HYDROGEN-PEROXIDE EPOXIDATION OF NATURAL OLEFINS CATALYZED BY A DINUCLEAR MANGANESE COMPLEX

**D. Mandelli,[1] K. B. Voitiski,[1] U. Schuchardt,[2]**
and G. B. Shul′pin[3]

The complex of Mn(IV) with the macrocyclic N-containing ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L) [L$_2$Mn$_2$O$_3$](PF$_6$)$_2$ catalyzes epoxidation of (+)-limonene in CH$_3$CN solution at room temperature. Adding CH$_3$COOH accelerates the reaction. The products are isomers of limonene epoxide with predominance of that with an epoxified ring double bond. Epoxidation of α- and β-pinene by this system is less effective, apparently due to extensive steric shielding of the double bonds in the pinenes.

Key words: terpenes, limonene, pinene, epoxidation, catalysis, hydrogen peroxide, manganese complexes.

Oxidation, in particular, the epoxidation of terpenes that is observed in many Brazilian tropical and subtropical plants, is an important process from a practical viewpoint because the products are valuable starting materials for the synthesis of fragrances and drugs [1]. The dinuclear complex of Mn(IV) with the macrocyclic N-containing ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L) [L$_2$Mn$_2$O$_3$](PF$_6$)$_2$ (**1**) catalyzes oxidation of saturated hydrocarbons, secondary alcohols, and sulfides by H$_2$O$_2$ in CH$_3$CN at room or even reduced temperature [2-7]. An organic acid, in particular, acetic, is mandatory.

We investigated oxidation by the above system of certain natural terpenes such as (+)-limonene (**2**) and α- and β-pinene (**6** and **9**, respectively). We have found that the hydrocarbon is practically inactive in the absence of a small quantity of acetic acid.

Epoxidation of limonene, which contains two different double bonds, gives products of addition to both the internal ring double bond and the double bond in the side chain (Table 1). The first product dominates. The ratio **3/4** varies from 1.4 (expt. No. 7), to 3.5 (expt. No. 9) depending on the reagent concentrations and the reaction time. The unoptimized maximum yield of both monoepoxides was almost 50% based on starting limonene. Use of an excess of H$_2$O$_2$ and a short reaction time formed in significant quantities the product of double epoxidation at both double bonds (**5**) (expts. No. 8, 9, and 10). The overall yield of epoxides was >75% based on starting limonene. Another product of unknown structure (the concentration of which in Table 1 is denoted by [*x*]) was formed in several experiments (4, 8, 9, 10). However, the amount of it was much less than those of the target epoxides (GC).

2   3   +   4   +   5

---
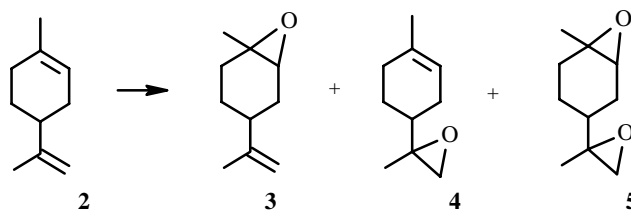
1) Institute of Biology and Chemistry, Catholic University, Campinas, Sao Paolo, 13020 904, Brazil, e-mail: dalmo.mandelli@uol.com.br; 2) Institute of Chemistry, State University, Campinas, Sao Paolo, 13083 970, Brazil, e-mail: ulf@iqm.unicamp.br; 3) N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow 119991, fax (7095) 137 61 30, e-mail: shulpin@chph.ras.ru.

