Journal of Catalysis **182,** 349–356 (1999)
Article ID jcat.1998.2355, available online at http://www.idealibrary.com on IDEAL®

Intramolecular Rearrangement of Epoxides Generated *in Situ* over Titanium Silicate Molecular Sieves

Asim Bhaumik and Takashi Tatsumi[1]

Department of Applied Chemistry, Graduate School of Engineering, The University of Tokyo, Yayoi, Tokyo 113, Japan

Received July 8, 1998; revised October 26, 1998; accepted November 9, 1998

Open chain unsaturated alcohols 1, having the general formula $R_1R_2C{=}CH(CH_2)_nCR_1R_2OH$ (where $R_1, R_2 = H$ or CH_3, and $n = 1$–3) and carbocyclic unsaturated alcohols of similar type have been efficiently cyclized to the corresponding hydroxytetrahydrofuran or hydroxytetrahydropyran over titanium silicate molecular sieves (TS-1 and Ti-beta), in one pot under mild liquid phase reaction conditions using dilute hydrogen peroxide as oxidant. When the hydroxy nucleophile may attack either of the activated carbon atoms of the epoxides generated *in situ*, to lead to a derivative of tetrahydrofuran or tetrahydropyran, the former exclusively formed. The regioselectively for such reaction is 100%. When R_1 or $R_2 = CH_3$, among the diasteroisomeric products *trans* predominates over *cis*. In this cyclization reaction titanium silicate epoxidizes the olefin and successively catalyzes the opening of the oxirane ring via intramolecular attack of hydroxy oxygen. Thus the behavior of titanium sites is bifunctional in nature. However, for bicyclic unsaturated alcohols, because of geometric restriction, activity of medium pore TS-1 is very low. Ti-beta synthesized by dry gel conversion has been found to be an efficient catalyst in oxidative cyclization of such bulky organic substrates as α-terpineol, isopulegol, and *trans-p*-menth-6-ene-2,8-diol to their corresponding tetrahydrofuranols or tetrahydropyranols with a very high regioselectivity.

Key Words: **TS-1; Ti–Al-beta; cyclization; tetrahydrofuran; tetrahydropyran.**

INTRODUCTION

The widespread occurrence of substituted tetrahydrofuran and tetrahydropyran rings in many classes of natural products have made them valuable building blocks for the synthesis of various biologically active organic target molecules (1). Thus, finding a new method for the synthesis of these oxacyclic compounds is an important area of research. A convenient route for the stereoselective synthesis of these compounds involves an electrophilic activation of the double bond (2, 3) in **1** followed by an intramolecular nucleophilic attack of the oxygen atom of the terminal hydroxyl group. Ring closure of substituted 4-penten-1-oxy and 5-hexen-1-oxy radicals (4, 5) is also a useful tool for the preparation of these compounds. For more than a decade, titanium silicate molecular sieve, TS-1 (6), having the medium pore MFI topology has been used as an efficient, clean, and selective oxidation catalyst under liquid phase heterogeneous reaction conditions in the presence of dilute hydrogen peroxide (7). Until now, as an outcome of the continuous effort to find a use for the TS-1/H_2O_2 system in a new class of organic transformations, it has been successfully employed for selective oxyfunctionalization of alkane (8), alkene epoxidation (9), hydroxylation of aromatics (10), ammoximation of carbonyls (11), and oxidation of amines (12) and sulfides (13). Some of these reactions have been commercialized or tested in a large pilot plant and the aim of the recent research is to find out their applicability to other transformations. Here, we report a highly efficient regioselective cyclization of such olefinic alcohols over titanium silicates, under mild reaction conditions using dilute hydrogen peroxide as an oxidant. TS-1 with the MFI structure has been very recently employed in the cyclization reactions for the synthesis of tetrahydrofurans and tetrahydropyrans using dilute hydrogen peroxide as an oxidant (14). Because the small pore size of this molecular sieve limits its application to molecules with kinetic diameters less than 5.5 Å, large pore Ti–Al-beta synthesized by the dry gel conversion (DGC) method (15, 16) has been employed for the synthesis of bulky bicyclic compounds, which cannot diffuse through the MFI pores. These molecular sieves with the BEA structure having pores approx. 7.0 Å in diameter allow the diffusion of the chosen bulky reactants and products through their channels. The double bond of olefinic alcohols was activated to the corresponding unstable epoxy alcohols by the electrophilic attack of the titanium hydroperoxo oxygen over TS-1 or Ti-beta. This in turn can easily undergo cyclization by the intramolecular attack of the hydroxy moiety present in the molecule to the activated carbon atom of the epoxy ring.

EXPERIMENTAL

TS-1 used in the present study was synthesized by modifying the standard literature procedure (6, 7). In a

[1] To whom correspondence should be addressed. Fax: 81-3-5800-6825. E-mail: tatsumi@catal.t.u-tokyo.ac.jp.

