



Olefin epoxidation catalyzed by an air stable-supported titanium catalyst

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Abstract

Grafting of $\text{Ti}(\text{O}^i\text{Pr})_4$ onto the surface of preactivated silica affords an efficient and selective solid olefin epoxidation catalyst. In conjunction with tert-butylhydroperoxide ($^t\text{BuOOH}$), it can effectively oxidize alkenes, dienes and allylic alcohols. The catalyst preparation is very simple and, once made, the material can be handled in air.

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1. Introduction

Epoxides are versatile reactive intermediates in organic synthesis since they are readily transformed into diols and polyols, polyethers, amino alcohols, etc. which are the basis for a wide variety of consumer products. As a consequence, catalytic epoxidation of alkenes has been the subject of many academic and industrial investigations [1–4]. Homogeneous-based systems include: (a) $\text{Ti}(\text{O}^i\text{Pr})_4$ with diethyltartrate ester (DET) which has been used for the asymmetric oxidation of allylic alcohols to epoxy alcohols in conjunction with tert-butylhydroperoxide $^t\text{BuOOH}$, resulting in high ee (90%) but modest yields [2]; (c) chiral manganese complexes with Schiff base ligands which can epoxidize simple olefins such as styrene derivatives [3]. However, homogeneous catalysts

must be separated in order to recover and recycle them, and reaction products must be purified. Heterogeneous catalysts have the advantage of ease of handling and recovery of both the catalyst and the products. Furthermore, heterogeneous catalysts have the potential to be used in gas phase processes (i.e. without solvent), which may result in appreciably lower operating cost [5].

A heterogeneous epoxidation catalyst developed at Shell has been tested with a wide variety of alkene substrates [6]. The catalyst is prepared by impregnation of silica by a titanium alkoxide compound followed by calcination. The supported catalyst, thus prepared, overcomes the problems of slow reaction rates and poor selectivity in the epoxidation of alkenes by homogeneous titanium isopropoxide and $^t\text{BuOOH}$. Unfortunately, the Shell catalyst is rapidly deactivated by moisture, necessitating the cumbersome use of strictly anhydrous reagents and inert atmospheres. Vanadium montmorillonite has been reported to catalyze the epoxidation of allylic alcohols [7], while titanium K10-montmorillonite is an efficient catalyst

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for the asymmetric epoxidation of primary alcohols in the presence of diethyltartrate ester [8]. Laszlo et al. [9] described the epoxidation of nonfunctionalized alkenes by vanadium oxide in moderate yields. Moisture-tolerant zeolite-based titanium catalysts such as TS-1 have been used for epoxidation in conjunction with anhydrous ^tBuOOH or aqueous H₂O₂ [10–14]. However, because the zeolite restricts access to the Ti sites, reactions are limited to unhindered olefins.

Recently, Mayoral and co-workers [15,16] described the preparation of SiO₂-supported titanium catalysts derived from Ti(OⁱPr)₄ which are active for the epoxidation of cyclohexene without calcining. The active sites were suggested to be (≡SiO)₂Ti(OⁱPr)₂. Bouh et al. [17] investigated the nature of the active sites generated by gas phase grafting of titanium isopropoxide onto aerosil silica. On silica partially dehydroxylated at 200 °C, the exclusive product is [(≡SiO)₂Ti(OⁱPr)₂]₂(O). In this paper, we present a study of alkene epoxidation using this catalyst.

2. Experimental

2.1. Materials

Ti(OⁱPr)₄ (99.99%, Aldrich) was stored in a Schlenk tube under N₂ and transferred into reaction vessels via the vapor phase using standard breakseal and vacuum techniques, as previously described by Bouh et al. [17]. Alkenes were distilled under vacuum and stored under argon over molecular sieves prior to use. All solvents were dried over sodium and benzophenone.

2.2. Characterization of the supported titanium catalyst

A nonporous pyrogenic silica (Degussa Aerosil-200, BET surface area 183 m²/g) was used as the support for all experiments. For in situ IR experiments, the silica was pressed at 125 kg/cm² into a self-supporting disk of diameter 1.6 cm, containing 2–4 mg of silica/cm². Transmission infrared spectra were recorded in an in situ cell (volume ~300 ml) on a dry air-purged Mattson Research series FTIR equipped with a DTGS detector. For both background

and sample spectra, 32 scans were recorded at a resolution of 2 cm⁻¹.

