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Shape selective oxidation using titanium silicates: epoxidation of dihydromyrcene and the model compounds 2-methylpent-2-ene and 3-methylpent-1-ene

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The regioselective epoxidation of dihydromyrcene has been studied in the presence of the titanium-containing silicates TS-1 and TiAlβ using aqueous hydrogen peroxide, *tert*-butyl hydroperoxide and urea–hydrogen peroxide as oxidants. Epoxides were observed with TS-1 and aqueous hydrogen peroxide, and with TiAlβ when used in conjunction with the urea–hydrogen peroxide complex and *tert*-butyl hydroperoxide. Epoxidation occurs exclusively at the more electron-rich double bond in the presence of both catalysts. The epoxidation of dihydromyrcene has also been studied under triphasic conditions (two immiscible liquid phases and one catalyst phase) rather than biphasic conditions (one liquid phase and one catalyst phase). The alcoholysis reaction of the resulting epoxide was found to proceed *via* the more stabilised cation intermediate under biphasic conditions. In contrast, alcoholysis under triphasic conditions proceeded to form both the favoured (major) and unfavoured (minor) ether alcohols in ratios up to 2 : 1. Model compounds, (2-methylpent-2-ene and 3-methylpent-1-ene) which simulate the electronic environment around each of the double bonds in dihydromyrcene, have been used to study the degree of epoxidation of each double bond separately and under competitive conditions. When the model substrates are studied separately, the rate of epoxidation of the two double bonds are comparable. When the model substrates are epoxidised in a competitive manner, the electron-deficient double bond is oxidised in preference which is different to that observed for dihydromyrcene.

Introduction

The epoxidation of alkenes is an important functional group transformation in the field of fine chemical synthesis as epoxides can be subsequently transformed to a wide variety of products.[1] Terpenes are of particular importance to the flavours and fragrance industries, and as this class of compounds usually contains several carbon–carbon double bonds, in addition to other functional moieties,[2] regioselective epoxidations are of particular interest. In the case of dihydromyrcene, epoxidation at the less electron-rich double bond is synthetically more useful as it provides a potential route to the fragrance intermediate citronellal,[3] which can be formed from the corresponding epoxide. In practice this is difficult to achieve as the more electron-rich double bond is more reactive towards oxidants.[4–9]

Zeotype based materials have been used to enhance the selectivity for a variety of reactions by product, reactant or transition state selectivity.[10] Regioselectivity in epoxidation reactions may be achieved by either reactant selectivity or transition state selectivity. The former can be achieved by selecting a pore dimension which will easily accommodate one alkene moiety in preference to a more bulky alkene moiety *i.e.* only one moiety can enter the pore. The latter can be achieved by selecting an internal channel diameter, which will restrict the size of the transition state allowing the preferential oxidation of one moiety over another. Many transition metal zeotypes exist and have been used for alkene epoxidation, but there are questions concerning the stability of some of these materials.[11–14] Amongst the most stable zeotype material is TS-1, the titanosilicate analogue of ZSM-5. This material has been demonstrated to be an effective catalyst for a variety of oxidation reactions, including alkene epoxidation.[15,16] Related to this is TiAlβ, a titanosilicate analogue of zeolite β, which has also been used for a variety of oxidation reactions, including epoxidation of alkenes.[17,18] The channel structures of TiAlβ and TS-1 are different and have maximum pore diameters of 6.7 and 5.6 Å respectively, and it would be expected that some difference in the reactant or transition state selectivity could be achieved as a result of these topological differences.

In this paper, we present a study of the epoxidation of dihydromyrcene (shown in Scheme 1) and related model compounds using a range of oxidants over TiAlβ and TS-1 catalysts, and, in particular, the effects of the pore geometry on regioselectivity are described.

Results and discussion

Epoxidation of dihydromyrcene

Triphasic reaction systems. Initial reactions were carried out using a 1 : 1 mol ratio of substrate to oxidant. This was found to give rise to a triphasic system (one solid and two initially immiscible liquid phases). This led to analytical problems as a result of sampling the heterogeneous mixture. As the reaction proceeded, dihydromyrcene was converted into more polar products, a biphasic system was obtained (one solid and one liquid phase). In all experiments carried out under these conditions with TS-1 and TiAlβ, epoxides were not directly observed (Table 1). However products from the methanolysis of

