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Tetrahedron: *Asymmetry* 17 (2006) 2833–2838

Tetrahedron: *Asymmetry*

Water soluble lanthanoid benzoate complexes for the kinetic separation of *cis*/*trans*-limonene oxide

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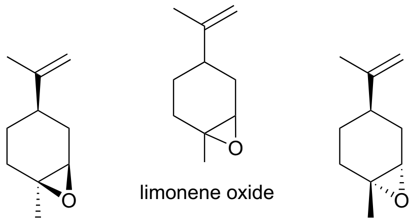
Received 2 October 2006; accepted 19 October 2006

Abstract—A new class of water soluble, environmentally friendly, lanthanoid 3,5-diacetamidobenzoate complexes (Ln = La, Gd, Yb) have been synthesized. The La and Gd complexes selectively catalyse hydrolysis of the *cis*-isomer of limonene oxide allowing for the separation of the *trans*-isomer (>98:2 dr) in up to 74% yield. Comparative studies with the corresponding chlorides and triflates reveal the lanthanoid benzoate complexes to be more active than the chlorides, but less active, though more selective, than the triflates.

1. Introduction

Homogeneous catalysis in non-volatile organic solvents is currently a field of active research due to interest in sustainable synthetic methods with low environmental impact.[1] In this respect, epoxide ring opening reactions in water have great potential owing to the vast number of enantiomerically pure compounds that are accessible via this simple transformation.[2] As catalysts, lanthanoid triflates appear to be an obvious choice since they have already been shown to be effective in a number of other aqueous based organic procedures.[3] From an industrial perspective though, triflates may not be ideal because of the highly corrosive nature of triflic acid. Lanthanoid benzoates[4] are a possible alternative with the potential to provide similar reactivity with improved selectivity. However, the relative insolubility of simple benzoates has inhibited comparative studies in this area.

The pure diastereomers **1** and **2** of limonene oxide (Fig. 1), a naturally occurring epoxide, have been used in the total syntheses of a number of natural products.[5–7] Although pure **1** and **2** are commercially available, they are expensive and are more commonly purchased and used as a mixture of the *cis*/*trans* (47:53) diastereomers. Efficient and commercially viable methods for separating the diastereomers have, therefore, been of some interest to both academic and industrial researchers and as such, a number of procedures now currently exist, with varying efficiencies, for their separation. These fall largely into two categories: (1) separation and recovery of each diastereomer based upon differing physical properties, for example, chromatography or distillation,[8] and (2) kinetic separation where one diastereomer reacts faster than the other, allowing for recovery of the pure unreacted diastereomer, for example, photo-assisted kinetic separation[9] and biocatalysis,[10] electrophilic mercuration,[11] amine addition[12] and molybdenum(VI) catalysis.[13]



1
trans
limonene oxide

2
cis
limonene oxide

Figure 1. Limonene oxide.

While the degree of separation in these chemical processes is generally >90%, they suffer from various drawbacks including being non-catalytic, requiring high reaction temperatures, the use of toxic reagents/catalysts, a need for derivatisation, and air/moisture sensitivity.

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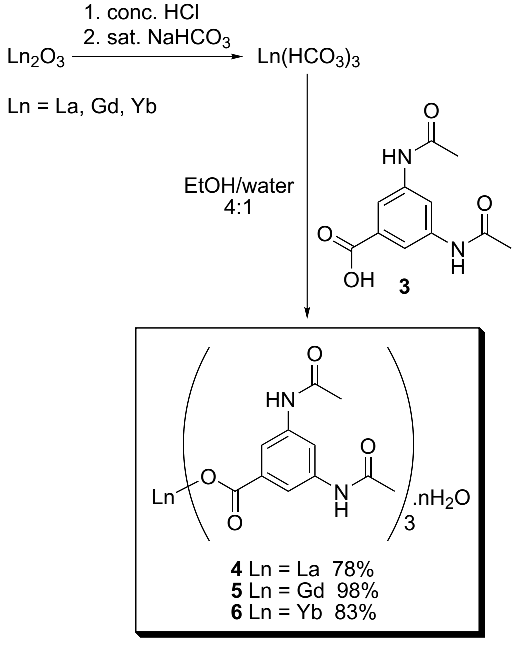
doi:10.1016/j.tetasy.2006.10.026

Herein, we report the first application of water soluble lanthanoid (Ln = La, Gd, Yb) benzoate complexes, derived from 3,5-diacetamidobenzoic acid, and their application as catalysts in the ring opening and consequent kinetic separation of limonene oxide.

