Scheme II

$$DCN^{*1} + CHD \longrightarrow \underset{\text{Exciplex}}{(DCN\cdots CHD)^{*1}} \quad (7)$$

$$(DCN\cdots CHD)^{*1} \longrightarrow DCN + CHD^{*3} \xrightarrow{CHD} \underset{\text{Dimers}}{\text{triplet}} \quad (8)$$

$$(DCN\cdots CHD)^{*1} \xrightarrow{CHD} \underset{\text{Triplex}}{(DCN\cdots CHD\cdots CHD)^{*1}} \quad (9)$$

$$(DCN\cdots CHD\cdots CHD)^{*1} \longrightarrow DCN + \text{mainly Dimer 1} \quad (10)$$

[CHD]) gives the bimolecular rate constant for reaction of $CHD^{+\cdot}$ with CHD (k_2, eq 2) equal to 3×10^8 M^{-1} s^{-1} from the slope of the linear plot.

The DCN-sensitized dimerization of CHD in benzene exhibits quite different properties. When the concentration of CHD is 0.11 M the major products (75%) are the triplet-derived [2 + 2] adducts and the ratio of endo to exo [4 + 2] dimers is 0.16. However, the yield of [4 + 2] adducts increases to 50% at 2.1 M CHD, and the endo to exo ratio becomes 1.30. The quenchers that inhibit formation of [4 + 2] dimer **1** in acetonitrile solution have no effect on the reaction in benzene. Finally, laser flash photolysis of DCN in benzene containing CHD shows quite clearly that no radical ion intermediates are formed.

The results suggest operation of the reaction sequence shown in abbreviated form in Scheme II. A key step in this sequence is the interception of an exciplex of CHD and DCN by CHD to form a triplex (eq 9). Triplexes have been observed before at high reagent concentrations,[19] and Jones[7] has suggested that one may participate in CHD dimerization.

These findings can be applied to the analysis of the aminium salt initiated dimerization of CHD in acetonitrile solution. The yield of Diels-Alder dimers is decreased more than fivefold when 2.8×10^{-2} M TMB is included with 0.21 M CHD and the reaction is initiated by addition of tris(*p*-bromophenyl)aminium hexachlorostibnate (1×10^{-2} M). This finding supports operation of the radical cation chain mechanism for the dimerization of CHD in acetonitrile. However, the maximum equilibrium concentration of $CHD^{+\cdot}$ (at 1 M CHD) under these conditions is only ca. 10^{-11} M. The large value we obtain for k_2 provides an explanation for how this low concentration of ions can give a good yield of dimers. However, in general this reaction will be sensitive to steric and electronic retardation and thus may often require much higher steady-state concentrations of active ions to give useful yields of dimer products by this mechanism.

Acknowledgment. This work was supported by a grant from the National Science Foundation.

Registry No. CHD, 592-57-4; TMB, 621-23-8; tris(*p*-bromophenyl)-aminium hexachlorostibnate, 40927-19-3.

(19) Weller, A.; Beens, H. *Chem. Phys. Lett.* **1968**, *2*, 140. Caldwell, R. A.; Creed, D.; DeMarco, D. C.; Melton, L. A.; Ohta, H.; Wine, P. H. *J. Am. Chem. Soc.* **1980**, *102*, 2369. Davidson, R. S. *Adv. Phys. Org. Chem.* **1983**, *19*, 43 and references therein.

Stereospecific, Regioselective, and Catalytic Monoepoxidation of Polyolefins by the Use of a P-450 Model, H_2-O_2-TPP·Mn-Colloidal Platinum

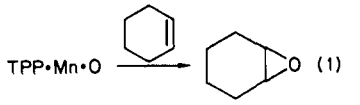
Iwao Tabushi* and Kozo Morimitsu

Department of Synthetic Chemistry, Kyoto University Sakyo-Ku, Kyoto 606, Japan

Received April 30, 1984

Although a variety of successful attempts have been made for the structure elucidation of the probable intermediates involved in the reductive activation of dioxygen by cyt P-450,[1] real activation of dioxygen by artificial porphyrin-metal complexes in the presence of reducing reagents had not been achieved until the recent finding of an efficient catalytic system consisting of dihydrogen-TPP·Mn (manganese complex of tetraphenylporphyrin)-methylimidazole-colloidal platinum.[2] Simple olefins were monooxygenated with the P-450 model system, giving the corresponding epoxides as the major products with excellent turnover (64.7 recycling number, i.e., 64.7 mol of cyclohexene oxide per 1 mol of TPP·Mn used), and with some loss of the catalyst (60% of the catalyst remained unchanged,[2] or 162 mol of the epoxide formed per 1 mol of TPP·Mn consumed).

$$TPP\cdot Mn^{III} \xrightarrow[\text{colloidal Pt}]{H_2} TPP\cdot Mn^{II} \xrightarrow[\text{colloidal Pt/EtOH}]{O_2,\ H_2}$$



(1)

Now the authors wish to report the stereospecific, regioselective, and efficiently catalytic (with large turnover) monoepoxidation of polyolefins by the use of the artificial P-450-type O_2 activating system (colloidal Pt, H_2, and $TPP\cdot Mn^{III}$). Aqueous $T_{SO_3Na}PP\cdot Mn^{III}$ was preferred to $TPP\cdot Mn^{III}$ in organic solvents, because colloidal platinum is much more stable in water than in organic solvents.