0021-9517/99 $30.00

typical synthesis 42 g tetraethyl orthosilicate was hydrolyzed with 67.7 g tetrapropyl ammonium hydroxyde (20% aqueous, Aldrich) with vigorous stirring for 1 h. Then 2.26 g tetrabutyl orthotitanate dissolved in 10 g isopropyl alcohol was added dropwise with vigorous stirring. After 2 h continuous stirring, 54 g water was added into the resulting clear liquid and the mixture was heated in a tumbling autoclave at 443 K for 24 h. After crystallization, the product was centrifuged and washed several times to make it free of occluded alkali. Then it was dried and calcined at 823 K for 12 h. The calcined TS-1 material thus obtained was thoroughly characterized through XRD, surface area measurements, and FTIR and UV–Vis spectroscopies. Ti–Al-beta was synthesized by the recently developed DGC method (16) using TEAOH as a structure directing agent. Typically, Ti–Al-beta was synthesized according to the following procedure: 0.58 g tetrabutyl orthotitanate (97 wt% Kanto) was first added to 4.0 g distilled water, and to the resulting suspension was added 2.0 g H_2O_2 (31 wt%, MGC) after 1 h. The mixture was stirred for 1 h, leading to solution A containing peroxide titanate. Solution B was prepared by dissolving 0.0124 g anhydrous $NaAlO_2$ (Koso) and 0.015 g of NaOH (96 wt%, Koso) in 8.0 g TEAOH (40 wt% in water, Alfa) at room temperature with stirring for 1 h. Then 3.0 g fumed silica (Aerosil-200, Nippon Aerosil) was added under vigorous stirring. A clear homogeneous solution obtained after 2 h was heated to 353 K and dried while stirring. When the gel became dry, it was ground into fine powder (chemical composition: $SiO_2 : TiO_2 : Al_2O_3 : Na_2O : TEAOH = 304 : 10 : 0.46 : 1.55 : 132.5$) and transferred into a Teflon beaker situated in a Teflon-lined special autoclave (16) where water (5.0 g) as a source of steam was poured into the bottom. The crystallization was carried out in steam first at 403 K for 96 h, and subsequently at 448 K for 18 h under autogeneous pressure. The recovered product (6.8 g, Si/Ti = 31.5, Si/Al = 156, Si/Na = 136) was washed with distilled water, dried at 308 K for 12 h, and calcined at 793 K for 10 h in the flow of air.

The liquid phase reaction was carried out in a two-necked glass reactor fitted with a water condenser under inert N_2 atmosphere at the required temperature (298 or 333 K) with vigorous stirring. In a typical reaction the following constituents were employed: 0.02 mol substrate, 0.02 mol H_2O_2 (30 wt% aqueous), catalyst (TS-1, Si/Ti = 29) 20 wt% with respect to the substrate, 10 g acetone, 2-butanol, or H_2O (in the three phase system). At various reaction times products were analyzed by a capillary gas chromatograph (Shimadzu 14 A, OV-1 Chiraldex G-TA columns with flame ionization detectors). Products were identified through GC retention times and GC-MS splitting patterns of the authentic samples. When authentic samples were unavailable, identification was made through ^1H NMR spectroscopy.

RESULTS AND DISCUSSION

Cyclization of Open Chain Unsaturated Alcohols

In Table 1 conversion and product selectivities of the cyclization of various unsaturated alcohols are reported. It is pertinent to mention that H_2O_2 conversion in all the cases is above 98%. Thus for clarity these data are not given in Table 1.

3-buten-1-ol. Cyclization of the simplest molecule of this series, 3-buten-1-ol, occurs at room temperature over TS-1/H_2O_2 system. In solvent 2-butanol the reaction rate is slow and it takes 18 h to reach a yield of 82%, 3-hydroxytetrahydrofuran **2** being the sole product (Scheme 1). However, in the presence of water as the dispersion medium (solid catalyst, aqueous H_2O_2, and organic substrate initially form three distinct phases) (17) reaction proceeds at a faster rate (94% conversion after 6 h) with selectivity toward **2** decreasing to 76%. In this case an oxirane ring opening via attack of external H_2O molecules of the medium competes with the intramolecular cyclization process, leading to dihydroxylation (1,2,4-butanetriol, 24% selectivity). Interestingly, increasing the reaction temperature to 333 K in the latter case decreases the yield of **2** to 2.5% with selective dihydroxylation (18). Unlike for the phenylsulfenyl chloride system (3), the cyclization of 3-butene-1-ol is quite efficient over the present TS-1/H_2O_2 system (14). Another important aspect of the TS-1 catalyzed cyclization is that, unlike radical addition reaction, the products are hydroxy-substituted oxacyclic compounds.

As shown in Scheme 1, the hydroxy nucleophile has two probabilities for intramolecular attack to the activated carbon atoms of intermediate epoxide. Path 1, the exo adduct

