The Use of Proton-exchanged X-Type Zeolite in Catalysing Ring-opening Reactions of 2-Substituted Epoxides with Nucleophiles and its Effect on Regioselectivity[†]

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The use of proton-exchanged X-type zeolite in catalysing ring-opening reactions of 2-alkyl substituted epoxides with nucleophiles gives a high regioselectivity and functional-selective catalysis giving allylic products from allylic nucleophiles. Mechanistic aspects are discussed.

Zeolites with large surface area, acidic nature, shape selectivity and so on have been used as catalysts for organic syntheses.[1–4] Ring-opening reactions of epoxides have been performed by the use of strong nucleophiles such as NH_3,[5,6] and NaN_3[7] and amines.[8] However, the ring-opening reaction of 2-alkyl substituted epoxides with weak nucleophiles such as alcohols and thiols took place by using H^+-exchanged X-type zeolite (H^+-zeolite X), although the reaction did not occur by using Na^+-zeolite X. The mechanistic aspects of both the regioselectivity of the ring-opening and the functional-selective catalysis have been discussed.

Results and Discussion

Ring-opening Reactions of Propylene Oxide **1** *with Nucleophiles in the Presence of* H^+*-Zeolite X.*—The ring-opening reactions of **1** with methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol, *tert*-butyl alcohol, hexan-1-ol, lauryl alcohol and allyl alcohol **2a–i**, ethanethiol and butane-1-thiol, *tert*-butyl mercaptan and allyl mercaptan **2j–m** and allylamine **2n** in the presence of H^+-zeolite X or H_2SO_4 gave secondary and primary alcohols **3** and **4** (Table 1). But, the reaction with *tert*-butyl alcohol (**2f**) or *tert*-butyl mercaptan (**2l**) did not yield the corresponding products (Table 1) because of the low nucleophilicity owing to steric hindrance to an attack of the bulky nucleophile. Only secondary alcohols **3m** and **3n** were formed from **2m** and **2n**, and the reaction with allylic nucleophiles in the presence of H_2SO_4 did not yield **3** and **4** (Table 1). The total yields of **3** and **4** and the ratio **3**/**4** are summarized in Table 1. The ratio **3**/**4** did not vary on treatment of a mixture of **3** and **4** under the reaction conditions, so that the ratio must reflect the regioselectivity of the ring-opening reaction.

Table 1 Ring-opening reactions of propylene oxide **1** with alcohols **2a–i**, thiols **2j–m** and amine **2n** using H^+-zeolite X

H^+-Zeolite X/mg	Nucleophile **2**	Yield[a] (%) **3** + **4**	Ratio **3**/**4**
150	**a**; MeOH	25 (40)	1.5 (0.91)
150	**b**; EtOH	27 (46)	1.5 (1.1)
250	**b**; EtOH	72	1.5
350	**b**; EtOH	92	1.5
150	**c**; PrOH	57 (63)	1.5 (1.1)
150	**d**; Pr^iOH	22 (30)	1.5 (1.3)
150	**e**; BuOH	65 (55)	1.6 (1.2)
250	**e**; BuOH	71	1.5
250[b]	**e**; BuOH	40 (46)	2.1 (1.4)
150	**f**; Bu^tOH	0 (0)	
250	**g**; HexOH	64 (58)	1.5 (1.2)
250	**h**; $C_{12}H_{25}OH$	56 (46)	1.7 (1.2)
350	**i**; $CH_2{=}CHCH_2OH$	67 (0)	1.5
350	**j**; EtSH	50 (37)	26 (1.2)
350	**k**; BuSH	61 (10)	39 (4.0)
150	**l**; Bu^tSH	0 (0)	
350	**m**; $CH_2{=}CHCH_2SH$	34[c] (0)	
150	**n**; $CH_2{=}CHCH_2NH_2$	65[c] (0)	
250	**n**; $CH_2{=}CHCH_2NH_2$	65[c]	
350	**n**; $CH_2{=}CHCH_2NH_2$	58[c]	

[a] Yields are based on **1** and the values in parentheses are yields in the reactions using H_2SO_4 (1.5 mmol) as a catalyst. [b] 1,2-Epoxydecane **1′** was used instead of **1**. [c] Only **3** was formed.

(*a*) *Regioselective catalysis by* H^+*-zeolite X.* The different regioselectivities for the reactions using H^+-zeolite X and H_2SO_4 can be interpreted as follows. A borderline mechanism[9–11] has been suggested for acid-catalysed ring-opening reactions of epoxides; the borderline mechanism obeys A-2 kinetics, but lies between the A-2 and A-1 routes, shown as step (*a*) and step (*b*), respectively (Scheme 1). The lack of catalytic activity of Na^+ -zeolite X (Table 1) shows that the proton of H^+ -zeolite X catalyses the reaction of the epoxy oxygen (see Scheme 1). In a homogeneous system, a nucleophile attacks predominantly at the less hindered carbon atom of the epoxide ring under neutral or basic conditions, while in an acidic solution, there is usually a great tendency for nucleophilic attack at the more substituted carbon atom.[12] Therefore, the high acidity of the catalyst may facilitate the bond-cleavage forming the more stabilised carbocation, favouring step (*b*) over step (*a*); in fact, the ratio **3**/**4** tended to decrease with increased acidity of pillared mica as mentioned in section (*b*). If the ring-opening is affected only by the acidity of the catalyst, the ratio should be lower in the case of H^+-zeolite X rather than H_2SO_4, because the zeolite ($H_0 < -8$)[13] is more acidic than H_2SO_4 (H_0 *ca.* -0.01) in the reaction. However, the ratio (1.5–1.7 for alcohol or 26–39 for thiol) using H^+-zeolite X was larger than that (0.9–1.2 for alcohol or 1.2–4.0 for thiol) using H_2SO_4 (Table 1).

