Hydroxy-assisted Chemo- and Stereo-selective Epoxidation Catalysed by a Titanium Silicate Molecular Sieve (TS-1)/H_2O_2 System†

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The TS-1/H_2O_2 system efficiently catalyses the hydroxy-assisted chemoselective epoxidation of α-hydroxyalkene in geraniol, and the stereoselective epoxidation of cyclopent-2-en-1-ol/cyclohex-2-en-1-ol producing the epoxide which is *cis* to OH with high selectivity (90 : 10 *cis*: *trans*).

The ability of molecular sieves to recognize, discriminate and organize molecules with high precision at > 1 Å scale, and the possibility of incorporating various transition metal ions with redox characteristics as active sites have brought the interface of heterogeneous catalysis with zeolites and organic synthetic transformations to the forefront.[1] Commonly, zeolite/molecular sieve catalysed transformations are restricted to mainly shape selective and/or regioselective control.[2] Recently, the epoxidation of allyl alcohol and methallyl alcohol over TS-1, a titanium silicate analogue of the ZSM-5 type molecular sieve, first synthesized by Taramasso *et al.*,[3] has been reported,[4–6] where epoxidation was preferred over oxidation of the OH group. Here, we report the TS-1/H_2O_2 catalysed hydroxy-assisted chemo- and stereo-selective epoxidation of hydroxy dialkenes (*viz. cis*- and *trans*-geraniol) and cyclic hydroxy alkenes (*viz.* cyclopent-2-en-1-ol and cyclohex-2-en-1-ol), respectively.

Titanium silicate molecular sieve (TS-1) was prepared from tetraethylorthosilicate, tetrabutylorthotitanate, tetrapropylammonium hydroxide and water according to literature procedure.[7] The Si : Ti molar ratio of the sample was 29. The X-ray powder pattern of the calcinated sample of TS-1 is characteristic of the MFI structure. The Al-free titanium silicate (TS-1) retained its orthorhombic symmetry after calcination. The scanning electron micrograph of the TS-1 sample exhibited the absence of any amorphous material. The particle size of the cuboid-shaped crystallites ranged from 0.2 to 0.3 µm. The UV–VIS spectrum of TS-1 showed a band at 209 nm, and the IR spectrum showed a characteristic absorption at 960 cm^{-1}.

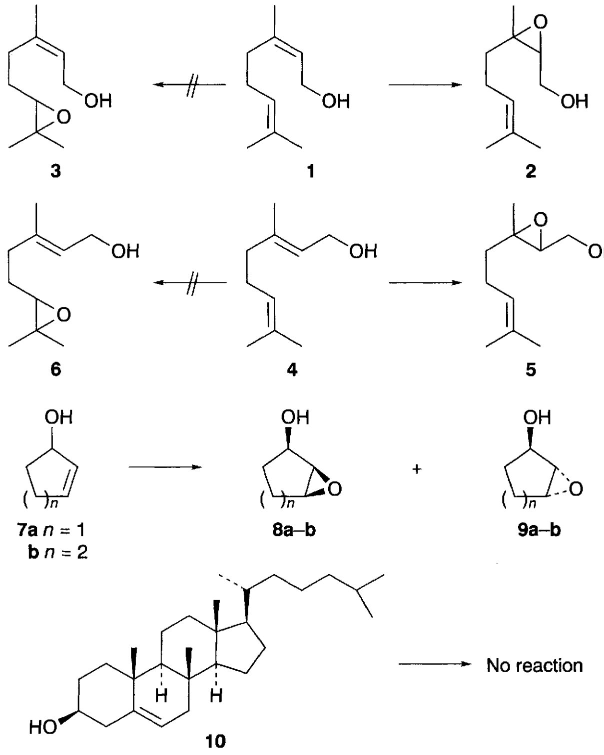
It is clear from Table 1 that both *cis*- and *trans*-stereoisomers of 1-hydroxy-3,7-dimethylocta-2,6-diene (**1** and **4**, respectively) undergo selective epoxidation, with only a small amount of oxidation of the OH group. While substrates **1** and **4** selectively form products **2** and **5**, respectively, **3** and **6** are not formed. Only α-hydroxyalkenes are epoxidized, with formation of the corresponding 2-epoxy products exhibiting high chemoselectivity, and the *cis* and *trans*-isomers of the reactant molecules retain their stereospecificity in the products (*i.e.* epoxides). Here it may be pertinent to mention that in all earlier reports[4–6] on the chemoselective oxidation of allylic alcohols, there were two functional groups, *viz.* C=C and OH. The present case of selective formation of **2** from **1** or **5** from **4** is an example of OH-assisted chemoselective epoxidation at the 2-position and not at the 6-position in **1** or **4** (entries 1 and 2, Table 1). As far as we know, this is the first report of OH-assisted chemoselective epoxidation over TS-1 and H_2O_2. Entries 3 and 4 (Table 1) demonstrate the stereoselective epoxidations of cyclopent-2-en-1-ol, **7a** and cyclohex-2-en-1-ol, **7b**, with quite high stereospecificity (90% **8a** and **8b**, where OH and epoxide are *cis*). These results are quite interesting from the viewpoint of stereospecific epoxidation catalysed by the heterogeneous TS-1/H_2O_2 system. However, when the corresponding unsaturated cyclic ketones (*viz.* cyclopent-2-en-1-one and cyclohex-2-en-1-one) were reacted under similar reaction conditions, no epoxidation occurred. With a view to examining whether oxidation is occurring within the pores of TS-1 or outside them, the epoxidation of a bulky homoallylic alcohol (cholesterol) was carried out. However, no epoxidation could be observed even after 2 days of refluxing under identical conditions (Scheme 1).