TABLE 1

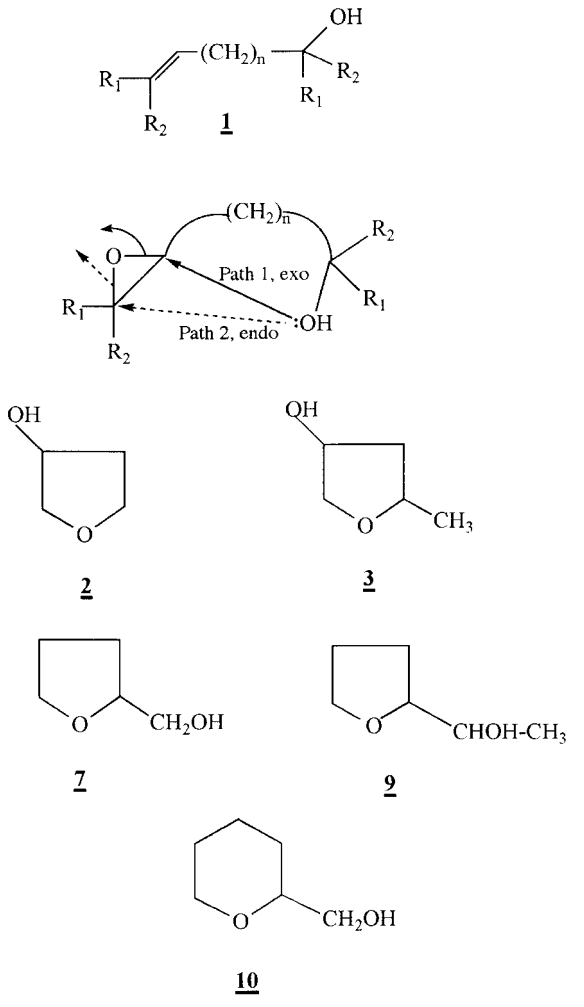
Cyclization of Various Unsaturated Alcohols over TS-1[a]

Substrate	Solvent/ medium	Time (h)	Conv. (mol%)	Product selectivity (%) Cyclized product[b]	Others
3-Buten-1-ol	H_2O	6	94.0	76.0 (**2**)	24.0
	2-Butanol	18	82.0	100 (**2**)	—
(±) 4-Penten-2-ol	H_2O	12	85.4	70.0 (**3**)	30.0
	Acetone	18	80.1	87.7 (**3**)	12.3
	2-Butanol	24	84.0	100 (**3**)	—
4-Penten-1-ol[c]	H_2O	3	98.0	100 (**7**)	—
	Acetone	4	96.5	100 (**7**)	—
cis-4-Hexen-1-ol[c]	Acetone	4	92.0	100 (**9**)	—
5-Hexen-1-ol[c]	Acetone	6	90.0	100 (**10**)	—

[a] Substrate : $H_2O_2 = 1 : 1$; catalyst TS-1 (20 wt% with respect to the substrate); temperature = 298 K unless otherwise stated.

[b] Formula of the corresponding product (as shown in the schemes) is given in parentheses.

[c] Reactions were carried out at 333 K.

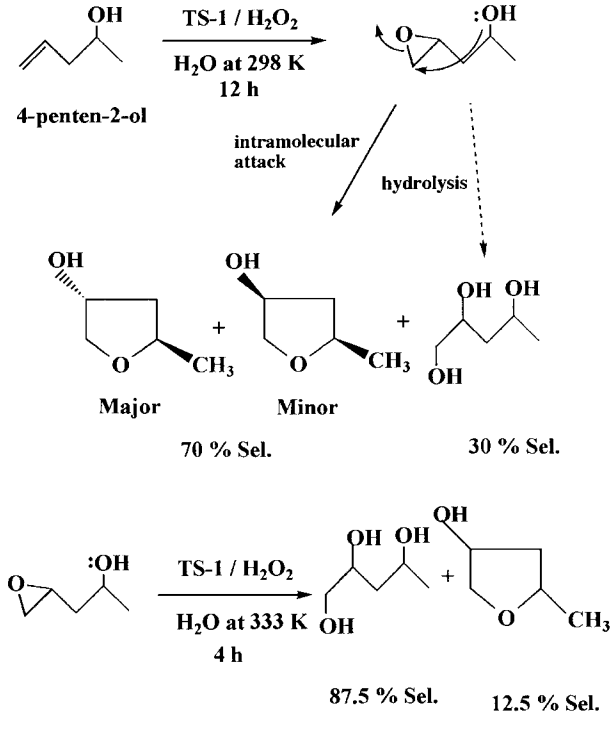


SCHEME 1. Different open chain unsaturated alcohols, reaction pathways, and cyclized products.

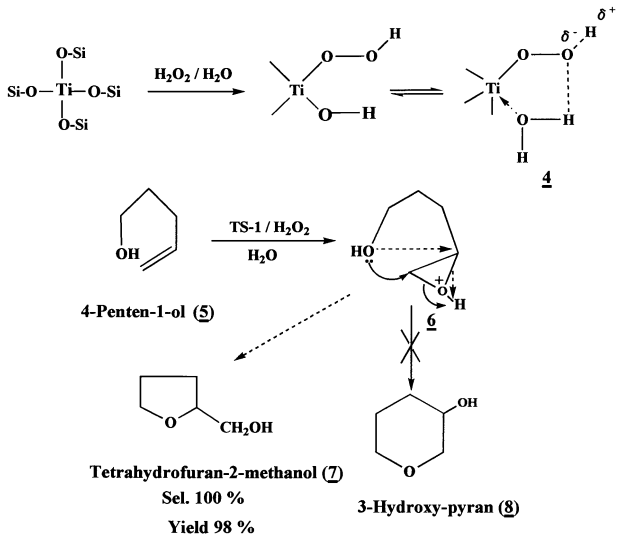
from the epoxide of 3-buten-1-ol, leads to the very unstable 4-membered ring compound. Thus it cannot form under the present reaction conditions. Path 2, the endo adduct, leads to the stable 5-membered tetrahydrofuran ring. Thus it is the only cyclized product in case of 3-buten-1-ol. However, as the endo product proceeds via terminal attack, for which transition state carbocation is not very stable, increasing reaction temperature from 298 to 333 K leads to the predominant dihydroxylation product when water is used as the dispersion medium.

