Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 7403–7408

TETRAHEDRON

# Selective epoxidation of monoterpenes with $H_2O_2$ and polymer-supported methylrheniumtrioxide systems

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Received 17 February 2003; revised 23 June 2003; accepted 17 July 2003

**Abstract**—A convenient and efficient synthesis of monoterpene epoxides by application of heterogeneous poly(4-vinylpyridine)/methyl rhenium trioxide (PVP/MTO) and polystyrene/methyl rhenium trioxide (PS/MTO) systems is described. Even highly sensitive terpenic epoxides were obtained in excellent yield. Environment friendly, easily available, and low cost $H_2O_2$ was used as oxidant. Catalysts were stable systems for at least five recycling experiments.

Terpenes are the basis for many of perfumes, detergents, flavours, agrochemicals, and therapeutically active substances.[1] In terpene chemistry the oxidative functionalization often starts with a selective epoxidation. The most commonly employed stoichiometric oxidants for this synthesis are organic peroxy acids that produce wastes and are not selective for the preparation of acid-sensitive epoxides.[2] To avoid these problems, catalytic systems including tungsten compounds,[3] titanium-silica and alumina supported catalysts,[4] peroxotungstophosphate (PCWP),[5] molybdenum, vanadium, and manganese complexes,[6] and metalloporphyrins,[7] have been used with varying degrees of success as well as limitations due to side reactions. Thus, there is a great interest in developing more efficient catalysts, mainly heterogeneous systems, for the selective synthesis of terpenic epoxides. In the last years methyl rhenium trioxide ($CH_3ReO_3$, MTO)[8] has been shown to possess interesting catalytic properties in oxidation reactions with hydrogen peroxide ($H_2O_2$) as oxygen atom donor.[9] The epoxidation of alkenes has been extensively studied.[10] The active catalytic forms are a monoperoxo metal $[MeRe(O)_2(O_2)]$ and a bisperoxo metal $[MeRe(O)(O_2)_2]$ complex and/or their adducts with solvent molecules.[10h] In this context, epoxidation of monoterpenes with MTO was described in homogeneous phase using urea/hydrogen peroxide adduct (UHP) as anhydrous oxygen atom donor,[11] or an excess of pyridine as Lewis base mediator of the oxidation.[12] MTO epoxidation of monoterpenes in fluorinated solvents, that usually increase the reactivity failed, probably because of the decomposition of the catalyst.[13] Recently, with the aim to develop clean oxidation processes, we described the preparation and characterization of novel heterogeneous rhenium compounds of general formula $(\text{polymer})_f/(\text{MTO})_g$ (the $f/g$ quotient express the ratio by weight of the two components) by heterogenation of MTO on poly(4-vinylpyridine) and polystyrene,[14] applying an extension of the 'mediator' concept,[15] and of the microencapsulation technique,[16] respectively. All the new MTO compounds were characterized by FT-IR, scanning electron microscopy (SEM), and wide-angle X-ray diffraction (WAXS).[14] Apart from silica supported MTO complexes,[17] and a NaY zeolite/MTO supercage system,[18] no further data is available in the literature about heterogeneous MTO catalysts. Polymer/MTO catalysts are efficient and selective systems for the epoxidation of simple olefins,[14] and for the oxidation of substituted phenol and anisole derivatives to *ortho*- and *para*-benzoquinones.[19] We report here on the applicability of different polymer/MTO systems, poly(4-vinylpyridine) 2% and 25% cross-linked (with divinylbenzene)/MTO (PVP-2%/MTO **1** and PVP-25%/MTO **2**, respectively), poly(4-vinylpyridine-*N*-oxide) 2% cross-linked/MTO (PVPN-2%/MTO **3**) and microencapsulated polystyrene 2% cross-linked/MTO (PS-2%/MTO **4**), to the $H_2O_2$ selective epoxidation of monoterpenes, including acid-sensitive ones. The structure of poly(4-vinylpyridine)/MTO and polystyrene/MTO catalysts **1–4** is represented in the schematic drawing in Figure 1.

Epoxidation with $H_2O_2$ were investigated using geraniol, nerol, *S*-(+)-carene, *R*-(+)-limonene and 1 (*R*)-α-pinene, as representative model substrates. As a general procedure, the terpene (1 mmol) to be oxidized and $H_2O_2$ (1.2 mmol, 35% water solution) were added to a suspension of the catalyst

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*Keywords*: terpenic epoxides; epoxidation; α-pinene oxide.

