Oxidation of α-hydroxy containing monoterpenes using titanium silicate catalysts: comments on regioselectivity and the role of acidity

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The regioselective epoxidation of monoterpenes in the liquid phase has been studied using the titanosilicates TS-1 and TiAlβ. A range of oxidants (hydrogen peroxide, *tert*-butyl hydroperoxide and urea–hydrogen peroxide complex) have been studied in detail. The allylic alcohols linalool and geraniol have been studied alongside the non-allylic alcohol citronellol and the diene dihydromyrcene to help determine the role of the hydroxy group in these reactions. Dihydromyrcene is selectively epoxidised at the more electron rich double bond regardless of the catalyst–oxidant–solvent system used. Geraniol can undergo allylic assisted epoxidation with TS-1–acetone–hydrogen peroxide and TiAlβ–acetonitrile–urea–hydrogen peroxide. With TiAlβ–hydrogen peroxide–methanol, the reaction shows an induction period in the conversion of geraniol which is considered to be characteristic of the autocatalytic removal of titanium from the catalyst framework. Reactions with citronellol show this titanium removal is entirely due to the presence of the allylic alcohol moiety. Finally, epoxidation of linalool and the subsequent *in situ* conversion of the epoxide to the furano- and pyrano-oxides were studied. The ratio of furano- and pyrano-oxides formed was considered to be due, in part, to the pore geometry and the Brønsted acidity of the catalyst.

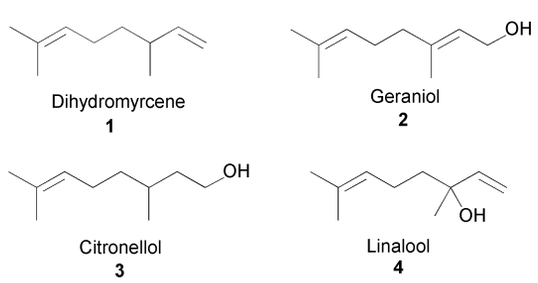
Introduction

Terpenes are a class of molecules with particular importance to the flavours and fragrance industries. One sub-group, the monoterpenes, is particularly interesting from a fine chemical synthesis viewpoint as they can contain alkene functional groups with different degrees of substitution. They can also contain other functionalities which may further alter the chemistry of the carbon–carbon double bonds. Thus, functionalised monoterpenes are useful test molecules for catalytic systems used in fine chemical synthesis. For this class of compounds, transformations need to be carried out under mild conditions since terpenes can be susceptible to rearrangements and isomerisations.

Many chemical transformations of acyclic monoterpenes are possible.[1] Recent examples include the preparation of ozonides,[2] 1,3-diol or 1,2-aminoalcohol derivatives *via* boroxy Fischer carbene complexes,[3] and Pt/Sn catalysed hydroformylation to linear aldehydes.[4] One of the more interesting transformations is the epoxidation of monoterpenes, which has been studied using heterogeneous,[5–17] homogeneous,[18,19] and enzymatic systems[20] with a variety of oxidants. The use of heterogeneous catalysts is particularly interesting because of the ease of separation of the catalyst from the reaction products. Examples include titanium containing silicates (TS-1,[21] Tiβ,[22] and TiMCM-41[23,24]). These materials have been shown to be useful catalysts for a variety of oxidation reactions, including the epoxidation of alkenes. Tungsten polyoxoanions immobilised within an ion exchange resin,[7] Mn triazacyclononane complex anchored onto silica[8] and vanadium-exchanged layered double hydroxides (LDAs) pillared using dodecylsulfate and dodecylbenzenesulfonate[11] have also been demonstrated to be useful heterogeneous catalysts for these types of reaction.

Careful consideration of the nature of reactants and products needs to be made when using heterogeneous catalysts in liquid phase oxidations since catalyst stability can be a particular problem. This was first revealed by Sheldon *et al.*,[25] and has recently been demonstrated in our laboratories.[26a–d] In these studies of alkene epoxidation, we reported that the presence of triol was responsible for the leaching of titanium into solution. These solution species could also contribute to the catalysis, although the main effect was to cause ring opening of the epoxides formed initially.[26d]

In this paper we present results obtained for the epoxidation of the α-hydroxy containing monoterpene alcohols geraniol (**2**) and linalool (**4**) (shown in Scheme 1), using microporous titanium silicates with a variety of hydroperoxide sources. The epoxidation of dihydromyrcene (**1**) and citronellol (**3**) was studied for comparison to determine the effect of the allylic hydroxy groups on the epoxidation of these substrates.



