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CATALYTIC OXIDATION OF DIENONES WITH TPPMn(III)Cl - PhIO SYSTEM

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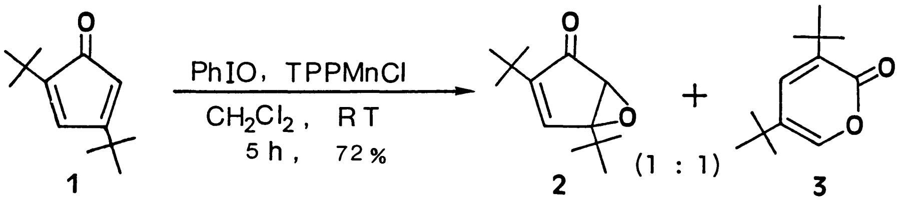
Several dienones were oxidized with iodosylbenzene (PhIO) in the presence of catalytic amount of tetraphenylporphinatomanganese(III) chloride (TPPMn(III)Cl), affording corresponding epoxides and pyrons.

The current interest has been focused on metalloporphyrin - monooxygen donor system which mimics monooxygenase reactions, e.g. hydroxylation and epoxidation.$^{1)}$ We have recently reported the efficient oxidation of sulfides with oxo-metalloporphyrins, in which the mechanism is not simply explained by common electrophilic reaction.$^{2)}$ Meanwhile, most of olefins capable of being oxidized with oxo-metalloporphyrins are electron-rich,$^{1)}$ and Groves reported 2-cyclohexenone, a typical enone, was inert toward iodosylbenzene - iron porphyrin system.$^{3)}$ We also noticed that little or no oxidation took place with some enones such as 3-methyl-2-cyclohexenone. In connection with high reactivity of stilbene, however, the radical mechanism relevant to the epoxidation with oxo-manganeseporphyrin$^{4)}$ made us presume that if some allylic stabilization of radical species formed initially is present, even enones can be oxidized. So an additional olefinic part was introduced into the enones and reactivities of the dienones thus formed were examined with TPPMn(III)Cl - PhIO system.

In this communication we wish to describe an efficient oxidation of several dienones with iodosylbenzene and catalytic TPPMn(III)Cl.

In a typical procedure, to a dichloromethane solution (20 ml) of 2,4-di-t-butylcyclopentadienone (1, 1.36 mmol)$^{5)}$ and TPPMn(III)Cl$^{6)}$ (0.14 mmol, 10 mol% vs. 1), iodosylbenzene$^{7)}$ (PhIO, 1.5 mmol) was added in several portions in 10 min. The heterogeneous mixture was stirred at ambient temperature for 5 h under an

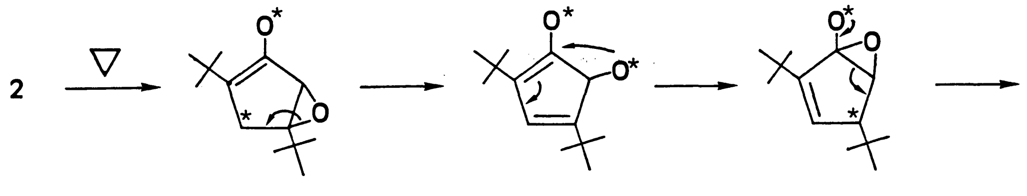


(1)

argon atmosphere,[8] giving a homogeneous solution. Careful chromotographic separation over silica gel afforded two products in a ca. 1 : 1 ratio in 72% yield based on the substrate used (Eq. 1).[5] One of the products was determined as an epoxide 2 from two separated signals of ring protons at 3.54 and 7.27 ppm in ^{1}H NMR as well as other spectroscopic data. The other was assigned to be a pyron 3 from IR, NMR and mass spectra. Regioisomeric epoxide was not observed. The epoxide 2 was thermally unstable and readily isomerized to the pyron 3 even under the work-up conditions. The pyron 3, therefore, must be the secondary product by the consecutive rearrangement of 2 as shown in Eq. 2, since thermal rearrangement to pyron and photochemical reversion of epoxides of such a type are known processes.[9]

In the similar manner, some dienones were converted to the corresponding epoxides and pyrons. Results are summarized in Table 1. In the case of 5, neither pyron derivative nor regioisomeric epoxide was detected (see Table 1, note g). trans-Chalcone (1,3-diphenyl-2-propen-1-one, 6), a substrate of another type, also underwent the epoxidation but less efficiently than the others. The reaction did not proceed without the catalyst, however, only in the case of 4 the oxidation products were produced in a rate ten times slower than that with the catalyst.