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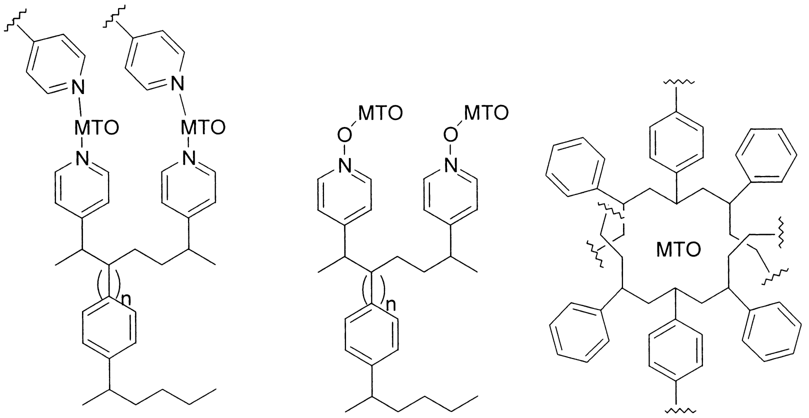
doi:10.1016/S0040-4020(03)01145-1



**PVP-2%/MTO 1 or PVP-25%/MTO 2** **PVPN-2%/MTO 3** **PS-2%/MTO 4**

**Figure 1.** Structures of polymer supported MTO catalysts.

(loading factor 1.0) in $CH_2Cl_2/CH_3CN$ (5 mL, 1:1 v/v), and the mixture was stirred at room temperature. In the tests for the recyclability of catalysts **1–4**, the solid was separated by filtration, washed with $CH_3CN$, dried and then reused in another reaction as described above. The oxidation results are summarized in Table 1 and Schemes 1 and 2. In the absence of the catalyst, less than 5% conversion of substrates took place under otherwise identical conditions. Previously performed terpene epoxidation with MTO in homogeneous phase[11,12] were used as references (Table 1, entries 1, 6, 11, 16, 17, and 22). The oxidation of monoterpenes geraniol **5**, and nerol **6**, afforded 6,7-epoxides, **5a** and **6a** as main products, in which the non-allylic double bonds were selectively oxidized. Only low amounts of 2,3-epoxides **5b–6b**, and diepoxides **5c–6c**, were recovered in the reaction mixture (Table 1, entries 2–5 and 7–10; Scheme 1). The regioselectivity demonstrated in the oxidation of **5** and **6**, is consistent with the results of MTO in homogeneous phase, in which case double bonds with the highest HOMO coefficients are oxidized (Table 1, entries 1 and 6).[20] Products of nucleophilic ring opening of the oxiranyl ring or acidic rearrangement of geraniol and nerol epoxides[21] were not recovered under our experimental conditions. Treatment of **5** with **1** afforded **5a** as the main product in 90% conversion and 77% yield (Table 1, entry 2). In a similar way, the oxidation performed with catalysts **2–4**

**Table 1**. Polymer-supported MTO catalysed epoxidation of monoterpenes **5–9**

| Entry | Catalyst[a] | Reaction time (h) | Substrate | Conversion(%) | Products(Yield)[b] |
|---|---|---|---|---|---|
| 1 | MTO/pyridine[c] | 1.0 | 5 | 92 | **5a**(66), **5b**(6), **5c**(11) |
| 2 | 1 | 1.0 | 5 | 90 | **5a**(77), **5b**(8), **5c**(5) |
| 3 | 2 | 1.0 | 5 | 90 | **5a**(74), **5b**(7), **5c**(7) |
| 4 | 3 | 1.5 | 5 | 92 | **5a**(79), **5b**(5), **5c**(3) |
| 5 | 4 | 1.0 | 5 | 96 | **5a**(82), **5b**(3), **5c**(6) |
| 6 | MTO/pyridine[c] | 0.5 | 6 | 89 | **6a**(62), **6b**(6), **6c**(13) |
| 7 | 1 | 1.0 | 6 | 90 | **6a**(87), **6b**(6), **6c**(1) |
| 8 | 2 | 1.5 | 6 | >98 | **6a**(83), **6b**(4), **6c**(4) |
| 9 | 3 | 1.5 | 6 | 95 | **6a**(88), **6b**(3), **6c**(2) |
| 10 | 4 | 1.0 | 6 | >98 | **6a**(81), **6b**(6), **6c**(3) |
| 11 | MTO/pyridine[d] | 1.0 | 7 | >98 | **7a**(75) |
| 12 | 1 | 3.5 | 7 | 68 | **7a**(85) |
| 13 | 2 | 2.5 | 7 | >98 | **7a**(96) |
| 14 | 3 | 2.5 | 7 | 75 | **7a**(84) |
| 15 | 4 | 3.0 | 7 | >98 | **7a**(91) |
| 16 | MTO[c] | 1.0 | 8 | – | **8a**(6) |
| 17 | MTO/pyridine[c] | 1.0 | 8 | – | **8a**(90) |
| 18 | 1 | 2.0 | 8 | 76 | **8a**(95) |
| 19 | 2 | 0.5 | 8 | 81 | **8a**(88) |
| 20 | 3 | 1.0 | 8 | 70 | **8a**(98) |
| 21 | 4 | 1.5 | 8 | >98 | **8a**(>98) |
| 22 | MTO/pyridine[c,e] | 1.0 | 9 | 96 | **9a**(79), diepoxide(13) |
| 23 | 1 | 1.5 | 9 | 75 | **9a**(83) |
| 24 | 2 | 1.5 | 9 | 79 | **9a**(89) |

All the reaction were performed in $CH_2Cl_2/CH_3CN$ (5 mL, 1:1 v/v) at room temperature, with $H_2O_2$ (35% aqueous solution), using a value of the catalyst loading factor of 1.0.