2. Results and discussion

To establish the effectiveness of lanthanoid benzoate catalysts in an aqueous medium, the ligands first had to be designed to allow solubility and stability. Convenient targets were the complexes derived from 3,5-diacetamidobenzoic acid **3**. The ligand was efficiently prepared by the acylation of 3,5-diaminobenzoic acid with acetic anhydride. Subsequent treatment of **3** with lanthanoid bicarbonate, prepared from the lanthanoid oxide, gave the appropriate La, Gd and Yb complexes **4**–**6** in good yield (Scheme 1).

For examination as catalysts in the ring opening and kinetic separation of *cis*/*trans*-limonene oxide, complexes **4**–**6** were dissolved in water (5 mol %, relative to total limonene oxide) and the 53:47 mixture of limonene oxides **1** and **2** added (Scheme 2).

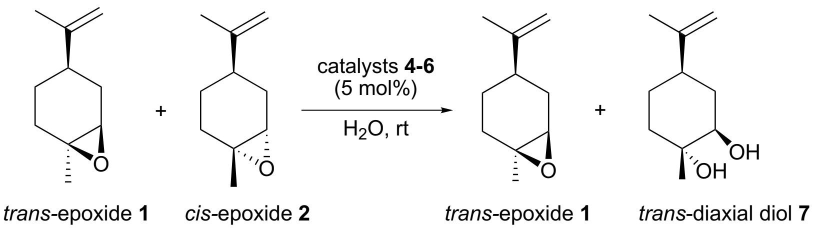


Scheme 1. Synthesis of 3,5-diacetamidobenzoate complexes **4**–**6**.

Since limonene oxide is only sparingly soluble in water (4.6×10^{-3} mol L^{-1} at 25 °C), the reaction mixtures are best described as dispersions rather than homogeneous solutions. The suspensions were vigorously stirred at room temperature and the reaction progress was monitored by ^{1}H NMR spectroscopy. A reliable analytical procedure involving extraction with ethyl acetate and in vacuo concentration was initially hindered by the volatility and significant loss of limonene oxide. After some experimentation, the most reliable and reproducible method involved an initial extraction with $CDCl_3$, to efficiently remove all the unreacted epoxide, followed by a second extraction with ethyl acetate to remove the remaining diol **7**. The ethyl acetate extraction was then evaporated to dryness leaving the non-volatile solid diol. This was re-combined with the $CDCl_3$ extract to form the sample for NMR analysis. With a good procedure for monitoring the reaction progress established, it was discovered that the only product of the reaction was the water soluble *trans*-diaxial diol **7** (Scheme 2), which was not unexpected since both *cis*- and *trans*-limonene oxides have been reported to open through a diaxial mechanism to yield the same diol.[14] Further NMR analysis revealed that the *cis*-diastereomer **2** reacts at a much faster rate than the *trans*-diastereomer **1** and that a kinetic separation of *trans*-limonene oxide **1** could be obtained if the reaction was stopped at the appropriate time. Under normal, non-analytical, reaction conditions the remaining unreacted *trans*-limonene oxide **1** could be isolated by pentane extraction of the aqueous layer (pure by NMR and >98:2 dr by GC analysis). The aqueous phase containing the catalyst was used for three consecutive reactions and extraction cycles without any significant reduction in the yield of diol or loss in the recovered fraction of *trans*-epoxide.

Figure 2 shows the reaction profile of the commercially available mixture of limonene oxides **1** and **2** with the lanthanum catalyst **4**. At $t = 0$, the species fractions of limonene oxide are *trans* = 0.53 and *cis* = 0.47. As the reaction proceeds there is a fast consumption of the *cis*-epoxide and a slow consumption of the *trans*-epoxide. After 13 h, the *cis*-epoxide is completely transformed to the diol and 74% of the original fraction of *trans*-epoxide is recovered.

