

Epoxide ring-opening and Meinwald rearrangement reactions of epoxides catalyzed by mesoporous aluminosilicates†

Mathew W. C. Robinson, A. Matthew Davies, Richard Buckle, Ian Mabbett, Stuart H. Taylor and Andrew E. Graham*

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Mesoporous aluminosilicates efficiently catalyze the ring-opening of epoxides to produce β -alkoxyalcohols in high yields under extremely mild reaction conditions. These materials also catalyze the corresponding Meinwald rearrangement in non-nucleophilic solvents to give aldehydes which can be trapped *in situ* to provide the corresponding acetals in an efficient tandem process.

Introduction

Epoxides are valuable synthetic intermediates and their ability to undergo ring-opening reactions with a variety of nucleophilic species to generate β -substituted alcohols with high regio- and stereoselectivity has been widely exploited.¹ The use of alcohols in epoxide ring-opening reactions is a well established route to β -alkoxyalcohols, however, the poor nucleophilicity of substrates means that these transformations often require harsh conditions and lack regioselectivity.² A variety of conditions have been developed, with the most practical and widely employed strategies utilizing Lewis acid promoters.³ Recently, the development of heterogeneous and polymer supported catalysts has provided an alternate and highly promising strategy to overcome these synthetic limitations with the added attractions of ease of work-up, facile catalyst recovery and recycling and improved atom efficiency.⁴ The advent of mesoporous silicate materials in particular has had a substantial impact in the area of heterogeneous catalysis where they have found use as high surface area inert supports and as catalysts in their own right.⁵ In particular, the physical properties of these materials, such as their Lewis acidity, pore size and surface areas, can be controlled during their synthesis by modification of the reaction conditions employed or by the introduction of metal dopants allowing the catalyst to be tailored to fit the specific requirements of the transformation under investigation.⁶ We have recently reported on the use of a mesoporous aluminosilicate material for the ring-opening reactions of epoxides,⁷ and in this paper we disclose our recent progress in this area.

Results and discussion

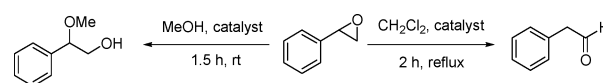
Two mesoporous aluminosilicate materials containing either a low aluminium content (AS-1, Si/Al ratio = 111:1) or a high aluminium content (AS-2, Si/Al ratio = 14:1), in addition to the corresponding silicate material (S-1), were synthesized using an evaporation-induced self-assembly (EISA) approach⁷ and characterized using a range of standard techniques. The

Table 1 Physical characteristics of the mesoporous aluminosilicate catalysts

Catalyst	Si/Al Ratio (theoretical)	Si/Al Ratio (actual) ^a	Pore width (nm) ^b	Surface area (m ² g ⁻¹) ^c
S-1	/	/	1.49	704
AS-1	102	111	1.48	927
AS-2	13	14	1.37	588

^a Determined by EDX analysis. ^b Pore width determined by the BJH method. ^c Surface areas were obtained by the BET method.

materials displayed physical characteristics typical of small pore mesoporous silicates and with values similar to previous reports (Table 1).⁶ The catalytic activity of these materials was then investigated using the formation of 2-methoxy-2-phenylethanol from styrene oxide and methanol as a model reaction (Scheme 1).



Scheme 1 Addition and rearrangement reactions of styrene oxide.


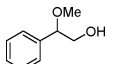

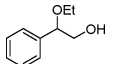

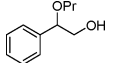

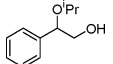

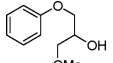

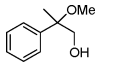

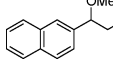

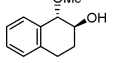

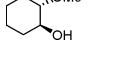

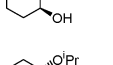

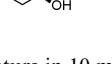
Initial experiments utilizing stoichiometric amounts of methanol in a variety of solvents gave poor yields of the desired β -alkoxyalcohol product with the starting material being recovered unchanged. Reactions carried out in neat methanol, however, resulted in high conversions to the β -alkoxyalcohol products with excellent regioselectivity for the expected Markovnikov product.⁸ In general, reactions employing the AS-2 material proved to be the most efficient (Table 1, entry 1), although significant quantities of product were generated using the AS-1 catalyst. The plain silicate material S-1 displayed no catalytic activity in agreement with previous literature reports.⁹ The synthetic utility of this process was next investigated using the AS-2 material to catalyze the addition of alcohols to a range of epoxides (Table 2).