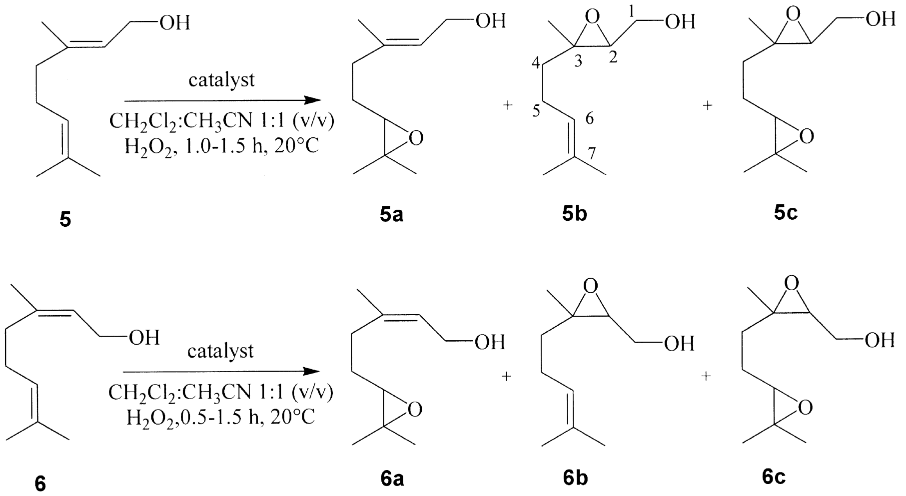
[a] Catalyst: PVP-2%/MTO **1**, PVP-25%/MTO **2**, PVPN-2%/MTO **3**, PS-2%/MTO **4**.

[b] Refers to isolated materials.

[c] Epoxide yields in the reaction of monoterpenes with $H_2O_2$ (35% aqueous solution) in THF or $CH_2Cl_2$ at room temperature catalyzed by MTO and MTO/pyridine; Ref. 12.

[d] Reaction performed under the experimental conditions described in Ref. 12.

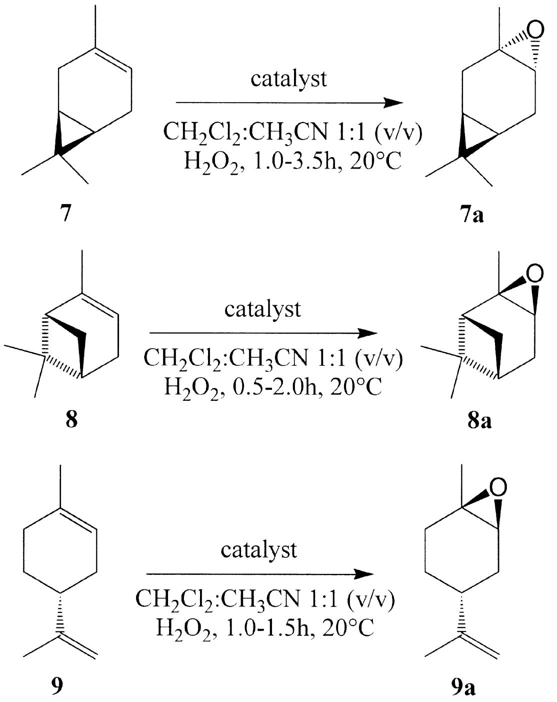
[e] (1,2):(8,9) epoxide=98:2; *cis* (1,2): *trans* (1,2) epoxide=1.3:1.0.



**Scheme 1.**

gave **5a** in 90–96% conversions, and 75–82% yields, respectively (Table 1, entries 3–5).

Under similar experimental conditions at least the same extent of conversions of **6** and yields of **6a** were achieved, with **1** and **4** being the most selective catalysts (Scheme 1, Table 1, entries 7–10). All polymer-supported MTO systems showed a high regiospecificity in the oxidation of **6**. In a test for checking the leaching of catalysts, the oxidation of **5** with catalyst **1** was stopped at ca. 50% conversion.[22] After centrifugation the colourless solution lost the catalytic activity. Table 2 shows that poly(4-vinylpyridine)/MTO catalysts are stable enough to perform al least five recycling experiments with similar conversion and selectivity. Even if only a very slight decrease in activity occurs during the first four recycling experiments with microencapsulated catalyst **4**, in the fifth recycling step the conversion was appreciably reduced, probably because of a partial decomposition of MTO.[14] Active methyl-(oxo)bis($\eta^2$-peroxo)rhenium(VII)/ligand intermediates have been prepared and characterized in homogeneous phase.[10h,23] In our case, catalytic activity was again observed when poly(4-vinylpyridine) and poly(4-vinyl-pyridine-*N*-oxide) were added to a solution where the rhenium peroxo species was already formed. This result indicates that the bisperoxo metal [$MeRe(O)(O_2)_2$] complex is stable in the presence of selected organic supports.



