, 744, 701 cm^{-1}.

12. Kumar, G. D. K.; Baskaran, S. *J. Org. Chem.* **2005**, *70*, 4520.
13. Otera, J.; Yoshihisa, N.; Hitosi, N. *Tetrahedron* **1991**, *47*, 7625.
14. Garcia, J. I.; Garcia-Marin, H.; Mayoral, J. A.; Perez, P. *Green Chem.* **2010**, *12*, 426.
15. Jeyakumar, K.; Chand, D. K. *Synthesis* **2008**, 807.