

## Microwave-assisted Oxidation of Saturated and Unsaturated Alcohols with *t*-Butyl Hydroperoxide and Zeolites

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**Abstract:** Under microwave irradiation 3Å molecular sieves promote the oxidation of secondary (linear and cyclic) and benzylic alcohols to the corresponding carbonyl compounds by *t*-butyl hydroperoxide. Under the same conditions,  $\alpha,\beta$ -unsaturated alcohols are converted into  $\alpha,\beta$ -epoxyalcohols in regio- and diastereoselective way. Both oxidative processes can be performed under solvent-free conditions; however, epoxidation of allylic alcohols is found to proceed with more satisfactory efficiency in saturated aliphatic hydrocarbon (n-hexane or cyclohexane). © 1997 Elsevier Science Ltd.

### Introduction

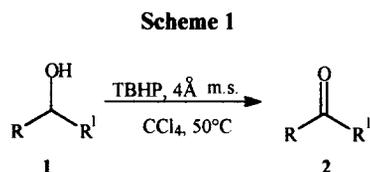
Most of the procedures for the oxidation of organic substrates use transition metals such as Cr (VI), Mn (VII), Mn (IV), Pb (IV), and Ag (I) salts.<sup>1</sup> However, too elevated reaction temperatures and basic or acidic conditions can promote undesired side reactions (especially in the presence of other sensitive functions). Furthermore, a large excess of oxidant is usually required to ensure adequate efficiency and serious environmental problems may derive from their toxicity, as for Cr (VI) reagents. Therefore, in recent years the attempt to eliminate all these disadvantages has led to the achievement of new, catalytic and less polluting methodologies involving the incorporation of transition metal compounds (Ti, V, Cr, Mn, etc) into inorganic supports, such as montmorillonite and zeolites.<sup>2</sup>

Previous investigations,<sup>3</sup> devoted to the elaboration of new acceptable procedures for oxidation of alcohols, have shown that zeolites are much more than inert supports and their intrinsic catalytic activity can be conveniently exploited in oxidative processes.

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### Oxidation of Benzylic Alcohols 1

At first, a series of experiments has been performed on benzylic alcohols **1** employing commercial 4Å molecular sieves as catalyst, and *t*-butyl hydroperoxide (TBHP) as the oxidant (Scheme 1).



As reported in Table 1, the conversion of alcohols **1** into ketones **2** proceeded with satisfactory yield and selectivity. Indeed, the formation of by-products of type  $\text{RR}'\text{-CH-O-O-t-Bu}$ , deriving from a competitive process of nucleophilic substitution, occurs in < 5%.

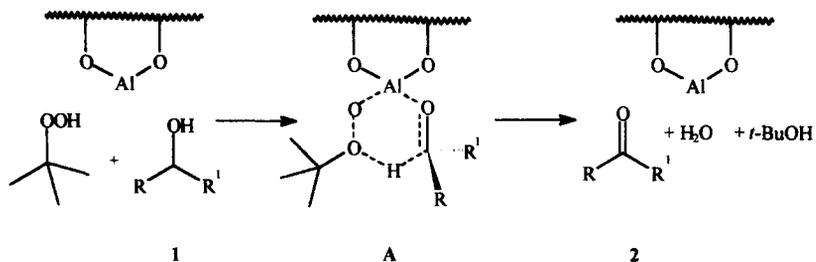
**Table 1.** Zeolite-catalyzed Oxidation of Alcohols **1**

Run	R	R <sup>1</sup>	Reac. time/h	Conversion (%)	Yield (%) <sup>a)</sup>
a	Ph	Me	120	70	55
b	Ph	Me	120	20	18 <sup>b)</sup>
c	Ph	Ph	156	100	97
d	Ph	Et	96	78	74
e	p-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Me	144	50	47
f		1-indanol	120	60	38
g		α-tetralol	120	45	35

<sup>a)</sup>All the yields are calculated on starting materials and refer to isolated chromatographically pure products, whose structures were confirmed by comparison with authentic samples. <sup>b)</sup>In this case no catalyst was added.