Scheme 1

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Table 1 Oxidation of dihydromyrcene

Entry	Catalyst[a]	Oxidant	Time/h	DHM conv. (%)	Selectivity (%)	
					2,2-Dimethyl-3-(3-methyl-pent-4-enyl)oxirane **7**	2-Methoxy-2,6-dimethyl-oct-7-en-3-ol **8**
1	None	H_2O_2	24	4.2	100	0
2	TS-1	H_2O_2	2	16.2	86	14
			24	22.6	29	71
3	TiAlβ	H_2O_2	2	2.6	0	100
			24	17.8	0	100
4	TiAlβ	TBHP	2	24.2	72	28
			24	44.7	72	28
5	TiAlβ	UHP	3	20.0	77	23
			25	36.4	77	23

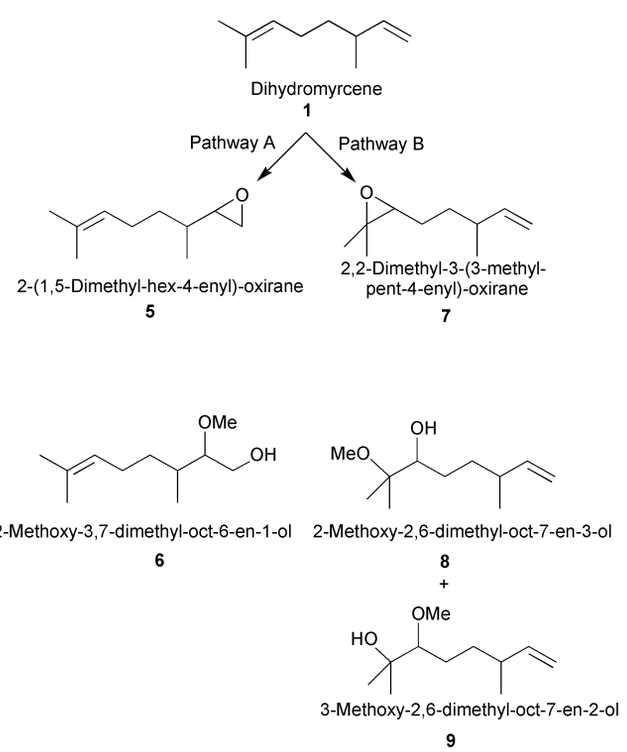
[a] Reaction conditions: dihydromyrcene (2.76 g, 20 mmol), catalyst (0.1 g), methanol (24 g), oxidant (10 mmol), 333 K. UHP: urea–hydrogen peroxide complex, TBHP: *tert*-butyl hydroperoxide (80% in di-*tert*-butyl peroxide–water 3 : 2).

Results and discussion

Epoxidation of dihydromyrcene

The data for the epoxidation of dihydromyrcene (**1**) show that TS-1 and TiAlβ are active epoxidation catalysts for these types of substrates (Table 1) and provide a benchmark for the epoxidation of the α-hydroxymonoterpenes. The hydrophobic/hydrophilic character of the two catalysts is demonstrated when these catalysts are used with aqueous hydrogen peroxide as proposed by Corma *et al.*,[27] where the smaller pore TS-1 shows greater activity than TiAlβ. This confirms that TS-1 can be used with aqueous hydrogen peroxide but TiAlβ is best used with non-aqueous peroxide sources.

Epoxidation is observed exclusively at the more electron rich double bond (pathway B in Scheme 2), in accordance with the accepted mechanism of electrophilic attack by the oxidant, to give 2,2-dimethyl-3-(3-methylpent-4-enyl)oxirane (**7**). This underwent subsequent alcoholysis to form two products. 2-Methoxy-2,6-dimethyloct-7-en-3-ol (**8**) was formed as the major product and 3-methoxy-2,6-dimethyloct-7-en-2-ol (**9**) as the minor product (typically only observed in trace amounts). These findings are consistent with an acid catalysed nucleophilic ring opening mechanism.[28] With TS-1, the epoxide can be obtained using short reaction times (up to 1 h), but with longer reaction times, significant formation of **8** is observed. In previous studies,[26] we have demonstrated that solution titanium is efficient at forming ring opened products from the starting alkene, however, for this system the filtrate was found to be inactive thus the selectivity observed is entirely due to the catalyst. Greater levels of titanium can be leached from TiAlβ when compared to TS-1 as reported by Carati *et al.*[29] and has been observed in our previous studies. In this case, acid catalysis can be caused by solution Ti species and framework aluminium sites.