The gadolinium complex **5** gave a similar reaction profile (Fig. 3) where complete consumption of the *cis*-epoxide **2** was achieved in ca. 15 h. In contrast to the La catalysed reaction, the fraction of *trans*-epoxide recovered, decreased to 0.25 (47%).



Scheme 2. Separation of *cis*/*trans*-limonene oxide **1**.

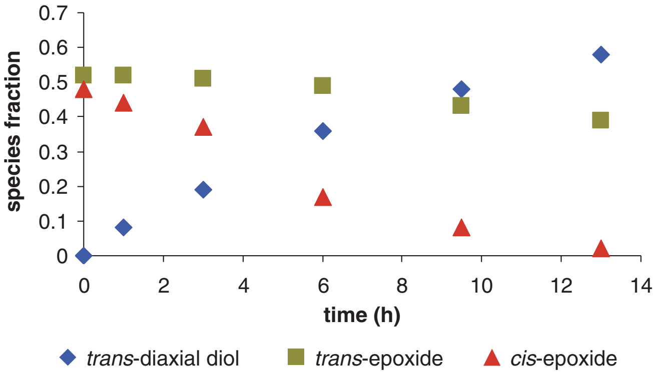


Figure 2. Reaction profile for the hydrolytic ring opening of limonene oxide mixtures **1** and **2** in the presence of 5% lanthanum catalyst **4**.

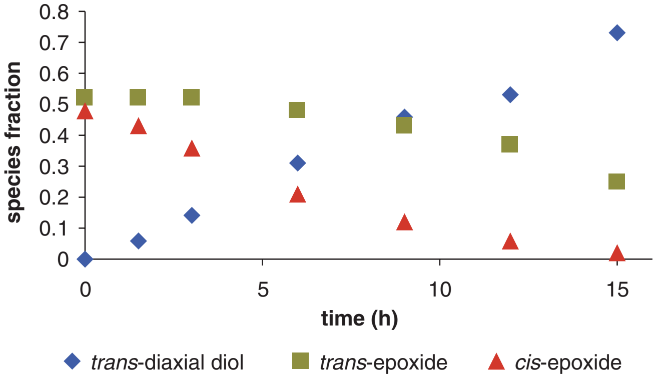


Figure 3. Reaction profile for the hydrolytic ring opening of limonene oxide mixtures **1** and **2** in the presence of 5% gadolinium catalyst **5**.

Surprisingly, the Yb complex **6** gave no appreciable reaction over a period of 2 days. Monitoring over a further period of 2 days revealed a very slow, and non-selective reaction which was not studied further.

It was important to compare the reactivity and selectivity of complexes **4**–**6** with their corresponding lanthanoid chlorides and triflates. The lanthanoid chlorides (La, Gd, Yb) proved to be inefficient catalysts with very little reaction occurring at room temperature over a period of 5 days. The triflates were prepared using an adaptation of the procedure described by Kobayashi.[15] The mixture of limonene oxides **1** and **2** were added to the lanthanoid triflates (5 mol %) in water and stirred vigorously. The reaction progress was again monitored by ^{1}H NMR spectroscopy. The reaction catalysed by La(OTf)$_3$ (Fig. 4) was faster than that catalysed by lanthanum benzoate complex **4** and complete consumption of the *cis*-epoxide **2** was achieved in a reaction time of 11 h. However, there was a decrease in the amount of *trans*-epoxide recovered (65%).

Gadolinium triflate also catalysed the hydrolysis of limonene oxide faster than the corresponding gadolinium benzoate complex **5** (Fig. 5). Complete consumption of the *cis*-epoxide **2** was achieved in 7 h, but again, increased reactivity of the *trans*-epoxide led to an inferior recovery of this diastereomer (61%).