Methanolysis reactions typically proceed rapidly to give β -methoxyalcohol products in excellent yields except in the case of the glycidyl ether (entry 5) which produced the expected secondary alcohol product by anti-Markovnikov addition.¹⁰ When higher molecular weight alcohols were employed, reactions were slower, requiring extended reaction times (entries 3–4), and yields were reduced by the formation of aldehydes generated by a competing

School of Chemistry, Cardiff University, Park Place, Cardiff, UK CF10 3AT. E-mail: GrahamAE@Cardiff.ac.uk; Fax: +44 (0)29 20874030

† Electronic supplementary information (ESI) available: ¹H and ¹³C NMR spectra. See DOI: 10.1039/b900719a

Table 2 Mesoporous aluminosilicate promoted alcoholysis of epoxides^a

Entry	Alcohol	Epoxide	Time (h)	Product ^b	Yield (%)
1	MeOH		1.5		95
2	EtOH		2.5		86 ^c
3	PrOH		2		68 ^c
4	iPrOH		3.5		52 ^c
5	MeOH		2		58 ^c
6	MeOH		3		97
7	MeOH		4.5		90 ^{c,d}
8	MeOH		1		99
9	MeOH		1		69 ^c
10	EtOH		1		96
11	iPrOH		3		90 ^c

^a Reactions were carried out at room temperature in 10 ml of the alcohol utilizing 50 mg/mmol of AS-2 catalyst. ^b All compounds gave satisfactory spectroscopic data. ^c Isolated yield after column chromatography. ^d Reaction carried out at 50 °C.

















Meinwald rearrangement reaction. In reactions employing very sterically hindered alcohols, such as the reaction of styrene oxide with *tert*-butanol, conversions were poor with significant quantities of the anti-Markovnikov addition product and phenylacetaldehyde being produced. The rate of alcoholysis of cyclohexene oxide with primary, secondary and tertiary alcohols followed a similar trend which was dependant upon the alcohol used. In the case of *tert*-butanol, the isolated yield of the β -alkoxyalcohol product was limited by a competing polymerization.^{2a}

Methanolysis reactions of *trans*-stilbene oxide under our standard conditions resulted in low yields of the β -alkoxyalcohol product. Interestingly, however, diphenylacetaldehyde dimethyl acetal was detected in these reactions produced by the Meinwald rearrangement of the epoxide and subsequent trapping of the aldehyde as its dimethyl acetal product. We have previously reported that carbonyl compounds are readily transformed to acetals by mesoporous aluminosilicates in the presence of both alcohols and diols^{7a} and we were intrigued by the possibility

of developing a tandem rearrangement/acetalization process in which both synthetic transformations are catalyzed by a single catalyst.

The rearrangement of epoxides to carbonyl compounds is a useful synthetic transformation, and several systems have been developed employing a range of promoters.¹¹ Recent interest has centred on the development of heterogeneous catalysts,¹² and indeed mesoporous materials have been shown to be effective promoters of this reaction, although no systematic studies have previously been undertaken.¹³ We initially investigated the use of aluminosilicates as catalysts for the Meinwald rearrangement process using a range of structurally diverse epoxides and were gratified to observe that, in most cases, the rearrangement reaction proceeded efficiently in non-polar solvents, such as dichloromethane, to give the aldehyde product. While the reactions did proceed at room temperature, it was most expeditious to carry out the reaction in dichloromethane at reflux temperatures. Under these conditions, both aluminosilicate materials displayed varying degrees of catalytic activity with a range of substrates giving high conversions of the epoxide to the aldehyde products in a number of cases. It was observed that the low aluminium containing AS-1 catalyst typically exhibited higher selectivity, and consequently, higher yields of aldehyde products than the high aluminium AS-2 material (Table 3). It has previously been observed that high selectivity for the carbonyl product is achieved in Meinwald rearrangement reactions of 1,2-epoxyoctane by employing MCM-41 materials with high aluminium loadings.¹⁴ It is proposed that

Table 3 Mesoporous aluminosilicate promoted Meinwald rearrangements of epoxides

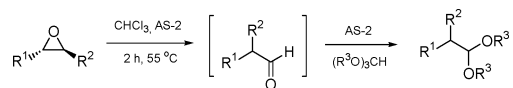
Entry	Epoxide	Catalyst	Time (h)	Product ^a	Conversion ^b (%)
1		AS-1	2		65 ^c
2		AS-1	2		98
3		AS-1	2		100 ^d
4		AS-1	3		85 ^e
5		AS-2	2		60 ^c
6		AS-2	2		93 ^d
7		AS-2	2		90 ^f
8		AS-2	3		12

^a Reactions were carried at reflux out in 10 ml dichloromethane using 50 mg/mmol AS-1 catalyst. ^b Determined from ¹H NMR and/or GC-MS analysis of the crude reaction mixtures. ^c Contains ~5% diol. ^d Contains ~5% polymeric material. ^e Approximately 75% campholenic aldehyde. ^f Contains ~10% polymeric material.

