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CATALYTIC EPOXIDATION OF ALIPHATIC TERMINAL OLEFINS WITH SODIUM HYPOCHLORITE

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Summary: Meso-tetra(halogenophenyl)porphyrinatomanganese complexes catalyze the epoxidation of terminal olefins by sodium hypochlorite at room temperature; moderate to good yields of epoxides are obtained.

The metalloporphyrin-catalyzed epoxidation of olefins with several single-oxygen donors has recently been described (e.g. with PhIO,[1] NaOCl,[2] p-cyano-N,N-dimethylaniline N-oxide,[3] nBu_4IO_4,[4] tBuOOH[5]). *However, until now the less reactive aliphatic terminal olefins could not be epoxidized catalytically in fair yields with these systems.* For example, in a previous paper[2] various di- and tri-substituted olefins were shown to be epoxidized in good yields with the NaOCl/Mn(TPP)OAc system, whereas 1-octene yielded only 1% epoxide. As in this system the epoxidation of the olefin and the oxidative decomposition of the catalyst are competing reactions, Mn(TPP)OAc is destroyed before the poorly reactive 1-octene can be epoxidized.

By modifying the porphyrin ligand we have now succeeded in epoxidizing 1-octene and other terminal olefins catalytically with sodium hypochlorite as the oxygen source. As can be seen in the Table, substitution of the phenyl groups considerably enhances the conversion of 1-octene and the yield of the corresponding epoxide.

In a typical experiment, 0.009 mmol of Mn(TFPP)Cl, 0.024 mmol of benzyldimethyltetradecylammonium chloride, 1.28 mmol of 1-octene and 0.20 mmol of pyridine are dissolved in 3 mL CH_2Cl_2; 9 mL of a 0.35 N aqueous NaOCl solution is added and the reaction mixture is stirred magnetically at room temperature. After 3 h, the two phases are separated, dodecane is added as reference and the mixture is analyzed by GLC.

Although para-substitution improves the epoxide yield, the results obtained with Mn(oFPP)Cl, Mn(TFPP)Cl and Mn(TCl_2PP)Cl demonstrate the importance of ortho-substituents on the phenyl groups of the catalyst. Indeed, with these catalysts non-functionalized olefins were converted to the corresponding epoxides with 50-80% yields. Even 4-pentenyl acetate could be epoxidized with moderate yield. The enhanced activity of Fe(TFPP)Cl and Mn(TFPP)Cl as compared to the (TPP)-analogues as catalysts in the oxidation of several hydrocarbons with iodosylbenzene has recently been mentioned by Chang et al.,[1d] who ascribed this phenomenon to an enhanced stability and electrophilicity of the complex. Our results show that in the case of the epoxidation of terminal olefins, substitution with one fluorine atom in the ortho position has a similar effect as perfluorination of the phenyl groups, which seems to indicate that steric effects play an important rôle in the stabilization of the catalyst. The presence of these ortho substituents probably renders more difficult the close approach of two catalyst molecules so as to decrease the intermolecular oxidative destruction.

Table. Metalloporphyrin-Catalyzed Epoxidation of Terminal Olefins with NaOCl.[6]

Olefin	Catalyst[a]	% Catalyst vs. Olefin	Conversion of Olefin (%)[b]	Yield of Epoxide (%)[b]	Selectivity (%)	Reaction time (h)[c]
1-octene	Mn(TPP)OAc[2]	0.6		1		4
	Mn(pFPP)Cl	0.8	43	21	49	3.75
	Mn(pTrifPP)Cl	0.7	71	34	48	3
	Mn(oFPP)Cl	0.8	88	59	67	1.75
	Mn(TFPP)Cl	0.7	>95	68	ca. 68	3
	Mn(TCl$_2$PP)Cl[d]		89	81	91	8.25
vinylcyclohexane	Mn(TFPP)Cl	0.6		50		4
propene	Mn(TFPP)Cl	0.6	100	51	51	3
5-bromo-1-pentene	Mn(TFPP)Cl	0.6	94	69	73	2.5
	Mn(oFPP)Cl	0.7	98	51	52	3.25
4-pentenyl acetate	Mn(TFPP)Cl	0.6	100	41	41	3.25

a) TPP = 5,10,15,20-tetraphenylporphyrinato dianion; in the other complexes phenyl groups are replaced by C_6F_5 (TFPP), p-F-C_6H_4 (pFPP), p-CF_3-C_6H_4 (pTrifPP), o-F-C_6H_4 (oFPP), 2,6-$Cl_2C_6H_3$ (TCl$_2$PP). b) Determined by GLC analysis; the yield is determined vs. the initial amount of olefin. c) Non-optimalized reaction times. d) Impure sample of catalyst.

Work is presently in progress to study the activity of these substituted porphyrins towards hydroxylation of saturated hydrocarbons.

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