A plausible catalytic cyclic mechanism which accounts for the efficient hydroxy-assisted chemoselective epoxidation is shown in Scheme 2. Some of the reactive species, *e.g.* **13** and **15**, originating from **11** and **12** in the presence of H_2O_2, are

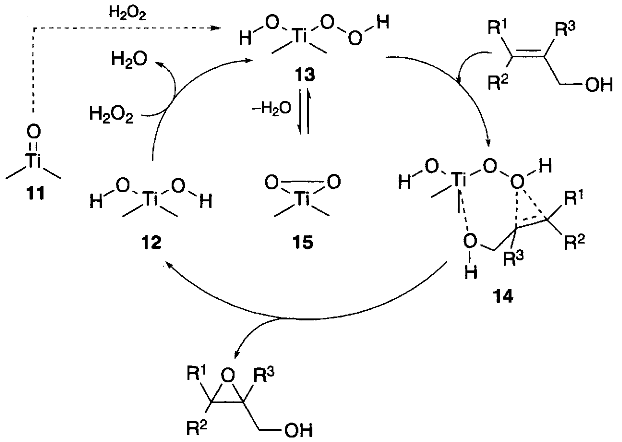
Table 1 Hydroxy-assisted epoxidation with TS-1 and H_2O_2[a]

				Product selectivity/ mol%	
Entry	Substrate	Products	Conversion[b] (%)	Epoxide	Aldehyde + acid
1	**1**	**2**	86	90	10
2	**4**	**5**	85	90	10
3	**7a**	**8a** : **9a** (9 : 1)[c]	80	75	—
4	**7b**	**8b** : **9b** (9 : 1)[c]	85	80	—

[a] A solution of substrate (10 mmol) and aq. H_2O_2 (30% *m/m*, 12 mmol) in acetone, along with the catalyst TS-1 (20% *m/m* with respect to substrate) was heated under reflux for 8 h, and the progress of the reaction was monitored by GC, TLC and/or ^1H NMR, after usual work-up. GC-MS was also used in certain cases. [b] Determined by GC. [c] A 9 : 1 mixture of **8a** and **9a** or **8b** and **9b** was observed (^1H NMR).



Scheme 1



Scheme 2 Probable mechanism for TS-1 induced epoxidation

routinely proposed for oxidation processes involving TS-1.[8–11] Presumably, the enhanced reactivity of OH-containing alkenes and OH-assisted chemoselectivity may be due to the possible formation of species, *e.g.*, **14**, which appears to be a probable reactive species explaining our results. The stereoselectivity in the epoxidation of cyclic alcohols **7a,b** also emphasizes a transition state bound to OH, similar to **14**.

In summary, a novel hydroxy-assisted heterogeneous catalytic chemo- and stereo-selective and stereospecific epoxidation of suitable alkenes with TS-1 and aqueous H_2O_2 (30% *m*/*m*) is demonstrated.

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