(±) 4-penten-2-ol. The tetrahydrofuran derivative 2-methyl-4-hydroxy-tetrahydrofuran **3** (*trans*:*cis* ratio 70:30) is formed from (±) 4-penten-2-ol when acetone is used as solvent (80% yield at room temperature after 18 h reaction time). In a water medium at room temperature, selectivity for **3** (Scheme 2) drops to 70% with *trans*:*cis* ratio of 67:33 after 12 h. At higher temperature in a water dispersion medium dihydroxylation product predominates in a similar manner to 3-buten-1-ol. Interestingly, here also the intermediate epoxide is highly reactive and undergoes a very rapid oxirane ring opening either via intramolecular cyclization or hydrolysis. However, when using 2-butanol as solvent, **3** forms as the sole product in 84% yield (*trans*:*cis* ratio 72:28). High *trans* selectivity between the diastereomers of **3** may be due to the higher stability of transition state at the active site. Scheme 2 compares the reaction sequences of (±) 4-penten-2-ol at 298 and 333 K using water as the dispersion medium.

4-penten-1-ol. In Scheme 3, the oxidative cyclization of 4-penten-1-ol **5** over TS-1/H_2O_2 is illustrated. Titanium hydroperoxide **4** is the proposed intermediate (19–21) generated in situ when titanium silicates come in contact with dilute aqueous hydrogen peroxide. As shown in Scheme 3, **6** is the proposed reaction intermediate. The cyclization of 4-penten-1-ol occurred regioselectively to the 5-exo product tetrahydro-2-furanmethanol **7**. The corresponding tetrahydropyran regioisomer of **7** (i.e., **8**, supposed to form via endo attack of the hydroxy nucleophile to the activated terminal carbon atom of the epoxide intermediate **6**) does not form at all. This is quite interesting, since 2,4,4,6-tetrabromo-1,5-cyclohexadienone (2) induced cyclization leads to a mixture of tetrahydopyran and tetrahydrofuran at a mole ratio of 3:1. Reaction medium has no effect; in 2-butanol, acetone, and water, **7** was exclusively obtained in 98–99% yield. In water at high temperature (333 K) no dihydroxylation product is formed.



SCHEME 2. Reaction pathways for the oxidation of 4-penten-2-ol over TS-1/H_2O_2.



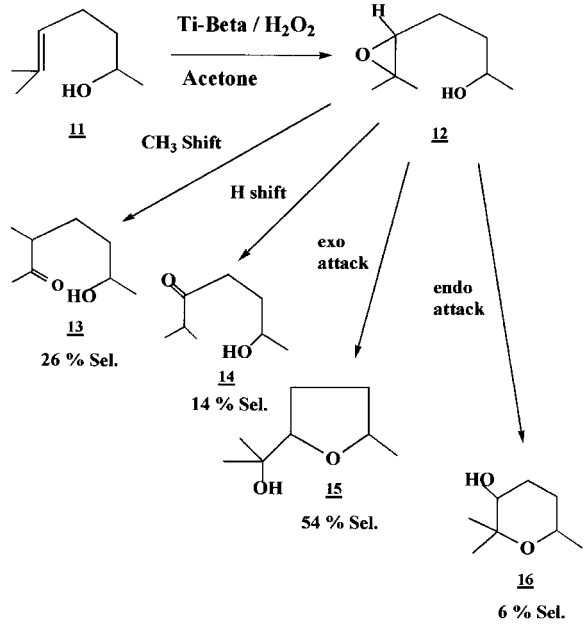
SCHEME 3. Possible reaction pathway for the oxidation of 4-penten-1-ol.

Cis-4-hexen-1-ol. One possible explanation for the 5-exo product formation from 4-penten-1-ol is the acidic nature of TS-1, apart from higher stability of 5-membered oxacycles over the 6-membered one. If the oxirane ring opening follows S_N1 pathways (involving initial protonation), a more preferential attack would be onto the more substituted carbon atom; the hydroxyl group would attack preferentially at the more substituted carbon atom due to the greater stability of the corresponding carbocation. On the contrary, alkyl group substitution at C_5 does not cause any change in the regioselectivity of cyclization as observed for *cis*-4-hexen-1-ol. Between the two possibilities of the intermediate oxirane ring opening the 5-exo product, tetrahydro-2-furan-1-ethanol **9** (Scheme 1), forms exclusively in 92% yield in acetone at 333 K. The 6-endo product, 2-methyl-3-hydroxytetrahydropyran, does not form at all, although it would have been formed via a more stable carbocation intermediate. As shown in Scheme 3 for **5**, the titanium hydroperoxo species here protonates the intermediate epoxide and thus activates it for the nucleophilic attack of the OH groups at C_4.

5-hexen-1-ol. In the case of 5-hexen-1-ol ($n = 3$ and R_1, $R_2 = H$), where two products, either tetrahydropyran or its 7-membered regioisomer tetrahydrohomopyran derivative, are possible, tetrahydro-2-pyranmethanol **10** only forms in 90% yield in acetone at 333 K (Scheme 1). Here the exo attack prevails to give 6-membered tetrahydropyran rather than the corresponding 7-membered regioisomer, which can form via endo attack.