The results can be well explained by acid–base bifunctional catalysis, considering the following basic property of H^+-zeolite X besides the acidic property. The interaction of the basic site of the zeolite with the H-atom of the nucleophile may enhance the nucleophilicity, resulting in the increase of the ratio **3**/**4** by the favourable A-2 route (Scheme 1). This interaction polarises the S–H bond more than O–H because the S–H bond is weaker, and enhances the nucleophilicity of that thiol more than the alcohol. Thus, the reaction of thiol interestingly gives such a high ratio 26–39. We also considered the possibility of simple surface catalysis as a means of accounting for the results, but we

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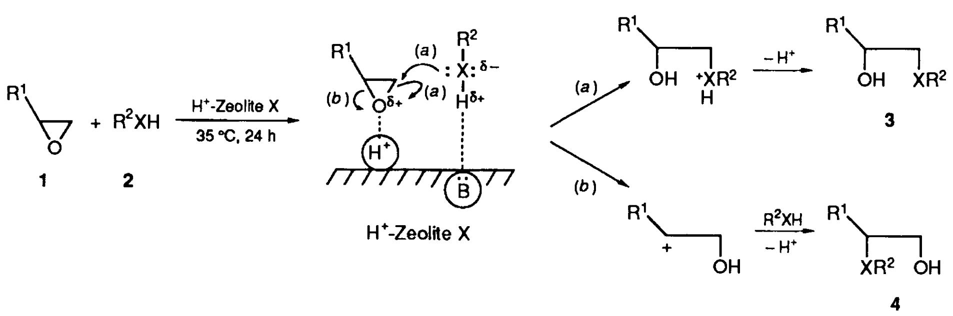

Scheme 1

feel that this explanation is less likely than acid–base catalysis on account of the fact that the reaction is effective even when an amine is the nucleophile.

(*b*) *Comparison with other solid catalysts.* The non-existent, or very poor, catalysis by H^{+}-zeolite A-3 or A-4, which has a smaller pore (Table 2), indicates that the reaction with H^{+}-zeolite X occurs not on the external surface but in the pore.

Alumina-pillared taeniolites, APT 1–4, having variable layer charges 0.41, 0.58, 0.64 and 0.82, respectively and acid-contents per Si_4O_{10} 1.07, 0.91, 0.56 and 1.9, respectively, were prepared as described in the experimental section. The original unpillared taeniolites (UPT 1 and 2) did not exhibit catalytic activity for the reaction of **1** with alcohols **2a** and **2b**, but APT 1–4 showed such activity (Table 2). The result implies that the pillar-space plays an important role in the reaction. The **3**/**4** ratio (0.54–0.91) for the reaction of **1** with alcohol **2b** using APT 1–4 was lower than that (1.5–1.6) using H^{+}-zeolite X, and the ratio (APT 1 > APT 2 > APT 3 > APT 4) decreased with an increase in the layer charge (the acidity may be proportional to the layer charge), not the acid content (*i.e.* the acid concentration) (Table 2). A similar result was observed in the reaction of **1** with alcohol **2a** when we used APT 1–4 (Table 2). Further, the ratio (8.0) for the reaction of **1** with thiol **2j** using APT 2 was much lower than that (26) using H^{+}-zeolite X (Table 2). These suggest that the **3**/**4** ratio is affected by the acidity of the solid catalysts since the higher acidity favours A-1 more than A-2 as mentioned in section (*a*), and that the pillared mica has high acidity compared to H^{+}-zeolite X because the basicities of each catalyst are probably not so different. Some of the SiO_4 tetrahedra in the host layer are inverted by pillar formation,[14] and thus we presume that the high acidity of the pillared mica is a result of such a drastic change in the layer.

The high ratio (5.1–6.7 in Table 2) for the reaction of **1** or 1,2-epoxydecane **1′** with **2b** or **2e** using Al_2O_3 arises from the basic and low acidic natures. In fact, the alumina reaction of 1,2-epoxybutane shows the ratio to be 6.[15] SiO_2 was an inactive catalyst (Table 2) because of its low acidic and basic natures.

(*c*) *Functional-selective catalysis by* H^{+}*-zeolite X.* The reactions of **1** with allyl alcohol, allyl mercaptan and allylamine **2i**, **2m** and **2n** produced allylic products **3i**, **3m** and **3n** and **4i** (Table 1). The formation of such allylic products indicates that the acidic site of H^{+}-zeolite X interacts selectively with the epoxide oxygen of **1** rather than the double-bond of the allylic nucleophile (Scheme 1). Such functional-selective catalysis is synthetically useful, and was not observed for the reaction using H_2SO_4, which causes polymerisation of the double-bond.

(*d*) *Shape selectivity of* H^{+}*-zeolite X.* The ratio **3**/**4** (2.1 in Table 1) for the reaction (using H^{+}-zeolite X) of a relatively large epoxide, 1,2-epoxydecane **1′**, with **2e** or that (1.7 in Table 1) of **1** with a large alcohol **2h** was slightly higher than that (1.5) for the reaction of **1** with the smaller *n*-alcohols **2a**–**e**, **2g** and **2i** (Table 1). Such a small variation of the ratio with the molecular size of alcohol or epoxide may result from a shape selectivity of H^{+}-zeolite X; the shape selectivity means that the less substituted epoxide carbon is preferentially attacked owing to the smaller transition state geometry.[1,2,4] The high ratio (3.1) for the reaction using H^{+}-zeolite A-4 which has the minimum pore diameter 4 Å (Table 2) also comes from the shape selectivity.

Ring-opening Reactions of Styrene Oxide **1″** *with Nucleophiles in the Presence of* H^{+}*-Zeolite X.*—The reactions of **1″** with alcohols **2b**, **2e**, **2g** and **2i** in the presence of H^{+}-zeolite X or H_2SO_4 gave only the primary alcohols **4″b**, **4″e**, **4″g** and **4″i** (Table 3). But, the reaction with allyl alcohol **2i** using H_2SO_4 did not produce **4″i**. The ring-opening of **1″** is affected by an electronic factor in which the C–O bond-breaking forms a stable benzyl carbocation, and thus produces only **4″** by the preferred A-1 route. The formation of allylic product **4″i** from **2i** is further evidence for the functional-selective catalysis of H^{+}-zeolite X.

Experimental

IR spectra were obtained on a Hitachi EPI-G3 spectrometer. NMR spectra (^{1}H and ^{13}C) were taken with a Nippondenshi JNM-FX-60Q NMR instrument. Mass spectra were recorded with a Hitachi M-80B spectrometer. GLC was performed with a Shimadzu GC-6A chromatograph using a glass column (1 m × 3 mm) packed with 10% polyethylene glycol (20 M) on 60–80 mesh Chromsosorb WAW DMCS. Two runs agreed within ±2% for the yields of the products which were determined by replicate GLC analyses. Preparative GLC was carried out with a Hitachi model 063-0012 unit using a column (2 m × 3 mm) packed with 10% polyethylene glycol (20 M) on 60–80 mesh Chromosorb WAW DMCS.