this selectivity arises as a consequence of the low conversion of the epoxide due to limited access of the substrate to the catalytic sites contained within the small-pore mesoporous material and is independent of the number or nature of catalytic sites. This would appear not to be the case here, since both of the mesoporous materials employed in this study display similar pore sizes. Studies are currently underway to understand better the role of pore size in reactions catalyzed by small-pore aluminosilicate materials.¹⁴

Disappointingly, only low conversions to carbonyl products were observed in the cases of cyclohexene oxide and tetrahydronaphthalene oxide which were recovered unchanged even after extended reaction times at elevated temperatures. The AS-1-catalyzed rearrangement of α -pinene oxide displayed moderate selectivity giving the campholenic aldehyde as the main product in addition to small quantities of fencholenal and *trans*-carveol (entry 4).

The protection of carbonyl compounds continues to attract interest despite the considerable attention that this transformation has received.¹⁵ However, few examples of tandem processes involving acetalization have been reported¹⁶ despite the considerable progress in the development of tandem reaction sequences, and the advantages in reducing the number of synthetic steps and the subsequent improvement in efficiency.¹⁷ An additional beneficial feature is that it is not necessary to isolate intermediate compounds that are volatile, toxic or unstable, allowing them to be prepared *in situ* and thus avoiding problems associated with their isolation and handling. Examples of sequential catalytic processes, however, in which one catalyst is responsible for catalyzing two distinctly different reactions, are much less common.¹⁸ We have previously reported that the high aluminium containing AS-2 material is a highly efficient catalyst for the conversion of carbonyl compounds to acetals in the presence of alcohols and diols^{5a} and is superior to materials containing low aluminium loadings in this transformation. We therefore initially investigated the use of this material in the tandem processes, even though the AS-1 material displayed slightly better selectivity in some cases, since it was envisaged that the aldehyde would be rapidly consumed and converted to the acetal product. We were delighted to observe that in the presence of an excess of either trimethyl- or triethyl orthoformate, these tandem Meinwald rearrangement/acetalization reactions proceeded efficiently to produce the corresponding acetals directly from the epoxides in high yields and with excellent selectivity (Scheme 2, Table 4). Indeed, the conversion of epoxide to acetal was so efficient that, in most cases, the final reaction mixtures did not require subsequent purification.



Scheme 2 Tandem Meinwald/acetalization reactions.

Conclusions

We have shown that small pore mesoporous aluminosilicate materials are efficiently made by an EISA approach and that the materials produced display the expected characteristics. The mesoporous aluminosilicate with a high aluminium content is a highly effective catalysts for the formation of β -alkoxyalcohols

Table 4 Tandem rearrangement/acetalization reactions of epoxides

Entry	Epoxide	Additive	Time (h)	Product ^a	Yield (%)
1		CH(OMe) ₃	5		98
2		CH(OMe) ₃	4.5		87
3		CH(OEt) ₃	5		96
4		CH(OMe) ₃	2		80

^a Reactions were carried out at 55 °C in 10 ml chloroform using 5 equivalents of the corresponding orthoformate and 50 mg/mmol AS-2 catalyst.

from epoxides and a range of alcohols under mild conditions, with high regioselectivity and in excellent isolated yield. We have also demonstrated that these aluminosilicate materials effectively catalyze the Meinwald rearrangement of epoxides to the corresponding aldehydes and that they can be employed as sequential catalysts for tandem rearrangement/acetalization processes of epoxides. In the latter case, it was found that it was to be more effective to use the high aluminium content material in these reactions as acetalization reactions proceeded more efficient with this catalyst. The facile synthesis of these materials using the EISA approach, their benign nature, the ease of handling and the simplified reaction and isolation procedures make them a highly attractive alternative to current methodologies.

Experimental

General experimental

Commercially available reagents were used without further purification. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography (TLC) was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF254 that were visualized under UV light (at 254 and/or 360 nm) or using potassium permanganate solution (1% in water) followed by charring. Infrared (IR) spectra were recorded between 4000–600 cm⁻¹ as neat oils or solids and are reported in cm⁻¹. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 400 MHz spectrometer in CDCl₃ at 25 °C and are reported in ppm; *J* values are recorded in Hz and multiplicities are expressed by the usual conventions. Low-resolution mass spectra (MS) were determined using the ionization technique stated. ES refers to electrospray ionization, CI refers to chemical ionization (ammonia) and EI refers to electron impact ionization. High resolution mass spectra (HRMS) were obtained courtesy of the EPSRC Mass Spectrometry Service, Swansea University using the ionization method specified. Removal of solvent refers to evaporation at reduced pressure using a rotary evaporator followed by the removal of trace volatiles using a vacuum pump. Melting points were recorded using a Sanyo Gallenkamp variable heater melting point apparatus with a digital

display, heating at a rate of 1 °C/minute. Specific surface areas were obtained by the BET method at liquid nitrogen temperatures using a Micromeritics Gemini or a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at 120 °C under a flow of helium for 2 hours prior to analysis. Pore sizes were obtained using a Quantachrome Autosorb-1 automated gas sorption instrument. Samples were degassed at room temperature under a stream of helium for 3 hours prior to analysis. Pore sizes were calculated from the desorption branch of the isotherm by the BJH Dv(d) method. Elemental compositions were obtained with a JOEL scanning electron microscope fitted with an EDX detector using a 20 KeV accelerating voltage.