Scheme 2

As expected with TiAlβ, no epoxide was observed and only the ring opened products were observed. Upon replacing the aqueous hydrogen peroxide with urea–hydrogen peroxide complex or *tert*-butyl hydroperoxide, the major product was observed to be the epoxide.

Epoxidation of geraniol and citronellol

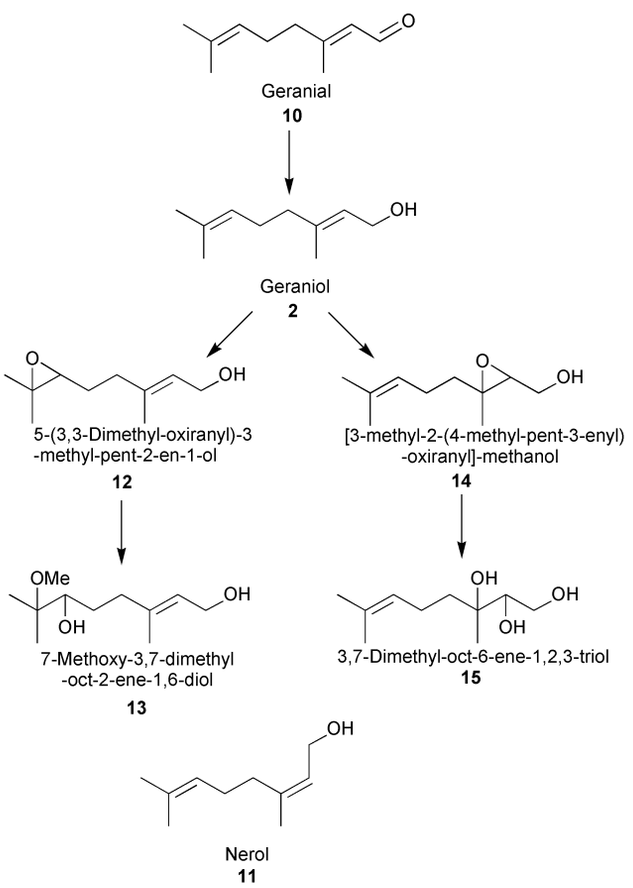
The epoxidation of geraniol (**2**) was studied using TS-1, TiAlβ and Alβ (as a blank). In the blank experiment system, very low conversions (≤ 2%) were observed (Table 2).

Using TS-1 with aqueous hydrogen peroxide in methanol, the ether diol **13** is observed as the major product (with epoxidation only observed at the double bond remote from the hydroxy group, demonstrating that allylic alcohol assisted epoxidation is insignificant in this system). The only other product observed was identified by GCMS as geranial (**10**) (Scheme 3). The formation of geranial and neral (as well as the corresponding unsaturated acids) from geraniol and the corresponding *Z*-isomer, nerol, has been reported previously by Kumar *et al.*[30] By using TS-1–aqueous hydrogen peroxide with acetone rather than methanol as the solvent, Kumar reported that high conversions were observed and the combined geranial (**10**) and geranoic acid selectivity was *ca.* 10%. As no ring-opened products were observed in the above reaction, this was repeated as part of our study. In agreement with Kumar *et al.*, no epoxide hydrolysis products were observed. However, where Kumar *et al.*[30] observed epoxidation only at the allylic alcohol double bond, we observed epoxidation at both double bonds, with a ratio of *ca.* 2 : 1 in favour of the non-allylic alcohol double bond. This demonstrates allylic epoxidation is possible in this system and the absence of allylic epoxidation in methanol suggests competitive co-ordination by the solvent occurs at the titanium site. In addition, a significant amount of nerol (**11**) was formed, presumably *via* isomerisation. Surprisingly, nerol was not observed in any of the experiments carried out with TiAlβ, suggesting that the acid strength of the catalysts is unimportant in this isomerisation. It is possible that nerol is more reactive than geraniol under these conditions, and it is for this reason that nerol is not observed. However, this is not the case since when geraniol is replaced by nerol and using TS-1 as