Methanol, ethanol, propan-1-ol, propan-2-ol, butan-1-ol and *tert*-butyl alcohol **2a**–**f** were purified by standard methods before use. Propylene oxide **1**, hexan-1-ol, lauryl alcohol, allyl alcohol, ethanethiol, butane-1-thiol, *tert*-butyl mercaptan, allyl mercaptan and allylamine **2g**–**n** and styrene oxide **1″** were purified by distillation.

H^{+}-zeolites X, A-3 and A-4 were prepared by the calcination (350 °C, 1 h) of NH_4^+-exchanged zeolites formed from Tōyōsōda synthetic powdery Na^{+}-zeolite F-9 (*i.e.* X), A-3 and A-4 which have minimum pore diameters 10, 3 and 4 Å, respectively.

The original unpillared taeniolites (UPT) had the following structural formulates: UPT-1, $Na_{0.41}Mg_{2.59}Li_{0.41}Si_4O_{10}F_2$; UPT-2, $Na_{0.64}Mg_{2.36}Li_{0.64}Si_4O_{10}F_2$. Alumina-pillared taeniolites, APT 1–4 were prepared by the calcination (450 °C, 1 h) of the following intercalated micas having Al-hydroxy groups, respectively: $Na_{0.02}[Al(OH)_{2.69}]_{1.23}Mg_{2.59}Li_{0.41}Si_4O_{10}F_2$, $Na_{0.07}[Al(OH)_{2.41}]_{0.91}Mg_{2.42}Li_{0.58}Si_4O_{10}F_2$, $Na_{0.07}[Al(OH)_{2.37}]_{0.47}Mg_{2.36}Li_{0.64}Si_4O_{10}F_2$ and $[Al(OH)_{2.35}]_{1.27}Mg_{2.18}Li_{0.82}Si_4O_{10}F_2$. The APT 1–4 had the basal spacing 18.0–18.5 Å, and layer charges 0.41, 0.58, 0.64 and 0.82, the pillared Al-contents per Si_4O_{10} 1.23, 0.91, 0.47

Table 2 Ring-opening reactions of propylene oxide **1** with nucleophiles **2** using solid-catalysts other than H^+-zeolite X

Catalyst	Catalyst /mg	Nucleophile **2**	Yield[a] (%) **3** + **4**	Ratio **3**/**4**
Na^+-zeolite X	250	**b**; EtOH	0	
H^+-zeolite A-3	250	**b**; EtOH	0	
H^+-zeolite A-4	250	**b**; EtOH	2.0	3.1
UPT 1	150	**a**; MeOH	0	
UPT 1	150	**b**;EtOH	0	
UPT 2	150	**a**; MeOH	0	
UPT 2	150	**b**; EtOH	0	
APT 1	150	**a**; MeOH	9.0	0.83
APT 2	150	**a**; MeOH	6.5	0.83
APT 3	150	**a**: MeOH	8.5	0.80
APT 4	150	**a**; MeOH	8.0	0.56
APT 1	150	**b**; EtOH	9.0	0.91
APT 2	150	**b**; EtOH	7.8	0.83
APT 3	150	**b**; EtOH	7.5	0.59
APT 4	150	**b**; EtOH	30	0.54
APT 2	150	**j**; EtSH	6.0	8.0
SiO_2[b]	250	**b**; EtOH	0	
Al_2O_3[c]	250	**b**; EtOH	2.5	6.7
Al_2O_3[d]	250	**e**; BuOH	73	5.1

[a] Yields are based on **1**. [b] Fuji Devison Silica Gel BW-350 for column chromatography was used after calcination (350 °C, 1 h). [c] Wako activated alumina for column chromatography was used after the above calcination. [d] The Al_2O_3-catalysed reaction of 1,2-epoxydecane **1′** instead of **1** was carried out at 100 °C.

Table 3 Ring-opening reactions of styrene oxide **1″** with alcohols **2** using H^+-zeolite X

Alcohol **2**	H^+-zeolite X/mg	Yield[a] of **4″** (%)
b; EtOH	150	20 (25)
b; EtOH	350	64
e; BuOH	350	51(42)
g; HexOH	350	44 (29)
i; CH_2=$CHCH_2OH$	150	68 (0)

[a] Yields are based on **1″**, and the values in parentheses are yields in the reactions using H_2SO_4 (1.5 mmol) as a catalyst.

and 1.27 and N_2 BET surface areas 257, 264, 91 and 192 m^2 g^{-1}, respectively.

1,2-Epoxydecane **1′** was prepared by the reaction of dec-1-ene with 3-chloroperbenzoic acid in the method described by Pasto and Cumbo,[16] and confirmed by the following data; ν_{max}(neat)/cm^{-1} 3020, 2910, 2840, 1460, 1410, 1375, 1260, 1130, 910, 830 and 720; δ_H($CDCl_3$–CCl_4) 0.9 (3 H, t Me), 1.0–1.7 (14 H, m, CH_2) and 2.3–3.1 (3 H, m, OCH and OCH_2); δ_C($CDCl_3$–CCl_4) 14.0, 22.5, 25.9, 29.1, 29.3, 31.7, 32.4, 46.6 (OCH_2) and 51.9 (OCH) (Found: C, 76.6; H, 12.9. Calc. for $C_{10}H_{20}O$: C, 76.85; H, 12.9%).

Ring-opening Reactions of Propylene Oxide **1** *and* 1,2-*Epoxydecane* **1′** *with Nucleophiles in the Presence of* H^+*-Zeolite X or* H_2SO_4.—The ring-opening reactions of **1** (3.75 mmol) with nucleophiles (3.5 cm^3), alcohols **2a–i**, thiols **2j–m** and amine **2n**, were carried out in the presence of H^+-zeolite X or H_2SO_4 under the conditions described in Table 1. The similar reaction of 1,2-epoxydecane **1′** with **2e** was also performed (Table 1). After filtration of H^+-zeolite X or neutralisation of H_2SO_4 by powdery Na_2CO_3, GLC analysis showed that the secondary alcohols **3** had the shorter retention times as compared to those of the corresponding primary alcohols **4**, and both the total yields of **3** and **4** and the ratio **3**/**4** were indicated in Table 1. The following products were isolated by preparative GLC, and the structures were confirmed by their spectroscopic data.