TABLE 1. Oxidation of (+)-Limonene by H_2O_2—**1**—CH_3COOH in CH_3CN at 25°C

No.	[1]	$[H_2O_2]_0$	t, min	E, %	[3]	[4]	[3]/[4]	[5]	[x]	ES, %	MB, %
1	5×10^{-5}	0.25 (anhydr.)	15	5	0.007	0.004	1.8	0.000	0.000	46	98
			60	11	0.018	0.010	1.8	0.000	0.000	75	96
2	5×10^{-5}	1.25 (anhydr.)	30	33	0.017	0.013	1.3	0.000	0.000	92	99
3	25×10^{-5}	0.25 (anhydr.)	30	15	0.024	0.014	1.7	0.001	0.002	86	98
4	25×10^{-5}	1.25 (anhydr.)	30	36	0.062	0.029	2.1	0.080	0.010	77	84
5	5×10^{-5}	0.11 (30% aq)	15	0	0.000	0.000		0.000	0.000		
			60	2	0.003	0.002	1.5	0.000	0.000	65	99
6	5×10^{-5}	0.43 (30% aq)	15	14	0.025	0.011	2.3	0.000	0.001	87	98
			60	18	0.032	0.014	2.3	0.005	0.002	86	97
7	5×10^{-5}	1.3 (30% aq)	15	1	0.002	0.000		0.000	0.000	66	100
			60	15	0.023	0.014	1.6	0.000	0.000	91	99
			120	14	0.021	0.015	1.4	0.000	0.000	59	90
8	20×10^{-5}	1.3 (30% aq)	15	37	0.066	0.027	2.4	0.042	0.006	62	71
			60	45	0.082	0.030	2.7	0.068	0.010	75	83
9	25×10^{-5}	1.25 (30% aq)	15	48	0.094	0.027	3.5	0.034	0.008	81	89
10	25×10^{-5}	1.25 (70% aq)	15	44	0.083	0.026	3.2	0.059	0.004	77	82

———

Concentrations (M) of reagents and products are given in square brackets. The index 0 denotes starting concentrations. In all experiments $[2]_0$ 0.25 M, $[CH_3COOH]$ = 0.25 M, t is the reaction time in min. The yield of isomeric monoepoxides (E, %) is calculated using $E = 100([3] + [4])/[2]_0$. The selectivity for formation of all epoxides (ES, %) is measured using $ES = 100([3] + [4] + [5])/([2]_0 - [2])$, where $[2]_0$ and [2] are the starting and instantaneous limonene concentrations. Mass balance (MB, %) was determined using $MB = 100([3] + [4] + [5] + [x])/([2]_0 - [2])$, where [x] is the concentration of an unknown side product estimated from GC. H_2O_2 was used as either the anhydrous product obtained by distillation of a 50% aqueous solution with further drying over anhydrous $MgSO_4$ or aqueous solutions (30 and 70%).

Epoxidation of both pinene isomers was less efficient (Table 2). The yield of target epoxide was <10%. Furthermore, significant quantities of side products (this product is cyclohexene derivative **8** for oxidation of α-pinene; the structure of the second product from oxidation of β-pinene was not established) appeared.
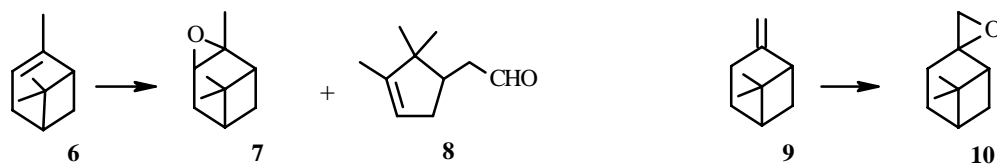
We propose that the low efficiency of this system for pinene oxidation is due to extensive steric hindrance by the substituents to approach of the bulky catalytic molecule. This indicates that epoxidation occurs via a mechanism that does not involve formation of free radicals. Their generation during oxidation of alkanes by t-butylhydroperoxide catalyzed by **1** (in the absence of CH_3COOH, although it slightly accelerates oxygenation of saturated hydrocarbon [7]) has been assumed. We observed that **1** does not catalyze epoxidation of limonene by t-butylhydroperoxide even in the presence of CH_3COOH in CH_3CN. This also is consistent with oxidation by H_2O_2 without formation of free radicals.

Thus, the results lead to the conclusion that the described catalytic system is useful for efficient epoxidation of sterically accessible olefins, including natural compounds.

