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MEDIATION OF ORTHOQUINONES IN THE MnTPPCl-CATALYZED EPOXIDATION WITH HYDROGEN PEROXIDE

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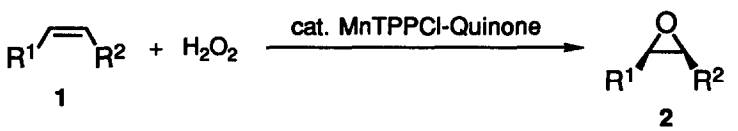
Summary: The MnTPPCl-catalyzed epoxidation of olefins with hydrogen peroxide is efficiently enhanced by mediation of orthoquinones.

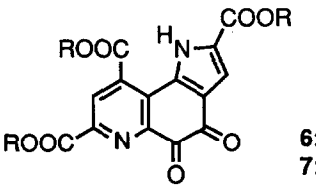
A variety of model systems for P-450 have been developed to elucidate the mechanism and provide a useful method for oxygenation reactions. Oxygen sources are molecular oxygen, hydrogen peroxide, *t*-butyl hydroperoxide, iodosylbenzene, sodium hypochlorite, and so on depending on the system,[1] but further improvement has been studied to achieve the more effective oxygen transfer.[2] We herein describe that orthoquinones efficiently mediated the MnTPPCl-catalyzed epoxidation reaction of olefins with hydrogen peroxide.



1 2

The MnTPPCl-catalyzed epoxidation of styrene (**1a**) proceeded whenever hydrogen peroxide was dropwise added to the reaction mixture.[3] The presence of phenanthrenequinone (**3**) resulted in about double the yield of styrene oxide (**2a**) as compared with that in the absence of **3**. The yield increase of epoxides with **3** is independent on the substrates. Cyclohexene (**1c**) was oxidized to cyclohexene oxide with ease as shown in Table 1. *cis*-Stilbene (**1b**) also underwent the facile epoxidation in the orthoquinone-mediated system. The efficiency of this system is considered to be based on orthoquinone function. The similar effect, however, was not observed with *p*-benzoquinone (**4**) employed. Use of 1,10-phenanthrolinequinone (**5**) substantially lowered the yield of **2a**.

The chemical behaviors of a novel coenzyme PQQ (**6**) have been disclosed in dehydrogenation reactions of amines, which is accounted for by autocycling redox of orthoquinone function under oxygen.[4,5] The trimethyl ester **7** of PQQ, soluble in organic solvent, worked as well in the present epoxidation with hydrogen peroxide.



6: R=H
7: R=Me

Although the mechanism for the effect of orthoquinones has to wait for further studies, the following observations are assumed to explain its role. The in situ formation of pyridine *N*-oxide is ruled out from the result of **5**. The addition of hydrogen peroxide to **7** in acetonitrile led to 7 nm blue shift of the peak at 357 nm and disappearance of the broad peak at 450 nm attributable n-π* of **7** in the UV-VIS spectrum (Fig. 1). The similar spectral change has been reported in the addition-adduct (α-glycol) of orthoquinones with water,[5] but was not observed with an equimolar amount of water as used in Fig. 1. The spectrum of **7** reappeared on treatment of thus obtained solution with Cu(I) chloride or Mn(II) chloride. These findings are presumably elucidated by the addition-adduct formation of orthoquinone moiety with hydrogen peroxide, which might be the more reactive oxidant. Under the present conditions, orthoquinones are protected against its self-oxidation. The orthoquinones are considered to work as a mediator to generate an effective oxygen source for the MnTPPCl-catalyzed epoxidation.[6]

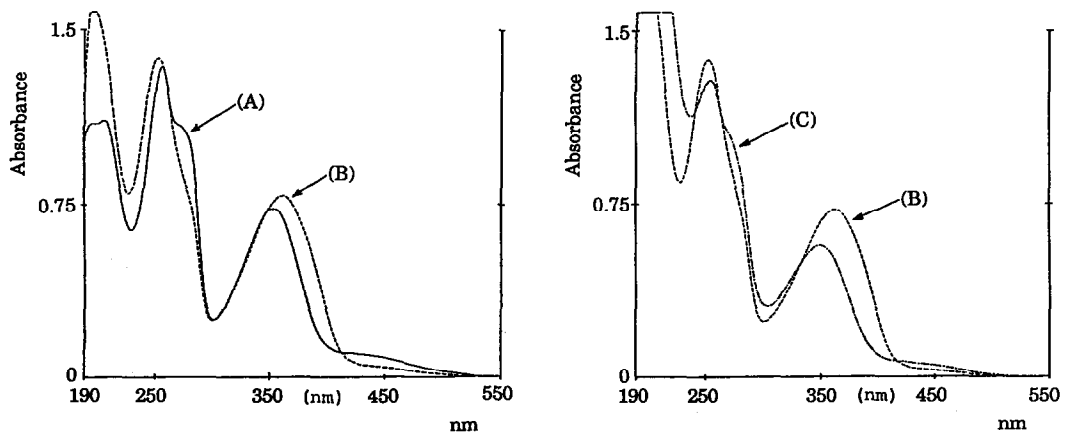
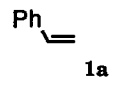
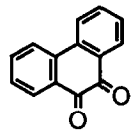
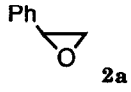
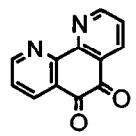
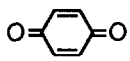
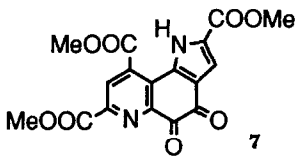
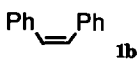
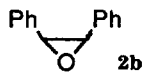
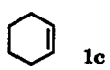
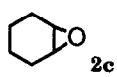


Fig. 1. UV-VIS spectra. (A) The spectrum of **7** (8 x 10^{-5} M, in acetonitrile under air at 30 °C). (B) Treatment of a solution of **7** with 30% H_2O_2 (17 equiv. to **7**). (C) Subsequent treatment with CuCl (9 x 10^{-5} M).

The mediation of orthoquinones provides a useful method for hydrogen peroxide activation. This result is interpreted from biological importance. The characterization of the active species of **7** helps to define the nature of the intermediate in the reoxidation step of

Table 1. The Mn(III)TPPCl-catalyzed epoxidation in the presence of quinones[a]

Olefin	Quinone	Product	Yield, %[b]
 1a	 3	 2a	59
1a	 4	2a	13
1a	 5	2a	38
1a	 7	2a	52
1a	—	2a	30
 1b	3	 2b	53 (89:11)[c] 5[d]
1b	7	2b	51(92:8)[c] 7[d]
1b	—	2b	34(92:8)[c] 4[d]
 1c	3	 2c	49
1c	7	2c	44
1c	—	2c	19

[a]To a solution of 1 (40 equiv), MnTPPCl (1 equiv), a quinone (2 equiv), and imidazole (4 equiv.) in acetonitrile-dichloromethane (2:1 V/V) was added 30% H_2O_2 (200 equiv) and imidazole (20 equiv) in acetonitrile-dichloromethane (2:1 V/V) in 6 portions every 10 min. The reaction mixture was stirred for 2 h after the initial addition of H_2O_2. [b]Yields were determined by GLC based on 1 unless otherwise stated. [c]Yields were determined by ^1H NMR. The numbers in parentheses are the ratio of *cis*:*trans*. [d]2-Phenylacetophenone was obtained as a byproduct. Yields were determined by ^1H NMR.

aerobic dehydrogenation reactions with **6**. Further investigations involving the mechanism are now in progress.

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