1-*Methoxypropan*-2-*ol* **3a**.[17] Liquid, δ_H($CDCl_3$–CCl_4) 1.15 (3 H, d, Me), 2.0–2.6 (1 H, br, OH), 3.1–3.6 (2 H, m, OCH_2), 3.45 (3 H, s, OMe) and 3.7–4.3 (1 H, m, OCH); δ_C($CDCl_3$–CCl_4) 18.5 (Me), 58.7 (OMe), 66.1 (OCH) and 78.2 (OCH_2).

2-*Methoxypropan*-1-*ol* **4a**.[17] Liquid, δ_H($CDCl_3$–CCl_4) 1.1 (3 H, d, Me), 2.3–2.7 (1 H, br, OH), 3.45 (3 H, s, OMe) and 3.2–4.8 (3 H, br, OCH_2 and OCH); δ_C($CDCl_3$–CCl_4) 15.1 (Me), 56.1 (OMe), 65.8 (OCH) and 77.3 (OCH_2).

1-*Ethoxypropan*-2-*ol* **3b**.[18] Liquid, ν_{max}(neat)/cm^{-1} 3400, 2960, 2850, 1450, 1380, 1325, 1280, 1110, 1020, 990, 950, 930, 885 and 845; δ_H($CDCl_3$–CCl_4) 1.25 (3 H, t, OCH_2*Me*), 1.15 (3 H, d, Me), 2.3–2.6 (1 H, br, OH), 3.0–3.8 (4 H, m, 2 × OCH_2) and 3.7–4.3 (1 H, m, OCH); δ_C($CDCl_3$–CCl_4) 15.1 (Me), 18.6 (OCH_2*Me*), 66.1 (OCH), 66.4 (O*C*H_2CH) and 76.0 (O*C*H_2Me).

2-*Ethoxypropan*-1-*ol* **4b**.[19] Liquid, ν_{max}(neat)/cm^{-1} 3400, 2950, 2900, 2840, 1450, 1365, 1330, 1090, 1040, 980, 945, 870 and 805; δ_H($CDCl_3$–CCl_4) 1.2 (3 H, t, OCH_2*Me*), 1.15 (3 H, d, Me), 1.9–2.2 (1 H, br, OH) and 3.2–4.2 (5 H, 2 × OCH_2 and OCH); δ_C($CDCl_3$–CCl_4) 15.5 and 15.8 (2 × Me), 63.8 (O*C*H_2OH), 66.1 (OCH) and 75.4 (*C*H_2Me).

1-(1-*Propyloxy*)*propan*-2-*ol* **3c**.[20] Liquid, ν_{max}(neat)/cm^{-1} 3380, 2920, 2850, 1460, 1450, 1405, 1375, 1325, 1255, 1110, 1050, 960, 850 and 750; δ_H($CDCl_3$–CCl_4) 1.1 (3 H, t, OCH_2CH_2*Me*), 1.15 (3 H, d, Me), 1.3–1.9 (2 H, m, OCH_2*C*H_2Me), 2.2–2.5 (1 H, br, OH), 3.4 (2 H, t, O*CH*$_2$$CH_2$Me), 3.4 (2 H, d, O*CH*$_2$CH) and 3.7–4.2 (1 H, m, OCH); δ_C($CDCl_3$–CCl_4) 10.5 (OCH_2CH_2*Me*), 18.5 (Me), 22.7 (OCH_2*C*H_2Me), 66.1 (OCH), 72.8 (O*C*H_2CH) and 76.1 (O*C*H_2CH_2).

2-(1-*Propyloxy*)*propan*-1-*ol* **4c**.[20] Liquid, ν_{max}(neat)/cm^{-1} 3270, 2920, 2850, 1480, 1465, 1450, 1410, 1380, 1345, 1240, 1100, 1000, 905, 845 and 760; δ_H($CDCl_3$–CCl_4) 0.95 (3 H, t, OCH_2CH_2*Me*), 1.15 (3 H, d, Me), 1.3–1.9 (2 H, m, OCH_2*CH*$_2$Me), 1.9–2.1 (1 H, br, OH), 3.1–4.0 (5 H, m, 2 × OCH_2 and OCH); δ_C($CDCl_3$–CCl_4) 10.6 (OCH_2CH_2*Me*), 15.7 (Me), 23.1 (OCH_2*C*H_2Me), 66.1 (OCH), 70.2 (*C*H_2OH) and 75.5 (O*C*H_2CH_2).

1-*Isopropyloxypropan*-2-*ol* **3d**.[20] Liquid, δ_H($CDCl_3$–CCl_4) 0.75–1.8 (11 H, 3 × Me and CHC*H*$_2$Me), 2.2–2.5 (1 H, br, OH), 2.95–3.7 (3 H, m, OCH_2 and OCH) and 3.6–4.2 (1 H, m, *C*HOH); δ_C($CDCl_3$–CCl_4) 9.7 (*Me*CH_2), 18.5 [*Me*CH(OH)-CH_2], 19.1 and 19.2 [*Me*CH(Et)O], 29.0 and 29.1 (Me*C*H_2), 66.2 and 66.4 [Me*C*H(OH)CH_2], 73.7 and 73.8 (OCH_2) and 76.8 (O*C*HMe_2).

2-*Isopropyloxypropan*-1-*ol* **4d**.[20] Liquid, δ_H($CDCl_3$–CCl_4) 0.75–1.7 (11 H, m, 3 × Me and MeC*H*$_2$), 1.8–2.2 (1 H, br, OH) and 3.1–3.9 (4 H, m, 2 × OCH and OCH_2); δ_C($CDCl_3$–CCl_4) 9.8 and 10.0 (*Me*CH_2), 16.3 and 17.1 [*Me*CH(CH_2OH)O], 19.7 and 20.6 [*Me*CH(Et)O], 29.3 and 30.18 (Me*C*H_2), 66.3 and 66.4 [Me*C*H(CH_2OH)O], 72.9 and 73.6 (*C*H_2OH) and 74.2 and 75.0 [O*C*HMe_2].