TABLE 2. Oxidation of α- (6) and β-Pinene (9) by H_2O_2—1—CH_3COOH in CH_3CN at 25°C

Substrate	[1]	$[H_2O_2]0$	t, min	E, %	[7] or [10]	[x]	ES, %	MB, %
α-Pinene	5×10^{-5}	1.3 (30% aq)	15	x	0.024	0.007	97	100
			30	x	0.019	0.013	69	91
			60	x	0.010	0.017	58	87
β-Pinene	5×10^{-5}	0.43 (30% aq)	15		0.005	0.002	64	98
			30	x	0.004	0.003		97
	25×10^{-5}	1.25 (anhydr.)	30		0.025	0.006	70	94

———

Concentration (M) of reagents and products are diven in brackets. The index o denotes starting concentrations. In all experiments $[Pinene]_0 = 0.25$ M, t is the reaction time in min. The epoxide yield (E, %) is calculated using $E = 100[7]/[6]_0$ and $E = 100[10]/[9]_0$. The selectivity for formation of epoxide (ES, %) is measured using $ES = 100[7]/([6]_0 - [6])$ and $ES = 100[10]/([9]_0 - [9])/$ Mass balance (MB, %) was determined using $MB = 100([7] + [8])/([6]_0 - [6])$ and $MB = 100([10] + [x])/([9]_0 - [9])$, where $[x]$ is the concentration of an unknown side product estimated from GC.

EXPERIMENTAL

Reactions were performed in cylindrical glass containers surrounded by a jacket through which thermostatted water was passed. The solution volume was 5 mL. Samples of the reaction mixture (0.5 mL) were taken at certain time intervals. These were treated (within several minutes) with an excess of solid manganese oxide to decompose unreacted H_2O_2 and analyzed by GC on a Hewlett—Packard Series II 5890 instrument with a reinforced quartz injector and quartz column packed with Carbowax 20M (25 m × 0.2 mm, 0.2 μm) using He carrier gas.

Complex 1 was synthesized as before [8, 9]. CH_3CN was distilled before use over P_2O_5.

ACKNOWLEDGMENT

REFERENCES

1. G. Sienel and R. Rieth, *Ulmann's Encyclopedia of Industrial Chemistry*, L. Kaudy, J. F. Rounsaville, and G. Schulz, Eds., VCH, Weinheim (1987), Vol. A9, p. 541.
2. J. R. Lindsay Smith and G. B. Shul′pin, *Tetrahedron Lett.*, 39, No. 27, 4909 (1998).
3. J. R. Lindsay-Smith and G. B. Shul′pin, *Izv. Akad. Nauk, Ser. Khim.*, No. 11, 2385 (1998); Engl. transl.: *Russ. Chem. Bull.*, 47, No. 11, 2313 (1998).
4. G. B. Shul′pin and J. R. Lindsay-Smith, *Izv. Akad. Nauk, Ser. Khim.*, No. 12, 2459 (1998); Engl. transl.: *Russ. Chem. Bull.*, 47, No. 12, 2379 (1998).
5. G. B. Shul′pin, G. Suss-Fink, and J. R. Lindsay Smith, *Tetrahedron*, 55, No. 17, 5345 (1999).
6. G. B. Shul′pin, G. Suss-Fink, and L. S. Shul′pina, *J. Mol. Catal. A: Chem.*, 170, No. 1-2, 17 (2001).
7. G. B. Shul′pin, *Neftekhimiya*, 41, No. 6, 440 (2001); Engl. transl.: *Petrol. Chem.*, 41, No. 6, 405 (2001).
8. K. Wieghardt, U. Bossek, B. Nuber, J. Weiss, J. Bonvoisin, M. Corbella, S. E. Vitols, and J. J. Girerd, *J. Am. Chem. Soc.*, 110, 7398 (1988).
9. J. H. Koek, S. W. Russell, L. van der Wolf, R. Hage, J. B. Warnaar, A. L. Spek, J. Kerschner, and L. DelPizzo, *J. Chem. Soc., Dalton Trans.*, 353 (1996).