Preparation of AS-2 catalyst

Cetyltrimethylammonium bromide (4.0 g, 11 mmol) was dissolved in a solution of hydrochloric acid (2.5 ml, 0.1 M) and ethanol (17.5 ml). Tetraethylorthosilicate (25 ml, 112 mmol) was then added and the mixture stirred for 10 minutes at 40 °C. The solution was cooled to room temperature and aluminium nitrate nonahydrate (3.35 g, 8.95 mmol) was added in one portion. The mixture was stirred for 20 minutes and then left to age at room temperature for 1 week. The resultant orange solid was crushed into a fine powder, dried overnight at 90 °C and then calcined in air at 550 °C for 12 hours to remove the organic template. The resulting white mesoporous aluminosilicate catalyst was characterized by EDX and MAS-NMR (^{27}Al and ^{29}Si) analysis. Surface area measurements and pore size distribution were obtained from BET experiments.

Synthesis of epoxides

α -Methyl styrene oxide¹⁹. α -Methyl styrene (2.96 g, 25 mmol) was added to a solution of *N*-bromosuccinimide (4.45 g, 25 mmol) in distilled water (40 ml) at room temperature and the reaction mixture was stirred vigorously at room temperature for 2 hours. After this time, the product bromohydrin was separated from the aqueous layer which was extracted with diethyl ether (2 \times 20 ml). The extracts were combined with the bromohydrin, dried over magnesium sulfate and the solvent removed under reduced pressure. The crude bromohydrin was then dissolved in sodium hydroxide (40 ml, 15% solution) and the mixture stirred for 1 hour at 60 °C. After this time, the epoxide product was separated from the aqueous layer which was extracted with diethyl ether (2 \times 20 ml). The ether extracts were combined with the crude epoxide, dried over magnesium sulfate and the solvent removed under reduced pressure. Distillation of the crude mixture gave the product α -methylstyrene oxide as a colourless oil (3.12 g, 92%); bp 37–41 °C, (0.1 mmHg) (lit 40–45 °C, 0.1 mmHg); ν_{max} (film)/cm⁻¹ (neat) 2985, 1497, 1445, 1124, 1061, 858, 757, 697 and 545; ^1H NMR (400 MHz; CDCl_3) δ = 7.30–7.14 (5H, m), 2.88 (1H, d, J = 5 Hz), 2.70 (1H, d, J = 5 Hz), 1.63 (3H, s); ^{13}C NMR (100 MHz; CDCl_3) δ = 141.6, 129, 127.9, 125.7, 57.5, 57.2 and 22.2; MS (EI) m/z 134 (M^+); HRMS (ES) calculated for $\text{C}_9\text{H}_{11}\text{O}$ ($\text{M} + \text{H}^+$)⁺ 135.0804, found ($\text{M} + \text{H}^+$)⁺ 135.0804.

Typical procedure for the mCPBA epoxidation of vinyl compounds: *trans*-Stilbene oxide²⁰. *trans*-Stilbene (3.60 g, 20 mmol) was dissolved in a suspension of sodium hydrogen carbonate (1.74 g) in dichloromethane (100 ml) and *meta*-chloroperbenzoic

acid (5.14 g, 23 mmol) was added and the reaction mixture stirred at room temperature for 48 hours. After this time, the reaction was washed sequentially with sodium metabisulfite (2 \times 100 ml, 5% solution) and sodium hydrogen carbonate solution (4 \times 75 ml, 5% solution). The organic layer was dried over magnesium sulfate and the solvent removed under reduced pressure to give the product *trans*-stilbene oxide as a white solid (2.75 g, 80% yield); mp 68–69 °C (lit 66–67 °C); ν_{max} (film)/cm⁻¹ (neat) 1725, 1452, 1244, 1176, 1071 and 846; ^1H NMR (400 MHz; CDCl_3) δ = 7.57–7.34 (10H, m), 3.91 (2H, s); ^{13}C NMR (100 MHz; CDCl_3) δ = 137.6, 129.0, 128.8, 126.2 and 63.3; MS (CI) m/z 214 ($\text{M} + \text{NH}_4^+$); HRMS (ES) calculated for $\text{C}_{14}\text{H}_{16}\text{NO}$ ($\text{M} + \text{NH}_4^+$), 214.1226, found 214.1228.