Table 2 Oxidation of geraniol

Entry	Catalyst[a]	Oxidant	Time/h	Geraniol conv. (%)	Selectivity (%)			Selectivity (%)		
					Allylic epoxide (**14**)	Non-allylic epoxide (**12**)	Allylic : non-allylic epoxide ratio	3,7-Dimethyloct-6-ene-1,2,3-triol (**15**)	7-Methoxy-3,7-dimethyloct-2-ene-1,6-diol (**13**)	Nerol (**11**)
1	Alβ	H_2O_2	24	2	0	0	—	0	0	0
2	TS-1	H_2O_2	24	35.8[d]	0	0	—	0	94.4	0
3	TS-1[b]	H_2O_2	24	39.4	20	48	0.4	0	0	32
4	TiAlβ	H_2O_2	2	0	0	0	—	0	0	0
			8	48.2[e]	0	0	—	29	27	0
			24	84.8[e]	0	0	—	41	16	0
5	TiAlβ	TBHP	2	7.3	27	63	0.6	0	0	0
			24	33.2	23	67	0.5	0	0	0
6	TiAlβ	UHP	2	10.4	58	42	1.4	0	0	0
			6	17.2	55	45	1.2	0	0	0
			26	34.6	51	49	1.0	0	0	0
7	TiAlβ[c]	UHP	6	24	37	63	0.6	0	0	0

[a] Reaction conditions: geraniol (3.10 g, 20 mmol), catalyst (0.1 g), methanol (24 g), oxidant (10 mmol), 333 K. UHP: urea–hydrogen peroxide complex, TBHP: *tert*-butyl hydroperoxide (3 M in isooctane). [b] In acetone. [c] In acetonitrile at 353 K. [d] 5.6% geranial formed in the reaction. [e] *ca.* 43–44% minor products (6 compounds in total not identified).



Scheme 3

a catalyst, no reaction was observed over 24 h. This is consistent with our earlier studies concerning the competitive epoxidation of *cis* and *trans* crotyl alcohol,[31] where the *cis* crotyl alcohol was by far the most reactive.

The oxidation of geraniol was also carried out using TiAlβ with aqueous hydrogen peroxide. At short reaction times (0–6 h), no products were observed. An increase in conversion (48%) occurred between 6–8 h, which increased further (to 84%) after 24 h which is characteristic of the autocatalytic removal of titanium from the catalyst framework.[26] The long induction period is likely to be due to the slow diffusion of the bulky titanium–triol or titanium–ether diol complex through the catalyst pores.

Two major products were observed (Scheme 3). 3,7-Dimethyl-oct-6-ene-1,2,3-triol (**15**) was formed *via* allylic epoxidation and subsequent ring opening by H_2O to form the corresponding triol. The other major product, 7-methoxy-3,7-dimethyloct-2-ene-1,6-diol (**13**), was formed *via* the epoxide formed at the more electron-rich double bond followed by alcoholysis. The different modes of ring opening observed for each epoxide are curious and may indicate that epoxidation is occurring at different locations within the catalyst. As the subsequent ring opening reaction is rapid (more rapid than epoxide formation as epoxides are not seen as intermediates under these specific epoxidation conditions), the ring-opened products may give an insight into the epoxidation location. The exclusive formation of ether diols is consistent with the ring opening reaction occurring in a hydrophobic environment, and as the $TO_2 : Al_2O_3$ is very low in this catalyst, this could be occurring within the pores of the β framework. Triol formation would be expected in water rich environments (external surface of the catalyst or in solution). The data obtained suggest that non-allylic epoxidation occurs preferentially within the pores, allylic assisted epoxidation occurs on the exterior surface of the catalyst or in solution.