Zeolites proved to play a decisive role in the process of oxidation: in fact, in the absence of any catalyst (run **b**), after five days acetophenone was recovered only in 18% yield. The conversion **1**→**2** could be reasonably explained assuming the coordination by unsaturated aluminium atoms of *t*-butyl hydroperoxide and alcohol (Scheme 2).

Scheme 2



Polarization of the O-O bond and activation of C-H bond by the metal center permits a hydride transfer (through a six-membered transition state) leading to oxidation product **2**. A similar mechanism has been proposed for the  $\text{Al(OR)}_3$  catalyzed oxidation of alcohols with TBHP.<sup>4</sup>

Since TBHP cannot penetrate the pores of zeolite,<sup>5</sup> oxidation must take place on the surface of the catalyst and the very reduced number of outer active sites can be considered responsible of the required long reaction times.<sup>6</sup> This mechanistic hypothesis has been confirmed by the observation that 4-*t*-butylcyclohexan-1-ol was converted into the corresponding ketone only in 9% yield after 3 days, while  $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{OH}$  was recovered almost completely unchanged. As known, hydride abstraction from nonactivated primary and secondary alcohols is a very slow process.<sup>7</sup>

In its present form, in spite of its cheapness and high selectivity, this methodology suffered from long reaction times, the applicability only to activated alcohols and the employment of toxic carbon tetrachloride, as the solvent.

Since microwave (MW) heating is often employed to carry out synthetic procedures, especially in term of remarkable reduction of reaction times and efficiency under solvent-free conditions,<sup>8</sup> we decided to examine the reactivity of zeolite/TBHP oxidant system using microwave irradiation.

### Microwave-assisted Oxidation of Alcohols 3

In order to circumvent the problems related to very low reaction rate and employment of carbon tetrachloride, no solvent was used (with exception of isooctane present in commercial TBHP) and, furthermore, reaction mixtures were submitted to MW irradiation for cycles of 20 minutes to avoid overheating (Scheme 3).

## Scheme 3



Table 2. Microwave-assisted Oxidation of Alcohols 3 with TBHP/Zeolite System

Entry	Alcohol 3	Reaction Time (min)	Yield (%) <sup>a,b</sup>
a		5x20	8% (90%) <sup>c</sup>
b		3x20	33% (45%)
c		3x20	12% (83%) <sup>c</sup>
d		3x20	68% (16%)
e		3x20	60% (20%)
f	$\text{CH}_3\text{CH}(\text{OH})\text{C}_6\text{H}_{13}$	3x20	38% (22%)
g		3x20	30% (58%)
h		3x20	36% (16%)
i	$\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{OH}$	4x20	No reaction
j	$\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2\text{OH}$	4x20	36% (64%) <sup>d</sup>

<sup>a</sup>All the yields are calculated on starting materials and refer to isolated chromatographically pure products, whose structures were confirmed by comparison with authentic samples. <sup>b</sup> Values in parentheses refer to recovered alcohols 3.

<sup>c</sup>These experiments were performed in absence of zeolite. <sup>d</sup>Yield refers to 4-hydroxy-butan-2-one.

As reported in Table 2, in control experiments performed in absence of any catalyst, on 4-*t*-butylcyclohexan-1-ol (entry a) and 1-(4-bromophenyl)-ethanol (entry c) oxidation proceeded with very poor efficiency, while a significant improvement was observed by microwave irradiation in the presence of 3Å molecular sieves (entries b and d). Comparable results have been obtained with 4Å molecular sieves.