(±) 6-methyl-5-heptene-2-ol. The nature of the intermediate epoxide formed plays a crucial role in the final product distribution. This is examplified by the reaction of bulky (±) 6-methyl-5-heptene-2-ol, **11** (Scheme 4), which may not diffuse easily through the MFI pore: the TS-1/H_2O_2/acetone system gives rise to only 30% conversion at 333 K after 4 h reflux. Large pore Ti–Al-beta (BEA structure with 12-membered rings of pore opening 6.9 × 7.4 Å, Si/Ti = 31.5, Si/Al = 156) synthesized by the DGC method improves the conversion drastically to 90% after 4 h reaction time at 333 K under identical conditions. Scheme 4 illustrates the reaction pathways. The protonated form of the epoxide formed from **11**, i.e., **12**, leads to a secondary carbocation, which undergoes CH_3 shift, producing the corresponding rearranged ketone **13** via a stabilized carbocation. Otherwise **12** gives a stable tertiary carbocation, which is converted to the ketone **14** via H shift. These ketones are obtained (**13** : **14** = 65 : 35) at 40% selectivity. The rest (60% selectivity) was the cyclized product 2-(1-hydroxy-1-methylethyl)-5-methyl-tetrahydrofuran **15**. Here also high regioselectivity for the *trans* diasteriomer (*trans* : *cis* = 70 : 30) is obtained. Over TS-1 the product distribution remained almost the same with a slightly higher *trans* : *cis* ratio (75 : 25) of **15**. Despite the higher stability for the intermediate carbocation, the tetrahydropyran derivative 5-hydroxy-2,2,6-trimethyltetrahydropyran **16** formed in a very low yield (6.5%, Scheme 4), indicating the high preference for the 5-exo product in the present cyclization system inside the zeolite pores. Thus there is a decreasing tendency toward the formation of 6-membered oxacyclices over 5-membered ones in the presence of microporous titanium silicates.

Corma *et al.* (22) have reported the oxidation of linalool to cyclic ethers catalyzed by Ti–Al-beta and

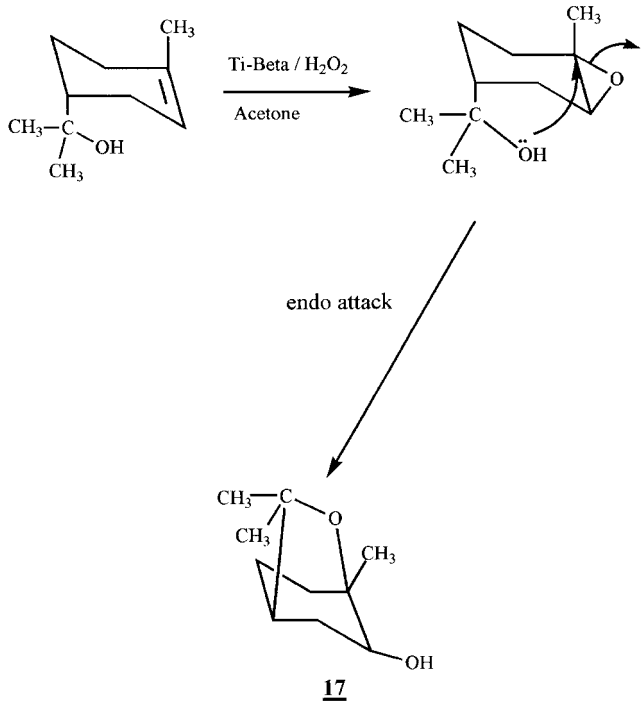


SCHEME 4. Reaction pathways for the oxidation of 6-methyl-5-heptene-2-ol over Ti-beta.

Ti–Al–MCM-41. Here acidity associated with framework Al was considered to be responsible for the cyclization after initial epoxidation of the double bond. It is noteworthy that TS-1 with neutral framework structure also catalyzes the cyclization of such unsaturated alcohols under mild liquid phase reaction conditions in the presence of hydrogen peroxide. Ti–Al-beta used for the present study is Na-form. So the acidity associated with the catalysis in the cyclization step could be attributed to that generated at the Ti sites rather than that of Al sites.

Cyclization of Carbocyclic Unsaturated Alcohols

α-terpineol. TS-1/H_2O_2 system used for the cyclization of open chain unsaturated alcohols shows poor activity in the case of unsaturated alcohol containing carbocyclic ring. Table 2 illustrates the results of oxidative cyclization of α-terpineol, isopulegol, and *trans-p*-menth-6-ene-2,8-diol. For α-terpineol over a TS-1/H_2O_2 system a conversion of 13% with very poor selectivity for cyclized product (Table 1, 5th column) was observed. In the case of α-terpineol over Ti–Al-beta (synthesized by the DGC method) the yield of product **17** (Scheme 5) is 50% (with 23% other product mixture including 16% uncyclized epoxide) vis-à-vis 7.6% over Ti–Al-beta (at 313 K after 8 h using *t*-butyl hydroperoxide, TBHP, as an oxidant in CH_2Cl_2 solvent) synthesized according to the hydrothermal synthesis method (23). Here it is pertinent to mention that since Ti–Al-beta synthesized by the DGC method is more hydrophobic (24), dilute aqueous H_2O_2 is a more suitable oxidant in the present case whereas for hydrothermally synthesized Ti–Al-beta (relatively hydrophilic) TBHP is the best oxidant. In Scheme 5 the probable pathway for α-terpineol oxidation is shown. In this bicyclic system, 6-endo product **17** (bicycle consisting of two 6-membered rings) predominantly forms over the exo product (5- and 7-membered rings). This may be due to the fact there is less strain in the former case. However, unlike the open chain system, here the hydroxy nucleophile may face more strain in an intramolecular attack because of the restricted geometry of the carbocycle. Hence, the epoxide intermediate is considerably more stable than that of the molecule at the transition state for intramolecular attack. This explains the observation of intermediate epoxide after the reaction as described above.