**Scheme 2.**

The oxidation of *S*-(+)-carene **7** with catalyst **1** gave the *trans*-3,4-epoxycarene **7a** as the only recovered product in 68% conversion and 85% yield (Scheme 2, Table 1, entry 12). The oxidation was selective and no traces of *cis*-3,4-epoxycarene or the corresponding diols were recovered in the reaction mixture. Better results were obtained with catalysts **2** and **4** (Table 1, entries 13 and 15), while **3** showed reactivity similar to **1** (Table 1, entry 14). It is noteworthy that in the oxidation of **7**, catalysts **1–4** were more selective than MTO (Table 1, entry 11). These results are in accord with the higher selectivity of polymer-supported /MTO systems with respect to MTO in the oxidation of cardanol derivatives, in part explained on the

**Table 2**. Stability of polymer-supported MTO catalysts in the oxidation of **5**

| Catalyst[a] | Conversion (%)[b] | | | | |
|---|---|---|---|---|---|
| | Run. no. 1 | Run. no. 2 | Run. no. 3 | Run. no. 4 | Run. no. 5 |
| 1 | 90 (77)[c] | 89 (78) | 91 (77) | 90 (76) | 91 (77) |
| 2 | 90 (74) | 90 (74) | 89 (72) | 88 (71) | 90 (73) |
| 3 | 92 (79) | 91 (79) | 93 (78) | 90 (77) | 92 (77) |
| 4 | 96 (82) | 96 (82) | 95 (80) | 91 (79) | 81 (75) |

The reaction were performed in $CH_2Cl_2$:$CH_3CN$ 1:1 (v/v) (5 mL) at 20% with $H_2O_2$ (35% aqueous solution) using a value of the catalysts loading factor of 1.0.

[a] Catalyst: PVP-2%/MTO **1**, PVP-25%/MTO **2**, PVPN-2%/MTO **3**, PS-2%/MTO **4**.

[b] Values of **5a** yields are given in parentheses and are normalized to 100% of conversion.

[c] The reaction were performed in $CH_2Cl_2$:$CH_3CN$ 1:1 (v/v) (5 mL) at 20% with $H_2O_2$ (35% aqueous solution) using a value of the catalysts loading factor of 1.0.

basis of supramolecular interactions between substrates and the heterogeneous catalyst.[19] Highly sensitive terpenic epoxides, such as α-pinene oxide, can be obtained in excellent yield using polymer supported MTO catalysts. Thus, the oxidation of 1(*R*)-α-pinene **8** with **1** afforded α-pinene oxide **8a** in 76% conversion and 95% yield as the only recovered product (Scheme 2, Table 1, entry 18). When the reaction was performed with **2** and **3**, epoxide **8a** was again obtained as the only recovered product in 81 and 70% conversion, and 88 and 98% yields, respectively (Table 1, entries 19 and 20). In this case, microencapsulated **4** was the best catalytic system affording **8a** in quantitative conversion and yield (Table 1, entry 21). Products of oxiranyl ring-opening (pinanediol) or oxiranyl ring rearrangement (campholenic aldehyde, isopinocamphone) were not recovered in the reaction mixture.

A higher selectivity of heterogeneous MTO compounds with respect to MTO was further observed in the oxidation of *R*-(+)-limonene **9** with **1** (Scheme 2). The *trans*-1,2-epoxide **9a** was obtained as the only recovered product in 75% conversion and 83% yield (Table 1, entry 23). Similar results were obtained in the oxidation of **9** with **2** (Table 1, entry 24). On the other hand, almost equal amount of *cis*- and *trans*-limonene oxides were recovered in the epoxidation with homogeneous MTO (Table 1, entry 22).[12,21] In conclusions, poly(4-vinylpyridine)/MTO and polystyrene/MTO systems are efficient and selective catalysts for the conversion of monoterpenes to the corresponding epoxides, using environment friendly, easily available, and low cost $H_2O_2$ as the oxygen atom donor. All catalysts were stable systems for at least fives recycling experiments and values of the loading factor of the catalyst higher than 1.0 did not give an appreciable increase in the conversion of substrates. Irrespective of the catalyst used, the oxidation of allylic monoterpenes **5** and **6** proceeds selectively at the more electron-rich 6,7-double bond in accord with the electrophilic character of the oxidant. To the best of our knowledge this is the first example described in the literature of heterogeneous catalysts with a peroxy acids like regioselectivity in the epoxidation of allylic monoterpenes.[4–6] In the oxidation of cyclic monoterpenes **7** and **9** polymer-supported MTO catalysts showed, in some cases, a higher reactivity and facial selectivity than their homogenous counterpart.