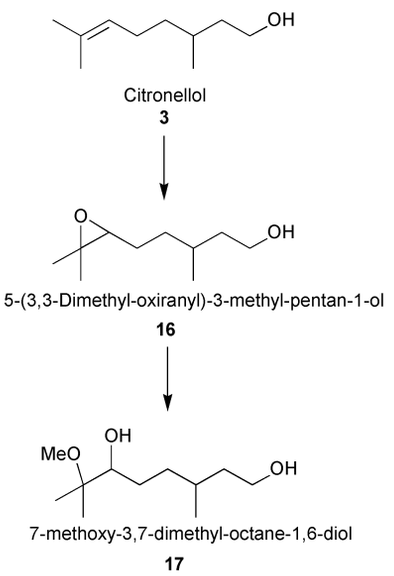
The selectivity observed for the triol increased between 8 and 24 h. After 8 h, no further ether diol is formed and geraniol is exclusively converted to additional triol and a number of minor products. As described above, the products observed may give an indication of the environment in which the reaction occurred. Up to 8 h, there is a contribution from Ti located both in the catalyst pores and in solution. After 8 h only conversion due to solution Ti species is observed. This differs from the data obtained for dihydromyrcene with the same catalyst, where conversion was observed from the start and no induction period was observed. This indicates that the Ti sites within the catalyst are active and no homogeneous Ti catalysed reaction is occurring. On this basis, it is concluded that triol formation leads to the leaching of Ti since triols cannot be formed from dihydromyrcene. We have previously shown that Ti can be leached by triol from TS-1.[26] To gain additional information on why this induction period exists for geraniol epoxidation using these conditions, the epoxidation of citronellol was studied (Scheme 4). Citronellol (**3**) is a hydrogenated form of geraniol (at the allylic alcohol double bond) and from the data shown in Table 3, no induction period was observed. This confirms that the by-products derived from the allyl alcohol moiety (ether diol, triol) are responsible for the catalytic results obtained with geraniol.

The epoxidation of geraniol was then studied using urea–hydrogen peroxide (Table 2) which has been reported by Adam *et al.*[32] to improve the selectivity to the epoxide when used in

Table 3 Oxidation of citronellol

Catalyst[a]	Oxidant	Time/h	Conv. (%)	Selectivity (%)	
				7-Methoxy-3,7-dimethyloctane-1,6-diol **17**	Minor products
TiAlβ	H_2O_2	2	11.8	85	15
		20	63.6	86	14
		48	82.6	78	22

[a] Reaction conditions: citronellol (3.28 g, 20 mmol), catalyst (0.1 g), methanol (24 g), oxidant (10 mmol), 333 K.