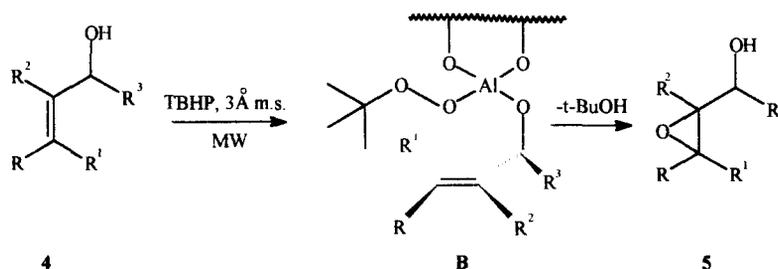
As expected on the ground of mechanistic pathway reported in Scheme 2, the best results have been obtained with benzylic alcohols ; in every case, the combined employment of MW and zeolite catalysis has allowed the extension of this methodology to linear and cyclic secondary alcohols, although in less satisfactory way. However, it is noteworthy that oxidation took place with similar yields in the case of 5 $\alpha$ -cholestan-3 $\beta$ -ol (entry g) although strong steric interactions with the aluminosilicate lattice had to be expected. In entries b and h, where starting materials 3 were used respectively as a mixture of cis/trans and endo/exo alcohols, no diastereoselective oxidation was observed.

At last, the almost complete unreactivity of primary alcohols (entry i) was conveniently exploited for highly selective oxidation of 1,3-diols presenting both primary and secondary alcoholic functions : in fact, 4-hydroxy-butan-2-one was obtained as exclusive product in entry j.

#### Epoxydation of Allylic Alcohols 4

Since allylic alcohols represent valuable test systems for checking the epoxidation versus dehydrogenation process, a significant support to the mechanistic pathway reported in Scheme 2 could be obtained by examination of their reactivity under the usual conditions: in fact, in a competitive Sharpless-type reaction, the proposed intermediate B could have afforded epoxyalcohols 5 by  $\pi$  electrons system attack on the polarized O-O bond (Scheme 4).

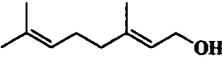
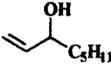
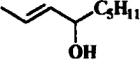
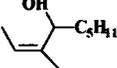
Scheme 4



Therefore a series of primary and secondary allylic alcohols 4 was submitted to the usual treatment. In all the experiments reported in Table 3 epoxidation proved to be the predominant process ( $\alpha,\beta$ -unsaturated carbonyl compounds were usually obtained in < 10% yield) and, more interestingly, to proceed in regio- and diastereoselective way. In fact, no evidence of formation of isomeric epoxide could be detected in entry c, while, as regards secondary allylic alcohols (entries d-g), the corresponding epoxyalcohols were obtained with the same diastereoselectivity observed in Sharpless epoxidation by TBHP/VO(acac)<sub>2</sub> oxidant. This result can be reasonably explained assuming that, although to a different extent, the same type of steric interactions of

the coordinated reagents with the zeolite lattice and with vanadium ligands is involved in the corresponding transition states leading to final products.

**Table 3.** Microwave-assisted Epoxidation of Allylic Alcohols by TBHP/Zeolite System

Entry	Alcohol 4	Reac. Time (min)	Yield (%) <sup>a,b)</sup>	TBHP/VO(acac) <sub>2</sub> C <sub>6</sub> H <sub>6</sub> , d.r. (E/T)
a		3x15 3x20	30 66 <sup>c)</sup>	
b		3x15 3x20	40 83 <sup>c)</sup>	
c		15 3x20	58 95 <sup>c)</sup>	
d		4x20 6x20	18 (69/31) 18 (69/31) <sup>c)</sup>	80/20
e		2x20 3x20	51 (55/45) 87 (55/45) <sup>c)</sup>	71/29
f		15 2x15	81 (88/12) 95 (85/15) <sup>c)</sup>	93/7
g		20	65 (13/87)	14/86
h	“	20	- <sup>d)</sup>	
i	“	20	- <sup>e)</sup>	

<sup>a)</sup>All the yields refer to isolated chromatographically pure compounds, whose structures have been confirmed by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. <sup>b)</sup> Values in parentheses refer to erythro/threo diastereoisomeric ratios. <sup>c)</sup> These experiments have been performed in cyclohexane (solvent/substrate 2.5 ml/2 mmol) and yields have been determined by <sup>1</sup>H-NMR-analysis. <sup>d)</sup>No zeolite. <sup>e)</sup> This experiment was performed under O<sub>2</sub> atmosphere in absence of TBHP.