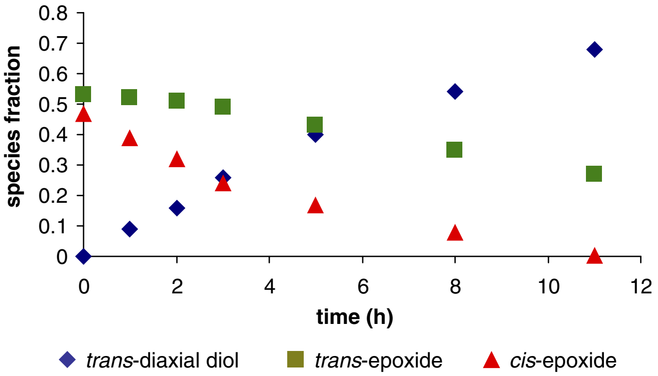


Figure 4. Reaction profile for the hydrolytic ring opening of limonene oxide mixtures **1** and **2** in the presence of 5% La(OTf)$_3$.

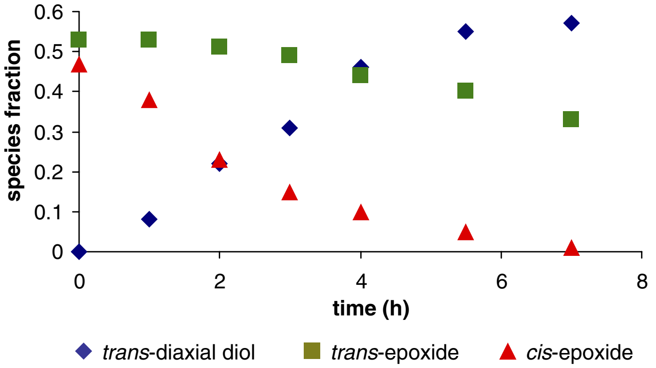


Figure 5. Reaction profile for the hydrolytic ring opening of limonene oxide mixtures **1** and **2** in the presence of 5% Gd(OTf)$_3$.

The increased reactivity of gadolinium triflate (7 h for completion) over lanthanum triflate (11 h for completion) is rationalised by the contraction in ionic radius and increased Lewis acidity of gadolinium over lanthanum. As was observed for the benzoates, the ytterbium triflate proved to be much less reactive (Fig. 6) than the La and Gd analogues. The reaction profile shows that after 9 h only ca. 50% of the *cis*-epoxide **2** had been hydrolysed. This observation is consistent with that obtained with ytterbium complex **6** and most likely results from the epoxide sub-

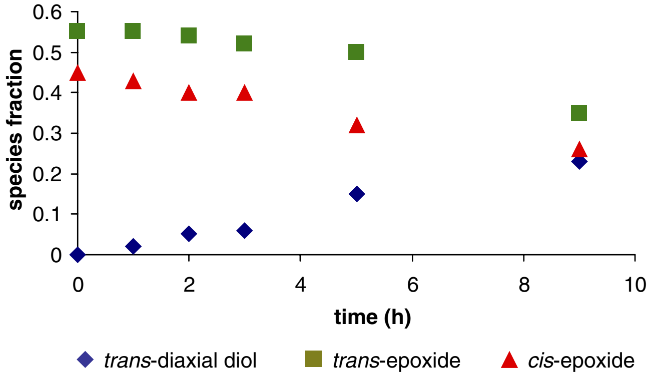


Figure 6. Reaction profile for the hydrolytic ring opening of limonene oxide mixtures **1** and **2** in the presence of 5% Yb(OTf)$_3$.

Table 1. Summary of reaction times, yields and dr for the separation of commercially available (+)-*cis*/*trans*-limonene oxide

Catalyst	Time (h)	dr (**1**:**2**)[a]	Fraction of *trans*-epoxide **1** recovered (%)	Yield of diol **7** (%)
4	13	>98:2	39[b] (74)[c]	61
5	15	>98:2	25[b] (47)[c]	75
6	>36	53:47[d]	—	<5
$LaCl_3$	>120	53:47[d]	—	<5
$GdCl_3$	>120	53:47[d]	—	<5
$YbCl_3$	>120	53:47[d]	—	<5
$La(OTf)_3$	11	>98:2	27[b] (65)[c]	73
$Gd(OTf)_3$	7	>98:2	32[b] (61)[c]	68
$Yb(OTf)_3$	>24	35:26	—	23

[a] Diastereomeric ratio of *trans*/*cis*-limonene oxide after given reaction time (h).