1-(1-*Butoxy*)*propan*-2-*ol* **3e**.[20] Liquid, ν_{max}(neat)/cm^{-1} 3350, 2900, 2840, 1450, 1370, 1320, 1250, 1105, 990, 950, 855 and 730; δ_H($CDCl_3$–CCl_4) 0.6–1.8 (10 H, m, 2 × Me and MeC*H*$_2$C*H*$_2CH_2$O), 2.1–2.6 (1 H, m, OH), 3.0–3.7 (4 H, m, 2 × OCH_2), 3.7–4.3 (1 H, OCH); δ_C($CDCl_3$–CCl_4) 13.8 (*Me*-CH_2), 18.5 (*Me*CHOH), 19.2 (Me*C*H_2), 31.6 (MeCH_2*C*H_2), 66.1 (OCH), 71.0 [O*C*H_2CH(OH)] and 76.2 (Pr*C*H_2O).

2-(1-*Butoxy*)*propan*-1-*ol* **4e**.[21] Liquid, ν_{max}(neat)/cm^{-1} 3370, 3910, 3850, 1450, 1370, 1335, 1300, 1230, 1085, 1040, 980, 910, 805 and 730; δ_H($CDCl_3$–CCl_4) 0.7–1.8 (10 H, m, 2 × Me and MeC*H*$_2$C*H*$_2$), 1.7–2.4 (1 H, br, OH) and 3.1–4.0 (5 H, 2 × OCH_2 and OCH); δ_C($CDCl_3$–CCl_4) 13.8 (*Me*CH_2), 15.8 (*Me*CH), 19.3 (Me*C*H_2), 32.1 (MeCH_2*C*H_2), 66.2 (OCH), 68.4 (CH_2OH) and 75.6 (Pr*C*H_2O).

1-(1-*Hexyloxy*)*propan*-2-*ol* **3g**. Liquid, ν_{max}(neat)/cm^{-1} 3370, 2910, 2850, 1460, 1375, 1330, 1260, 1110, 950, 845 and 725; δ_H($CDCl_3$–CCl_4) 0.7–1.9 (14 H, m, 2 × Me and

Me(C*H*$_2$)$_4$, 2.0–2.5 (1 H, br, OH), 3.0–3.7 (4 H, m, 2 × OCH$_2$) and 3.7–4.3 (1 H, m, OCH); δ_C(CDCl$_3$–CCl$_4$) 13.9 (*Me*CH$_2$), 18.5 (Me), 22.5 (Me*C*H$_2$), 25.7 (MeCH$_2$*C*H$_2$), 29.5 (MeCH$_2$CH$_2$*C*H$_2$), 31.6 (MeCH$_2$CH$_2$CH$_2$*C*H$_2$), 66.1 (OCH) and 71.2 (O*C*H$_2$CH) and 76.2 (O*C*H$_2$CH$_2$) (Found: C, 67.5; H, 12.5. $C_9H_{20}O_2$ requires C, 67.45; H, 12.6%).

2-(1-*Hexyloxy)propan*-1-*ol* **4g**. Liquid, ν_{max}(neat)/cm^{-1} 3370, 2900, 2850, 1450, 1370, 1340, 1260, 1130, 1090, 1045, 985, 900 and 720; δ_H(CDCl$_3$–CCl$_4$) 0.65–1.9 [14 H, m, 2 × Me and Me(C*H*$_2$)$_4$], 1.8–2.3 (1 H, br, OH) and 3.1–4.0 (5 H, m, 2 × OCH$_2$ and OCH); δ_C(CDCl$_3$–CCl$_4$) 13.9 (*Me*CH$_2$), 15.7 (Me), 22.5 (Me*C*H$_2$), 25.8 (MeCH$_2$*C*H$_2$), 29.9 (MeCH$_2$CH$_2$*C*H$_2$), 31.6 (MeCH$_2$CH$_2$CH$_2$*C*H$_2$), 66.1 (OCH), 68.6 (O*C*H$_2$CH) and 75.5 (O*C*H$_2$CH$_2$) (Found: C, 67.3; H, 12.65. $C_9H_{20}O_2$ requires C, 67.45; H, 12.6%).

1-*Lauryloxypropan*-2-*ol* **3h**. Liquid, ν_{max}(neat)/cm^{-1} 3350, 2900, 2830, 1455, 1370, 1110, 845 and 720; δ_H(CDCl$_3$–CCl$_4$) 0.7–2.2 [27 H, m, 2 × Me, OCH$_2$(C*H*$_2$)$_{10}$ and OH] and 3.1–4.1 (5 H, m, OCH and 2 × OCH$_2$); δ_C(CDCl$_3$–CCl$_4$) 14.0 (*Me*CH$_2$), 18.5 (Me), 22.6 (Me*C*H$_2$), 26.0 (MeCH$_2$*C*H$_2$), 29.2 (MeCH$_2$CH$_2$*C*H$_2$), 29.5 [O(CH$_2$)$_2$*C*H$_2$)$_6$], 31.8 (OCH$_2$*C*H$_2$), 66.1 (OCH), 71.2 [O*C*H$_2$CH(OH)Me] and 76.2 (O*C*H$_2$CH$_2$) (Found: C, 73.55; H, 13.25. $C_{15}H_{32}O_2$ requires C, 73.7; H, 13.2%).

2-*Lauryloxypropan*-1-*ol* **4h**. Liquid, ν_{max}(neat)/cm^{-1} 3350, 2900, 2830, 1450, 1330, 1140, 1085, 1040, 980, 900 and 715; δ_H(CDCl$_3$–CCl$_4$) 0.7–2.2 [27 H, m, 2 × Me, O(CH$_2$)$_{10}$ and OH] and 3.2–4.0 (5 H, m, OCH and 2 × OCH$_2$); δ_C(CDCl$_3$–CCl$_4$) 14.0 (*Me*CH$_2$), 15.7 (Me), 22.6 (Me*C*H$_2$), 26.1 (MeCH$_2$*C*H$_2$), 29.2 (MeCH$_2$CH$_2$*C*H$_2$), 29.5 [O(CH$_2$)$_2$(*C*H$_2$)$_5$], 30.0 (OCH$_2$CH$_2$*C*H$_2$), 31.8 (OCH$_2$*C*H$_2$), 66.1 (OCH), 68.6 (CH$_2$OH) and 75.5 (O*C*H$_2$CH$_2$) (Found: 73.75; H, 13.05. $C_{15}H_{32}O_2$ requires C, 73.7; H, 13.2%).