Change of the central metal of the catalyst from manganese to iron did not result in the oxidation at all, presumably because of fast decomposition of the active species due to very high reactivity that we reported previously in the sulfide oxidation.[2]



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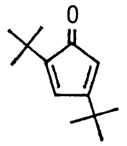
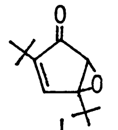
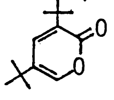
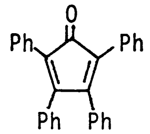
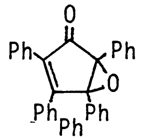
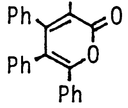
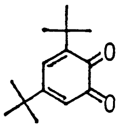
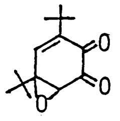
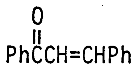
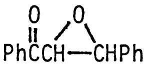
* : +, - or ·

Table 1. Catalytic oxidation of dienones with TPPMn(III)Cl - PhIO system in dichloromethane at room temperature

Susbstrate	Time/h	Isolated[a] yield/%	Product(ratio)[b,c]	Selected spectral[d] characteristics
 1	5.0	72[e]	 2 (50)	IR: 1710(C=O) ^{1}H NMR: 7.27(s,1H), 3.54 (s,1H)[f]
			 3 (50)	IR: 1695(C=O); ^{1}H NMR: 7.31(d,1H), 7.23 (d,1H)
 4	3.0	78	 7 (30)	^{13}C NMR: 72.7(s), 67.7(s) MS: m/e 400(M$^+$)
			 8 (70)	IR: 1695(C=O) MS: m/e 400(M$^+$)
 5	4.0	82[g]	 9	^{1}H NMR: 7.20(s,1H), 3.86 (s,1H) ^{13}C NMR: 67.0(s), 55.6(s) IR: 1730, 1680(C=O)[h]
 $PhC(=O)CH=CHPh$ 6 (trans)	10.0	25[i]	 10 (trans)	IR: 1680(C=O) ^{1}H NMR: 4.33(d,1H), 4.10 (d,1H)

a) The yield was based on the substrate used. b) Ratio of the two products was variable depending on the conditions of the reaction and the work-up. c) Melting point. 3: 64.0-64.5 °C; 7: 140-142 °C; 8: 163.5-165.5 °C; 9: 99-100 °C; 10: 78.5-80 °C. d) Spectra were obtained under the following conditions unless stated otherwise. IR: $CDCl_3$, cm^{-1}; NMR: $CDCl_3$, δ. e) The yield was based on 5 which was a precursor of 1 (see Ref. 5). f) CCl_4 solvent. g) The value indicates the total yield of two products, 9 (61%) and unknown structure 9' (39%) which was converted to 9 by passing through a silica gel column. h) KBr. i) The starting material was recovered in 66% yield (conversion yield: 74%).

Sodium hypochlorite as a monooxygen donor[10] could be served for iodosylbenzene, however, the yield of 9 was considerably low (<10%) in a two phase system (CH_2Cl_2 - H_2O) containing a small amount of a phase transfer catalyst.

The results thus obtained undoubtedly support the hypothesis of the allylic stabilization of the radical formed by the addition of the active species[11] to olefinic part, which eventually leads to the epoxidation. Steric hindrance appears to exert little influence on the product formation, while it clearly affects the regiospecificity of the epoxide formation.

References

1) See the recent papers and references cited therein: J. T. Groves and D. V. Subramanian, J. Am. Chem. Soc., 106, 2177(1984); M. F. Powell, E. F. Pai, and T. C. Bruice, ibid., 106, 3277, 6123(1984).

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6) The visible spectrum of TPPMn(III)Cl was the same as that reported by Hill et al.: C. L. Hill and B. C. Schaldt, J. Am. Chem. Soc., 102, 6374(1980).

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8) The product yield was little influenced by air, room light, or temperature ranging from -20 to 25 °C.

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11) The structure of the active species is reported by Hill et al.[4)]

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