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Mesoporous aluminosilicate promoted alcoholysis of epoxides

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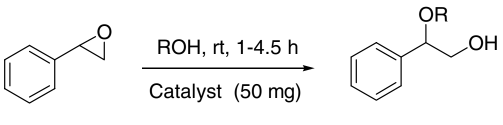
Abstract—Mesoporous aluminosilicates efficiently catalyze the ring-opening of epoxides with a range of alcohols to give the corresponding β-alkoxyalcohols in high yields under extremely mild conditions and in short reaction times.

Epoxides are highly versatile synthetic intermediates in organic synthesis and undergo ring-opening reactions to give β-substituted alcohols with a variety of nucleophilic species with high regio- and stereoselectivity.[1] The addition of alcohols to epoxides to produce β-alkoxyalcohols is a widely studied reaction, however, its application is limited due to the poor nucleophilicity of alcohols which requires the use of strongly acidic or basic conditions or Lewis acid promoters.[2] These protocols are often far from ideal, and suffer from disadvantages such as high toxicity and corrosiveness of the acids employed, the requirement to use stoichiometric quantities, long reaction times or inconvenient handling procedures.[3] Therefore, the introduction of new methods for the nucleophilic ring-opening of epoxides that work under mild conditions is of great importance. The use of heterogeneous catalysts provides an ideal solution to these limitations and the use of solid acid catalysts such as Amberlyst-15, pillared clays, functionalized alumina or silica and polymer supported ferric chloride or copper sulfate has shown great promise in this area.[4] The recent advent of the mesoporous aluminosilicate materials has had a substantial impact in the area of heterogeneous catalysis, and they have been shown to promote a range of synthetic transformations.[5] However, there is no precedent in the literature for the use of mesoporous aluminosilicates as catalysts for ring-opening reactions of epoxides.[6] In this study, we wish to report the facile conversion of epoxides into β-alkoxyalcohols (Scheme 1) utilizing a mesoporous aluminosilicate catalyst.

A small range of mesoporous aluminosilicate materials were synthesized using the literature procedures,[7] and their ability to catalyze the nucleophilic ring-opening of styrene oxide with methanol was studied. It was found that the reaction was successfully catalyzed to varying degrees by all of the aluminosilicate materials. However, under the conditions studied to date, materials with Si/Al ratios = 14, as measured by EDX analysis, were found to be the most efficient. Interestingly, the plain silicate material displayed little catalytic activity and starting material was recovered unchanged from these reactions,[8] suggesting that the transformation is dependent on the Lewis acid nature of the catalyst rather than simple Brönsted acid activity.[9] The few reports that utilize Brönsted acid catalysis typically require forcing conditions, microwave irradiation or report low yields.[10]

Reactions utilizing catalytic quantities of this mesoporous aluminosilicate catalyst in methanol at room temperature readily transformed styrene oxide into 2-methoxy-2-phenyl-ethanol in a highly efficient manner (Table 1). This protocol was also found to be effective when higher molecular weight alcohols were used,



Scheme 1.

Keywords: Aluminosilicates; Epoxides; β-Alkoxyalcohols; Heterogeneous catalysis.

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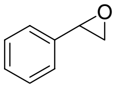
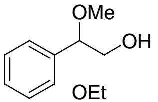
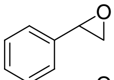
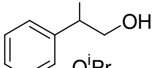
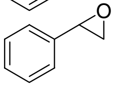
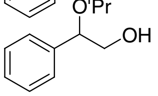
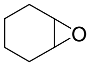
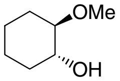
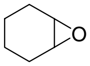
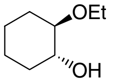
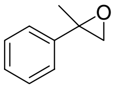
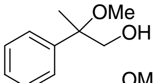
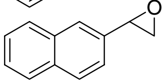
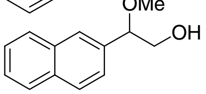
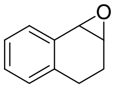
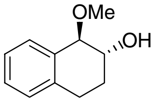
Table 1. Mesoporous aluminosilicate promoted alcoholysis of epoxides

Entry	Epoxide[a]	Time (h)	Product[b,c]	Yield[d] (%)
1		1.5		95
2		2.5		86
3		3.5		52
4		1		69
5		1		96
6		3		97
7		4.5		90[e,f]
8		1		99

[a] All epoxides were used as supplied or synthesized according to the literature procedures.[14]

[b] Reactions at room temperature in 10 mL of the alcohol (MeOH, EtOH, ^{i}PrOH) utilizing 50 mg of catalyst.

[c] Regioselectivity was determined from crude ^{1}H NMR spectra.

[d] All compounds gave satisfactory spectroscopic data.

[e] Isolated yield after column chromatography.

[f] Reaction at 50 °C.

however, sterically hindered alcohols, such as 2-propanol, gave low isolated yields of addition products due to a competing Meinwald rearrangement.[11] Gratifyingly, the alcoholysis of a range of both cyclic and acyclic epoxides with methanol proceeded readily at room temperature to produce the expected β-alkoxyalcohols in high yields and with high regioselectivity.[3d,12] Furthermore, in a number of cases the crude products did not require chromatographic purification, further demonstrating the synthetic utility of this protocol. Reactions of cyclohexene oxide with higher molecular weight alcohols resulted in low isolated yields even though NMR analysis of the crude reaction mixtures indicated complete conversion of the starting material to the desired β-alkoxyalcohol. This may be attributed to the organophilicity of these materials where the product remains adsorbed on the aluminosilicate.[13] Attempts to remove the product from the catalyst by washing did not lead to improved isolated yields.

In conclusion, it has been shown that mesoporous aluminosilicates efficiently catalyze the regioselective addition of alcohols to epoxides to produce β-alkoxyalcohols in high yields and in short reaction times. The facile synthesis of these catalysts, their benign nature, the ease of handling and the simplified reaction and isolation procedures make them a highly attractive alternative to current methodologies.

Typical procedure for the formation of β-alkoxyalcohols: Styrene oxide (120 mg, 1 mmol) was dissolved in methanol (10 mL) at room temperature. The catalyst (50 mg) was added and the reaction mixture stirred at room temperature and monitored by TLC. Upon completion of the reaction the catalyst was removed by filtration through a Celite plug which was washed with dichloromethane (2 × 5 mL) and the combined solvents were removed under reduced pressure to give the product *2-methoxy-2-phenyl-ethanol* (114 mg, 95%) as a colourless oil; ^{1}H NMR (400 MHz; $CDCl_3$) $\delta = 7.44$–7.29 (5H, m), 4.34 (1H, dd, $J = 4$ and 5 Hz), 3.74–3.59 (2H, m), 3.34 (3H, s), 2.45 (1H, br s); ^{13}C NMR (100 MHz; $CDCl_3$) $\delta = 138.7$, 129.4, 129.3, 128.9, 127.4, 127.3, 85.1, 67.8, 57.3; MS (CI+NH_3) m/z 170 ($M+NH_4^+$); HRMS (CI+NH_3) calculated for $C_9H_{16}NO_2$ ($M+NH_4^+$) 170.1176, found ($M+NH_4^+$) 170.1176.

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