

A new titanium–silica catalyst for the epoxidation of alkenes

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Abstract

Silica gel treated with $\text{Ti}(\text{O}^i\text{Pr})_4$ is an efficient catalyst for the TBHP epoxidation of non-functionalized alkenes, dienes, and allylic alcohols. This catalyst is more efficient than those obtained from other titanium precursors; it must be activated at 140°C prior to use, it can be recovered and stored in the open air. The reactivity of different olefinic substrates is compared and is shown to be dependent on the structure, which allows the selective epoxidation of compounds containing different kinds of double bonds.

Keywords: Epoxidation; Titanium silica; TBHP; Non-activated alkenes

1. Introduction

Epoxides are versatile and useful intermediates in organic synthesis and, as a consequence, the epoxidation of alkenes is a field of both academic and industrial importance. This has led to great interest in the development of new heterogeneous systems able to catalyze these reactions [1]. Vanadium-exchanged montmorillonites have been used in the epoxidation of allylic alcohols [2], and it has been reported [3] that titanium K10 montmorillonite is an efficient catalyst in the asymmetric epoxidation of primary allylic alcohols, in the presence of chiral tartrates. Laszlo et al. [4] have obtained moderate chemical yields for the epoxidation of

non-functionalized alkenes catalyzed by vanadium oxide. The preparation of catalysts able to promote the epoxidation of alkenes with hydrogen peroxide has attracted much attention. Excellent results have been described using titanium silicalite TS-1 as a catalyst [5], but the reaction is limited to unhindered olefins [6]. The larger pore size of titanium-beta zeolite [7,8] makes it useful to promote the oxidation of bulkier organic molecules. However, neither the conversion nor the selectivity, for the epoxide, described are high [9].

Recently, large-pore Ti-zeolites, such as Ti-beta [8] and Ti-MCM-41 [10], have been used to promote alkene epoxidation with *tert*-butyl hydroperoxide, which greatly increases the selectivity in the epoxide with regard to the oxidant. Titanium–silica aerogels, with highly dispersed titanium, have been tested in the epoxidation of olefins with cumene hydroperoxide. In particu-

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lar, the mixed oxide containing 20% TiO₂ displays high activity and selectivity [11].

The heterogeneous catalyst that has been tested in the epoxidation of the broadest range of alkenes is the titanium–silica catalyst developed by Shell [12], prepared by impregnation and further calcination. It has been claimed [13] that this catalyst overcomes some of the problems of slow reaction rates and formation of byproducts observed when epoxidation of non-activated olefins is carried out using alkyl hydroperoxides and titanium alkoxides in homogeneous phase. It has been suggested [1] that the active centers of this solid consist of titanyl groups (Ti^{IV}=O) bound to siloxane ligands, which catalyze the epoxidation of non-functionalized alkenes, allyl chloride and allylic alcohols with organic hydroperoxides at high temperatures. We have described the preparation of several titanium–silica and titanium–alumina supported solids which catalyze Diels–Alder reactions [14]. Very recently we have reported that Ti(OⁱPr)₄ supported on silica gel is an efficient catalyst for the epoxidation of olefins at room temperature and we have shown the presence of isopropyl groups in the solid [15]. In this paper we present a complete study of this catalyst and other related solids.

2. Experimental

2.1. Preparation of the catalyst

Silica gel (Merck 60) was heated at 140°C under vacuum overnight prior to use. The corresponding titanium compound (Table 2, 7.5 mmol) was added under argon to a suspension of activated silica gel (5 g) in anhydrous toluene (50 ml) and the mixture was refluxed for 48 h. After cooling to room temperature, the solution was removed with a syringe, the solid filtered off and repeatedly washed with anhydrous toluene. The titanium–silica catalysts were activated at 50, 140 or 600°C under vacuum overnight prior to use.