TBHP/zeolite can be considered the effective oxidant system: in fact, no significant reaction was observed when the most reactive allylic alcohol was submitted to two control experiments in the absence of catalyst (entry h) and under O<sub>2</sub> atmosphere in absence of TBHP (entry i).

In conclusion, the combined exploitation of microwave and molecular sieves catalysis has allowed the achievement of a very simple, cheap and environmentally safe oxidative procedure, which can be considered

of synthetic value because of the short reaction times under solvent free conditions and the satisfactory chemo- regio- and diastereoselectivity observed in the case of allylic alcohols.

**Caution:** Although in more than 100 experiments no particular safety problem (ignition, explosion, reaction vessel deformation) has been encountered, careful attention should be paid to avoid risks of overheating and excessive pressure deriving from too prolonged reaction times or too high irradiation power.

### Experimental Section

**General Information.** All secondary linear, cyclic and benzylic alcohols, as well as primary allylic alcohols, were commercially available (Fluka or Aldrich) and were used without any previous purification. Secondary allylic alcohols were prepared by routine procedures involving addition of the appropriate Grignard reagent to the corresponding  $\alpha,\beta$ -unsaturated aldehyde. After purification by silica gel column chromatography their structures were confirmed by  $^1\text{H-NMR}$ . TBHP (3M in isooctane solution) and 3Å and 4Å molecular sieves were respectively purchased from Fluka and Aldrich. Silica gel (230-400 mesh Merck) was used for flash chromatography. Analytical thin layer chromatography (TLC) were carried out on Merck Kieselgel F<sub>254</sub> plates. Spots on TLC were visualized under iodine and by spraying with  $\text{H}_2\text{SO}_4$  (10% in ethanolic solution) followed by heating.  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra were recorded with Varian Gemini-200 spectrometer. Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), qp (quintet), hept (heptuplet), m (multiplet), dd (double doublet), ss (sharp singlet), bs (broad singlet), bdd (broad double doublet). Chemical shifts are reported in ( $\delta$ ) ppm relative to internal  $\text{CHCl}_3$ ,  $\delta$  (7.27) for  $^1\text{H-NMR}$  and  $\text{CDCl}_3$ ,  $\delta$  (77.0) for  $^{13}\text{C-NMR}$ .

**General procedure for oxidation of benzylic alcohols 1 in  $\text{CCl}_4$  solution.** Commercial 4Å molecular sieves (1 g), after activation by heating at 200°C for 6h under a reduced pressure (0.1 mmHg), were added to a solution of alcohol (2 mmol) and TBHP (3 M isooctane solution, 6 mmol) in  $\text{CCl}_4$  (10 ml) under argon atmosphere. The reaction was monitored by TLC and/or GLC. Then 0.1 N aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  (7.5 ml) was added and the mixture was stirred for 0.5 h. After evaporation under reduced pressure of organic phase, the crude product was purified by silica gel column chromatography by elution with n-pentane/diethyl ether mixtures.

**General procedure for MW-assisted oxidation of alcohols 3.** Commercial 3Å molecular sieves (0.5 g), without any previous activation, were added to a solution of alcohol **3** (1 mmol) and TBHP (3M isooctane solution, 1.5 mmol) in on Ace pressure tube (Aldrich). The tube was placed inside the MW oven (2450 MHz) and irradiated at 180 Watt for 20 minutes. The mixture was allowed to cool to room temperature and the reaction was monitored by TLC or by GC. The procedure was repeated several times as shown in Table 2. Then, dimethyl sulphide (3 eq.) was added to the organic phase and the mixture was stirred at room temperature for 1h. Then, after evaporation under reduced pressure, the crude product was directly poured onto the top of a silica gel chromatographic column. Elution with n-hexane/ diethyl ether mixtures afforded pure ketones.