***cis*-Stilbene oxide²¹.** (88% yield); mp 35–37 °C (lit 37–68 °C); ν_{max} (film)/cm⁻¹ (neat) 1727, 1496, 1253, 1178, 1026 and 895; ^1H NMR (400 MHz; CDCl_3) δ = 7.11–7.0 (10H, m), 4.24 (2H, s); ^{13}C NMR (100 MHz; CDCl_3) δ = 134.8, 128.7, 127.6, 127.3, 60.2; MS (CI) m/z 214 ($\text{M} + \text{NH}_4^+$); HRMS (ES) calculated for $\text{C}_{14}\text{H}_{13}\text{O}$ ($\text{M} + \text{H}^+$)⁺, 197.0961, found 197.0961.

1,2-Dihydronaphthalene oxide²⁰. (97% yield); ν_{max} (film)/cm⁻¹ (neat) 2999, 2933, 1493, 1433, 1278, 1132, 1035, 937, 851, 795; ^1H NMR (400 MHz; CDCl_3) δ = 7.44 (1H, d, J = 7 Hz), 7.33–7.21 (2H, m), 7.13 (1H, d, J = 7 Hz), 3.89 (1H, d, J = 4 Hz), 3.77 (1H, t, J = 4 Hz), 2.83–2.79 (1H, m), 2.59–2.55 (1H, m), 2.49–2.41 (1H, m), 1.80–1.76 (1H, m); ^{13}C NMR (100 MHz; CDCl_3) δ = 137.1, 132.9, 129.9, 129.8, 128.8, 126.5, 55.5, 53.2, 24.8 and 22.2; MS (EI) m/z 146 (M^+); HRMS (EI) calculated for $\text{C}_{10}\text{H}_{10}\text{O}$ (M^+)⁺ 146.0726, found (M^+)⁺ 146.0724.

2-Vinylnaphthalene oxide²². (99% yield); ν_{max} (film)/cm⁻¹ (neat) 2975, 1525, 1401, 1303, 1259; ^1H NMR (400 MHz; CDCl_3) δ = 7.74–7.67 (4H, m), 7.40–7.33 (2H, m), 7.22 (1H, dd, J = 2 and 9 Hz), 3.91 (1H, dd, J = 3 and 4 Hz), 3.10 (1H, dd, J = 4 and 6 Hz), 2.79 (1H, dd, J = 3 and 6 Hz); ^{13}C NMR (100 MHz; CDCl_3) δ = 135.5, 133.8, 133.6, 128.2, 127.3, 126.8, 126.5, 125.7, 123.1, 53.1 and 51.7; MS (EI) m/z 170 (M^+)⁺.

Typical procedure for the alcoholysis of epoxides: 2-Methoxy-2-phenylethanol^{3b}. Styrene oxide (120 mg, 1 mmol) was dissolved in methanol (10 ml) at room temperature. The mesoporous catalyst AS-2 (50 mg) was added and the reaction mixture stirred at room temperature. After completion of the reaction (TLC), the catalyst was removed by filtration through a Celite plug which was washed with dichloromethane (2 \times 5 ml). The combined solvents were removed under reduced pressure to give the product 2-methoxy-2-phenylethanol as a colourless oil (114 mg, 95%); ν_{max} (film)/cm⁻¹ (neat) 3421, 2933, 1454, 1109, 1062, 1025, 757, 699 and 544; ^1H NMR (400 MHz; CDCl_3) δ = 7.44–7.29 (5H, m), 4.34 (1H, dd, J = 4 and 9 Hz), 3.74–3.59 (2H, m), 3.34 (3H, s), 2.45 (1H, br s); ^{13}C NMR (100 MHz; CDCl_3) δ = 138.7, 129.4, 128.9, 127.5, 85.1, 67.8 and 57.3; MS (EI) m/z 152 (M^+); HRMS (ES) calculated for $\text{C}_9\text{H}_{10}\text{NO}_2$ ($\text{M} + \text{NH}_4^+$)⁺ 170.1176, found ($\text{M} + \text{NH}_4^+$)⁺ 170.1176.

2-Ethoxy-2-phenylethanol¹⁰. (86% yield); ν_{max} (film)/cm⁻¹ (neat) 3425, 2974, 2871, 1454, 1127, 1099, 1066, 756 and 700; ^1H NMR (400 MHz; CDCl_3) δ = 7.32–7.19 (5H, m), 4.34 (1H, dd, J = 4 and 8 Hz), 3.62–3.48 (2H, m), 3.47–3.28 (2H, m), 2.51 (1H, br s), 1.14 (3H, t, J = 8 Hz); ^{13}C NMR (100 MHz; CDCl_3) δ = 139.4, 128.7, 128.4, 127.2, 83.2, 67.8, 64.9 and 15.7; MS (EI) m/z

166 (M)⁺; HRMS (ES) calculated for C₁₀H₁₈NO₂ (M + NH₄)⁺ 184.1332, found (M + NH₄)⁺ 184.1332.