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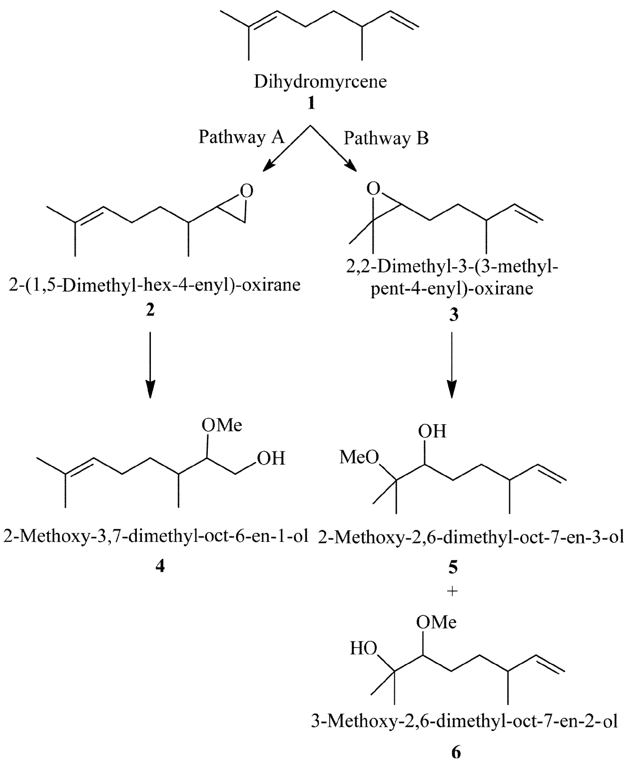
Table 1 Oxidation of dihydroxymyrcene under triphasic conditions

					Selectivity (%)	
Entry	Catalyst[a]	Oxidant	Time/h	DHM conv. (%)	2-Methoxy-2,6-dimethyloct-7-en-3-ol **5**	3-Methoxy-2,6-dimethyloct-7-en-2-ol **6**
1	S-1	H_2O_2	24	4.7	71	29
2	TS-1	H_2O_2	4	6.6	83	14
3	TS-1	H_2O_2	24	32.5	75	25
4	TiAlβ	H_2O_2	2	32.0	72	28
5	TiAlβ	H_2O_2	24	45.7	67	33

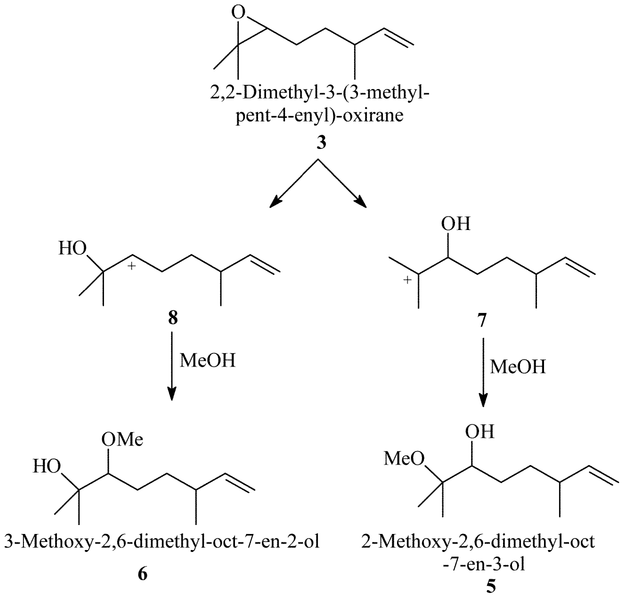
[a] Reaction conditions: dihydromyrcene (2.78 g, 20 mmol), catalyst (0.1 g), methanol (24 g), oxidant (10 mmol), 333 K.



Scheme 1

the epoxide **3** were 2-methoxy-2,6-dimethyloct-7-en-3-ol, **5** (major) and 3-methoxy-2,6-dimethyloct-7-en-2-ol, **6** (minor) were identified (Scheme 1).

Under acidic conditions, it was to be expected that product **5** would be selectively formed as this reaction proceeds *via* the more stable cationic intermediate. Initially, it was thought that the presence of the less-favoured isomer must be a consequence of the initial triphasic nature of the reaction system, as **6** was not observed in any of our biphasic studies using dihydromyrcene or α-hydroxy substituted terpenes.[19] We consider that this difference in selectivity is not entirely a consequence of using the triphasic system, since with both TS-1 and TiAlβ, the selectivity to the less favoured product **6** increases with time. Over the same time period, the phase separation of the two liquid phases decreases as the formation of polar products facilitates the mixing of the two liquid phases. If the formation of **6** were dependent on the presence of a triphasic system, then as the reaction proceeds and phase mixing occurs the selectivity to **6** should decrease. Holderich *et al.*[20] reported the transformation of cyclohexanone oxime into caprolactam over boron substituted ZSM-5. The reaction product was too large to diffuse out of the zeolite pores and thus this process was shown to occur selectively in the pore mouths. This demonstrates the difference in selectivities that can be achieved between reactions in pores, pore mouths and on the external surface. A similar state of affairs could explain the formation of **6** in the present work.