1-*Allyloxypropan*-2-*ol* **3i**.[22] Liquid, δ_H(CDCl$_3$–CCl$_4$) 1.15 (3 H, d, Me), 2.0–2.3 (1 H, br, OH), 3.0–3.6 [2 H, m, OC*H*$_2$CH(OH)Me], 3.6–4.4 (3 H, m, OCH and OC*H*$_2$=CH), 5.05–5.6 (2 H, m, C*H*$_2$=CH) and 5.6–6.4 (1 H, m, CH$_2$=C*H*); δ_C(CDCl$_3$–CCl$_4$) 18.5 (Me), 66.2 (OCH), 71.9 [O*C*H$_2$CH(OH)Me], 75.6 (O*C*H$_2$CH=CH$_2$), 116.9 (*C*H$_2$=CH) and 134.3 (CH$_2$=*C*H).

2-*Allyloxypropan*-1-*ol* **4i**.[22] Liquid, δ_H(CDCl$_3$–CCl$_4$) 1.15 (3 H, d, Me), 1.8–2.2– (1 H, br, OH), 3.2–3.9 (2 H, m, OC*H*$_2$CH=CH$_2$), 3.9–4.6 (3 H, m, C*H*$_2$OH and OCH), 5.0–5.6 (2 H, m, C*H*$_2$=CH) and 5.6–6.4 (1 H, m, CH$_2$=C*H*); δ_H(CDCl$_3$–CCl$_4$) 15.7 (Me), 66.1 (OCH), 69.5 (CH$_2$OH), 75.1 (O*C*H$_2$CH=CH$_2$), 116.5 (*C*H$_2$=CH) and 134.8 (CH$_2$=*C*H)

1-*Ethylthiopropan*-2-*ol* **3j**.[23] Liquid, δ_H(CDCl$_3$–CCl$_4$) 1.25 (3 H, d, *Me*CH), 1.3 (3 H, t, *Me*CH$_2$), 2.1–2.4 (1 H, br, OH), 2.2–3.0 (4 H, m, 2 × SCH$_2$) and 3.5–4.1 (1 H, m, OCH); δ_C(CDCl$_3$–CCl$_4$) 14.8 (*Me*CH$_2$), 21.9 (*Me*CH), 25.9 (S*C*H$_2$Me), 41.3 (S*C*H$_2$CH) and 65.0 (OCH); GLC–MS (EI method): *m*/*z* 120 (M$^+$), 76, 61, 48, 47, 45, 43, 32, 28 and 18; (CI method): *m*/*z* 121 (M$^+$ + 1).

2-*Ethylthiopropan*-1-*ol* **4j**. The yield of this product was very low, and thus the structure was confirmed by the following mass spectroscopy; GLC–MS (EI method): *m*/*z* 120 (M$^+$), 89 (M$^+$ – CH$_2$OH), 61 and 28; (CI method): *m*/*z* 121 (M$^+$ + 1). The yield of **4j** was obtained by assuming that **3j** and **4j** have the same area-sensitivity for GLC analysis.

1-(1-*Butylthio)propan*-2-*ol* **3k**.[23] Liquid, δ_H(CDCl$_3$–CCl$_4$) 0.9 (3 H, t, *Me*CH$_2$), 1.25 (3 H, d, *Me*CH), 1.1–1.9 (4 H, m, MeC*H*$_2$C*H*$_2$), 2.0–3.0 (5 H, m, 2 × SCH$_2$ and OH) and 3.5–4.2 (1 H, m, OCH); δ_C(CDCl$_3$–CCl$_4$) 13.6 (*Me*CH$_2$), 21.8 (*Me*CH), 31.7 (Me*C*H$_2$), 31.8 (MeCH$_2$*C*H$_2$), 41.8 (S*C*H$_2$CH$_2$) and 65.1 (S*C*H$_2$CH); GLC–MS (EI method): *m*/*z* 148 (M$^+$), 104, 75, 61, 57, 56, 45, 41, 29 and 27; (CI method): *m*/*z* 149 (M$^+$ + 1).

2-(1-*Butylthio)propan*-1-*ol* **4k**. The structure of this product was confirmed by the following mass spectroscopy because the yield was very low; GLC–MS (EI method): *m*/*z* 148 (M$^+$), 117 (M$^+$ – CH$_2$OH), 75, 61, 41, 28 and 18; (CI method): *m*/*z* 149 (M$^+$ + 1). The yield of **4k** was also determined by assuming that **3k** and **4k** have the same area-sensitivity for GLC analysis.

1-*Allylthiopropan*-2-*ol* **3m**. Liquid, ν_{max}(neat)/cm^{-1} 3350, 2950, 2800, 1700, 1630, 1400, 1365, 1260, 1225, 1115, 1060, 1035, 985, 915 and 740; δ_H(CDCl$_3$–CCl$_4$) 1.2 (3 H, d, Me), 2.0–2.5 (1 H, br, OH), 2.3–2.9 [2 H, m, SC*H*$_2$CH(OH)Me], 3.15 (2 H, d, SC*H*$_2$CH=CH$_2$), 3.5–4.1 (1 H, m, OCH), 4.9–5.5 (2 H, m, C*H*$_2$=CH) and 5.5–6.3 (1 H, m, CH$_2$=C*H*); δ_C(CDCl$_3$–CCl$_4$) 21.9 (Me), 34.6 (S*C*H$_2$CH=CH$_2$), 39.8 [S*C*H$_2$CH(OH)Me], 65.1 (OCH), 117.2 (*C*H$_2$=CH) and 133.9 (CH$_2$=*C*H) (Found: C, 54.5; H, 9.4. $C_6H_{12}OS$ requires C, 54.5; H, 9.15%).