2-Propoxy-2-phenylethanol¹⁰. (68% yield); ν_{\max} (film)/cm⁻¹ (neat) 3419, 2953, 1447, 1119, 1099 and 1025; ¹H NMR (400 MHz; CDCl₃) δ = 7.31–7.19 (5H, m), 4.32 (1H, dd, J = 4 and 8 Hz), 3.62–3.48 (2H, m), 3.34–3.19 (2H, m), 2.48 (1H, br s), 1.59–1.47 (2H, m), 0.84 (3H, t, J = 8 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 139.4, 129.8, 128.9, 127.4, 83.3, 71.3, 67.9, 23.5 and 11.1; MS (CI) m/z 198 (M + NH₄)⁺; HRMS (ES) calculated for C₁₁H₂₀NO₂ (M + NH₄)⁺ 198.1489, found (M + NH₄)⁺ 198.1490.

2-iso-Propoxy-2-phenylethanol^{3b}. (52% yield); ν_{\max} (film)/cm⁻¹ (neat) 3432, 2971, 1453, 1123, 1091 and 1056; ¹H NMR (400 MHz; CDCl₃) δ = 7.30–7.20 (5H, m), 4.50 (1H, dd, J = 4 and 8 Hz), 3.60–3.45 (3H, m), 2.40 (1H, br s), 1.15 (3H, d, J = 7 Hz), 1.05 (3H, d, J = 7 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 139.2, 129.1, 128.3, 127.1, 80.3, 69.9, 67.7, 23.1 and 21.1; MS (CI) m/z 198 (M + NH₄)⁺; HRMS (ES) calculated for C₁₁H₁₇O₂ (M + H)⁺ 181.1223, found (M + H)⁺ 181.1224.

2-Methoxy-3-phenoxypropan-1-ol²³. (58% yield); ν_{\max} (film)/cm⁻¹ (neat) 3425, 2927, 1599, 1496, 1242, 1108, 1040, 752 and 691; ¹H NMR (CDCl₃, 400 MHz) δ = 7.30–7.20 (2H, m), 6.95–6.85 (3H, m), 4.09 (1H, dt, J = 5 and 2 Hz), 3.94 (2H, dd, J = 2 and 5 Hz), 3.54–3.44 (2H, m), 3.34 (3H, s), 2.60 (1H, br s); ¹³C NMR (CDCl₃, 100 MHz) δ = 159.0, 129.9, 121.5, 115.0, 73.9, 69.4, 69.2, 59.7; MS (ES) m/z 183 (M + H)⁺; HRMS (ES) calculated for C₁₀H₁₅O₃, (M + H)⁺, 183.1016, found 183.1016.

2-Methoxy-2-phenylpropan-1-ol²⁴. (97% yield); ν_{\max} (film)/cm⁻¹ (neat) 3421, 2940, 1446, 1072, 1047, 1024, 761, 735, 699 and 552; ¹H NMR (400 MHz; CDCl₃) δ = 7.44–7.26 (5H, m), 3.68 (1H, d, J = 11 Hz), 3.52 (1H, d, J = 11 Hz), 3.15 (3H, s), 2.72 (1H, br s), 1.64 (3H, s); ¹³C NMR (100 MHz; CDCl₃) δ = 142.4, 128.7, 127.8, 126.9, 80.2, 71.7, 50.8 and 19.6; MS (CI, NH₃) m/z 184 (M + NH₄)⁺; HRMS (ES) calculated for C₁₀H₁₈NO₂ (M + NH₄)⁺ 184.1332, found (M + NH₄)⁺ 184.1334.

2-Methoxy-2-naphthalen-2-ylethanol²⁵. (90% yield); ¹H NMR (400 MHz; CDCl₃) δ = 7.77–7.70 (3H, m), 7.67 (1H, s), 7.40–7.36 (2H, m), 7.32 (1H, dd, J = 1 and 9 Hz), 4.37 (1H, dd, J = 4 and 9 Hz), 3.68 (1H, dd, J = 9 and 11 Hz), 3.55–3.45 (1H, m), 3.24 (3H, s), 2.44 (1H, br s); ¹³C NMR (100 MHz; CDCl₃) δ = 135.6, 133.2, 133.1, 128.3, 127.8, 127.6, 126.2, 126.1, 126.0, 124.3, 84.7, 67.1 and 56.9; MS (EI) m/z 202 (M)⁺; HRMS (ES) calculated for C₁₃H₁₈NO₂ (M + NH₄)⁺ 220.1332, found (M + NH₄)⁺ 220.1332.