[b] Yield as % of total limonene oxide starting material (max = 53%).

[c] Yield as % of only *trans*-limonene oxide starting material.

[d] No appreciable reaction with no change in limonene oxide fraction.

strate not being able to successfully compete with water and the sulfonate ligands for co-ordination to the smaller, more Lewis acidic ytterbium centre.

The reaction times and yields obtained with each of the lanthanoid 3,5-diacetamidobenzoate complexes **4**–**6** and the lanthanoid triflates and chlorides are summarised in Table 1. As can be seen, the La benzoate catalyst **4** is the most efficient, followed by the La and Gd triflates, both of which are marginally better than the Gd benzoate complex **5**, while the chlorides are ineffective.

3. Conclusion

This new procedure provides a high yielding and environmentally benign procedure for the formation of *trans*-axial diol **7** and consequent kinetic separation of *trans*-limonene oxide. The La benzoate complex proved to be the most efficient, outperforming all three metal triflate complexes. While the degree of kinetic separation may not be as high as those reported for other chemical systems this new reaction process provides the benefits of being catalytic in water, can be carried out at ambient temperature, minimizes the use of volatile organic compounds with no need for reagent derivatisation, and importantly does not involve the use of toxic reagents/catalysts. Significantly, lanthanide tris-2,5-diacetamidobenzoate complexes represent a new class of water soluble catalysts, for which this study provides an initial assessment. Further investigations are currently underway in our laboratories to develop and test analogous complex systems in ring opening reactions, and to compare the reactivity and selectivity of these catalysts with lanthanoid triflates in a variety of other organic transformations.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR were recorded at 300 and 75 MHz, respectively, on a Bruker AM 300 spectrometer. Melting points were recorded on a Kofler hot stage apparatus and are uncorrected. Mass spectrometry (ESI) was performed on a Micromass Platform QMS spectrometer. High resolution mass spectra (HRMS) were recorded on a Bruker BioApex 47e FTMS. Infrared spectra (IR) were recorded on a Bruker Equinox 55 ATR spectrometer. GC–MS were performed on a Varian 3700 gas chromatograph using a 30QC5/BPX5 1.0 μm column of internal diameter 0.53 mm and length 30 m at a linear velocity of 40.6 cm/s. Elemental microanalyses were performed by the University of Otago, Dunedin, New Zealand. Lanthanoid oxides and (+)-limonene oxide, mixture of *cis*/*trans*-diastereomers were obtained from Sigma–Aldrich and used as supplied.

4.2. 3,5-Diacetamidobenzoic acid 3

To a stirred suspension of 3,5-diaminobenzoic acid (5.0 g, 32.9 mmol) in distilled water (150 mL) was added K_2CO_3 (13.3 g, 98.7 mmol). After stirring for 0.5 h, the solution became homogeneous and acetic anhydride (7.80 mL, 82.6 mmol) was slowly added. The reaction was stirred at rt o/n after which time all the water was removed under reduced pressure and the residual solid re-crystallised from boiling ethanol/water (5:1) to give a grey solid (7.06 g, 91%). ^{1}H NMR (300 MHz): δ 2.04 (s, 6H), 7.89 (d, $J = 1.8$ Hz, 2H), 8.10 (t, $J = 1.8$ Hz, 1H), 10.08 (br s, 2H). ^{13}C NMR (75 MHz): δ 23.0, 113.5, 114.6, 131.4, 139.7, 167.1, 168.6. IR (ATR) 3313s, 2894m, 1684s, 1627s, 1572m, 1533s, 1479m, 1452m, 1353m, 1321m, 1286s, 1158m, 1115w, 1036s, 934w, 912m, 871m, 645m, 625m cm^{-1}. MS calcd for $C_{11}H_{12}N_2O_4Na^+ = 259.1$, found: 259.0. HRMS calcd for $C_{11}H_{12}N_2O_4Na^+ = 259.0695$, found: 259.0695.