The silica pellet was first dehydroxylated under dynamic vacuum for at least 4 h at 200 °C. An excess of Ti(OⁱPr)₄ vapor was brought in contact with silica powder for several hours, then unreacted material and volatile products were transferred to a liquid nitrogen cold trap. An excess of anhydrous ^tBuOOH (99%, 5–6 M in decane, Aldrich) was introduced into the reactor in order to form the corresponding titanium tert-butylperoxo complex. 2-Propanol and excess ^tBuOOH were removed by simple evacuation.

2.3. Preparation of the catalyst for reactivity studies

The catalyst was prepared as described above, except that instead of being pressed into a thin pellet, ca. 1 g of silica was first compacted in a pellet die, then coarsely ground in a mortar to make it easier to handle.

2.4. Titanium analysis

About 20 mg of solid catalyst was stirred in 5 ml of 10% H₂SO₄ solution for 30 min. The suspension was treated with 30% aqueous H₂O₂ (0.03 ml/ml of sample solution) to form the yellow peroxotitanium complex [18]. After filtration and dilution to a known volume with distilled water, the absorbance at λ_{max} = 408 nm was measured. The absorbance was converted to titanium concentration using a calibration curve prepared from a 1 g/l standard Ti solution (Aldrich) under the same conditions.

2.5. Oxidation reactions (liquid olefins)

About 100 mg of catalyst (0.2 wt.% Ti loading) was transferred into a Schlenk tube inside a glove box. The alkene (3 mmol) was added by syringe on a Schlenk line (nitrogen atmosphere) with constant stirring. Finally, 3–4 mmol ^tBuOOH (5–6 M in decane) was added (nitrogen atmosphere) with constant stirring. The reaction mixture was heated to the desired reaction temperature for the specified time. The catalyst was removed by filtration and washed with dry THF. Reaction mixtures were analyzed by gas chromatography (GC) after diluting a small amount

of sample with THF. In some cases (allylic alcohols), the epoxide was purified by column chromatography using diethyl ether as the eluant.

2.6. Oxidation of propylene

About 100 mg of catalyst and 3 mmol of *t*BuOOH were added to a glass autoclave inside a glove box. The reactor was flushed three times with N₂, then pressurized with propylene (3 bar). The autoclave was heated to 60 °C. After 16 h, the reaction was stopped and the gaseous products analyzed by GC as well as GC-mass spectrometry (MS) using a gas-tight syringe.

2.7. Gas chromatography

Reaction products were analyzed on an Agilent Gas Chromatograph, 19091J-413, equipped with a HP-S capillary column (5% phenylmethylsiloxane), of dimensions 30.0 m × 32.0 μm × 0.25 μm. A typical GC program is 30 °C (5 min)–10 °C/min–250 °C (5 min).

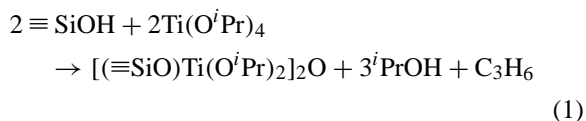
2.8. NMR Data

All NMR spectra were recorded in CDCl₃ with TMS as an internal standard on Gemini 200 spectrometer.

The spectra of 1,2-epoxyhexane, styrene oxide, cyclohexene oxide, 1,2-epoxydecane, 1,2-epoxyoctane, trans-2,3-epoxy-1-butanol, trans-2,3-epoxy-3-phenylbutanol, 2,3-epoxy-3,7-dimethyl-6-octanol were in accord with literature data.

3. Results and discussion

Grafting of titanium(IV) isopropoxide onto silica at room temperature under vacuum (10⁻⁴ Torr) results in irreversible chemisorption and formation of grafted titanium complexes. The stoichiometry of grafting has been measured and is consistent with the reaction shown in Eq. (1) [17].

