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Microwave-assisted Aminolysis of Epoxides Under Solvent-free Conditions Catalyzed by Montmorillonite Clay†

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The reaction of primary and secondary amines with epoxides in the presence of montmorillonite K10 clay, under solvent-free condtions and microwave irradiation affords high yields of β-amino alcohols.

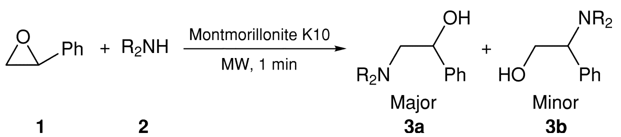
β-Amino alcohols are important organic compounds in biological and pharmaceutical processes. One of the best routes to synthesize these compounds involves the regioselective ring opening of oxiranes at elevated temperatures[1,2] or in the presence of metal salts such as lithium perchlorate,[3] samarioum iodide,[4] cobalt(II) chloride,[5,6] lithium methanetrifluorosulfonate,[7] titanium tetraisopropoxide,[8] and polymer-supported reagents.[9] In many of these cases, the ring opening of epoxides is carried out in a solvent, and normally requires many hours at reflux temperature under environmentally unfriendly conditions.

Montmorillonite K10 clay has long been known to show strong solid acidity, and has been used as a catalyst in organic reactions. Microwave-assisted treatment of liquid and solid samples has been a very helpful method for organic and inorganic synthesis and its application in rapid synthetic organic chemistry has received much attention in recent years.[10–12]

In this paper we report a new, simple, and fast procedure for ring opening of epoxides with a cheap and convenient heterogeneous catalyst. These reactions are performed in a domestic conventional microwave oven, under solvent-free conditions, although more sophisticated microwave reactors are now commercially available.

When epoxide **1** were treated with 1.0 equivalent of a primary or secondary amine **2** in the presence of 0.2 g montmorillonite K10 clay under microwave irradiation, without any solvent, complete reaction took place, leading to β-amino alcohols **3a**–**m** (Scheme 1).

The reaction takes place in the solid phase, in an open vessel, and the products can be extracted from the support by solvent. The starting epoxides, products and yields are shown in Table 1.

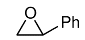
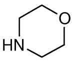
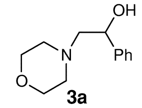
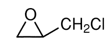
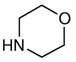
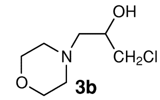
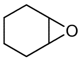
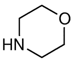
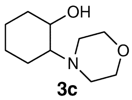
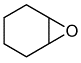
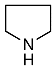
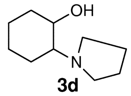
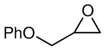
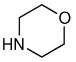
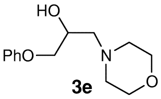
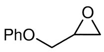
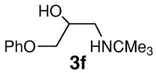
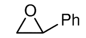
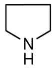
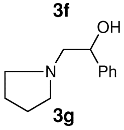
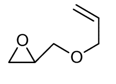
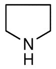
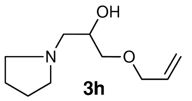
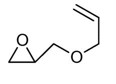
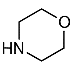
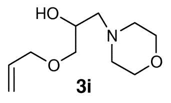
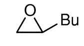
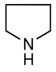
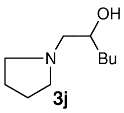
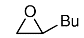
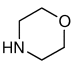
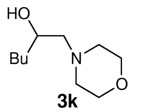
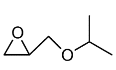
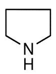
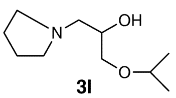
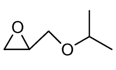
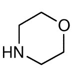
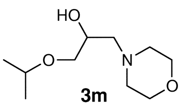


1 **2** **3a** **3b**

Scheme 1

Distribution of the products in Table 1 shows that the regioselectivity of ring opening of the epoxide is low in some cases. Ring opening of epoxides in entries 8, 9 and 12, 13 occur with very high regioselectivity. Only one product was obtained in these cases. The low yield of **3j** and **3k** may be due to evaporation of starting epoxide during microwave heating, since no epoxide was found in the product after microwave irradiation. Increasing the amount of epoxide in