Colloidal platinum supported on poly(vinyl alcohol) (PVA) or poly(vinylpyrrolidone) (PVP) was prepared according to the literature[3] (with slight modifications[2]). Experimental results and reaction conditions employed are listed in Table I.

The most important finding is the large size of the recycling numbers obtained for the present catalyst systems, especially in aqueous ethanol. After 48 h, 30-150 mol of the epoxide was formed per unit mol of $TPP\cdot Mn^{III}$ used, where loss of $TPP\cdot Mn^{III}$ was less than 27% (the theoretical recycling number is 280-533 mol product/mol of TPP·Mn consumed). The electron-transfer activity of colloidal Pt was also preserved. Under appropriate conditions, colloidal Pt was still active after 264 recyclings (products mol/Pt atom equiv used). Therefore, preservation of the activities of both catalysts, TPP·Mn and colloidal Pt, were quite satisfactory in the protic solvents. In an aprotic solvent like benzene, preservation of catalytic activity of colloidal Pt was somewhat lower than in a protic solvent.

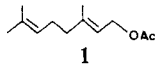
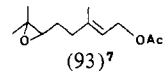
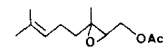
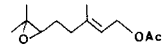
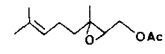
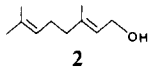
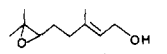
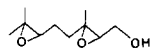
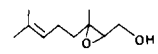
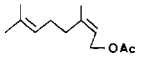
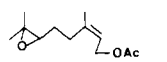
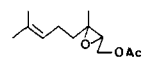
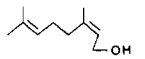
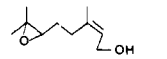
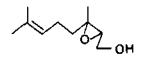
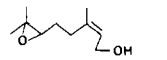
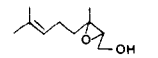
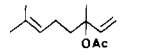
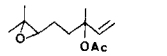
The second advantage of the present H_2-O_2 epoxidation is the almost exclusive monoepoxidation of the polyolefins. In aqueous ethanol, formation of diepoxides from nerol and geraniol was negligible or very small (almost none and less than 3%, respectively), when 85% of the diolefin was converted to the epoxides, based on the GLC analyses.

In addition to these remarkable characteristics, the present P-450-type monoepoxidation preserves two important characteristics which were observed in appropriate noncatalytic epoxidizing reagents,[4] regioselectivity and stereospecificity.[5] The regioselectivity in the present monoepoxidation of geraniol and related compounds was high, as determined by 400-MHz ^1H

(1) (a) White, R. E.; Coon, M. J. *Annu. Rev. Biochem.* **1980**, *49*, 315. (b) Guengerich, F. P.; Macdonald, T. L. *Acc. Chem. Res.* **1984**, *17*, 9.
(2) Tabushi, I.; Yazaki, A. *J. Am. Chem. Soc.* **1981**, *103*, 7371.
(3) Rampino, L. D.; Nord, F. F. *J. Am. Chem. Soc.* **1941**, *63*, 2745.
(4) See review: Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2.
(5) Monoepoxidation of cyclododecatriene and limonene using ferric porphyrins, see: Groves, J. T.; Nemo, T. E. *J. Am Chem. Soc.* **1983**, *105*, 5786. Regioselective intramolecular oxidation of the alkyl chain attached to ferric porphyrin system: (a) Groves, J T.; Nemo, T. E.; Myers, R. S. *Ibid.* **1979**, *101*, 1032. (b) Chang, C. K.; Kuo, M.-S. *Ibid.* **1979**, *101*, 3413.
(6) The regioselectivity of the reaction described here is opposite to that of Sharpless's epoxidation: Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63.
(7) Mousseron-Canet, M.; Mousseron, M.; Levallois, C. *Bull. Soc. Chim. Fr.* **1964**, *297*.
(8) Sharpless, K. B.; Michaelson, R. C. *J. Am. Chem. Soc.* **1973**, *95*, 6136.
(9) Cicala, G.; Curci, R.; Fiorentino, M.; Laricchiuta, O. *J. Org. Chem.* **1982**, *47*, 2670.
(10) Kametani, T.; Kurobe, H.; Nemoto, H. *J. Chem. Soc., Perkin Trans. 1* **1981**, 756.