Scheme 2

For dihydromyrcene, alcoholysis of the corresponding epoxide would be expected to occur *via* intermediate **7** (Scheme 2), the more stable carbocation, as opposed to intermediate **8**. It is well known that materials such as TS-1 cannot utilise bulky oxidants such as *tert*-butyl hydroperoxide as the tertiary carbon centre is too large to enter and efficiently diffuse through the catalyst pores.[17] It is therefore reasonable to expect that the transition state where the methanol interacts with the more electrophilic carbon of the epoxide ring to initiate the ring opening is restricted within the pores of TS-1 as this would be sterically crowded. That is to say that the pore size constraints limit the size of the transition state. As the intermediate which results in the formation of the less favoured ether alcohol proceeds *via* attack at a less hindered carbocation, this transition state is more likely to be accommodated within the pores of the catalyst. A tertiary carbon centre is still formed but this is an alcohol rather than an ether moiety, which is less bulky This reaction can proceed relatively unimpeded on the outer surface of the TS-1 crystallites or at the pore openings. Thus, it is proposed that ring opening can occur both on the surface and in the pore openings of the catalyst and within the pores of the catalyst and different ring opened products can be expected to be formed from the two sites. Compound **5** is formed on the exterior surface and **6** is formed within the pores. By increasing the pore diameter of the catalyst, *i.e.* by using TiAlβ rather than TS-1, one of two effects are expected. Either, both transition states can be accommodated within the pores and the selectivity reverts back to the favoured product, or the selectivity to the less favoured product **6** is enhanced due to a combination of an improved rate of diffusion (due to the catalyst pore diameter), with continued suppression of the reaction of intermediate **7**. The reaction data shows that the latter is observed (Table 1

Table 2 Oxidation of dihydroxymyrcene under biphasic conditions

					Selectivity (%)	
Entry	Catalyst[a]	Oxidant	Time/h	DHM conv. (%)	2,2-Dimethyl-3-(3-methylpent-4-enyl)oxirane **3**	2-Methoxy-2,6-dimethyloct-7-en-3-ol **5**
1	TS-1	H_2O_2	2	16.2	86	14
2			24	22.6	29	71
3	TS-1[b]	H_2O_2	24	4.4	100	0[c]
4	Alβ	H_2O_2	24	2.6	0	100
5	TiAlβ	H_2O_2	1	0	0	0
6			2	2.6	0	100
7			24	17.8	0	100
8	TiAlβ[d]	H_2O_2	1	0	0	0
9			21	7.2	0	100
10			77	25.6	16	84
11	TiAlβ	TBHP	2	24.2	72	28
12			24	44.7	72	28
13	TiAlβ	UHP	3	20.0	77	23
14			25	36.4	77	23
15	Filtrate[e]	H_2O_2	16	25.24	0	87[f]

[a] Reaction conditions: dihydromyrcene (2.76 g, 20 mmol), catalyst (0.1 g), methanol (24 g), oxidant (10 mmol), 333 K. UHP: urea–hydrogen peroxide complex, TBHP: *tert*-butyl hydroperoxide (80% in: di-*tert*-butyl peroxide : water 3 : 2). [b] Ethanol used as solvent. [c] Ethoxy product not methoxy product. [d] At 303 K. [e] From TiAlβ catalysed epoxidation of 2-methylpent-2-ene. 1.6% of the other ring-opened product also observed. [f] Also 13% selectivity to the less favoured ether diol 3-methoxy-2,6-dimethyloct-7-en-2-ol **6**.

entries 2, 4 and entries 3, 5), together with a much higher rate of conversion of dihydromyrcene. The data obtained with the pure silica analogue of TS-1, silicalite (which has the weakest acid sites), and TiAlβ (which has the strongest acid sites) demonstrate the relative amounts of **5** and **6** are independent of acid strength as shown in Table 1.

Although an explanation for the observed selectivity can be made for the data obtained under these conditions, the change in selectivity with time is more difficult to explain. One possibility may be due to the poisoning of the acid sites located on the exterior surface of the catalyst resulting in a greater level of alcoholysis occurring within the catalyst pores. However, it is clear that by carefully optimising the pore diameter with respect to the size of the alkene moiety, it should be possible to increase further the selectivity to the less favoured product. This is especially relevant in systems in which the active sites on the exterior surface of the catalysts are removed by *e.g.* silanisation.

Biphasic reaction systems. Initial experiments for the oxidation of dihydromyrcene (Table 2) reveal that when TS-1 is used as the catalyst (Table 2 entry 1–2), dihydromyrcene is epoxidised exclusively at the more electron-rich double bond to give 2,2-dimethyl-3-(3-methylpent-4-enyl)oxirane **3**. Subsequent methanolysis occurs to form 2-methoxy-2,6-dimethyloct-7-en-3-ol **5** and as the reaction time increases, the selectivity to the ring opened ether alcohol increases as expected. The data obtained in the previous section strongly suggests that the alcoholysis reaction is occurring outside the pores of the catalyst, most probably on the external surface of the catalyst, where there are no pore constraints on the transition state.