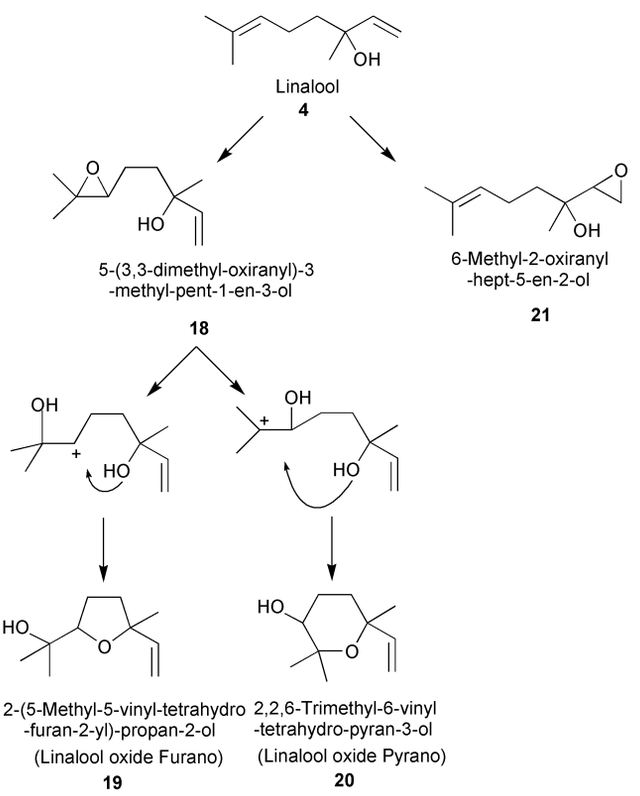
Scheme 4

conjunction with TiAlβ. This change in selectivity may occur because the urea neutralises the acid sites responsible for catalysing the ring opening reactions. During the course of this reaction the ratio of allylic epoxidation (**14**) to non-allylic epoxidation (**12**) (more reactive double bond) is initially 1.4, but decreases to unity by the time the reaction is complete. As the more reactive double bond is preferentially epoxidised in dihydromyrcene, the data obtained suggest two competing reactions are occurring, namely allylic assisted and direct epoxidation. A related study by Jacobs *et al.*[8,9] reported the formation of diepoxides. No diepoxides were observed in this study as a consequence of our substrate : oxidant ratio being 2 : 1. Results obtained with anhydrous *tert*-butyl hydroperoxide (3 M in isooctane) in methanol gave no ring-opened products, only the epoxides being formed. These experiments were repeated using acetonitrile instead of methanol as solvent. Again, no ring-opened products were observed. As no ring-opened products were observed, several possibilities exist. The lower amount of water in these systems prevents leaching of titanium from the catalyst framework as the Ti–O–Si bonds require water to complete the hydrolysis. This is consistent with the absence of an induction period (unlike that observed in the TiAlβ–hydrogen peroxide system). Alternatively, urea and *tert*-butyl alcohol make the solution Ti inactive by competing with the substrate and oxidant for active sites on the titanium. Finally, urea and *tert*-butyl alcohol moderate the acidity, thereby preventing ring opening. This occurs by a Lewis base–proton interaction which increases the steric bulk around the acid sites, especially in a confined system such as a zeolite pore. The approach of the epoxide is hindered by this interaction, thus the acid site is effectively 'neutralised' without any specific acid–base interaction occurring. The determination of which of the above is occurring in this system is beyond the scope of this study and will be addressed in future work.

The ratio of the two epoxides formed is a function of oxidant and solvent in the case of TiAlβ. For urea–hydrogen peroxide in acetonitrile and *tert*-butyl hydroperoxide in methanol, the non-allylic epoxide is the preferred product (selectivity of 60–70%). With urea–hydrogen peroxide in methanol the allylic epoxide is formed initially (selectivity of 58%), but with longer reaction times this reduces to 51%.

Epoxidation of linalool

The data (Table 4) show that no allylic assisted epoxidation of linalool (**4**) occurs under our reaction conditions. This may be due to the steric situation around the hydroxy group. As with dihydromyrcene, epoxidation occurred exclusively at the more substituted double bond for both TS-1 and TiAlβ. The non-allylic epoxide of linalool is rarely observed as it readily undergoes intra-molecular cyclisation to form furano linalool oxide (**19**) (five membered heterocyclic ring) or pyrano linalool oxide (**20**) (six membered heterocyclic ring) as shown in Scheme 5.



Scheme 5

Alβ was found to be inactive for the epoxidation and subsequent ring closure as the data obtained were consistent with those observed in the absence of catalyst, although significant isomerisation to nerol was observed.

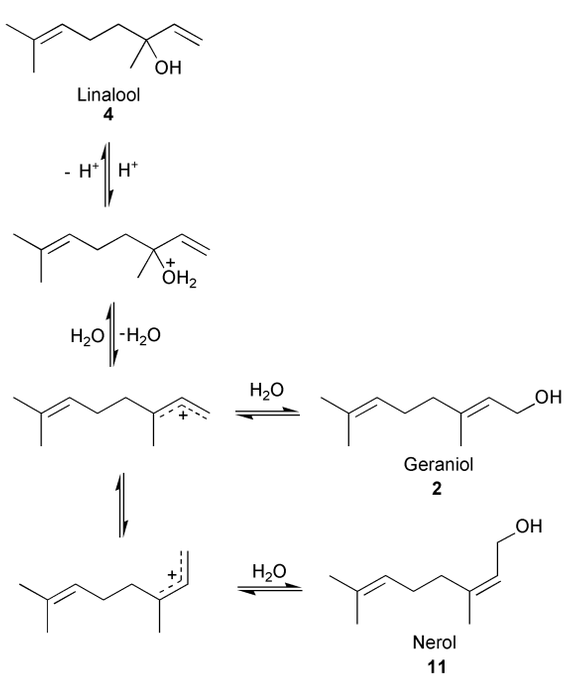
Upon replacing Alβ with TiAlβ, higher levels of conversion were obtained but the selectivity to nerol is markedly decreased. The presence of nerol was extremely surprising although blank experiments with hydrogen peroxide in the absence of a catalyst, and hydrogen peroxide with Alβ revealed that the acid sites were responsible for the isomerisation reaction, which was not the case for geraniol isomerisation (Table 2 entry 3).