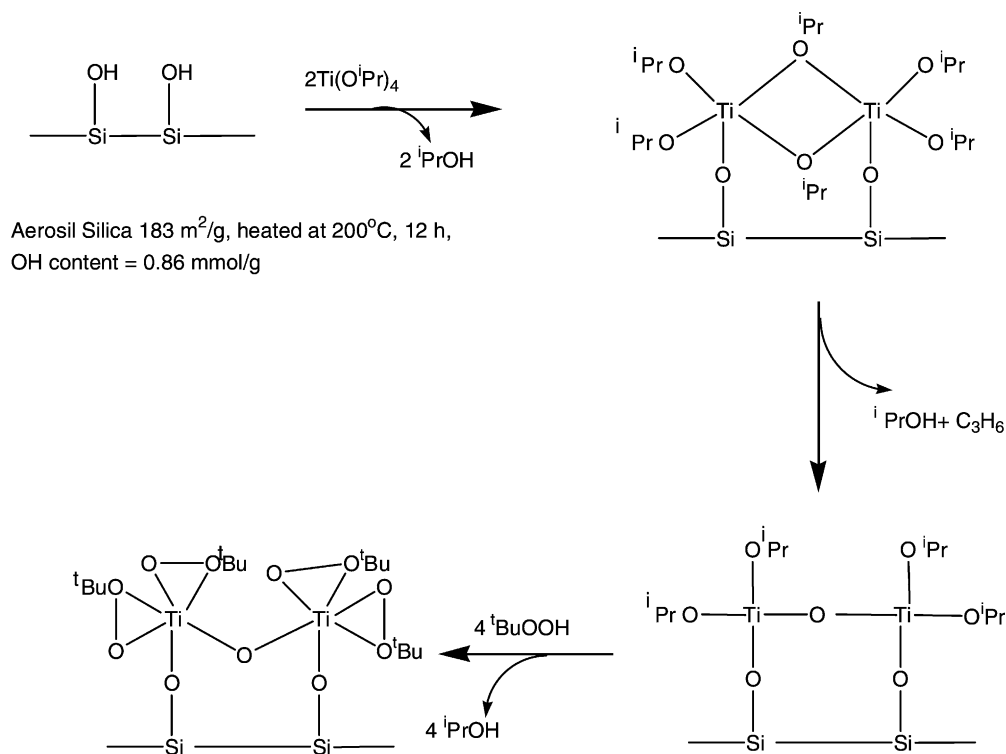


Commercial Aerosil-200 silica, partially dehydroxylated at 200 °C, contains 0.86 mmol accessible OH/g [17]. Grafting of Ti(O^{*i*}Pr)₄ onto this silica resulted in typical titanium loadings from 0.2 to 0.5 wt.% Ti loading (powder experiments) up to 3.9 wt.% Ti (pellet experiments). The variation in titanium loading is a consequence of the vastly different amounts of silica used in the two kinds of experiments (silica pellets weigh 10–20 mg, while up to 1 g of silica was used for powder experiments). The formation of the catalyst active sites is shown in Scheme 1.

We previously demonstrated that, regardless of the extent of reaction of the surface hydroxyl groups, grafting of Ti(O^{*i*}Pr)₄ occurs according to the stoichiometry shown in Eq. (1) [17]. Treatment of the catalyst with *t*BuOOH results in the quantitative displacement of the alkoxide ligand and formation of the titanium active sites (Scheme 1).

The grafting reaction can be followed by in situ IR spectroscopy. The IR spectrum of a silica pellet partially dehydroxylated at 200 °C shows a peak at 3747 cm⁻¹, corresponding to the stretching vibration of the surface hydroxyl groups (Fig. 1). Grafting of Ti(O^{*i*}Pr)₄ onto the surface results in the disappearance of this absorbance and the appearance of new peaks at ca. 2900 cm⁻¹ and 1300–1500 cm⁻¹, due to vibrations of the 2-propoxide ligands. The (Ti–O–Ti) vibration appears at 680 cm⁻¹, and is difficult to observe due to its proximity to intense silica lattice modes in this region. Upon exposure of the catalyst to *t*BuOOH, the appearance of the bands in the C–H stretching and deformation regions changes, demonstrating the formation of tert-butyl peroxotitanium complexes on the silica surface. In addition a new absorbance appears at ca. 855 cm⁻¹, assigned to ν(O–O) vibration [19]. Finally, addition of an excess of 1-decene results in oxygen atom transfer, as shown by the formation of 1,2-epoxydecane (confirmed by GC and GC-MS), and by the complete disappearance of the ν(O–O) band at 855 cm⁻¹.