A greater rate of reaction and final conversion is observed in the triphasic system (Table 1 entries 2–5) when compared to the corresponding biphasic system (Table 2 entries 1–2 and 5–7). As identical catalysts have been used in each study, this increase must be due to the nature of the triphasic system influencing the absorption of reagents and diffusion of products within the pore system.

As the purpose of this study was to investigate the role of shape selectivity on alkene epoxidation, one possible route is to control the steric bulk around the titanium centre by changing the solvent used for the reaction. It has been reported[21] that protic solvents coordinate to the peroxytitanium species, hence, a more bulky solvent could lower the accessibility of the active site. Ethanol was selected as a more bulky solvent than methanol. Epoxidation was still found to occur exclusively at the more electron-rich double bond. Ethanol did have an effect on the rate of conversion of dihydromyrcene, which was much lower when compared with methanol as solvent (4.4 *vs.* 22.6% over 24 h), and no alcoholysis products were observed. Comparing the data obtained in ethanol with that of methanol demonstrates that regioselective transition state control is not occurring in this system, since no epoxidation occurred at the less reactive and less bulky double bond. The only effect of the ethanol was to suppress the rate of epoxidation. For TS-1 catalysed epoxidations, the replacement of methanol with ethanol is beneficial because the alcoholysis reaction is reported to be slower with ethanol.[22] As the more reactive double bond is epoxidised exclusively, the solvent does not appear to participate in the transtion state. Thus the catalysis is occurring at a location where there is little possibility of transition state control, *i.e.* pore openings, the external surface or in solution. This is illustrated by data obtained for the epoxidation of the model substrates, which is discussed in a later section. This may indicate the importance of the role of surface titanium species in the epoxidation of large and bulky alkenes.

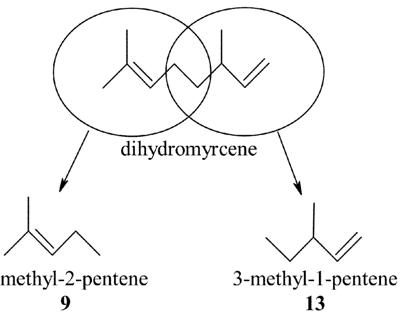
TiAlβ was also tested using aqueous hydrogen peroxide as the oxidant, and as expected, only the ring-opened product **5** was observed. At short reaction times, no conversion was observed which possibly suggests that the catalysis observed in this system at longer reaction times may be partly due to a solution species *via* a homogeneously catalysed reaction. To confirm this, the reaction filtrate from a model substrate reaction (2-methylpent-2-ene with aqueous hydrogen peroxide) catalysed by TiAlβ was stirred with an aliquot of dihydromyrcene. This was found to be active for the epoxidation and subsequent ring opening reaction (Table 2 entry 15) to form mainly the ether alcohol **5** (25% conversion over 16 h with a selectivity of 87%). Again, epoxidation occurred exclusively at the most electron-rich double bond. This shows conclusively that a solution species, formed by titanium leaching from TiAlβ, contributes to the epoxidation catalysis observed. The presence of Ti in solution is consistent with the work of Carati *et al.*[14] and our previous studies[13b–d] and suggests the contribution to the observed catalysis by solution titanium species can be significant. The ether diol formed also showed that epoxidation occurred exclusively at the more electron-rich double bond. Upon decreasing the reaction temperature from

333 to 303 K, some epoxide was also observed, but again the epoxidation occurred at the more electron-rich double bond.

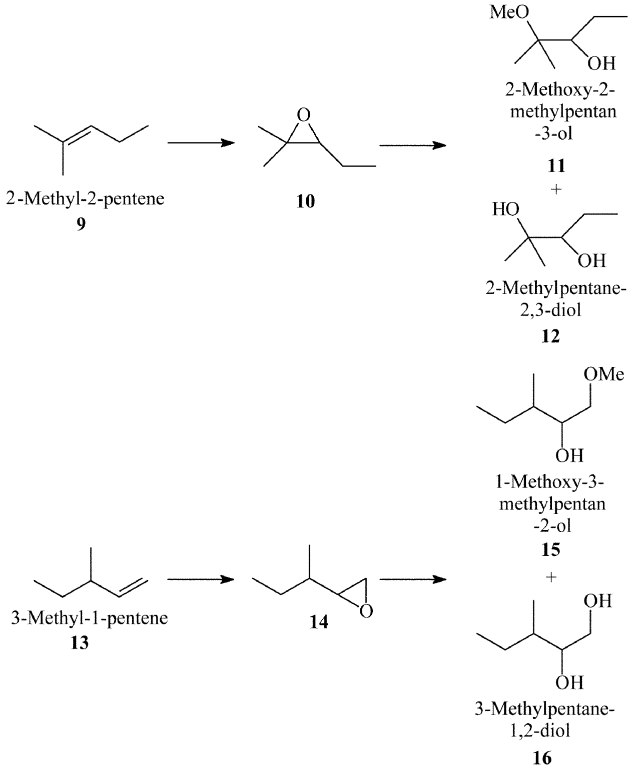
The use of urea–hydrogen peroxide complex or *tert*-butyl hydroperoxide (in di-*tert*-butyl peroxide) instead of hydrogen peroxide (Table 2, entries 11 to 14) resulted in a mixture of epoxide and ether alcohol (*ca.* 70–75% selectivity to the epoxide) derived from epoxidation at the more electron-rich double bond. In our previous studies of the epoxidation of α-hydroxy terpenes,[19] the same increases in selectivity to the epoxides were observed when using these oxidants.