## 1. Experimental

All commercial products were of the highest grade available and were used as such. Hydrogen peroxide was a 35% aqueous solution (Aldrich). NMR spectra were recorder on a Bruker (200 MHz). Gas chromatography and gas chromatography-mass spectroscopy (GC-MS) of the reaction products were performed using a SPB column (25 m×0.30 mm and 0.25 mm film thickness) and isothermal temperature profile of 80°C for the first 2 min, followed by a 10°C/min temperature gradient to 200°C for 10 min. The injector temperature was 200°C. Chromatography grade helium was used as the carrier gas. In GC calculations, all peaks amounting to at least 0.3% of the total products were taken into account. When necessary, chromatographic purification were performed on columns packed with silica gel, 230–400 mesh, for flash technique. Mass spectra were recorded with an electron beam of 70 eV.

### 1.1. Starting materials

Poly(4-vinylpyridine)/MTO and polystyrene/MTO catalysts were prepared as previously reported.[14] In summary, to a suspension of 600 mg of the appropriate resin in 4 mL of ethanol (tetrahydrofuran in the case of polystyrene) was added 77 mg (0.3 mmol) of MTO, and the mixture was stirred for 1 h using a magnetic stirrer. Coocervates were found to envelop the solid core dispersed in the medium and 5.0 mL of hexane were added to harden the capsule walls. The solvent was removed by filtration, and the solid residue was washed with ethyl acetate and finally dried under high vacuum. The suspension was stirred for 1 h at this temperature and then slowly cooled to 0°C. In each case, MTO had completely become bound to the polymer. This result was confirmed by spectroscopic analysis of the residue obtained after evaporation of the organic layers. The catalyst was used without any further purification. Terpene derivatives **5–9** were obtained from a commercial source (Aldrich).

### 1.2. Synthesis of terpene epoxides. General procedure

To the suspension of 146 mg of the appropriate catalyst (loading factor 1.0) in 5.0 mL of $CH_3CN/CH_2Cl_2$ (ratio 1:1 v/v) at 25°C were added the terpene (1 mmol) to be oxidised and $H_2O_2$ (1.2 mmol, 35% water solution). The suspension was filtered and the recovered catalyst washed with ethyl acetate. After drying under high vacuum, the catalyst was used for further reaction to evaluate its stability. The solvent was dried over $Na_2SO_4$. After the evaporation of the solvent, the crude product was analysed by gas chromatography-mass spectroscopy and when necessary purified by flash-chromatography. Identity of epoxide products was confirmed by 200 MHz $^1H$ and $^{13}C$ NMR and mass-spectroscopy (EI) analyses. Spectra were compared with those of authentic compounds. Listed data are available for α-pinene oxide,[23] epoxygeraniols,[7] epoxynerols,[7] 3-carene oxide,[25] and 1,2-limonene oxide.[24,25]

**1.2.1. 6,7-Epoxygeraniol 5a.** Oil, bp 243–244°C [lit.,[26] bp 243°C], $\delta_H$ [$CDCl_3$, 200 MHz] 1.24–1.35 and 1.73–1.80 (2H, 2×m, H-5), 1.31 and 1.35 (6H, 2×s, H-8,9), 1.73 (3H, s, H-10), 2.06–2.34 (2H, m, H-4), 2.73 (1H, s broad, H-6), 4.23 (2H, s broad, H-1), 5.49 (1H, s broad, H-2). $\delta_C$ [$CDCl_3$, 200 MHz] 16.2 (C-10), 18.7, 24.8 and 27.1 (C-5, 8, 9), 36.3 (C-4), 58.6 (C-1), 59.4 (C-7), 64.1 (C-6), 124.6 (C-2), 138.8 (C-3). MS (EI) *m/z* 170 ($M^+$, 1), 97 (22), 81 (75), 71 (52), 59 (95), 41 (100).

**1.2.2. 2,3-Epoxygeraniol 5b.** Oil, bp 238–241°C [lit.,[27] bp 238°C], $\delta_H$ [$CDCl_3$, 200 MHz] 1.30 (3H, s, H-10), 1.28–1.32 and 1.42–1.52 (2H, 2×m, H-5), 1.61 (3H, s, H-8), 1.68 (3H, d, $J$=1.2 Hz, H-9), 2.04–2.12 (2H, m, H-4), 2.98 (1H, m, H-2), 3.66 (1H, m, H-1), 3.82 (1H, m, H-1), 5.08 (1H, m, H-6). $\delta_C$ [$CDCl_3$, 200 MHz] 16.6 (C-10), 17.5, 23.6 and 25.6 (C-5, 8, 9), 38.4 (C-4), 61.2 (C-3), 61.3 (C-1), 63.1 (C-2), 123.2 (C-6), 132.0 (C-7). MS (EI) *m/z* 170 ($M^+$, 1), 95 (22), 82 (34), 67 (61), 55 (33), 41 (100).