In order to further explore its robustness and effectiveness, the catalyst was prepared by grafting Ti(O^{*i*}Pr)₄ onto larger quantities of powdered silica. The catalyst was used for the epoxidation of alkenes in conjunction with anhydrous *t*BuOOH. The results are shown in Table 1, while the catalytic process is depicted in Scheme 2.



Scheme 1. Procedure for the preparation of silica-supported titanium catalyst.

Although the conversion was relatively low high selectivity for the epoxide was observed in all cases. The use of more polar solvents such as dichloromethane or tetrahydrofuran drastically reduced catalytic activity. Even the use of a nonpolar solvent such as cyclohexane reduced the catalytic activity. Therefore, epoxidations were carried out without solvent, by suspending the catalyst in neat olefin. Gas phase epoxidation of propene using the supported catalyst led to 40% conversion, based on the analysis of the gaseous product obtained from the reaction mixture. The rather low conversion may be due to our inability to stir the catalyst in the autoclave.

Low conversion to the epoxide was observed when reactions were carried out at room temperature with the catalyst and ^tBuOOH/decane. However, at 60–65 °C, 98% conversion of cyclohexene to cyclohexene oxide was obtained, with a turnover number of 62.5. Reactions with other terminal alkenes (1-decene, styrene) under identical conditions gave more than 80% conversion with acceptable turnover

numbers. Among all the alkenes studied, cyclohexene shows the highest reactivity. Surprisingly, the catalyst demonstrated poor reactivity towards 1-hexene and 1-octene. Sterically crowded alkenes, such as 2,5-dimethyl-3-hexene, did not show any conversion, probably due to the difficulty with which the olefin approaches the active site. Isolated double bonds can also be epoxidized with high selectivity for the epoxide but the reactivity depends on the stereochemistry around the double bond as well the purity of the substrates. Finally in agreement with the report of Cativiela et al. [15], we find that the catalyst is air-stable, and can be used in air on the bench top (Table 1, entry 14). The insensitivity of the catalyst to moisture is attributed to its dinuclear oxo-bridged structure, since metal oxoalkoxides are more resistant to hydrolysis than metal alkoxides.

Allylic alcohols such as geraniol, nerol, crotyl alcohol and cinnamyl alcohol are effectively epoxidized in the presence of the supported catalyst and ^tBuOOH. Reactions with geraniol and nerol were carried out