Epoxidation of 2-methylpent-2-ene and 3-methylpent-1-ene

These compounds were selected as models to study the epoxidation of alkene moieties with environments similar to those found in dihydromyrcene as shown in Schemes 3 and 4. The oxidation of these model compounds was studied individually and as a mixture with terminal alkene : secondary alkene : oxidant ratio of 0.25 : 0.25 : 1. Blank experiments revealed the epoxidation of both substrates was ≤ 3% in the absence of a catalyst, or when Alβ was present as a blank catalyst material.



Scheme 3



Scheme 4

Data obtained for the epoxidation of 2-methylpent-2-ene **9** and 3-methylpent-1-ene **13** individually with TS-1 (Table 3), revealed that, for a given reaction time, a higher conversion of **13** was obtained compared to **9**. In this system, the less alkylated double bond was epoxidised preferentially, which was considered to be due to the formation of a less hindered transition state when compared to the usually more active but more encumbered double bond. This was surprising considering that with dihydromyrcene no epoxidation at the less sterically hindered double bond was observed. To test this hypothesis the reactions were repeated using TiAlβ. As this material has wider pores than TS-1, any steric effects on the transition state should be decreased and so the conversion of 2-methylpent-2-ene **9** should increase relative to 3-methylpent-1-ene **13** as this is the more reactive molecule. The results, shown in Table 4, confirm this to be the case, with the rates of reaction for **9** and **13** being the same.

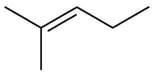
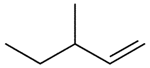
The two model compounds also show interesting differences in product selectivity. For 2-methylpent-2-ene only ring-opened products were observed regardless of the acidity of the catalysts studied. In the case of TiAlβ, initially only one product was observed, 2-methoxy-2-methylpentan-3-ol **11**, which is the expected product formed by the acid-catalysed nucleophilic attack by the methanol on the epoxide. As the reaction time increases, the selectivity towards diol increases. With TS-1, the selectivity to **11** was lower, with a significant amount of diol observed. The product distribution for the epoxidation of 3-methylpent-1-ene with TiAlβ was also surprising as epoxide **14** was formed and was stable despite the presence of the strong acid sites located in the pores of the catalyst. Although this epoxide is considered more difficult to form, it is also more stable to alcoholysis. Reactions carried out using TS-1 showed excellent (≥98%) epoxide selectivities, although the TiAlβ catalysed epoxidation did result in alcoholysis / hydrolysis.

Competitive epoxidation reactions

The competitive epoxidation reaction between the two model substrates was also studied. From the data obtained in the dihydromyrcene experiments (Table 2), it would be expected that 2-methylpent-2-ene would be exclusively epoxidised. However, precedent from the individual epoxidation experiments would suggest a mixture of the two epoxides (or products derived from them) would be obtained, with the exact ratio dependent on the pore size of the catalyst. The data obtained for TS-1 and TiAlβ shows that both alkenes are epoxidised, although not in the ratio that would be expected based on the data obtained for each substrate individually or from the ratio observed in dihydromyrcene. With TS-1, 2-methylpent-2-ene was oxidised in preference to 3-methylpent-1-ene. In the non-competitive experiments, the conversion of **9** and **13** was 5.9% and 12.3% respectively after *ca.* 24 h (Table 3). However, in the competitive epoxidation experiments the conversions were 10.0% and 6.9% (Table 5, entry 7), although the total conversion in the competitive and non-competitive experiments was comparable. The same trend was also observed for TiAlβ, although with significantly reduced conversion (Table 6).