SCHEME 5. Oxidative cyclization of α-terpineol over Ti-beta.

TABLE 2

Cyclization Reaction over Ti–Al-Beta[a]

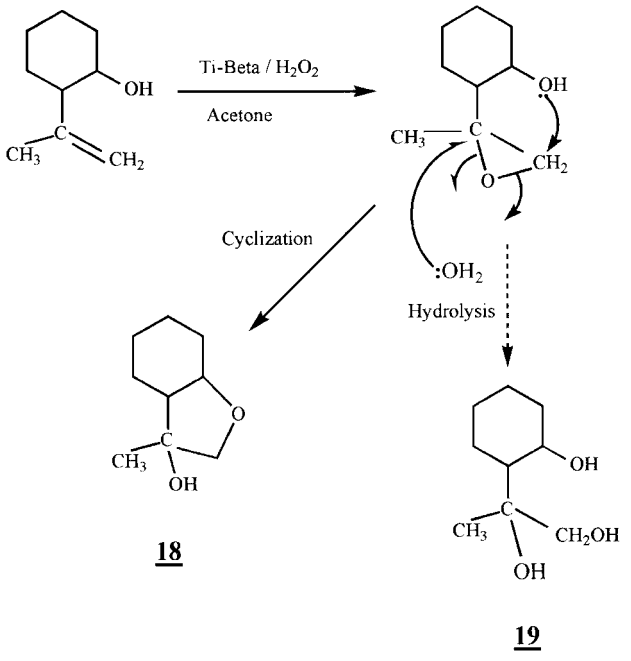
Substrate	Conv. (mol%)	Product selectivity (%) Cyclized product	Epoxide	Triol	Others
α-Terpineol[b]	17.8	26.8	60.3	—	12.9
α-Terpineol	73.4	68.4	21.8	—	9.8
Isopulegol	53.7	61.4	6.6	28.3	3.7
trans-p-Menth-6-ene-2,8-diol	90.0	95.0	—	—	5.0

[a] Reaction conditions: catalyst (Si/Ti = 31.5, Si/Al = 156); reaction time = 4–6 h; substrate : H_2O_2 : acetone or acetone/dichloromethane (1 : 1) = 1 : 1 : 5; temperature = 333 K.

[b] Catalyst TS-1 (Si/Ti = 29).

Isopulegol. In Scheme 6 the pathways for oxidative cyclization of isopulegol are shown. Only **18** formed as the major product from isopulegol. The cyclized product **18** is an endo product; a corresponding exo attack would have given rise to a very unstable 4-membered oxirane. The unstable epoxide intermediate undergoes dihydroxylation to the corresponding triol **19** to a considerable extent. Results of oxidative cyclization on this unsaturated alcohol containing one carbocyclic ring over Ti–Al-beta/H_2O_2 is in close agreement to that obtained in the case of an open system (3-buten-1-ol and 4-penten-2-ol). As shown in Table 2, the selectivity for triol in this case is high, which may be due to the more open structure of the initially formed epoxide. However, in this case acetone is used as a solvent, which is unlikely to favor dihydroxylation as observed in other substrates.

trans-p-Menth-6-ene-2,8-diol. Oxidation of *trans-p*-menth-6-ene-2,8-diol in the presence of an acetone and CH_2Cl_2 solvent mixture (used to avoid the phase seperation) leads to a very high selectivity for the cyclized product **20** (90% conversion after 6 h reaction time at 333 K). The reaction pathway is shown in Scheme 7. The selectivity toward cyclization is as high as 95%. Among the diastereomers the

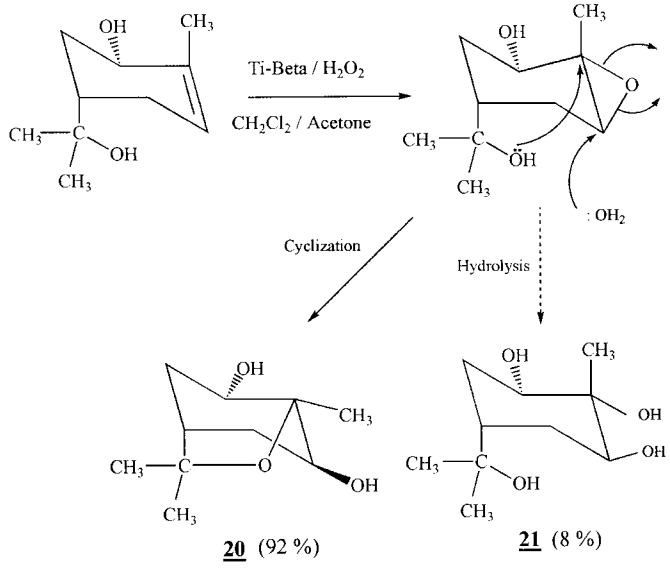


SCHEME 6. Oxidative cyclization of isopulegol over Ti-beta.

selectivity ratio is 86 : 14 (*cis*-dihydroxy vs *trans*-dihydroxy). Intermediate epoxide undergoes dihydroxylation to produce the corresponding diol **21** to some extent (8.0% selectivity).