**1.2.3. 2,3,6,7-Diepoxygeraniol 5c.** Oil, bp 258–261°C, $\delta_H$ [$CDCl_3$, 200 MHz] 1.25–1.34 (9H, 3×s, H-8, 9, 10), 1.21–1.33 and 1.53–1.90 (4H, m, H-4,5), 2.75 (1H, s broad, H-6), 3.01 (1H, s broad, H-2), 3.73–3.82 (2H, m, H-1). $\delta_C$ [$CDCl_3$, 200 MHz] 16.5 (C-10), 18.6, 24.6, 29.7 (C-5, 8, 9), 35.65 (C-4), 60.7, 62.5, 63.5, 64.3, 64.6 (C-1,2,3,6,7). MS (EI) *m/z* 186 ($M^+$, 1), 111 (15), 84 (47), 71 (37), 59 (30), 53 (100).

**1.2.4. 6,7-Epoxynerol 6a.** Oil, bp 243–245°C [lit.,[26] bp 243°C], $\delta_H$ [$CDCl_3$, 200 MHz] 1.31 (3H, s, H-8), 1.28 (3H, s, H-9), 1.52–1.81 (2H, m, H-5), 1.78 (3H, s broad, H-10), 2.18–2.34 (2H, m, H-4), 2.74 (1H, dd, $J$=5.1, 7.7 Hz, H-6), 4.07–4.21 (2H, m, H-1), 5.52 (1H, t, $J$=7.2 Hz, H-2). $\delta_C$ [$CDCl_3$, 200 MHz] 18.8 and 24.8 (C-8,9), 23.3 (C-10), 26.9 (C-5), 28.4 (C-4), 58.8 (C-1), 58.9 (C-7), 63.8 (C-6), 125.2 (C-2), 138.9 (C-3). MS (EI) *m/z* 170 ($M^+$, 3), 153 (34), 143 (66), 125 (41), 110 (63), 81 (89), 71 (93), 59 (100).

**1.2.5. 2,3-Epoxynerol 6b.** Oil, bp 238–240°C [lit.,[26] bp 238°C], $\delta_H$ [$CDCl_3$, 200 MHz] 1.35 (3H, s, H-10), 1.48 (1H, ddd, $J$=7.2, 9.7, 13.8 Hz, H-5), 1.62–1.75 (1H, m, H-5), 1.62 (3H, s, H-8), 1.69 (3H, s, H-9), 1.99–2.19 (2H, m, H-4), 2.97 (1H, dd, $J$=4.3, 6.9 Hz, H-2), 3.66 (1H, dd, $J$=6.9, 12.1 Hz, H-1), 3.82 (1H, dd, $J$=4.3, 12.1 Hz, H-1), 5.10 (1H, tq, $J$=1.3, 7.2 Hz, H-6). $\delta_C$ [$CDCl_3$, 200 MHz] 18.8 and 24.8 (C-8,9), 23.3 (C-10), 26.9 (C-5), 28.4 (C-4), 58.8 (C-1), 58.9 (C-7), 63.8 (C-6), 125.2 (C-2), 138.9 (C-3). MS (EI) *m/z* 170 ($M^+$, 1), 109 (35), 82 (33), 69 (57), 41 (100).

**1.2.6. 2,3,6,7-Diepoxynerol 5c.** Oil, bp 258–261°C, $\delta_H$ [$CDCl_3$, 200 MHz] 1.30–1.37 (9H, 3×s, H-8,9,10), 1.54–1.87 (4H, m, H-4,5), 2.74–2.81 (1H, m, H-6), 2.98–3.05 (1H, m, H-2), 3.76 (2H, m, H-1). $\delta_C$ [$CDCl_3$, 200 MHz] 18.6, 22, 23.1 and 28.9 (C-5-8-9-10), 29.4 (C-4), 59.3, 60.5 and 61 (C-1, 3, 7), 63.6 and 64 (C-2,6). MS (EI) *m/z* 186 ($M^+$, 1), 173 (4), 167 (8), 149 (12), 143 (54), 125 (40), 111 (59), 97 (55), 85 (93), 71 (96), 59 (100).

**1.2.7. α-3,4-Epoxycarene 7a.** Oil, bp 182–184°C [lit.,[28] bp 182°C], $\delta_H$ [$CDCl_3$, 200 MHz] 0.45 (1H, ddd, $J$=2.2, 8.9, 9.1 Hz, H-1 eq), 0.53 (1H, ddd, $J$=2.3, 8.9, 9.1 Hz, H-6 eq), 0.73 (3H, s, H-8), 1.01 (3H, s, H-9), 1.26 (3H, s, H-10), 1.49 (1H, dd, $J$=2.2, 16.2 Hz, H-2 eq), 1.64 (1H, dt, $J$=2.3, 16.4 Hz, H-5 eq), 2.15 (1H, dd, $J$=9.1, 16.2 Hz, H-2 ax), 2.30 (1H, ddd, $J$=1.9, 8.9, 16.4 Hz, H-5 ax), 2.85 (1H, t, $J$=1.9 Hz, H-4). $\delta_C$ [$CDCl_3$, 200 MHz] 13.8 (C-1), 14.6 (C-8), 15.9 (C-6), 16.0 (C-7), 19.1 (C-5), 23.1 (C-10), 23.3 (C-2), 26.7 (C-9), 56.1 (C-3), 58.3 (C-4). MS (EI) *m/z* 152 ($M^+$, 2), 137 (42), 109 (62), 91 (24), 81 (45), 67 (82), 43 (100), 39 (56).