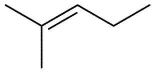
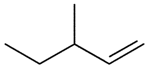
A simple analysis of the rates of the above reactions for the competitive and non-competitive experiments (Table 7) sheds some light on the processes. For substrate **9** the calculated rates for the competitive reaction (0.050 mmol h^{-1}) and non-competitive reaction (0.049 mmol h^{-1}) are identical, whereas the calculated rates for substrate **13** are very different (0.045 and 0.098 mmol h^{-1} respectively). This suggests that for **9**, the reaction occurs where the effects of competition are minimised *i.e.* predominantly on the exterior surface of the catalyst. It is proposed that for **13**, the reaction can take place in the pores and on the exterior surface. As this is the less reactive alkene, **9** is preferentially epoxidised on the exterior surface in the competitive experiments. The dihydromyrcene selectivity data in Table 2 gives a good indication of how much more favoured the epoxidation of **9** is compared to **13** on the exterior surface of the catalyst. The reduction in rate for **13** is considered to be due to the competitive adsorption of **9** into the zeolite pores and the

Table 3 Epoxidation of model substrates using TS-1

				Selectivity (%)			
Entry	Substrate[a]	Reaction time/h	Conversion (%)	2-Methoxy-2-methylpentan-3-ol **11**	2-Methylpentane-2,3-diol **12**	1-Epoxy-3-methylpentane **14**	1-Methoxy-3-methylpentan-2-ol **15**
1	 **9**	6	3.1	79	21	—	—
2		24	5.9	64	36	—	—
3		44	11.5	60	40	—	—
4		72	11.7	60	40	—	—
5		46[b]	32.0	82	18	—	—
6	 **13**	5	5.2	—	—	100	0
7		25	12.3	—	—	100	0
8		46	15.1	—	—	98	2
9		72	15.1	—	—	98	2
10		42[b]	0	—	—	0	0

[a] Reaction conditions: 2-methylpent-2-ene or 3-methylpent-1-ene (1.72 g, 20 mmol), TS-1 (0.1 g), methanol (24 g), hydrogen peroxide (30 wt%) (10 mmol), 313 K. [b] Homogeneous reaction carried out with Ti(OPr)$_4$.

Table 4 Epoxidation of model substrates using TiAlβ

				Selectivity (%)			
Entry	Substrate[a]	Reaction time/h	Conversion (%)	2-Methoxy-2-methylpentan-3-ol **11**	2-Methylpentane-2,3-diol **12**	1-Epoxy-3-methylpentane **14**	1-Methoxy-3-methylpentan-2-ol **15**
1	 **9**	6	10.8	100	0	—	—
2		24	29.0	93	7	—	—
3		45	50.8	92	8	—	—
4		70	55.4	91	9	—	—
5	 **13**	5	11.6	—	—	58	42
6		25	29.4	—	—	23	77
7		46	48.8	—	—	11	79[b]
8		72	56.8	—	—	7	82[c]

[a] Reaction conditions: 2-methylpent-2-ene or 3-methylpent-1-ene (1.72 g, 20 mmol), TS-1 (0.1 g), methanol (24 g), hydrogen peroxide (30 wt%) (10 mmol), 313 K. [b] Homogeneous reaction carried out with Ti(OPr)$_4$. Also 3-methylpentane-1,2-diol observed with a selectivity of 12%. [c] Also 3-methylpentane-1,2-diol observed with a selectivity of 11%.

Table 5 Competitive epoxidation of the model substrates over TS-1

		Conversion[a] (%)		Selectivity (%)			
Entry	Time/h[a]	3-Methylpent-1-ene **13**	2-Methylpent-2-ene **9**	1-Epoxy-3-methylpentane **14**	1-Methoxy-3-methylpentan-2-ol **15**	2-Methoxy-2-methylpentan-3-ol **11**	2-Methylpentane-1,2-diol **16**
1	1	3.2	6.5	33	0	41	26
2	2	4.1	7.0	37	0	39	24
3	3	4.2	8.0	34	0	44	22
4	4	4.2	8.2	33	0	44	23
5	7	4.2	8.5	33	0	44	23
6	11	5.3	8.8	29	9	40	22
7	20	6.9	10.0	27	13	40	20

[a] Reaction conditions: 2-methylpent-2-ene (0.85 g, 10 mmol) and 3-methylpent-1-ene (0.85 g, 10 mmol), TS-1 (0.1 g), methanol (24 g), hydrogen peroxide (30 wt%) (10 mmol), 313 K.

Table 6 Competitive epoxidation of the model substrates over TiAlβ

		Conversion[a] (%)		Selectivity (%)			
Entry	Time/h[a]	3-Methylpent-1-ene **13**	2-Methylpent-2-ene **9**	1-Epoxy-3-methylpentane **14**	1-Methoxy-3-methylpentan-2-ol **15**	2-Methoxy-2-methylpentan-3-ol **11**	2-Methylpentane-1,2-diol **16**
1	1	0	1.0	0	0	100	0
2	2	0.7	1.5	32	0	68	0
3	3	0.9	2.1	30	0	70	0
4	4	1.0	2.7	27	0	73	0
5	7	2.5	5.0	23	10	67	0
6	11	4.3	9.9	13	18	63	6
7	20	4.0	10.4	10	18	66	6

[a] Reaction conditions: 2-methylpent-2-ene (0.85 g, 10 mmol) and 3-methylpent-1-ene (0.85 g, 10 mmol), TiAlβ (0.1 g), methanol (24 g), hydrogen peroxide (30 wt%) (10 mmol), 313 K.