Table 1
Retention times (R.T.) of reagents and products from gas chromatographic analyses

Olefin	R.T. olefin (min)	R.T. epoxidation products (min)
1-Hexene	2.55	5.96
Styrene	7.28	9.35 (epoxides), 8.99 (acetophenone), 7.93 (benzaldehyde)
Cyclohexene	3.72	6.69
Norbornene	4.60	7.89
Cyclododecene	11.26, 11.35 ^a	12.41, 12.56 ^a
<i>cis</i> -2-heptene	4.53	7.09
<i>trans</i> -2-heptene	4.39	6.74
1-methylcyclohexene	5.57	7.14
(<i>R</i>)-carvone ^b	10.82	13.64, 13.73
(<i>R</i>)-limonene	8.93	9.92, 9.97 (major), 10.20, 10.23 (minor)
(<i>R</i>)- β -citronellol	10.21	10.91, 10.93
1,3-cyclohexadiene	3.25	6.60
Crotyl alcohol	3.31	5.18
Nerol	10.22	10.83 (major), 11.41 (minor)

^a *cis* + *trans*.

^b In this case the following oven temperature program was used: 45°C (4 min) — 25°C/min — 150°C (7 min) — 25°C/min — 250°C (5 min).

The surface area of the Ti(OⁱPr)₄-modified silica, calculated from BET nitrogen isotherms, determined at 77 K, is 360 m² · g⁻¹. Neither X-ray diffraction patterns nor normalized XANES spectra at the Ti–K edge indicate the presence of TiO₂.

2.2. Gas chromatographic methods

Most of the reactions were monitored by gas chromatography (GC) (FID from Hewlett-Packard 5890 II), using a cross-linked methyl silicone column (25 m × 0.22 mm × 0.33 μm), helium as carrier gas (18 psi), injector temperature 230°C, detector temperature 250°C, oven temperature program: 45°C (4 min) — 25°C/min — 250°C (5 min). Isooctane (retention time = 4.03 min) was used as internal standard and TBHP (retention time = 4.21 min) as the oxidant. The retention times of the olefins and the oxidation products are given in Table 1.

2.3. Reactions with non-functionalized olefins

2.3.1. General procedure

Under argon, the titanium–silica catalyst (1 g) was added to a mixture of an olefin (36 or 96 mmol, Tables 2 and 6) and 4 ml of a 3 M solution of TBHP in isooctane (12 mmol). The mixture was shaken and the reaction monitored by GC. The catalyst was removed by filtration and washed with dry methylene chloride. The reagent excess was eliminated by evaporation under reduced pressure to furnish the product or product mixture. In some cases the epoxide had to be purified by column chromatography on silica gel using the following eluents: hexane/diethyl ether 4/6 [(*S*)- β -citronellol], methylene chloride [(*R*)-carvone], hexane/methylene chloride 1/1 [(*R*)-limonene].

Products were characterized by GC-MS and by $^1\text{H-NMR}$ (CDCl_3 , δ ppm).

- 1,2-epoxyhexane: 2.89 (bs, 1H), 2.72 (t, 1H; 4.5 Hz), 2.44 (dd, 1H; 4.8 Hz, 2.7 Hz), 1.1–1.6 (m, 6H), 0.89 (t, 3H; 7.1 Hz).
- Phenylloxirane: 7.3 (m, 5H), 3.85 (dd, 1H; 3.9 Hz, 2.8 Hz), 3.13 (dd, 1H; 5.4 Hz, 4.4 Hz), 2.79 (dd, 1H; 5.5 Hz, 2.6 Hz).