1-*Allylaminopropan*-2-*ol* **3n**. Liquid, ν_{max}(neat)/cm^{-1} 3250, 2950, 2900, 1720, 1635, 1440, 1410, 1370, 1325, 1275, 1075, 990, 920 and 880; δ_H(CDCl$_3$–CCl$_4$) 1.15 (3 H, d, Me), 2.1–2.6 (2 H, br, OH and NH), 2.4–2.9 [2 H, m, NHC*H*$_2$CH(OH)Me], 3.3 (2 H, d, NHC*H*$_2$CH=CH$_2$], 3.5–4.1 (1 H, m, OCH), 5.0–5.5 (2 H, m, CH=C*H*$_2$) and 5.6–6.4 (1 H, m, C*H*=CH$_2$); δ_C(CDCl$_3$–CCl$_4$) 20.6 (Me), 51.8 (N*C*H$_2$CH=CH$_2$), 56.0 [N*C*H$_2$CH(OH)Me], 65.2 (OCH), 116.4 (CH=*C*H$_2$) and 135.9 (*C*H=CH$_2$) (Found: C, 62.8; H, 11.2; N, 11.85. $C_6H_{13}NO$ requires C, 62.55; H, 13.4; N, 12.15%).

1-(1-*Butoxy)decan*-2-*ol* **3′e**. Liquid, ν_{max}(neat)/cm^{-1} 3400, 2910, 2845, 1460, 1375, 1300, 1115, 880, 875 and 720; δ_H(CDCl$_3$–CCl$_4$) 0.6–1.9 [24 H, m, *Me*(C*H*$_2$)$_7$CH and *Me*(C*H*$_2$)$_2$CH$_2$O], 1.9–2.5 (1 H, br, OH) and 3.0–4.0 (5 H, m, 2 × CH$_2$ and OCH); δ_C(CDCl$_3$–CCl$_4$) 13.8 (Me), 14.0 (Me), 19.1 [Me*C*H$_2$(CH$_2$)$_2$O], 22.6 [Me*C*H$_2$(CH$_2$)$_6$CH], 25.4 [MeCH$_2$*C*H$_2$(CH$_2$)$_5$CH], 29.1 [Me(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_4$CH], 29.4 [Me(CH$_2$)$_3$ *C*H$_2$(CH$_2$)$_3$CH], 29.6 [Me(CH$_2$)$_4$*C*H$_2$(CH$_2$)$_2$CH], 31.6 [MeCH$_2$*C*H$_2$CH$_2$O], 31.8 [Me(CH$_2$)$_5$*C*H$_2$CH$_2$CH], 33.0 [Me(CH$_2$)$_6$*C*H$_2$CH], 70.0 (OCH), 70.9 (*C*H$_2$CHOH) and 75.0 (O*C*H$_2$CH$_2$) (Found: C, 72.95; H, 13.1. $C_{14}H_{30}O_2$ requires C, 73.0; H, 13.15%).

2-(1-*Butoxy)decan*-1-*ol* **4′e**. Liquid, ν_{max}(neat)/cm^{-1} 3370, 2910, 2840, 1460, 1375, 1100, 1040 and 720; δ_H(CDCl$_3$–CCl$_4$) 0.6–2.3 [25 H, m, *Me*(C*H*$_2$)$_7$CH, *Me* (C*H*$_2$)$_2$CH$_2$ and OH] and 3.1–4.1 (5 H, m, 2 × Me and OCH); δ_C(CDCl$_3$CCl$_4$) 13.8 [*Me*(CH$_2$)$_3$O], 14.0 [*Me*(CH$_2$)$_7$CH], 19.3 [Me*C*H$_2$(CH$_2$)$_2$O], 22.5 [Me*C*H$_2$(CH$_2$)$_6$CH], 25.3 [MeCH$_2$*C*H$_2$(CH$_2$)$_5$CH], 29.1 [Me(CH$_2$)$_2$*C*H$_2$(CH$_2$)$_4$CH], 29.4 [Me(CH$_2$)$_3$*C*H$_2$(CH$_2$)$_3$CH], 29.7 [Me(CH$_2$)$_4$*C*H$_2$(CH$_2$)$_2$CH], 30.7 [Me(CH$_2$)$_5$*C*H$_2$CH$_2$CH], 31.7 [Me(CH$_2$)$_6$*C*H$_2$CH], 32.2 [MeCH$_2$*C*H$_2$CH$_2$O], 64.0 (OCH), 69.0 (CH$_2$OH) and 79.8 [O*C*H$_2$(CH$_2$)$_2$Me] (Found: C, 72.8; H, 13.2. $C_{14}H_3O_2$ requires C, 73.0; H, 13.15%).

A mixture consisting of **3e** and **4e** (the amount of **3e** and **4e** were almost the same as that formed in the reaction) was treated with H$^+$-zeolite X (250 mg) under the reaction conditions, but the ratio **3e**/**4e** was not changed by the treatment.

Ring-opening Reactions of Propylene Oxide **1** *or* 1,2-*Epoxydecane* **1′** *with Nucleophiles Using* Na$^+$-*zeolite X*, H$^+$-*zeolites A-3 and A-4, APT-1-4, UPT1 and 2,* SiO$_2$ *and* Al$_2$O$_3$.—Na$^+$-zeolite X, H$^+$-zeolites A-3 and A-4, APT 1–4, UPT 1 ($Na_{0.41}Mg_{2.59}Li_{0.41}Si_4O_{10}F_2$), UPT 2 ($Na_{0.64}Mg_{2.36}Li_{0.64}Si_4O_{10}F_2$), SiO$_2$ and Al$_2$O$_3$ were used instead of H$^+$-zeolite X. The conditions and results are in Table 2. The structures of the products were confirmed by the method described above.

Ring-opening Reactions of Styrene Oxide **1** *with Nucleophiles in the Presence of* H$^+$-*Zeolite X*.—The reactions of **1″** (3.75 mmol) with nucleophiles (3.5 cm^3), ethanol **2b**, butan-1-ol **2e**, hexan-1-ol **2g** and allyl alcohol **2i**, were carried out. The detailed conditions and results are shown in Table 3. The structures of the products were characterised as follows.

2-*Ethoxy*-2-*phenylpropan*-1-*ol* **4″b**.[24] Liquid, ν_{max}(neat)/

cm^{-1} 3400, 3060, 3025, 2970, 2870, 1495, 1455, 1405, 1375, 1350, 1315, 1230, 1200, 1160, 1110, 1070, 1050, 940, 865, 790, 765, 705, 640 and 550; $\delta_H(CCl_4)$ 1.2 (3 H, t, Me), 2.0–2.4 (1 H, br, OH), 3.1–3.9 (4 H, m, $MeCH_2$ and CH_2OH), 4.5 (1 H, t, OCH) and 7.3–7.8 (5 H, br s, Ph); $\delta_C(CDCl_3)$ 15.0 (Me), 64.5 (OCH), 67.4 (CH_2OH), 82.7 (OCH_2Me) and 126.7, 127.9, 128.4 and 139.2 (C-2, -4, -3 and -1 of phenyl group).