Table 7 Rate data for catalysed and uncatalysed reaction

Entry	Substrate	Catalyst	Reaction time/h	Substrate/mmol	Conversion (%)	Rate/mmol h^{-1}
1	**9**	TS-1	24	20	5.9	0.049
2	**13**	TS-1	25	20	12.3	0.098
3	**9**[a]	TS-1	20	10	10.0	0.050
4	**13**[a]	TS-1	20	10	6.9	0.045
5	**9**	TiAlβ	24	20	29.0	0.242
6	**13**	TiAlβ	25	20	29.4	0.235
7	**9**[a]	TiAlβ	20	10	10.4	0.052
8	**13**[a]	TiAlβ	20	10	4.0	0.020

[a] Competitive epoxidation experiment.

bulky oxidation products of this compound decreasing the rates of diffusion of other reagents. From the above data it is proposed that **13** is epoxidised mainly within the pores of TS-1 and **9** is mainly epoxidised on the exterior surface.

The product distribution for **9** after 20 h in the competitive oxidation experiments (Table 5, entry 7) is close to that observed in the non-competitive experiments after 24 h (Table 3, entry 2) *i.e.* a ratio 2 : 1 for **11** : **16**. Again this is consistent with the reaction occurring at the same site in both types of reaction. The selectivity data for **13** after 20 h in the competitive experiments shows an increased selectivity to the ether alcohol **15** (Table 5, entry 7) compared to the non-competitive experiments after 25 h (Table 3, entry 8) where only the epoxide is formed. In the non-competitive reaction the epoxidation may occur predominantly within the zeolite pore to form preferentially the corresponding epoxide, with a low conversion occurring on the exterior surface to give mainly ring opened products (as observed with **9**). In the competitive experiments, the reaction in the pores is suppressed leaving an increased contribution from the exterior surface, which results in a reduction in rate and a change in selectivity towards the ring opened products.

The non-competitive epoxidation of **9** and **13** over TiAlβ give similar rates of reaction (0.242 and 0.235 mmol h^{-1}, respectively), which is very different to the calculated rates observed for the competitive reaction (0.052 and 0.020 mmol h^{-1}, respectively). The difference in the rates for the non-competitive experiments over TS-1 and TiAlβ are likely to be due to the increased pore diameter of the TiAlβ catalyst, although the similarity between the two is surprising considering the differences in reactivity. There may still be reactions occurring on the exterior surface and in the pores but the effect is less pronounced in TiAlβ because of the wider pores. The fact that TiAlβ leeches titanium into solution more readily than TS-1 makes it difficult to unravel the observed effects. The same is also true for the competitive experiments and any discussions concerning selectivity. We are confident that any Ti leaching from TS-1 has very little effect on the above data as Ti leaching in this system has been shown to be relatively low in the absence of diols and triols.

Conclusions

Dihydromyrcene can be efficiently epoxidised at the more reactive double bond using titanium-containing molecular sieves. The product distribution can be altered by varying factors such as framework type, oxidant and amount of solvent. The alcoholysis reaction appears to take place exclusively on the outer surface of the catalyst unless specific reaction conditions (two immiscible liquid phases) are used. This is determined from the formation of alcoholysis products.

All attempts to control the observed regioselectivity of dihydromyrcene oxidation by altering the pore size to change the diffusion characteristics, and influence the transition state were not successful. The observed products are due to, or derived from, epoxidation at the more electron-rich double bond in accordance with the accepted mechanism of epoxidation *via* electrophilic attack of the oxidant. Studies carried out using the model substrates demonstrate that it is possible to epoxidise both alkene moieties, and by altering the pore size of the catalyst it is possible to preferentially epoxidise the less bulky (and less active) alkene. The data obtained for the competitive epoxidation experiments with both titanosilicates show an even greater preference for epoxidation of the less active alkene. The preferred explanation for the data obtained with dihydromyrcene is that epoxidation of this molecule is occurring in a region where there are no pore restrictions to influence molecular orientation within the pore or the transition state. The reaction could be occurring either at the pore mouths or on the exterior surface in the case of dihydromyrcene, whereas for the model substrate reactions may be occurring at the pore mouths, exterior surface and within the pores. For **9** it is proposed the reaction takes place mainly on the exterior surface of the catalyst, and for **13**, the reaction occurs mainly within the pores.