- 1,2-epoxycyclohexane: 3.08 (bs, 2H), 1.88 (m, 2H), 1.79 (m, 2H), 1.37 (m, 2H), 1.20 (m, 2H).
- 1,2-epoxycyclododecane (*cis* + *trans*): 2.86 (m, 1H*cis*), 2.68 (1H*trans*), 1.76 (m, 2H), 1.2–1.5 (m, 18H).
- *exo*-2,3-epoxybicyclo[2.2.1]heptane: 3.03 (bs, 2H), 2.41 (bs, 2H), 1.43 (m, 2H), 1.1–1.3 (m, 3H), 0.67 (d, 1H; 9 Hz).
- *cis*-2,3-epoxyheptane: 3.01 (m, 1H), 2.86 (m, 1H), 1.3–1.5 (m, 6H), 1.22 (d, 3H; 5.4 Hz), 0.89 (t, 3H; 7.1 Hz).
- *trans*-2,3-epoxyheptane: 2.91 (d, 1H; 2.9 Hz), 1.82 (m, 4H), 1.65 (m, 2H), 1.38 (m, 2H), 1.25 (s, 3H).
- 1,2-epoxy-3-cyclohexene: 5.90 (m, 2H), 3.47 (bs, 1H), 3.19 (bs, 1H), 2.0–2.2 (m, 2H), 1.55 (m, 2H).
- (*R*)-1-methyl-1-[4-(2-methyl-1-oxo-2-cyclohexenyl)]oxirane (mixture of diastereomers): 6.66 (bs, 1H), 2.62 (d; 4.6 Hz) + 2.59 (d; 4.6 Hz)(1H), 2.52 (d) + 2.50 (d)(1H), 2.0–2.4 (m, 5H), 1.68 (bs, 3H), 1.24 (s) + 1.23 (s)(3H). Isolated yield: 47%.
- 1,2-epoxy-1-methyl-(*R*)-4-isopropenyl-cyclohexane (mixture of diastereomers): 4.63 (bs, 2H), 3.02 (bs) + 2.96 (d; 5.3 Hz)(1H), 1.2–

Table 2

Results obtained for the TBHP epoxidation of cyclohexene at room temperature using 12 mmol of TBHP (3 M solution in isooctane) and 1 g of catalyst

Catalyst precursor	Activation	Silylating agent	Olefin/TBHP	<i>t</i> (h)	Conv. TBHP ^a (%)	S_{peroxide} (%)	Conv. cyclohexene ^b (%)	S_{alkene} (%)
Ti(O ^{<i>i</i>} Pr) ₄ ^c	—	—	8:1	1.0	4	—	—	—
	50°C	—	8:1	1.0	67	—	—	—
	140°C	—	8:1	1.0	100	85	87	98
	600°C	—	8:1	1.0	100	75	84	89
	140°C	HMDS	8:1	1.5	18	—	—	—
	140°C	HMDS	8:1	7.0	55	—	—	—
	140°C	BDMSC	8:1	7.0	52	—	—	—
	140°C	—	3:1	1.0	67	94	64	98
	140°C	—	3:1	3.5	86	90	79	98

^a Determined by GC.

^b Referred to the maximum.

^c The catalyst contains 1.18 mmol of Ti per gram, determined by plasma emission spectroscopy.

2.1 (m, 7H), 1.66 (s) + 1.64 (s)(3H), 1.29 (s) + 1.27 (s)(3H).

- (*R*)-1-methyl-1-[4-(1-methyl-1-cyclohexenyl)]oxirane (mixture of diastereomers): 5.33 (bs, 1H), 2.61 (d; 4.4 Hz) + 2.60 (d; 4.4 Hz)(1H), 2.53 (d; 4.8 Hz) + 2.50 (d; 4.8 Hz)(1H), 1.2–2.1 (m, 7H), 1.61 (s, 3H), 1.24 (s) + 1.23 (s)(3H).

- 6,7-epoxy-(*S*)-3,7-dimethyloctanol (mixture of diastereomers): 3.62 (m, 2H), 2.66 (t, 1H; 6.0 Hz), 1.85 (bs, 1H), 1.3–1.6 (m, 7H), 1.26 (s, 3H), 1.22 (s, 3H), 0.87 (d, 3H; 6.2 Hz). In this case, the diastereomers cannot be distinguished by ¹H-NMR, but they can be by ¹³C-NMR (CDCl₃, δ ppm): 64.67 + 64.64, 60.84, 58.43 + 58.29, 39.79 + 39.54, 33.69 + 33.65, 29.39 + 29.19, 26.39 + 26.17, 19.64 + 19.43, 18.67 + 18.62. Isolated yield: 65%.

2.3.2. In methylene chloride

Under argon, the catalyst (0.25 g) was added to a solution of cyclohexene (1.48 g, 18 mmol) and TBHP (3 ml of a 3 M solution in isooctane, 9 mmol) in dry methylene chloride (4.2 ml). The mixture was shaken and the reaction analyzed as described above. The catalyst, separated by filtration and thoroughly washed with dry methylene chloride, was activated at 140°C and reused. The selectivities are calculated as $S_{\text{reagent}} (\%) = 100 \cdot [\text{epoxide}] / ([\text{reagent}]_i - [\text{reagent}]_t)$. All concentrations are molar, *i* states for the initial value and *t* for the value at the time given, and reagent can be the olefin or the epoxide.