4.3. General procedure for the synthesis of benzoate complexes

To solid Ln_2O_3 (0.5 mmol) was added concd HCl (12 M, 1 mL). Stirring was continued until all the solid had dissolved and then satd $NaHCO_3$ (~40 mL) was added until the pH reached 8.5. The precipitated $Ln(HCO_3)_3$ was collected on a sintered funnel and washed with distilled water (3 × 5 mL), acetone (3 × 5 mL) and ether (3 × 5 mL) and then dried under vacuum for 2 h at rt. It was then added to a solution of 3,5-diacetamidobenzoic acid (2 mmol) in refluxing ethanol/water (4:1, 300 mL). The reaction was heated at reflux for a further 3 h after which any unreacted solid was removed by filtration and the ethanol/water removed under reduced pressure. The residual solid was suspended in THF and heated to reflux for 1 h before being filtered and washed with boiling THF (3 × 50 mL). The resulting grey powdery solid was dried under reduced pressure at rt for 2 days.

4.4. Lanthanum tris-3,5-diacetamidobenzoate 4

Following the general procedure as above with 3,5-diacetamidobenzoic acid **2** (1.00 g, 4.23 mmol) and La_2O_3 (173 mg, 0.53 mmol), lanthanum tris-3,5-diacetamido benzoate **4** was obtained as a greyish pink powder (0.7 g, 78%).

Mp 250 °C (decomp.). ^{1}H NMR (300 MHz): δ 2.03 (s, 6H), 7.78 (d, $J = 1.9$ Hz, 2H), 8.07 (t, $J = 1.9$ Hz, 1H), 9.91 (br s, 2H). ^{13}C NMR (75 MHz): δ 23.9, 112.1, 114.8, 137.4, 138.9, 168.2. IR (ATR) 3270s, 3090s, 1660s, 1612s, 1530s, 1493s, 1367s, 1266s, 1037m, 992m, 878m, 787m, 710m cm^{-1}. MS calcd for $C_{33}H_{33}N_6O_{12}LaNa^+ = 867.1$, found: 867.0. Calcd for $C_{33}H_{34}N_6O_{12}La^+ = 845.1$, found: 845.0. Anal. Calcd for $C_{33}H_{33}N_6O_{12}La{\cdot}3H_2O$ = C, 45.01; H, 4.24; N, 9.54. Found: C, 45.22; H, 4.56; N, 9.50.

4.5. Gadolinium tris-3,5-diacetamidobenzoate 5

Following the general procedure above with 3,5-diacetamidobenzoic acid **2** (2.08 g, 8.8 mmol) and Gd_2O_3 (400 mg, 1.10 mmol), gadolinium tris-3,5-diacetamido benzoate **5** was obtained as a greyish pink powder (2.01 g, 98%). Mp 250 °C (decomp.). IR (ATR) 3270s, 3095s, 1662s, 1612s, 1532s, 1444s, 1368s, 1269s, 1169m, 1037w, 991w, 878w, 789m, 698w cm^{-1}. MS calcd for $C_{33}H_{33}N_6O_{12}GdNa^+ = 886.1$, found: 886.2. HRMS calcd for $C_{33}H_{34}N_6O_{12}Gd^+ = 864.1476$, found: 864.1462. Anal. Calcd for $C_{33}H_{33}N_6O_{12}Gd{\cdot}H_2O$ = C, 44.99; H, 4.00; N, 9.54. Found: C, 45.15; H, 4.21; N, 9.39.