trans-1-Methoxy-1,2,3,4-tetrahydronaphthalen-2-ol²⁶. (99% yield); ν_{\max} (film)/cm⁻¹ (neat) 3397, 2931, 1455, 1108, 1072, 1039, 956 and 745; ¹H NMR (400 MHz; CDCl₃) δ = 7.43–7.38 (1H, m), 7.27–7.22 (2H, m), 7.14–7.10 (1H, m), 4.25 (1H, d, J = 7 Hz), 4.05–3.95 (1H, m), 3.45 (3H, s), 2.88–2.82 (2H, m), 2.21–2.12 (2H, m), 1.85–1.75 (1H, m); ¹³C NMR (100 MHz; CDCl₃) δ = 136.5, 134.5, 128.3, 128.2, 127.4, 125.9, 82.6, 68.8, 56.6, 27.8 and 26.3; MS (EI) m/z 177.1 (M-H)⁺; HRMS (ES) calculated for C₁₁H₁₈NO₂ (M + NH₄)⁺ 196.1322, found (M + NH₄)⁺ 196.1322.

trans-2-Methoxycyclohexanol^{3b}. (69% yield); ν_{\max} (film)/cm⁻¹ (neat) 3438, 2931, 2861, 1450, 1376, 1125, 1099, 1077, 1027 and 840; ¹H NMR (400 MHz; CDCl₃) δ = 3.43–3.29 (4H, m), 3.02 (1H, br s), 2.93–2.85 (1H, m), 2.11–2.02 (1H, m), 1.99–1.88 (1H, m),

1.72–1.58 (2H, m), 1.30–1.09 (3H, m); 1.09–0.96 (1H, m); ¹³C NMR (100 MHz; CDCl₃) δ = 85.5, 74.0, 56.7, 32.5, 28.7, 24.4 and 24.3; MS (CI, NH₃) m/z 148 (M + NH₄)⁺; HRMS (ES) calculated for C₇H₁₄O₂Na (M + Na)⁺ 153.0886, found (M + Na)⁺ 153.0885.

trans-2-Ethoxycyclohexanol²⁷. (96% yield); ν_{\max} (film)/cm⁻¹ 3433, 2931, 2861, 1452, 1190, 1094, 995, 913 and 845; ¹H NMR (400 MHz; CDCl₃) δ = 3.77–3.68 (1H, m), 3.48–3.30 (2H, m), 3.07–2.90 (1H, m), 2.78 (1H, br s), 2.14–1.90 (2H, m), 1.72–1.60 (2H, m), 1.26–0.97 (7H, m); ¹³C NMR (100 MHz; CDCl₃) δ = 83.8, 74.0, 64.4, 32.5, 29.6, 24.7, 24.6 and 16.0; MS (CI, NH₃) m/z 162 (M + NH₄)⁺; HRMS (ES) calculated for C₈H₁₆O₂Na (M + Na)⁺, 167.1043; found (M + Na)⁺ 167.1043.

trans-2-iso-Propoxycyclohexanol^{3b}. (90% yield); ν_{\max} (film)/cm⁻¹ (neat) 3435, 2930, 2861, 1450, 1134, 1071 and 911; ¹H NMR (400 MHz; CDCl₃) δ = 3.69 (1H, hept, J = 6 Hz), 3.38–3.30 (1H, m), 3.10–3.02 (1H, m), 2.73 (1H, br s), 2.05–1.94 (2H, m), 1.73–1.62 (2H, m), 1.40–1.12 (10 H, m); ¹³C NMR (100 MHz; CDCl₃) δ = 81.3, 73.7, 69.5, 32.0, 30.3, 24.4, 24.0, 23.8 and 22.3; MS (EI) m/z 159 (M + H)⁺.

Typical procedure for the Meinwald rearrangement of epoxides: 2,2-diphenylacetaldehyde²⁸. The mesoporous catalyst AS-1 (50 mg) was added to a solution of *trans*-stilbene oxide (120 mg, 1 mmol) in dichloromethane (10 ml) and the reaction mixture was heated to reflux. On completion of the reaction (TLC), the mixture was cooled to room temperature and the catalyst was removed by filtration through a Celite plug which was washed with further amounts of dichloromethane (2 × 5 ml). The combined solvents were removed under reduced pressure to give the product *2,2-diphenylacetaldehyde* as a colourless oil (78 mg, 65%); ν_{\max} (film)/cm⁻¹ (neat) 3063, 3032, 1724, 1495, 1452, 1285, 1250, 1155, 744, 694 and 613; ¹H NMR (400 MHz; CDCl₃) δ = 10.0 (1H, d, J = 2 Hz), 7.45–7.20 (10H, m), 4.95 (1H, d, J = 2 Hz); MS (EI) m/z 196 (M)⁺; HRMS (ES) calculated for C₁₄H₁₆NO (M + NH₄)⁺, 214.1226; found (M + NH₄)⁺ 214.1228.