2.4. Reactions with allylic alcohols. General procedure

Under argon, the titanium–silica catalyst (1 g) was added to a solution of the allylic alcohol (2 mmol) and TBHP (1 ml of a 3 M solution in isooctane) in dry methylene chloride (3 ml). The reaction was shaken and monitored by GC (crotyl alcohol and nerol) or TLC in diethyl ether (cinnamyl alcohol). The catalyst was removed by filtration and thoroughly washed with

methylene chloride. 2,3-epoxy-1-butanol was obtained by evaporation under reduced pressure. The products obtained from cinnamyl alcohol were purified by column chromatography on silica gel using diethyl ether as an eluent. The products obtained from nerol were separated by column chromatography on silica gel using diethyl ether as an eluent.

Products were characterized by GC-MS and by ¹H-NMR (CDCl₃, δ ppm).

- *trans*-2,3-epoxy-1-butanol: 3.85 (d, 1H; 12.6 Hz), 3.56 (d, 1H; 12.6 Hz), 3.01 (dc, 1H; 5.2 Hz, 2.3 Hz), 2.86 (ddd, 1H; 4.5 Hz, 2.4 Hz, 2.2 Hz), 2.52 (bs, 1H), 1.30 (d, 3H; 5.3 Hz).

- *trans*-2,3-epoxy-3-phenylbutanol: 7.3 (m, 5H), 4.02 (dd, 1H; 12.8 Hz, 1.6 Hz), 3.91 (d, 1H; 2.1 Hz), 3.76 (bd, 1H), 3.21 (ddd, 1H; 3.9 Hz, 2.1 Hz, 2.1 Hz).

- 2,3-epoxy-3,7-dimethyl-6-octenol: 5.06 (t, 1H; 7.2 Hz), 3.78 (bd, 1H), 3.61 (dd, 1H; 12.3 Hz, 6.9 Hz), 2.93 (dd, 1H; 6.9 Hz, 4.2 Hz), 2.21 (bs, 1H), 2.07 (m, 2H), 1.65 (s, 3H), 1.58 (s, 3H), 1.47 (m, 2H), 1.31 (s, 3H). Isolated yield: 42%.

- 6,7-epoxy-3,7-dimethyl-2-octenol: 5.47 (t, 1H; 7.2 Hz), 4.09 (m, 2H), 2.70 (dd, 1H; 5.1 Hz, 7.8 Hz), 2.23 (m, 2H), 1.94 (bs, 1H), 1.73 (s, 3H), 1.60 (m, 2H), 1.27 (s, 3H), 1.24 (s, 3H). Isolated yield: 7%.

2.5. Competitive reactions

Under argon, the titanium–silica catalyst (0.5 g) was added to a mixture of 9 mmol of each olefin (Table 7) and TBHP (2 ml of a 3 M solution in isooctane). Reactions were shaken and analyzed by GC at regular times, 15 min after the start of the reaction.

3. Results and discussion

3.1. Selection of the catalyst

Silica gel (Merck, silica gel 60, 63–200 nm) was treated with Ti(O^{*i*}Pr)₄ (see the experimen-

Table 3

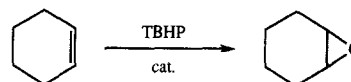
Results obtained for the TBHP (9 mmol) epoxidation of cyclohexene (18 mmol), in CH₂Cl₂ (4.2 ml) at 15°C, using 0.25 g of catalyst

Activ. T (°C)	Result	Reaction time (h)				
		0.5	1.0	2.0	7.0	24.0 ^a
140°C	conv. TBHP (%)	23	31	42	64	80
	S _{peroxide} (%)	81	82	81	83	91
	conv. cyclohexene (%)	19	25	36	57	75
	S _{cyclohexene} (%)	97	98	96	98	98
600°C	conv. TBHP (%)	39	47	60	82	93
	S _{peroxide} (%)	75	77	75	75	81
	conv. cyclohexene (%)	31	41	56	77	90
	S _{cyclohexene} (%)	87	89	88	89	89

^a The final results are determined after thoroughly washing the catalyst to remove the reagents and products adsorbed. Indeed, some TBHP is adsorbed, which accounts for the increase in selectivity.

tal section). Catalysts were tested as obtained or activated by heating under vacuum at 50, 140 or 600°C overnight prior to use. Some samples of catalysts activated at 140°C were ‘end-capped’ by treatment with hexamethyldisilazane (HMDS) or *tert*-butyldimethylsilyl chloride (BDMSC). The catalytic activity of all these solids was compared to the TBHP epoxidation of cyclohexene (Scheme 1).