Experimental

Catalyst preparation

Preparation of TS-1. TS-1 with a Si : Ti ratio of 50 : 1 was prepared following the method proposed by Taramasso *et al.*[23] Tetraethyl orthosilicate (TEOS) (86.4 g, Aldrich) was placed into a beaker into which titanium ethoxide (1.92 g, Aldrich) was carefully added with continuous stirring. The mixture was then covered and stirred for a period of 2 h. A portion (~10 ml) of this mixture was then added dropwise to tetrapropylammonium hydroxide (TPAOH) (40 wt% in water, 96 ml, Alfa) followed by the addition of deionised water (20 ml). The remainder of the mixture was then carefully added to the TPAOH solution and the total volume of the resulting mixture was noted. This volume was maintained *via* the addition of water whilst the mixture was stirred for a period of 3 h at room temperature. The solution was heated to 333 K for a period of 3 h with continuous stirring. The resulting solution was then aged for 18 h prior to being heated at 448 K under autogeneous pressure in a Teflon-lined autoclave for 2 d without stirring. The white solid obtained after this period was isolated by filtration, dried at 373 K for ~8 h and calcined at 823 K in air for 24 h prior to use.

Preparation of TiAlβ. TiAlβ with a Si : Ti ratio 30 : 1 and a $TO_2 : Al_2O_3$ ratio of 800 : 1 (where T represents both Ti and Si) was prepared following the method proposed by Corma and co-workers.[24] TEOS (12.5 g, Aldrich) was placed into a beaker to which hydrochloric acid (4.5 ml, 0.1 M, Fisher) was added and the resulting mixture stirred for 20 min. The mixture was then cooled to 273 K before the dropwise addition of a solution containing titanium butoxide (TBOT) (0.68 g, Aldrich) in propan-2-ol (9 g, Fisher), the mixture was then stirred for a further 15 min at 273 K. The resulting clear yellow solution was allowed to warm to room temperature before the dropwise addition of a portion of tetraethylammonium hydroxide

(TEAOH) (10 ml, Alfa). Upon addition of ~3 ml of TEAOH a white gel was formed. The gel was dried (373 K, 6 h) before aluminium isopropoxide (0.03 g) and the remainder of the TEAOH (10 ml) was added. The resulting thick paste was mixed thoroughly then placed into a Teflon-lined autoclave and heated at 408 K under autogeneous pressure without stirring for a period of 7 d. The resulting white solid was isolated using a centrifuge, dried at 373 K for 12 h and calcined at 823 K for 24 h prior to use.

Characterisation of the materials by powder XRD and FTIR revealed the materials to be consistent with those reported in the literature.

Oxidation of dihydromyrcene

The catalytic reactions were carried out in a 50 ml two-necked round bottom flask fitted with a water-cooled condenser and rubber septum for sampling. The mixtures were stirred and heated using a hotplate stirrer, magnetic follower and oil bath.

Triphasic conditions. Reactions were typically carried out as follows; dihydromyrcene (2.8 g, 20 mmol Quest), catalyst (0.1 g), and solvent (10 ml) were added to the round bottom flask, followed by 30 wt% aqueous hydrogen peroxide (2.4 g, 20 mmol, BDH). This mixture was then heated to 333 K. Samples were taken at timed intervals and diluted in acetone prior to analysis.

Biphasic conditions. Reactions were carried out as described in the section above except 23.5 g of methanol was used and 10 mmol of oxidant. The values for the conversion are based on the moles of oxidant *i.e.* 100% conversion is equivalent to the formation of 10 mmol of product.

Oxidation of 3-methylpent-1-ene and 2-methylpent-2-ene

Initially these reactions were carried out using the method used for dihydromyrcene epoxidation. Due to the low boiling point of these substrates, it was found that significant loss of starting material occurred regardless of the efficiency of the condenser. Instead, the reactions were carried out in boiling tubes fitted with a rubber septum, which were stirred by magnetic follower and heated by immersion in a thermostated water bath. Reactions were typically carried out as follows; substrate (20 mmol), catalyst (0.1 g), solvent (24 g) and 30 wt% aqueous hydrogen peroxide (10 mmol, 1.2 g BDH) were added to the boiling tube which was sealed and heated to 313 K.

The competitive epoxidation of 3-methylpent-1-ene and 2-methylpent-2-ene was also carried out using the above method. The total number of moles of substrate remained at 20 mmol (10 mmol of each substrate was used).

To minimise the loss of starting material in all model substrate experiments, eight identical experiments were set up (one for each sampling time). Only one sample was taken from each reaction to give the conversion and selectivity data with respect to time.

Analysis of all samples was by GC (Varian 3400) fitted with a split / splitless injector and a FID with helium as the carrier gas. For dihydromyrcene reactions (split ratio 1 : 50), the column used was a HP1 (30 m, ID 0.23 mm), and for the model substrates (split ratio 1 : 100), a BP-1 column was used (30 m, ID 0.23 mm). In both analysis 0.1 µl of reaction sample diluted in methanol was injected onto the column. Reaction products were identified by GCMS (HP5890 GC coupled to a TRIO 1 mass spectrometer) using the column and carrier gas stated above.

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