**1.2.8. α-Pinene oxide 8a.** Oil, bp 102–104°C /50 mm [lit.,[29] bp 102–103°C/50 mm], $\delta_H$ [$CDCl_3$, 200 MHz] 0.91 (3H, s, $CH_3$), 1.30 (3H, s, $CH_3$), 1.32 (3H, s, $CH_3$), 1.59 (1H, m, CH), 1.72 (1H, m, CH), 1.90–2.05 (4H, m, $CH_2$), 3.08 (1H, m, CH). $\delta_C$ [$CDCl_3$, 200 MHz] 60.23 (s, C-1), 56.7 (d, C-2), 44.9 (d, C-6), 40.4 (s, C-10), 39.6 (d, C-4), 27.64 (t, C-5), 26.72 (q, C-9), 25.87 (t, C-3), 22.41 (q, C-8), 20.18(q, C-7). MS (EI) *m/z* 152 ($M^+$).

**1.2.9. Limonene oxide 9a.** Oil, bp 113–114°C /50 mm [lit.,[30] bp 113–114°C/50 mm], $\delta_H$ [$CDCl_3$, 200 MHz] 4.65 (2H, m, $CH_2$), 3.10 (1H, m, CH), 2.97 (1H, m, CH), 2.20–1.40 (6H, 3×m, $CH_2$), 1.55 (3H, s, $CH_3$), 1.20 (3H, s, $CH_3$). $\delta_C$ [$CDCl_3$, 200 MHz] 20.19 (q, C-7), 22.05 (q, C-8), 25.81 (t, C-3), 28.53 (t, C-5), 30.66 (t, C-6), 40.68 (d, C-4), 57.35 (s, C-1), 59.24 (d, C-2), 109.0 (d, C-8), 148.78 (s, C-7). MS (EI) *m/z* 152 ($M^+$).

## References

1. Bauer, K.; Garbe, D.; Surburg, H. *Common Fragrance and Flavour Materials*. Wiley: New York, 1997.
2. *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed., Electronic Release, Wiley: New York, 1998.
3. For a recent review of alkene epoxidation using hydrogen peroxide see: (a) Grigoropoulou, G.; Clark, J. H.; Elings, J. A. *Green Chem.* **2003**, *5*, 1–7. (b) Villa, P. A. L.; Sels, B. F.; De Vos, D. E.; Jacobs, P. A. *J. Org. Chem.* **1999**, *64*, 7267–7270.
4. (a) Suh, Y.-W.; Kim, N.-K.; Ahn, W.-S.; Rhee, H.-K. *J. Mol. Catal. A: Chem.* **2001**, *174*, 249–254. (b) Cativiela, C.; Fraile, J. M.; García, J. I.; Mayoral, J. A. *J. Mol. Catal. A: Chem.* **1996**, *112*, 259–267. (c) Guidotti, M.; Conti, L.; Fusi, A.; Ravasio, N.; Psaro, R. *J. Mol. Catal. A: Chem.* **2002**, *182-183*, 151–156. (d) Kumar, R.; Pais, G. C. G.; Panoley, B.; Kumar, P. *J. Chem. Soc., Chem. Commun.* **1995**, 1315–1316.
5. Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. *J. Org. Chem.* **1996**, *61*, 5307–5311.
6. Banthorpe, D. V.; Barrow, S. E. *Chem. Ind.* **1981**, *14*, 502.
7. Martins, R. R. L.; Neves, G. P. M. S.; Silvestre, A. J. D.; Simões, M. M. Q.; Silva, A. M. S.; Tomé, A. C.; Cavaleiro, J. A. S.; Tagliatesta, P.; Crestini, C. *J. Mol. Catal. A: Chem.* **2001**, *172*, 33–42.
8. Beattie, I. R.; Jones, P. *J. Inorg. Chem.* **1979**, *18*, 2318.
9. (a) Herrmann, W. A.; Fischer, R. W.; Marz, D. W. *Chem. Rev.* **1997**, *97*, 3197–3246. (b) Kuhn, F. E.; Santos, A. M.; Goncalves, I. S.; Rõmao, C. C.; Lopes, A. D. *Appl. Org. Chem.* **2001**, *15*, 43–50.
10. See for example: (a) Al-Ajlouni, A. M.; Espenson, J. H. *J. Org. Chem.* **1996**, *61*, 3969–3976. (b) Gisdakis, P.; Antonczak, S.; Köstlmeier, S.; Herrmann, W. A.; Rösch, N. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2211. (c) Adam, W.; Mitchell, C. M. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 533–535. (d) Saladino, R.; Carlucci, P.; Danti, M. C.; Crestini, C.; Mincione, E. *Tetrahedron* **2000**, *56*, 10031–10037. (e) Herrmann, W. A.; Fischer, R. W.; Rauch, M. U.; Scherer, W. *J. Mol. Catal.* **1994**, *86*, 243–266. (f) Copèret, C.; Adolfsson, H.; Sharpless, K. B. *J. Chem. Soc., Chem. Commun.* **1997**, 1915. (g) Ferreira, P.; Xue, W.-M.-; Bencze, E.; Herdtweck, E.; Kühn, F. E. *Inorg. Chem.* **2001**, *40*, 5834–5841. (h) Herrmann, W. A.; Fischer, R. W.; Scherer, W.; Rauch, M. U. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1157–1160. For recent computational studies on MTO epoxidation see: (i) Gisdakis, P.; Yudanov, I. V.; Rösch, N. *Inorg. Chem.* **2001**, *40*, 3755–3765. (j) Di Valentin, C.; Gandolfi, R.; Gisdakis, P.; Rösch, N. *J. Am. Chem. Soc.* **2001**, *123*, 2365–2376.
11. Boehlow, T. R.; Spilling, C. D. *Tetrahedron Lett.* **1996**, *37*, 2717–2720.
12. Villa de P., A. L.; De Vos, D. E.; Montes, C. C.; Jacobs, P. A. *Tetrahedron Lett.* **1998**, *39*, 8521–8524.
13. Iskra, J.; Bonnet-Delpon, D.; Bégué, J.-P. *Tetrahedron Lett.* **2002**, *43*, 1001–1003.