The results obtained (Table 2) show that the solids obtained from Ti(O^{*i*}Pr)₄ activated at 140 and 600°C are the most efficient catalysts. Activation at lower temperature or end-capping leads to solids with lower catalytic activity.



Scheme 1.

The behavior of the solids treated at 140 and 600°C is closely similar, which is probably due to the fact that, under the experimental conditions used, the reaction is very fast with both solids. In order to compare them, both catalysts were used under ‘worse’ conditions. The results obtained (Table 3) show that the solid treated at 600°C leads to higher conversions, but to lower selectivities and, as a consequence, the yield of epoxide finally obtained is almost the same. In view of this we decided to use the catalyst activated at 140°C, which is easier to obtain and also more selective.

It is important to note that with all these catalysts, high selectivities in the epoxide with regard to the TBHP are obtained. Furthermore, they can be stored in the open air keeping their catalytic activity unchanged.

3.2. Comparison with other titanium-based epoxidation catalysts

In view of the good results described for the epoxidation of olefins with organic peroxides using large-pore titanium–zeolites [8,10] and titania–silica mixed oxides [11], we decided to compare them with our solid activated at 140°C.

Table 4

Results obtained for the epoxidation of cyclohexene with organic peroxides using different titanium catalysts

Catalyst (mg)	Ti (mmol)	Cyclohexene (mmol)	TBHP (mmol)	T (°C)	Time (h)	Conv. cyclohexene (%) ^a	Epoxide (%) ^a
Ti-MCM-41 (300) ^b	0.075	56.3	14.00	60	5.0	14 (25.3)	12.6
Ti-Beta (300) ^c	0.124	25.0	6.25	50	5.0	34 (17.2)	33.6
SiO ₂ + Ti(O ^{<i>i</i>} Pr) ₄ (80) ^d	0.094	56.0	14.00	60	5.0	96 (142.5)	92
SiO ₂ –TiO ₂ 20LT (100) ^e	0.240	77.0	13.40 ^f	60	1.5	93 (51.9)	93
SiO ₂ + Ti(O ^{<i>i</i>} Pr) ₄ (250) ^d	0.295	77.0	13.50	60	1.5	97 (44.4)	93

^a Referred to the maximum.

^b Data from Ref. [10].

^c Data from Ref. [8].

^d This work.

^e Data from Ref. [11].

^f *tert*-cumyl hydroperoxide is used instead of TBHP.

Table 5

Results obtained for the TBHP (9 mmol) epoxidation of cyclohexene (18 mmol), in CH₂Cl₂ (4.2 ml) at 15°C, using 0.25 g of recovered catalyst

Recovery No.	Ti (mmol · g ^{±1a})	Conv. cyclohexene (%)			Conv. TBHP (%)			Epoxide ^b (%)		
		1 h	7 h	24 h	1 h	7 h	24 h	1 h	7 h	24 h
0	1.18	25	57	75	31	64	80	25	56	73
1	1.16	19	48	70	22	53	73	19	47	69
2	1.15	11	44	69	17	48	70	11	43	67
3	1.08	10	36	57	14	39	59	10	36	55
4	1.11	7	31	51	9	32	51	7	30	50
5	1.11	—	—	—	—	—	—	—	—	—

^a Determined by plasma emission spectroscopy.

^b Referred to the maximum.

The results obtained are gathered in Table 4. With all these catalysts high selectivities in the epoxide (more than 90%), with regard to the TBHP, are obtained. The silica-based catalysts are by far more active than the zeolites, the titania–silica mixed oxide leading to slightly higher turnover and selectivity.