**General procedure for MW epoxidation of allylic alcohols 4.** Commercial 3Å molecular sieves (0.5 g), without any previous activation, were added to a solution of allylic alcohol **4** (1 mmol) and TBHP (3M isooctane solution, 2 mmol) in on Ace pressure tube (Aldrich). The tube was placed inside the MW oven (2450 MHz) and irradiated at 180 Watt, for the selected time. The mixture was allowed to cool to room temperature and the reaction was monitored by TLC. The procedure was repeated several times as shown in Table 3. Then, dimethyl sulphide was added to the organic phase and the mixture was stirred at room temperature for 1h. After evaporation under reduced pressure, the crude product was directly poured onto the top of a silica gel chromatographic column. Elution with n-hexane/diethyl ether mixtures afforded pure epoxyalcohol **5**.

**5a:**  $^1\text{H-NMR}$  data: 0.93 (3H, t,  $J=7.0$  Hz); 1.30-1.58 (4H, m); 2.98-3.08 (1H, m); 3.10-3.18 (1H, m); 3.62 (1H, dd,  $J_1=11.7$  Hz,  $J_2=6.7$  Hz); 3.82 (1H, dd,  $J_1=11.7$  Hz,  $J_2=6.7$  Hz).  $^{13}\text{C-NMR}$  data: 13.83, 19.86, 29.84, 56.94, 57.12, 60.81. Anal. Calcd. for  $\text{C}_6\text{H}_{12}\text{O}_2$ : C, 62.04; H, 10.41%. Found: C, 62.10; H, 10.38%.

**5b:**  $^1\text{H-NMR}$  data: 0.90 (3H, t,  $J=7.1$  Hz); 1.50-1.58 (4H, m); 2.50 (1H, bs); 2.82-2.95 (2H, m); 3.54 (1H, dd,  $J_1=12.5$  Hz,  $J_2=4.5$  Hz); 3.85 (1H, dd,  $J_1=12.5$  Hz,  $J_2=2.4$  Hz).  $^{13}\text{C-NMR}$  data: 13.61, 18.98, 33.34, 55.78, 58.49, 61.69. Anal. Calcd. for  $\text{C}_6\text{H}_{12}\text{O}_2$ : C, 62.04; H, 10.41%. Found: C, 62.10; H, 10.35%.

**5c:**  $^1\text{H-NMR}$  data: 1.27 (3H, s); 1.58 (3H, s); 1.66 (3H, s); 2.05 (4H, bq); 2.94 (1H, dd,  $J_1=6.7$  Hz,  $J_2=4.3$  Hz); 3.59-3.70 (1H, m); 4.99-5.10 (2H, m).  $^{13}\text{C-NMR}$  data: 16.92, 17.82, 23.87, 25.86, 38.73, 61.53, 61.76, 63.33, 123.81, 132.69. Anal. Calcd. for  $\text{C}_{10}\text{H}_{18}\text{O}_2$ : C, 70.55; H, 10.66%. Found: C, 70.50; H, 10.62%.

**5d** (*inseparable mixture of two diastereomers*):  $^1\text{H-NMR}$  data (*erythro isomer*): 0.85 (3H, bt); 1.10-1.70 (8H, m); 2.67-2.72 (1H, m); 2.77-2.82 (1H, m); 2.97-3.02 (1H, m); 3.77-3.87 (1H, m).  $^1\text{H-NMR}$  data (*threo isomer*):

0.85 (3H, bt); 1.10-1.70 (8H, m); 2.67-2.72 (1H, m); 2.77-2.82 (1H, m); 2.92-2.97 (1H, m); 3.35-3.45 (1H, m). <sup>13</sup>C-NMR data (*erythro isomer*): 13.81, 22.38, 24.80, 31.69, 33.25, 43.26, 54.44, 68.34. <sup>13</sup>C-NMR data (*threo isomer*): 13.81, 22.38, 24.80, 31.62, 34.24, 45.27, 55.42, 71.63. Anal. Calcd. for C<sub>8</sub>H<sub>16</sub>O<sub>2</sub>: C, 66.63; H, 11.18%. Found : C, 66.68; H, 11.22%.