Table 4 Oxidation of linalool

Entry	Catalyst[a]	Oxidant	Time/h	Linalool conv. (%)	Selectivity (%)				Furano : pyrano ratio
					Furano	Pyrano	Nerol	Others	
1	None	H_2O_2	24	2.2	100	0	0	0	∞
2	Alβ	H_2O_2	31	12.4	19	0	81	0	∞
3	TS-1	H_2O_2	2	0	0	0	0	0	—
			24	2.9	4.2	67	33	0	1.72
4	TiAlβ	H_2O_2	2	42.8	66	12	12	10	5.5
			24	98	66	14	12	8	4.7
5	TiAlβ	TBHP[b]	24	5	100	0	0	0	∞
			44	13.4	100	0	0	0	∞
6	TiAlβ[c]	TBHP[d]	2	11.8	61	39	0	0	1.6
			5.5	18.6	62	38	0	0	1.5
7	TiAlβ	UHP	2	3.1	61	39	0	0	1.6
			24	4.2	67	33	0	0	1.7

[a] Reaction conditions: linalool (3.12 g, 20 mmol), catalyst (0.1 g), methanol (24 g), oxidant (10 mmol). UHP: urea–hydrogen peroxide complex. TBHP: *tert*-butyl hydroperoxide. [b] *tert*-Butyl hydroperoxide (3 M in isooctane). [c] At 353 K in acetonitrile. [d] *tert*-Butyl hydroperoxide (70% in water).

For the reaction of linalool in TS-1–hydrogen peroxide systems, low conversion was observed which is consistent with the size of the substrate relative to the pore dimensions. It is likely that the catalytic reaction observed with TS-1 occurs at Ti sites on the exterior surface of the catalyst. The formation of the ring closure products (furano oxide : pyrano oxide ratio of 1.72 : 1) must also be occurring on the exterior surface of the catalyst crystallites as the transition state for the formation of either the furano or pyrano oxide cannot be accommodated within the pores of the TS-1 catalyst. Reactions carried out with TiAlβ–hydrogen peroxide–methanol resulted in a much higher conversion than in the TS-1 case. An induction period was not observed. Initially, the major product was furano linalool oxide, and the two minor products were pyrano linalool oxide and nerol. Other products were observed at low levels and these include intermolecular ring opened products to give ether alcohols as observed with the other monoterpenes in this study. The furano : pyrano ratio was found to decrease with reaction time (5.5 : 1 after 2 h, 4.7 : 1 after 24 h). A small amount (*ca.* 2%) of the furano product was found to be due to the non-catalytic epoxidation of linalool. Isomerisation of linalool occurs because it is a tertiary alcohol, facilitating the formation of an allylic carbocation as shown in Scheme 6. Stereoisomerisation of the allylic cation and re-hydroxylation give rise to nerol. Geraniol would be the expected product as it has a '*trans*' arrangement of the two bulkiest groups around the double bond, which indicates the isomerisation process may be under kinetic control as the alkene '*cis*' isomer, nerol is formed preferentially. The formation of nerol may be enhanced by the pore constraints of the catalyst as nerol may have a better fit within the pore structure of the microporous catalyst.



Scheme 6

The epoxidation of linalool was repeated using anhydrous TBHP in methanol. Very low linalool conversions were observed (*ca.* 2.5% after 24 h) with the only product observed being furano linalool oxide. Presumably, water plays an indirect role in the catalysis as it can be implicated in the Ti leaching process. If water is excluded from the system then hydrolysis of the Si–O–Ti bonds cannot take place, thus leaching should be minimised. In this case, we are probably observing the 'true' contribution of framework species to the overall catalysis as none of the required components for leaching are present.

In addition, the work of Corma *et al.*[27] was reproduced as part of our study with *tert*-butyl hydroperoxide (70% aqueous) using acetonitrile as the solvent at 353 K. Interestingly, no isomerisation to nerol was observed; hence, it is considered that passivation of the acid sites occurs in this reaction system and this prevents the isomerisation process from occurring. This may involve an interaction with the solvent, or may be due to basic impurities in the acetonitrile itself.

The furano : pyrano ratio varies significantly under the conditions used in this and related studies.[6] As mentioned earlier with the TiAlβ–H_2O_2 system, a ratio of 5.5 to 4.7 was observed (Table 4 entry 4), depending on the reaction time. In experiments using *m*-chloroperbenzoic acid (MCPBA) as the oxidant in the absence of a catalyst, a furano : pyrano ratio of 12 was obtained. Upon switching to the non-aqueous system, a ratio of 1.6 was obtained which varied little with reaction time (unlike in the aqueous system). The reaction carried out using acetonitrile and TBHP is considered to be a direct repeat of work carried out by Corma *et al.*[6] and an identical furano : pyrano ratio was obtained. Corma *et al.*[6] also carried out this reaction using TiMCM-41 and a furano : pyrano ratio of 0.9 was reported, which is lower than that observed in the TiAlβ system. This difference was attributed to a reduction in the pore constraints upon moving to the mesoporous system, but the ratio obtained with MCPBA (ratio of 12) indicates this may not be the case.