3.3. Recovery of the catalyst

In order to test the possibility of recovering and reusing of the catalyst, the solid activated at 140°C was separated by filtration after the reaction, thoroughly washed, and reactivated at 140°C before use. The results obtained (Table

Table 6

Results obtained for the TBHP epoxidation of several olefins, at room temperature, catalysed by silica gel treated with Ti(OⁱPr)₄

Olefin	Olefin/TBHP	<i>t</i> (h)	Conv. TBHP ^a (%)	S _{peroxide} (%)	S _{alkene} (%)
1-hexene	8:1	24	73	62 ^b	96 ^b
Styrene	8:1	3	95	65 ^c	80 ^c
Norbornene	3:1	4	91	92 ^d	100 ^d
Cyclododecene ^e	3:1	5	70	80 ^e	95 ^e
<i>cis</i> -2-heptene	2:1	7	83	96 ^b	97 ^b
<i>trans</i> -2-heptene	2:1	24	83	72 ^b	96 ^b
1-methylcyclohexene	3:1	2	83	94 ^b	98 ^b
(<i>R</i>)-carvone	3:1	2	39	77	
		72	86	84	95
(<i>R</i>)-limonene	3:1	4	93	90	98 ^f
(<i>R</i>)-β-Citronellol	3:1	24	89	100 ^b	100 ^b
1,3-cyclohexadiene	3:1	24	91	93 ^g	90 ^g
Crotyl alcohol	3:2	1	90	100 ^b	100
Cinnamyl alcohol	3:2	24	33	68 ^{b,h}	68 ^{b,h}
Nerol	3:2	3.5	95	70	96
1-penten-3-ol	3:2	24	87	0 ⁱ	0 ⁱ
Cyclohexenol	3:2	24	100	0 ⁱ	0 ⁱ

^a Determined by GC using isoocane as the internal standard.

^b Calculated from the isolated yield.

^c Phenylacetaldehyde (15%) and benzaldehyde (3%) are also obtained.

^d Only *exo* epoxide.

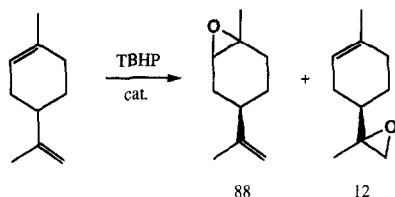
^e *cis/trans* mixture.

^f A mixture of epoxides is obtained

^g Oligomers of the diene are obtained as byproducts and the excess of diene cannot be recovered. The reaction is carried out at –10°C.

^h Some epoxide is opened by the cinnamyl alcohol, which reduces the selectivity in epoxide.

ⁱ Ketones are the only reaction products.



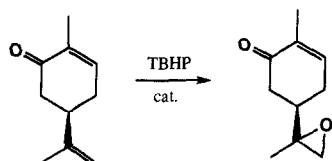
Scheme 2.

5) indicate that the catalytic activity of the solid is reduced, and consequently the reaction is slower. In spite of this, the yield in epoxide obtained after 24 h of reaction is, after using five times the catalyst, 68% that obtained with the freshly prepared catalyst, and the selectivity in the epoxide with regard to the TBHP remains high.

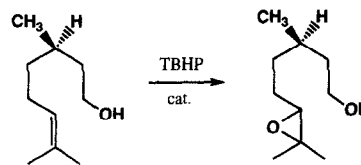
The decrease in catalytic activity is not due to the leaching of titanium from the solid, as the analyses show, and it may be due to two main reasons. First of all, the change in the structure of the active centers. In fact, during the reaction, the $\text{Ti}(\text{O}^i\text{Pr})$ groups shall be substituted by $\text{Ti}(\text{O}^i\text{Bu})$ groups, which reduces the activity because the ^iBuO is a worse leaving group than the ^iPrO one. Furthermore, the former group increases the steric hindrance in the surroundings of the titanium atoms. Both facts make the coordination of the reagents to the active centers more difficult. Second, the adsorption of byproducts on the active centers.

3.4. Epoxidation of different olefins

The above-described results show that silica gel treated with $\text{Ti}(\text{O}^i\text{Pr})_4$, and activated at 140°C is a good catalyst for the epoxidation of cyclohexene, therefore we tested its catalytic activity for the epoxidation of different kinds of



Scheme 3.