14. Saladino, R.; Neri, V.; Pelliccia, A. R.; Caminiti, R.; Sadun, C. *J. Org. Chem.* **2002**, *67*, 1323–1332.
15. Herrmann, W. A.; Fritz-Meyer-Weg, D. M.; Wagner, M.; Küchler, J. G.; Weichselbaumer, G.; Fischer, R. US Patent 5, 155, 247, October 13, 1992.
16. Donbrow, M. *Microcapsules and Nanoparticles in Medicine and Pharmacy*; CRC: Boca Raton, FL, 1992.
17. (a) Takaaki, S.; Chyongjin, P. *Kawamura Rikagaku Kenkyusho Hokoku* **2000**, 59–64. (b) Wang, T.-J.; Li, D.-C.; Bai, J.-H.; Huang, M.-Y.; Jiang, Y.-Y. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 531–538.
18. Adam, W.; Saha-Möller, C. R.; Weichold, O. *J. Org. Chem.* **2000**, *65*, 2897–2899.
19. Saladino, R.; Neri, V.; Mincione, E.; Filippone, P. *Tetrahedron* **2002**, *58*, 8493–8500.
20. Bhaumik, A.; Kumar, R.; Ratnasamy, P. *Stud. Surf. Sci. Catal.* **1994**, *84*, 1883.
21. Battioni, P.; Renaud, J. P.; Batoli, J. F.; Reina-Artiles, M.; Fort, M.; Mansuy, D. *J. Am. Chem. Soc.* **1988**, *110*, 8462.
22. Catalysts **2**–**4** behave in a similar way.
23. Herrmann, W. A.; Correira, J. D. G.; Rauch, M. U.; Artus, G. R. J.; Kühn, F. E. *J. Mol. Catal. A* **1997**, *118*, 33–45.
24. Pouchert, C.; Behnke, J. *The Aldrich Library of $^{13}$C and $^{1}$H FT-NMR Spectra*; Aldrich Chemical: Milwaukee, 1993.
25. Folil, N.; Romane, A.; Allaoud, S.; Karim, A.; Castanet, Y.; Mortreux, A. *J. Mol. Catal.* **1996**, *108*, 15.
26. Nohara, I.; Eniura, M.; Toyota, T.; Kanisawa, T. *J. Essent. Oil Res.* **1997**, *9*, 727–729.
27. Ishikowa, A.; Katsuki, T. *Tetrahedron Lett.* **1991**, *32*, 3547–3550.
28. Martins, R. R. L.; Neves, M. G. P.; Silvestre, A. J. D.; Simoes, M. M. Q.; Silva, A. M. S.; Tome, A. C.; Cavaleiro, J. A. S.; Tagliatesta, P.; Crestini, C. *J. Mol. Catal. A: Chem.* **2001**, *172*, 33–42.
29. *Beil.* 5, 152. The product was identical to an authentic commercially sample (Aldrich, Co.).
30. *Beil.* 17, 44. The product was identical to an authentic commercially sample (Aldrich, Co.).