We consider that the observed furano : pyrano ratio could be a function of acid strength of the reagents/catalysts used. The furano oxide is the kinetically favoured product[33] since the formation of 5-membered heterocycles is known to be preferred over 6-membered heterocycles, although the 6-membered ring has the lower strain energy. The ring closure involves proto-

nation of the epoxide ring, epoxide C–O bond cleavage and furano/pyrano bond termination. Under strongly acidic conditions, the early transition state requires modest epoxide cleavage and C–OH bond formation. Under this regime (as the furano oxide is the kinetic product), the furano isomer is formed preferentially. As the acid strength is decreased, attack at the furano carbon becomes less favourable as the ring forming process is under a much greater influence from the strain energy released by cleavage of the 3-membered ring and the lower strain energy of the 6-membered ring product. TiMCM-41 only contains weak Lewis acid sites and this is therefore consistent with the lowest furano : pyrano ratio (0.9 : 1) observed with the catalysts studied.[6] The acid strengths in the TiAlβ–MeCN–TBHP, TiAlβ–MeOH–TBHP and TiAlβ–MeOH–UHP systems are expected to be lower than the acid strength in the TiAlβ–MeOH system because of neutralisation of acid sites, as described previously. The actual ratios obtained are in agreement with this observation (Table 4 entries 4–7).

Conclusions

For the oxidation of monoterpenes, it has been shown that titanosilicates are effective catalysts when using a variety of oxidants. Dihydromyrcene is selectively epoxidised at the more electron rich double bond and significant amounts of ring opened products are observed with both TS-1 and TiAlβ with aqueous hydrogen peroxide. Upon replacing the aqueous hydrogen peroxide with urea–hydrogen peroxide complex or *tert*-butyl hydroperoxide, the epoxide can be obtained as the major product. The epoxidation of geraniol can occur at either double bond. As observed in the dihydromyrcene experiments, the subsequent ring opening reaction can be prevented by using *tert*-butyl hydroperoxide, urea–hydrogen peroxide complex, or aqueous hydrogen peroxide in conjunction with acetone. With aqueous hydrogen peroxide in methanol, the epoxides rapidly undergo hydrolysis to ether diols or triol. Indirect evidence of leaching in the TiAlβ–H_2O_2 system was observed. Reactions carried out using citronellol show this is entirely due to the allylic alcohol functional group. Finally, the epoxidation of linalool occurred exclusively at the more electron rich double bond. This was found to undergo rapid intra-molecular cyclisation to a five and a six membered heterocycle. Although the catalysts used for this transformation are porous, the ratio of the two products was thought to be dependent on the catalyst pore size, but data obtained in this study suggest the acid strength of the support plays a far greater role.

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.*[21] 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, then aged for 18 h. The gel was then heated at 448 K under autogeneous pressure in a Teflon lined autoclave for 2 d under static conditions. 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 of 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.[32] 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 and 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) were 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.

Both TS-1 and TiAlβ were characterised by powder XRD and FTIR and were found to be consistent with materials reported in the literature.

Catalytic reactions

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

Reactions were typically carried out as follows; substrate (20 mmol), catalyst (0.1 g), and solvent (24 g) were added to the round bottomed flask, followed by the oxidant (10 mmol). This mixture was then heated to 333 K when methanol or acetone was used as the solvent or 353 K when acetonitrile was used as the solvent. Samples were taken at timed intervals and diluted in acetone prior to analysis. Analysis was by GC (Varian 3400) fitted with a split/splitless injector (split ratio 1 : 50) and a FID. The column used was an HP1 (30 m, id 0.23 mm) with helium as the carrier gas. Conversions were based on mmol of oxidant (*i.e.* 100% conversion corresponds to 50% conversion of reactant and 100% conversion of oxidant). Reaction products were analysed by GCMS (HP5890 GC coupled to a TRIO 1 mass spectrometer) using the column and carrier gas mentioned above and identified by means of library fitting and comparison with authentic samples.

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