Scheme 4.

olefins. The results obtained (Table 6) show that isolated double bonds are efficiently epoxidized with a high selectivity in the epoxide with regard to the TBHP, but the reactivity depends on the structure around the double bond. These differences are shown in the epoxidation of (*R*)-limonene, which is preferentially epoxidized in the endocyclic double bond (Scheme 2).

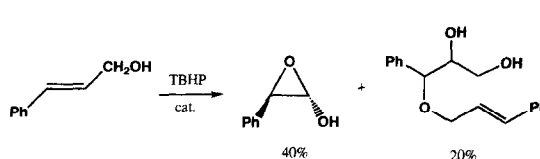
In the epoxidation of styrene 15% phenylacetaldehyde, coming from the Lewis acid-catalyzed rearrangement of the epoxide, as well as 3% benzaldehyde, are obtained.

α,β -unsaturated carbonyl compounds are not epoxidized under these conditions, which allows the selective epoxidation of the exocyclic double bond of (*R*)-carvone (Scheme 3).

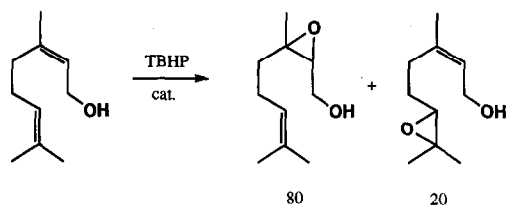
The epoxidation of the 1,3-cyclohexadiene at room temperature leads to a complex mixture of products. However, the monoepoxide is the only oxidation product although oligomers of cyclohexadiene are also obtained, which is logical if the acidic properties of the catalyst are taken into account.

(*R*)-citronellol is epoxidized without oxidation of the primary alcohol (Scheme 4).

Primary allylic alcohols are also efficiently epoxidized. A byproduct, originating from the opening of the epoxide ring with the alcohol, is also obtained in the case of the cinnamyl alcohol. The solid can act as an acid catalyst for this



Scheme 5.



Scheme 6.

reaction, which is favored by the stability of the benzylic cation intermediate (Scheme 5).

Allylic alcohols react faster than isolated double bonds as shown for the epoxidation of nerol (Scheme 6).

The catalysts do not epoxidize secondary allylic alcohols and ketones are the only products obtained for these reactions.

3.5. Competitive reactions

The results described so far show that primary allylic alcohols are epoxidized faster than non-functionalized alkenes and that α,β -unsaturated carbonyl compounds do not react under these conditions. Furthermore, they show that non-functionalized alkenes are epoxidized at different rates depending on their structures. In order to analyze the different reactivities of these compounds, we carried out some competitive experiments using two alkenes in equimolecular amounts and analyzing the mixture from short reaction times.

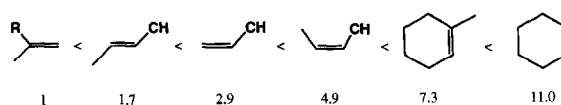
The results obtained from these experiments (Table 7) are complemented by the epoxidation of (*R*)-limonene, which show that methylcyclo-

Table 7

Results obtained for the competitive epoxidation of pairs of olefins (9 mmol of each one) with TBHP (6 mmol), catalysed by silica treated with $\text{Ti}(\text{O}^i\text{Pr})_4$ (0.5 g) at room temperature

Olefin A	Olefin B	Epoxide A/ epoxide B ^a
Cyclohexene	1-methylcyclohexene	1.5:1
Cyclohexene	1-hexene	3.8:1
1-methylcyclohexene	<i>cis</i> -2-heptene	1.5:1
1-hexene	<i>trans</i> -2-heptene	1.7:1

^a Determined by GC.



Scheme 7.

hexene is oxidized more than seven times faster than a *gem*-disubstituted double bond. It can be concluded that cyclic double bonds react faster than exocyclic ones, and that *cis*-disubstituted are epoxidized faster than *trans*- or *gem*-disubstituted double bonds. Scheme 7 gives an approximate quantification of the relative rates of epoxidation of the different kinds of alkenes.

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