Effect of Temperature

For 3-buten-1-ol and 4-penten-2-ol, where there is no possibility of exo attack in the intermediate epoxide, as this would give rise to unstable 4-membered oxacycles,



SCHEME 7. Cyclization pathway for *trans-p*-menth-6-ene-2,8-diol.

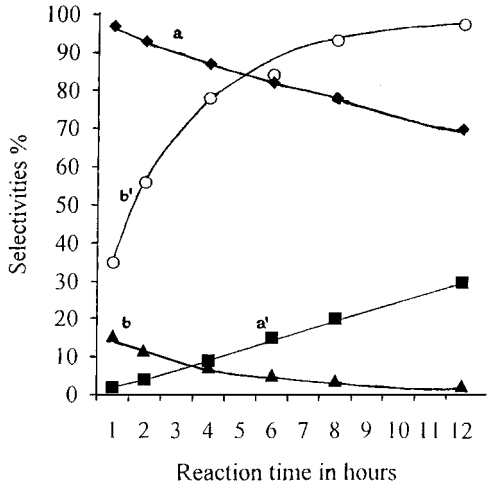


FIG. 1. Effect of temperature on selectivities in the oxidation of 3-butan-1-ol.

cyclization is favored at low temperatures only. In Fig. 1 the kinetics of oxidative cyclization for 3-buten-1-ol is shown. Curves a and a′ correspond to the selectivities for 3-hydroxytetrahydrofuran and 1,2,4-butanetriol, respectively, at 298 K. Curves b and b′ correspond to the same at 333 K. As seen from the figure, increasing the temperature from 298 to 333 K results in the dihydroxylation products being predominant. From the figure it is clear that the selectivity loss of 3-hydroxytetrahydrofuran does not correspond to the gain in selectivity for 1,2,4-butantriol, indicating that the triol formed mainly from the intermediate epoxide directly rather than via hydrolysis of 3-hydroxytetrahydrofuran.

Mechanistic Aspects

Although theoretical calculation on the transition state energies for 4-penten-1-oxyl radical (4) indicates the 5-exo product is strongly favored, in the TS-1/H_2O_2 system oxidation is believed to occur through titanium hydroperoxo species **4** (19, 20) (Scheme 3) and thus to be essentially ionic in nature. It is noteworthy that a different type of coordination of alcohol has been proposed recently (21). Restricted geometry inside the TS-1 channel (the MFI topology with intersecting 10-membered rings of 5.3 × 5.6 and 5.1 × 5.5 Å pore diameters and 0.10 cm^3/g internal void volume helps in bending the chain) might play a crucial role in the regioselective cyclization. The decreasing trend of the ratio of tetrahydropyrans to tetrahydrofurans from mesoporous MCM-41 (internal void volume very high, 0.95 cm^3/g) to large pore beta (22) followed by exclusive formation of tetrahydrofuran rings over medium pore TS-1 supports the above proposition.

In the oxidative cyclization (bifunctional behavior, epoxidation followed by acid catalyzed cyclization) observed

in the oxidation of linalool (22) over Ti–Al-beta and Ti–Al–MCM-41 the acidity at the Al sites was responsible for the oxirane ring opening leading to cyclized product. Since TS-1 employed here contains no Al (tetraethyl orthosilicate used as Si source is absolutely free of Al), the protonic character of the titanium hydroperoxo species **4** seems to promote the cyclization. In the transition state of the acid-catalyzed S_N2 cleavage of the oxirane ring, bond breaking proceeds faster than bond making, and carbon has acquired a considerable positive charge. Thus the reaction has considerable S_N1 character and the nucleophilic attack is easy to occur at the crowded carbon atom that can best accommodate the positive charge. However, for 3-buten-1-ol and (±) 4-penten-2-ol, the attack of the OH group on such a carbon leading to the 4-membered ring is unfavorable. The attack on the less crowded carbon occurs instead. At high temperatures the attack of water predominates over the attack of the intramolecular OH group. In contrast, for 4-penten-1-ol the attack of the OH group on the crowded carbon to produce **7** is favorable, excluding the occurrence of dihydroxylation even at high temperature.

In the case of products **2** and **3**, where dihydroxylation product predominates at higher temperature in the water medium, the lower stability of the endo adduct can be accounted for according to the Baldwin rule (25). For them the exo adduct is very unstable, as it would lead to 4-membered oxacycles, and dihydroxylation is the most favored pathway at higher temperature. In contrast, for the substrates of formula **1**, having $n = 2$, a favorable exo adduct leads to 5-membered oxacyles and having $n = 3$, a favorable exo adduct leads to 6-membered oxacycles following the Baldwin rule. Restricted geometry inside the zeolite pore further assists these processes. Interestingly, no intermediate epoxide is detected either while studying the kinetics of various constituents of the reaction mixture in the open chain unsaturated alcohols by GC, indicating that TS-1 catalyzed the present cyclization process at a very fast rate and ring closure takes place inside the cages of the zeolite immediately after the epoxidation.