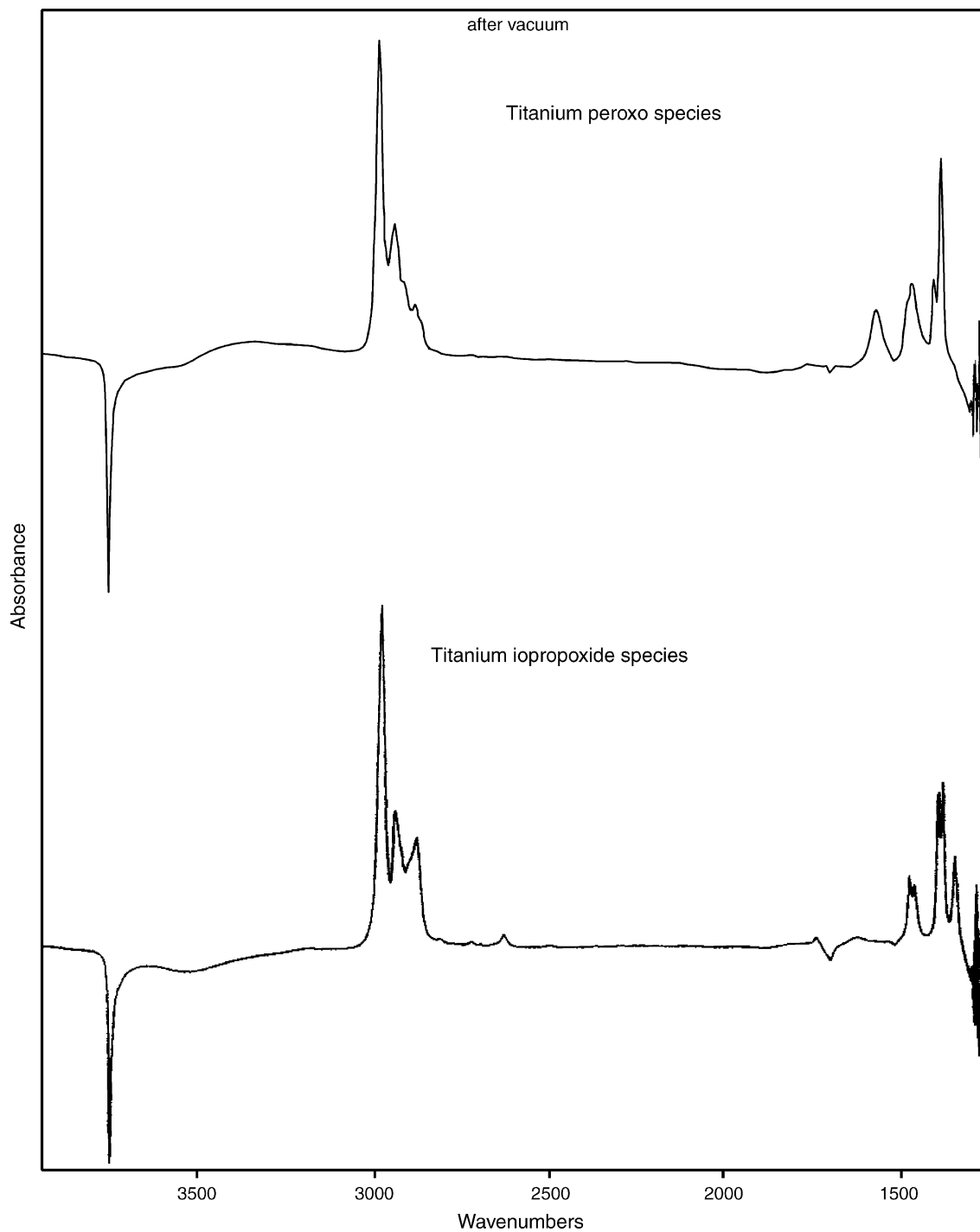


Fig. 1. In situ IR difference spectra of a self-supporting disk of silica-200; (a) treated with $\text{Ti}(\text{O}^i\text{Pr})_4$; (b) $\text{Ti}(\text{O}^i\text{Pr})_4$ treated with $^t\text{BuOOH}$ to give Ti-peroxy species. The reference spectrum of silica-200 has been subtracted such that negative peaks correspond to vibrations, which are no longer present on the silica surface after reaction.

Table 1
Catalytic activity of Ti/SiO₂ for epoxidation of olefins^a

Entry no.	Substrate	Amount of Ti (mmol)	Temperature (°C)	Time (h)	Conversion (%)	TON mmol/mmole Ti/h	Selectivity alkene (%)
1	Cyclohexene	0.003	r.t.	5	3		
				24	11		
				48	52		
				72	47	10	–
						62.5	100
2	Cyclohexene	0.003	50	16	98		
3	1-Decene	0.004	65	3	37		
				5	56		
				20	77		
				24	80	25	94
					30		98
5	Styrene	0.004	60	20	86	32.2	87
6	2,5-Me ₂ -3-hexene	0.004	50	24	–		
7	1-Octene	0.004	60	20	54		
				36	70		
				40	72	13.1	98
				20	40		96
					40		96
8	Propene	0.004	60	20	40		
9	Geraniol	0.004	r.t.	20	94 ^b	62.5	96
					4 ^c		
					62 ^b , 3 ^c		
10	Nerol	0.004	–20 °C	20	62 ^b , 3 ^c		
				40	73 ^b , 10 ^c	13.7	87
11	Cinnamyl alcohol	0.004	r.t.	16	0		
				60	44	21.1	
					56		
12	Crotyl alcohol	0.004	60	20	45	16.8	100
13 ^d	Styrene	–	r.t.	20	0		
14 ^e	Styrene	0.004	60	5	45	67.5	