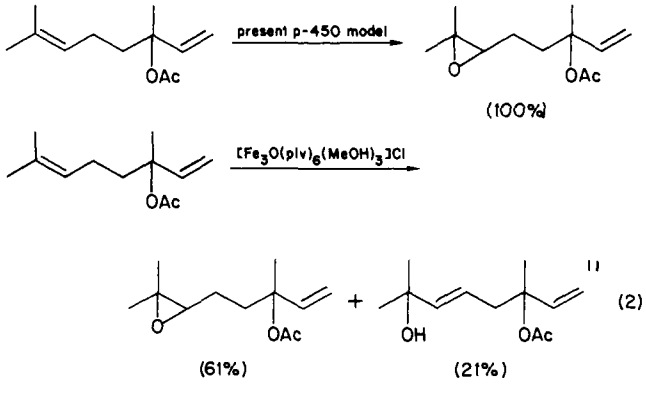
0002-7863/84/1506-6871$01.50/0

Table I. Metalloporphyrin-Catalyzed Epoxidation of Polyolefins

substrates (mol)	solvents, mL	porphyrin[a] (mol)	colloidal Pt (g equiv)	reaction time, h	conversion, %	yield, %[b]	products (ratio, %)[d]	
 1 (2.8×10^{-3})	ethanol, 10; water, 5	TSO_3NaPP (2.8×10^{-5})	Pt/PVA (9×10^{-6})	72	56	5.600 (28.600)[c]	 (93)[7]	 (7)[8]
1 (2.8×10^{-3})	benzene, 4; ethanol, 1	TPP (2.8×10^{-5})	Pt/PVP (6×10^{-6})	60	33	3.300 (34.000)	 (90)	 (10)
 2 (2.8×10^{-3})	ethanol, 5; water, 5	TSO_3NaPP (2.8×10^{-5})	Pt/PVA (9×10^{-6})	48	85	8.500 (53.800)	 (79)[9]  (3)[9]	 (18)[8]
 3 (2.8×10^{-3})	ethanol, 10; water, 5	TSO_3NaPP (5.6×10^{-5})	Pt/PVA (9×10^{-6})	24	81	4.050 (40.500)	 (93)[7]	 (7)[8]
 4 (2.8×10^{-3})	ethanol, 5; water, 5	TSO_3NaPP (2.8×10^{-5})	Pt/PVA (9×10^{-6})	42	88	8.800 (46.300)	 (90)[9]	 (10)[8]
4 (6.5×10^{-3})	ethanol, 5; water, 5	TSO_3NaPP (2.8×10^{-5})	Pt/PVA (9×10^{-6})	72	62	14.390 (53.300)	 (79)	 (21)
 5 (2.8×10^{-3})	ethanol, 10; water, 5	TSO_3NaPP (2.8×10^{-5})	Pt/PVA (9×10^{-6})	82	30	3.000 (45.400)	 (100)[10]	

[a] Amount of 1-methylimidazole is 26 times as much as the metalloporphyrin used. [b] Based on the metalloporphyrin used. [c] In parentheses, the yield based on the metalloporphyrin consumed is shown. [d] Structure of each epoxide was determined by NMR and GLC. Each authentic epoxide was prepared, separated, and purified according to the literature cited.

NMR (see Table II), and ω-terminal epoxidation was much favored[6] (see Table I). Relatively high regioselective terminal epoxidation by a solid catalyst was recently reported.[11] However, the reported system is self-sacrificing (olefins are consumed as electron donors) and selectivity is appreciably lower than the present P-450 model, as shown in eq 2. Stereospecific epoxidation



of simple olefin was previously reported for artificial P-450 systems.[2,12] The stereospecificities determined by the 400-MHz ^1H NMR demonstrate the exclusive formation of the *trans*-epoxides at the internal *trans*-ethylenic linkages. Judging from the peak height of the sharp singlet absorption of the methyl directly attached to the epoxide ring (e.g., δ 1.342 and 1.302 for the cis (**4**) and trans (**2**) isomer, respectively), it was concluded that the present epoxidation proceeded stereospecifically at least 99.9% and 97.0% for the corresponding cis and trans olefins, respectively (these numbers were obtained taking base-line noise into account).

Table II. ^1H NMR Data on Epoxides

	2,3-epoxygeraniol			2,3-epoxynerol		
	δ (from Me_4Si)		coupling pattern	δ (from Me_4Si)		coupling pattern
$C^{10}H_3$	1.30	3 H	s	1.34	3 H	s
C^4H_2	1.44-1.70	2 H	m	1.44-1.70	2 H	m
C^9H_3	1.61	3 H	s	1.62	3 H	s
C^8H_3	1.69	3 H	s	1.69	3 H	s
C^5H_2	2.06-2.11	2 H	m	2.03-2.19	2 H	m
C^2H	2.98	1 H	m	2.97	1 H	m
	(X part of ABX system, J_{AX} = 6.72 Hz, J_{BX} = 4.28 Hz)			(X part of ABX system, J_{AX} = 6.96 Hz, J_{BX} = 4.15 Hz)		
C^1H_2	3.68, 3.83 (AB part, J_{AB} = 12.12 Hz)	2 H	m	3.65, 3.81 (AB part, J_{AB} = 12.15 Hz)	2 H	m
C^6H	5.08	1 H	m	5.09	1 H	m

(11) Ito, S.; Inoue, K.; Matsumoto, M. *J. Am. Chem. Soc.* **1982**, *104*, 6450.
(12) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791.