2-Phenylpropionaldehyde²⁸. (98% yield); ν_{\max} (film)/cm⁻¹ (neat) 2978, 1718, 1493, 1452, 1267, 1020, 759 and 697; ¹H NMR (400 MHz; CDCl₃) δ = 9.62 (1H, d, J = 2.0 Hz), 7.40–7.20 (5H, m), 3.55 (1H, dq, J = 2 and 7 Hz), 1.45 (3H, d, J = 7 Hz); ¹³C NMR (100 MHz; CDCl₃) δ = 201.6, 138.12, 129.5, 128.7, 127.5, 53.4 and 15.0; MS (EI) m/z 134 (M)⁺; HRMS (ES) calculated for C₉H₁₄NO (M + NH₄)⁺ 152.1070, found (M + NH₄)⁺ 152.1070.

Phenylacetaldehyde²⁸. (95% yield); ν_{\max} (film)/cm⁻¹ (neat) 2993, 1704, 1510, 1452 and 1127; ¹H NMR (400 MHz; CDCl₃) δ = 9.70 (1H, t, J = 2 Hz), 7.30–7.10 (5H, m), 3.60 (2H, d, J = 2 Hz); MS (EI) m/z 121 (M + H)⁺; HRMS (EI) calculated for C₈H₈O (M)⁺ 120.0570, found (M)⁺ 120.0568.

Typical procedure for the tandem rearrangement/ acetalization of epoxides: 2,2-diphenylacetaldehyde dimethyl acetal²⁹. The mesoporous catalyst AS-2 (50 mg) was added to a mixture of *trans*-stilbene oxide (199 mg, 1.02 mmol) and trimethyl orthoformate (541 mg, 5.10 mmol) in chloroform (10 ml) at room temperature and the reaction mixture stirred at 50 °C for 5 hours. After this time, the mixture was cooled to room temperature and the catalyst removed by filtration through a Celite plug which was washed with dichloromethane (2 × 5 ml). The washings were combined and the solvent was removed under reduced pressure to give the crude

product 2,2-diphenylacetaldehyde dimethyl acetal (240 mg, 98%) as a colourless oil; ν_{\max} (film)/ cm^{-1} (neat) 2970, 1720, 1431, 1109, 1057 and 745; ^1H NMR (400 MHz; CDCl_3) δ = 7.33–7.06 (10H, m), 4.91 (1H, d, J = 8 Hz), 4.15 (1H, d, J = 8 Hz) 3.21 (6H, s); ^{13}C NMR (100 MHz; CDCl_3) δ = 141.6, 129.7, 128.9, 126.2, 106.9, 55.0 and 54.5; MS (CI) m/z 260 ($\text{M} + \text{NH}_4$) $^+$; HRMS (ES) calculated for $\text{C}_{16}\text{H}_{22}\text{NO}_2$ ($\text{M} + \text{NH}_4$) $^+$, 260.1645; found ($\text{M} + \text{NH}_4$) $^+$ 260.1644.

2,2-Diphenylacetaldehyde diethyl acetal²⁹. (96% yield); ν_{\max} (film)/ cm^{-1} (neat) 2975, 1727, 1496, 1451, 1113, 1057, 745 and 696; ^1H NMR (400 MHz; CDCl_3) δ = 7.26–7.06 (10H, m), 4.99 (1H, d, J = 8 Hz), 4.15 (1H, d, J = 8 Hz), 3.59–3.49 (2H, m), 3.39–3.31 (2H, m), 0.98 (6H, t, J = 7 Hz); ^{13}C NMR (100 MHz; CDCl_3) δ = 141.9, 129.3, 128.4, 126.6, 105.2, 62.8, 55.8, 15.5; MS (ES) m/z 288 ($\text{M} + \text{NH}_4$) $^+$; HRMS (ES) calculated for $\text{C}_{18}\text{H}_{26}\text{NO}_2$ ($\text{M} + \text{NH}_4$) $^+$, 288.1958; found ($\text{M} + \text{NH}_4$) $^+$ 288.1958.

2-Phenylpropionaldehyde dimethyl acetal³⁰. (80% yield); ν_{\max} (film)/ cm^{-1} (neat) 2935, 1605, 1452, 1058, 760 and 698; ^1H NMR (CDCl_3 , 400 MHz) δ = 7.37–7.05 (5H, m), 4.29 (1H, d, J = 7 Hz), 3.29 (3H, s), 3.16 (3H, s), 2.93 (1H, pent, J = 7 Hz), 1.20 (3H, d, J = 7 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ = 142.1, 127.4, 126.9, 125.1, 107.6, 53.5, 53.0, 41.9, 15.8; MS (ES) m/z 198 ($\text{M} + \text{NH}_4$) $^+$.

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