4.6. Ytterbium tris-3,5-diacetamidobenzoate 6

Following the general procedure above with 3,5-diacetamidobenzoic acid **2** (0.80 g, 3.37 mmol) and Yb_2O_3 (250 mg, 0.63 mmol), Ytterbium tris-3,5-diacetamido benzoate **6** was obtained as a greyish pink powder (0.65 g, 83%). Mp 300 °C (decomp.). IR (ATR) 3263s, 3094s, 1659s, 1616s, 1540s, 1367s, 1271s, 1242s, 1170m, 995w, 878, 788m, 693w cm^{-1}. MS calcd for $C_{33}H_{34}N_6O_{12}Yb^+ = 880.1$, found: 880.0. HRMS calcd for $C_{33}H_{34}N_6O_{12}Yb^+ = 880.1623$. Anal. Calcd for $C_{33}H_{33}N_6O_{12}Yb{\cdot}5H_2O$ = C, 40.91; H, 4.47; N, 8.67. Found: C, 40.90; H, 4.20; N, 8.50.

4.7. General procedure for reaction optimisation in the kinetic separation of (+)-*trans*-limonene oxide 1

The catalyst (**4**–**6** or $Ln(OTf)_3$) (0.017 mmol, 5 mol %) was dissolved in water (20 mL) and commercially available *cis*/*trans* (47:53) limonene oxide **1** or **2** (50 mg, 0.33 mmol) is added. The suspension was vigorously stirred for a given time period and then extracted with $CDCl_3$. The extraction mainly contains all the unreacted epoxide and some of the product diol **7**. The aqueous phase is then exhaustively extracted with EtOAc (2 × 20 mL) and the solvent removed under reduced pressure. This extract contains the residual diol and is dissolved using the $CDCl_3$ extract. Benzonitrile is added (0.033 mL, 0.33 mmol) as an internal NMR standard. A sample for ^{1}H NMR analysis is taken from this solution. The amount of *trans*-epoxide **1** was determined by integration of the methine doublet at 2.98 ppm. The amount of *cis*-epoxide **2** was determined by integration of the methine triplet at 3.05 ppm, and the *trans*-diaxial diol **7** by integration of the methine doublet at 3.63 ppm. All integrations were measured relative to the five hydrogens of benzonitrile.

4.8. Ring opening and kinetic separation of *trans*-limonene oxide 1 by lanthanum catalyst 4

Catalyst **4** (0.153 mmol, 5 mol %) was dissolved in water (180 mL) and *cis*/*trans* (47:53) limonene oxides **1** and **2** (0.45 g, 2.97 mmol) added. The suspension was vigorously stirred for 13 h and then extracted with pentane (2 × 50 mL). The organic phase was washed with brine (2 × 10 mL) and the solvent then carefully removed under reduced pressure to yield the (+)-*trans*-limonene oxide as a colourless liquid (0.18 g, 74%). $[\alpha]_D = +78$ (neat) (lit.[9] +77). ^{1}H NMR (200 MHz): δ 1.32 (s, 3H), 1.67 (s, 3H), 1.41–1.51 and 1.71–2.29 (m, 6H), 2.98 (d, J 5.0 Hz, 1H), 4.65 (br s, 2H).

4.9. Synthesis of lanthanoid triflates

An adaptation of the procedure of Kobayashi was followed.[15] Trifluoromethanesulfonic acid (0.5 mL, 5.65 mmol) was added to a suspension of lanthanoid oxide (0.34 g, 1.03 mmol) in water (2 mL). The suspension was stirred at reflux for 1 h and was then filtered to remove unreacted oxide. The remaining filtrate was concentrated under reduced pressure and the residual solid dried under reduced pressure (1 mmHg, 2 h) to yield the appropriate lanthanoid triflate hydrate as a white powder.

Lanthanum triflate. ^{13}C NMR (50 MHz): δ 120.2 (q, J 315 Hz, O_3SCF_3) IR (ATR) 3409s, 2228s, 1659w, 1633w, 1225s, 1185s, 1026s, 632w cm^{-1}.

Gadolinium triflate. IR (ATR) 3404s, 2538s, 2654s, 1457w, 1224s, 1183s, 1025s, 632w cm^{-1}.

Ytterbium triflate. ^{13}C NMR (50 MHz): δ 120.2 (q, J 316 Hz, O_3SCF_3). IR (ATR) 3382s, 2495s, 1650w, 1458w, 1222s, 1173s, 1022s, 631m cm^{-1}.

Acknowledgements

The authors acknowledge the support of Monash University and the Australian Research Council.

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