In the case of isopulegol, from which a considerable amount of triol formed (28% in acetone), the intermediate epoxide is more hydorphobic than its open chain analogs (for 3-buten-1-ol 24% in H_2O and for 4-penten-2-ol 30% in H_2O, 0% in acetone). In our earlier results (18) we had shown that more hydrophobic epoxide undergoes rapid hydrolysis over the TS-1/H_2O_2/H_2O triphase system. This is because of the fact that compared to the intermediate the product triol is highly water soluble. Thus the presence of water facilitates the removal of the product from the catalyst. Since the endo adduct of isopulegol is relatively unstable, even the presence of water coming from dilute H_2O_2 and its decomposition product results in the formation of considerable dihydroxylation product.

CONCLUSIONS

In the presence of aqueous H_2O_2, TS-1 generates titanium hydroperoxo species **4**, which not only efficiently epoxydizes the double bond of the unsaturated alcohols of type **1** but also catalyzes the oxirane ring opening via intramolecular attack of hydroxy nucleophile, leading to oxacyclic ring formation. The reaction sequence indicates that when there is a choice between hydroxytetrahydrofuran and tetrahydropyran, the former exclusively formed under the present reaction conditions. However, when there is no possibility of smaller oxacycles other than the 6-membered one, hydroxytetrahydropyran forms exclusively. Large pore titanium silicate Ti-beta synthesized by the DGC method effectively catalyzes the oxidation of bulky unsaturated alcohols to the corresponding bicyclic compounds with high selectivity. Because the number of acid sites of this material is very low and pure titanium silicate TS-1 also catalyzes this type of cyclization, it is believed that the titanium sites are solely responsible for this reaction. The nature of the substituent groups present in the intermediate epoxide plays a crucial role in guiding the final product selectivities. The lower stability of **12** in turn may be responsible for the formation of hydroxytetrahydropyran (6-endo product) in this case to a considerable extent, which is not observed in other examples of open chain unsaturated alcohols, studied here. More open structured carbocyclic unsaturated alcohols, where endo attack is the only possibility of cyclization, lead to considerable dihydroxylation product even in the presence of a reactant amount of water.

ACKNOWLEDGMENT

A.B. thanks the Japan Society for the Promotion of Science (JSPS) for a postdoctoral fellowship.

REFERENCES

1. Lord, M. D., Negri, J. T., and Paquette, L. A., *J. Org. Chem.* **60**, 191 (1995).
2. Ting, P. C., and Bartlett, P. A., *J. Am. Chem. Soc.* **106**, 2668 (1984).
3. Tuladhar, S. M., and Fallis, A. G., *Tetrahedron Lett.* **28**, 523 (1987).
4. Hartung, J., Stowasser, R., Vitt, D., and Bringmann, G., *Angew. Chem. Int. Ed. Engl.* **35**, 2820 (1996).
5. Trost, B. M., and Li, C. J., *J. Am. Chem. Soc.* **116**, 10819 (1994).
6. Taramaso, M., Perego, G., and Notari, B., U.S. Patent 4410501 (1983).
7. Thangaraj, A., Kumar, R., Mirajkar, S. P., and Ratnasamy, P., *J. Catal.* **130**, 1 (1990).
8. Tatsumi, T., Nakamura, M., Negishi, S., and Tominaga, H., *J. Chem. Soc. Chem. Commun.*, 476 (1990).
9. Huybrechts, D. R. C., DeBruycker, L., and Jacobs, P. A., *Nature* **345**, 240 (1990).
10. Tatsumi, T., Yako, M., Nakamura, M., Yuhara, Y., and Tominaga, H., *J. Mol. Catal.* **78**, L41 (1993).

11. Tatsumi, T., and Jappar, N., *J. Catal.* **161**, 570 (1996).
12. Reddy, J. S., and Jacobs, P. A., *J. Chem. Soc. Perkin Trans. 1*, 2665 (1993).
13. Reddy, R., Reddy, J. S., Kumar, R., and Kumar, P., *J. Chem. Soc. Chem. Commun.*, 84 (1992).
14. Bhaumik, A., and Tatsumi, T., *Chem. Commun.*, 463 (1998).
15. Tatsumi, T., Xia, Q., and Jappar, N., *Chem. Lett.*, 677 (1997).
16. Jappar, N., Xia, Q., and Tatsumi, T., *J. Catal.*, in press.
17. Bhaumik, A., and Kumar, R., *J. Chem. Soc. Chem. Commun.*, 349 (1995).
18. Bhaumik, A., and Tatsumi, T., *J. Catal.* **176**, 305 (1998).
19. Bellussi, G., Carati, A., Clerici, M. G., Maddinelli, G., and Millini, R., *J. Catal.* **133**, 220 (1992).
20. Tantanak, D., Vincent, M. A., and Hillier, *Chem. Commun.*, 1031 (1998).
21. Vayssilov, G. N., and Van Santen, R. A., *J. Catal.* **175**, 170 (1998).
22. Corma, A., Iglesias, M., and Sanchez, F., *J. Chem. Soc. Chem. Commun.*, 1635 (1995).
23. Corma, A., Navarro, M. T., Pérez-Pariente, J., and Sánchez, F., *Stud. Surf. Sci. Catal.* **84A**, 69 (1994).
24. Tatsumi, T., and Jappar, N., *J. Phys. Chem. B* **102**, 7126 (1998).
25. Baldwin, J. E., *J. Chem. Soc. Chem. Commun.*, 734 (1976).