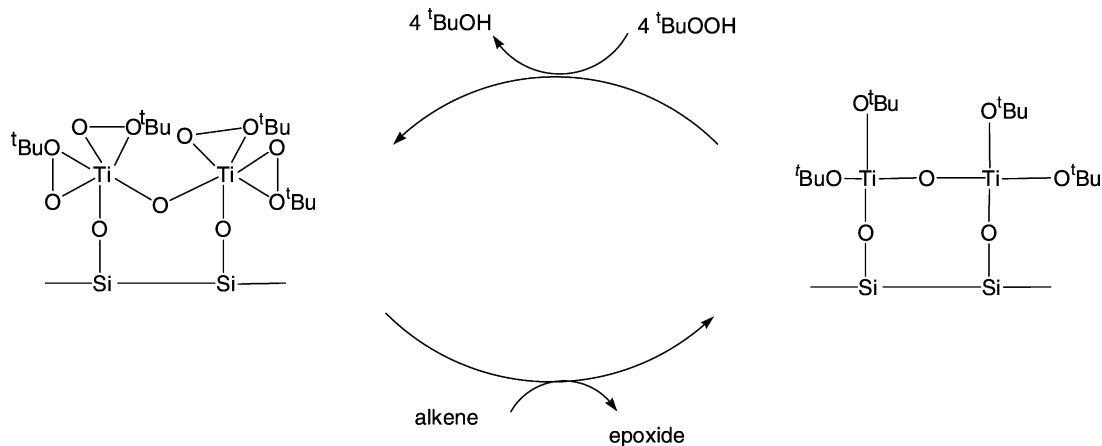
^a Conditions: reactions were carried out without solvent. Alkene: 3 mmol, ^tBuOOH: 3–4 mmol.

^b Allylic epoxidation.

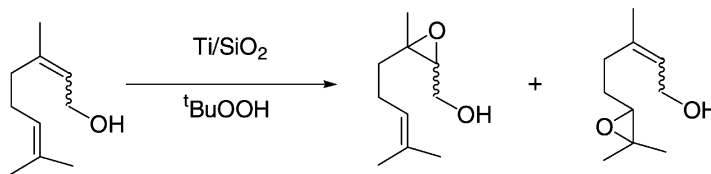
^c Terminal epoxidation.

^d No reaction with homogeneous Ti(OⁱPr)₄ and ^tBuOOH.

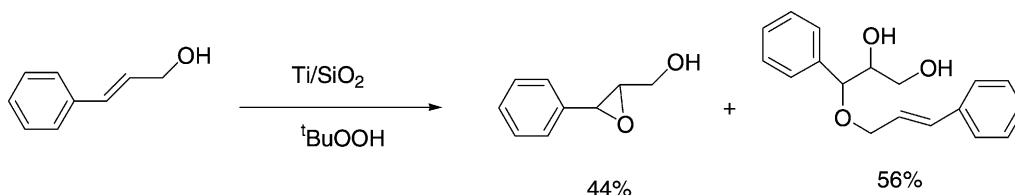
^e Catalyst was exposed for 2 h to open air.



Scheme 2. Catalytic cycle for olefin epoxidation.



Scheme 3. Epoxidation of nerol or geraniol.



Scheme 4. Epoxidation of cinnamyl alcohol.

at room temperature, since addition of $t\text{BuOOH}$ at 60°C to the mixture of catalyst and allylic alcohol resulted in significant heat evolution and as a result, more byproducts (a result of terminal epoxidation) were formed. Generally, allylic alcohols reacted faster than isolated double bonds. Two different epoxide products were observed by GC for nerol and geraniol. Higher temperatures favor the epoxidation of the double bond at the C_6 position over the allylic one (Scheme 3).

In the case of cinnamyl alcohol, a byproduct resulted from opening of the epoxide ring by the alcohol (Scheme 4). Unreacted hydroxyl groups on the catalyst surface may act as acid catalysts for this reaction, which is favored by the stability of the benzylic cation intermediate. Under identical conditions, reaction of crotyl alcohol led to only 45% conversion.

In summary, grafting of $\text{Ti}(\text{O}^i\text{Pr})_4$ onto silica partially dehydroxylated at 200°C leads to the formation of titanium surface complexes which are effective for the epoxidation of isolated double bonds as well as allylic alcohols, in the absence of added solvent and even in the gas phase. The catalyst shows highest activity towards cyclohexene, geraniol and nerol.

Acknowledgements

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