Table 1 Distribution of the ring opening products of epoxides by primary and secodary amines

Entry	Epoxide	Amine	Major product	Ratio of major to minor product	(%) Yield (total)
1			 **3a**	1.7	85
2			 **3b**	1.7	54
3			 **3c**	—[b]	65
4			 **3d**	—[b]	46
5			 **3e**	—[b]	91
6		H_2NCMe_3	 **3f**	1.2	53
7			 **3g**	2.9	69
8			 **3h**	—[b]	80[a]
9			 **3i**	—[b]	74
10			 **3j**	1.9	30
11			 **3k**	1.8	25
12			 **3l**	—[b]	79
13			 **3m**	—[b]	77

[a]The yield after 3 h at 70 °C (oil bath) was only 25%. [b]The only product.

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†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1999, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

entries 10 and 11 did not change the yield in these reactions. However irradiation for 30 s with a 2 min interval gave a 35% yield of β-amino alcohol **3k**.

Experimental

Montmorillonite K10 clay was activated in the microwave oven for 5 min just before use. The products were purified by column chromatography, using aluminium oxide, eluting with light petroleum, if needed. All compounds were identified by NMR and IR spectroscopy.[13]

General Procedure for the Preparation of β-Amino Alcohols.—A mixture of epoxide (1 mmol), amine (1 mmol) and montmorillonite K10 clay (0.2 g) was placed in a Teflon container with a screw cap. Then the mixture was irradiated with high power (900 W) in a conventional microwave oven for 1 min. After the mixture was cooled to room temperature, it was washed with dichloromethane (2 × 10 ml). The solvent was evaporated and the product(s) were identified.

In conclusion, ring opening of epoxides with primary and secondary amines can be achieved within 1 min under environmentally friendly solvent-free conditions under microwave irradiation in the presence of montmorillonite K10 clay as solid support. These organic reactions are safe and take place more rapidly and with higher yields compared to conventional heating.

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12 C. R. Strauss and R. W. Trainor, *Aust. J. Chem.*, 1995, **48**, 1665.
13 *Selected Spectroscopic Data.*—Compounds **3a**–**3g**, **3j** and **3k** have been synthesized previously.[3,4] The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC80 instrument using $CDCl_3$ as solvent. Chemical shifts are in ppm relative to TMS. **3h**: δ_H 1.28–1.51 (m, 4H), 1.98–2.52 (m, 6H), 3.01–3.18 (m, 2H), 3.42–3.63 (m, 1H), 3.63–3.90 (m, 3H), 4.70–5.12 (m, 2H), 5.34–5.88 (m, 1H). δ_C 23.46 (CH_2), 54.34 (CH_2), 59.18 (CH_2), 67.94 (CH_2), 72.24 (CH_2), 72.94 (CH), 116.82 (CH_2), 134.76 (CH). **3i**: δ_H 2.12–2.75 (m, 6H), 3.31 (t, $J = 5.8$ Hz, 4H), 3.41–4.06 (m, 6H), 4.85–5.38 (m, 2H), 5.52–6.11 (m, 1H). δ_C 53.88 (CH_2), 61.53 (CH_2), 66.29 (CH_2), 66.75 (CH_2), 77.23 (CH_2), 77.33 (CH), 116.88 (CH_2), 134.69 (CH). **3l**: δ_H 1.01 (d, $J = 6.0$ Hz, 6H), 1.61–1.88 (m, 4H), 2.27–2.76 (m, 6H), 3.34–3.98 (m, 3H), 4.51 (s, 1H). δ_C 21.92 (CH_3), 23.99 (CH_2), 54.20 (CH_2), 59.10 (CH_2), 68.10 (CH_2), 70.91 (CH), 71.92 (CH). **3m**: δ_H 1.20 (d, $J = 6.1$ Hz, 6H), 2.40–2.86 (m, 6H), 3.30–3.58 (m, 5H), 3.58–4.10 (m, 4H). δ_C 21.73 (CH_3), 53.67 (CH_2), 61.37 (CH_2), 66.22 (CH_2), 66.60 (CH_2), 70.42 (CH), 71.75 (CH).