2-*Butoxy*-2-*phenylpropan*-1-*ol* **4″e**.[25] Liquid, $\delta_H(CDCl_3–CCl_4)$ 0.9 (3 H, t, Me), 1.0–1.9 [4 H, m, $Me(CH_2)_2CH_2O$], 1.9–2.4 (1 H, br, OH), 3.45 (2 H, t, OCH_2CH_2), 3.65 (2 H d, CH_2OH), 4.45 (1 H, t, OCH) and 7.0–7.9 (5 H, br s, Ph); $\delta_C(CDCl_3–CCl_4)$ 13.8 (Me), 19.3 ($MeCH_2$), 31.9 ($MeCH_2CH_2$), 67.3 (OCH), 68.7 (CH_2OH), 82.8 (OCH_2CH_2) and 126.5, 127.7, 128.2 and 138.8 (C-2, -4, -3 and -1 of phenyl group).

2-(1-*Hexyloxy*)-2-*phenylpropan*-1-*ol* **4″g**. Liquid, ν_{max}(neat)/cm^{-1} 3480, 2900, 2840, 1490, 1450, 1380, 1345, 1220, 1100, 1030, 875, 755, 700 and 635; $\delta_H(CDCl_3)$ 0.9 (3 H, t, Me), 1.0–2.0 (8 H, m, $Me(CH_2)_4$), 1.9–2.4 (1 H, br, OH), 3.45 (2 H, t, OCH_2CH_2), 3.7 (2 H, d, OCH_2CH), 4.5 (1 H, t, OCH) and 7.3–8.0 (5 H, br s, Ph); $\delta_C(CDCl_3)$ 14.0 (Me), 22.6 ($MeCH_2$), 5.8 ($MeCH_2CH_2$), 29.8 [$Me(CH_2)_2CH_2$], 31.6 [$Me(CH_2)_3CH_2$], 67.4 (OCH), 69.2 (CH_2OH), 82.7 (OCH_2CH) and 126.7, 127.9, 128.4 and 138.9 (C-2, -4, -3 and -1 of phenyl group) (Found: C, 75.65; H, 9.95. $C_{14}H_{22}O_2$ requires C, 75.65; H, 9.95%).

2-*Allyloxy*-2-*phenylpropan*-1-*ol* **4″i**.[26] Liquid, $\delta_H(CDCl_3–CCl_4)$ 1.9–2.4 (1 H, br, OH), 3.2–4.2 (4 H, m, 2 × CH_2), 4.45 (1 H, t, OCH), 4.8–5.6 (2 H, m, $CH{=}CH_2$), 5.6–6.3 (1 H, m, $CH{=}CH_2$) and 7.0–7.9 (5 H, m, Ph); $\delta_C(CDCl_3–CCl_4)$ 67.2 (OCH), 69.5 (CH_2OH), 82.1 ($OCH_2CH{=}CH_2$), 116.9 ($CH{=}CH_2$), 126.6, 127.9, 128.3 and 138.3 (C-2, -4, -3 and -1 of phenyl group) and 134.3 ($CH{=}CH_2$).

References

1 H. van Bekkum and H. W. Kouwenhoven, *Recl. Trav. Chim. Pay-Bas*, 1989, **108**, 283.
2 K. Smith, *Bull. Soc. Chim. Fr.*, 1989, 272.
3 M. Onaka and Y. Izumi, *Yukogoseikagaku*, 1989, **47**, 233.
4 W. Hölderich, M. Hesse and F. Naumann, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 226.
5 F. L. Johnson, US-PAT. 4438281 (March 20, 1984).
6 L. Vamling and L. Cider, *Ind. Eng. Chem. Prod. Res. Dev.*, 1986, **25**, 424.
7 M. Onaka, K. Sugita and Y. Izumi, *Chem. Lett.*, 1986, 1327.
8 M. Onaka, M. Kawai and Y. Izumi, *Chem. Lett.*, 1985, 779.
9 G. Berti, G. Camici, B. Macchia, F. Macchia and L. Monti, *Tetrahedron Lett.*, 1972, 2591.
10 G. A. Cockayne and P. J. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1972, 2173.
11 A. P. Kozikowski, H. Ishida and K. Isobe, *J. Org. Chem.*, 1979, **44**, 2788.
12 R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 1959, 737.
13 K. Tanabe, *Solid Acids and Bases, their catalytic properties*, Kodansha Academic Press, Tokyo, 1970.
14 T. J. Pinnavaia, S. D. Landau and M.-S. Tzou, *J. Am. Chem. Soc.*, 1985, **107**, 7222.
15 G. H. Posner and D. Z. Rogers, *J. Am. Chem. Soc.*, 1977, **99**, 8208.
16 D. J. Pasto and C. C. Cumbo, *J. Org. Chem.*, 1965, **30**, 1271.
17 W. Reeve and A. Sadle, *J. Am. Chem. Soc.*, 1950, **72**, 1251.
18 H. C. Chitwood and B. T. Freure, *J. Am. Chem. Soc.*, 1946, **68**, 680.
19 A. Dewael, *Bull. Soc. Chim. Belg.*, 1930, **39**, 395.
20 H. C. Cox, W. L. Nelson and L. H. Cretcher, *J. Am. Chem. Soc.*, 1927, **49**, 1080.
21 H. Adkin and G. Krsek, *J. Am. Chem. Soc.*, 1949, **71**, 3051.
22 D. Swern, G. N. Billen and H. B. Knight, *J. Am. Chem. Soc.*, 1949, **71**, 1152.
23 L. A. Walter, L. H. Goodson and R. J. Fosbinder, *J. Am. Chem. Soc.*, 1945, **67**, 661.
24 K. Mislow, *J. Am. Chem. Soc.*, 1951, **73**, 3954.
25 W. Reeve and I. Christoffel, *J. Am. Chem. Soc.*, 1950, **72**, 1480.
26 F. N. Hayes and C. Gutberlet, *J. Am. Chem. Soc.*, 1950, **72**, 3321.

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