**5e** (*inseparable mixture of two diastereomers*): <sup>1</sup>H-NMR data (*erythro isomer*): 0.85 (3H, bt); 1.10-1.60 (11H, m); 2.10 (1H, bs); 2.68 (1H, dd, *J*<sub>1</sub>=2.5 Hz, *J*<sub>2</sub>=5.4 Hz); 3.03 (1H, dq, *J*<sub>1</sub>=2.5 Hz, *J*<sub>2</sub>=5.3 Hz); 3.78-3.30 (1H, m). <sup>1</sup>H-NMR data (*threo isomer*): 0.85 (3H, bt); 1.10-1.60 (11H, m); 2.27 (1H, bd); 2.64 (1H, dd, *J*<sub>1</sub>=2.32, *J*<sub>2</sub>=5.4); 2.93 (1H, dq, *J*<sub>1</sub>=2.32, *J*<sub>2</sub>=5.3); 3.35-3.42 (1H, m). <sup>13</sup>C-NMR data (*erythro isomer*): 13.77, 17.01, 22.34, 24.76, 31.67, 33.32, 50.91, 61.88, 68.59. <sup>13</sup>C-NMR data (*threo isomer*): 13.77, 17.01, 22.34, 24.76, 31.60, 34.10, 52.76, 68.77, 71.31. Anal. Calcd. for C<sub>9</sub>H<sub>18</sub>O<sub>2</sub>: C, 68.31; H, 11.47%. Found: C, 68.37; H, 11.40%.

**5f** (*erythro isomer*): <sup>1</sup>H-NMR data: 0.88 (3H, bt); 1.15-1.68 (11H, m); 2.15 (1H, s); 3.13 (1H, q, *J*=5.6 Hz); 3.60 (1H, bs). <sup>13</sup>C-NMR data: 13.51, 13.97, 14.05, 22.52, 25.23, 31.85, 32.62, 54.91, 62.70, 72.59. Anal. Calcd. for C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>: C, 69.72; H, 11.70%. Found: C, 69.76; H, 11.68%.

**5f** (*threo isomer*): <sup>1</sup>H-NMR data: 0.88 (3H, bt); 1.10-1.68 (11H, m); 2.1 (1H, s); 2.96 (1H, q, *J*=5.6 Hz); 3.15 (1H, bs). <sup>13</sup>C-NMR data: 13.52, 13.99, 14.09, 22.49, 25.32, 31.77, 32.97, 57.67, 63.60, 76.95. Anal. Calcd. for C<sub>10</sub>H<sub>20</sub>O<sub>2</sub>: C, 69.72 ; H, 11.70%. Found: C, 69.75 ; H, 11.75%.

**5g** (*inseparable mixture of two diastereomers*): <sup>1</sup>H-NMR data (*erythro isomer*): 1.18 (3H, d, *J*= 6.2 Hz); 1.24-1.34 (6H, m); 2.60 (1H, d, *J*= 7.8 Hz); 2.90-3.00 (1H, bs); 3.52-3.66 (1H, m). <sup>1</sup>H-NMR data (*threo isomer*): 1.18 (3H, d, *J*= 6.2 Hz); 1.24-1.34 (6H, m); 2.68 (1H, d, *J*= 8.0 Hz); 2.90-3.00 (1H, bs); 3.52-3.66 (1H, m). <sup>13</sup>C-NMR data (*erythro isomer*): 18.62, 20.84, 24.75, 59.23, 66.07, 67.04. <sup>13</sup>C-NMR data (*threo isomer*): 19.00, 19.11, 24.84, 59.23, 66.88, 68.56. Anal. Calcd. for C<sub>6</sub>H<sub>12</sub>O<sub>2</sub>: C, 62.04; H, 10.41%. Found : C, 61.97; H, 10.38%.

## References and Notes

<sup>⊙</sup> Diastereoisomeric ratios have been determined on the ground of isolated epoxyalcohols (**5f**) or by <sup>1</sup>H-NMR analysis of the crude mixture, involving accurate integration of the signals relative to CH—OH of *threo* and *erythro* epoxyalcohols for **5d** and **5e**, relative to CH<sub>2</sub>CH(OH)- for **5g**.

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