

HEMATOPORPHYRIN Mn(IV) COMPLEX AS A POWERFUL AND UNIQUE OXIDIZING REAGENT

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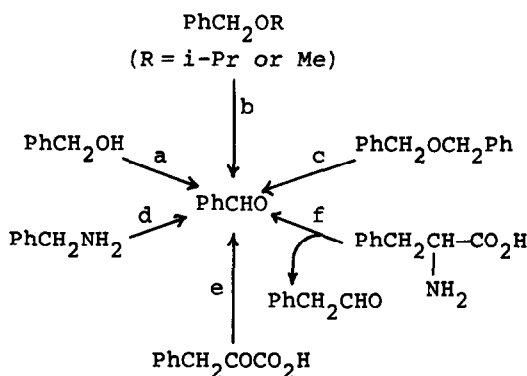
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The very important but still not fully understood contribution of some Mn-protein to the oxidative decomposition of water in the photosystem II of the plant photosynthesis¹ urges chemists to investigate appropriate model systems² in order to gain further insights into the mechanistic characteristics of Mn(IV)³⁻⁵ species as such potent oxidants as to be able to oxidize water. Among the models investigated, hematoporphyrin·Mn(IV) complex 1, (hereafter it is abbreviate as HmMn(IV)) seems to be extremely important, since its oxidation potential was found to increase very sharply on lowering pH to overcome water potential near pH 8.4.⁶⁻⁸ The authors were especially attracted by the significant characteristics of HmMn(IV) as a powerful oxidant which has driven us to further investigate systematically scope of its oxidation reactions in neutral or acid solution to find that it is a very interesting and useful synthetic reagent.

In this paper, the authors wish to report that a variety of substituted methylene group, CH₂X involving various ethers, can be readily oxidized to CHO by HmMn(IV) as illustrated in Scheme 1. Among the reactions studied especially important and interesting was the reaction of the ethers where ether linkage was very readily cleaved to afford benzaldehyde *at room temperature within a minute* under Ar (Scheme 1, b and c), the details of which was shown in Table I together with those for various substrates. The unique characteristics of the

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present potent oxidant is not only limited to the oxidative cleavage of ethers but is also extended to the interesting and ready oxidative cleavage of C-C linkages (Scheme 1, e and f).



Scheme 1. Illustration of Typical Oxidation Reactions with HmMn(IV).

TABLE I. HmMn(IV) Oxidation

Substrate	Solvent ^a (rel. vol.)	Yield of benzaldehyde (%) ^b
PhCH ₂ OH	H ₂ O (1) MeOH (1.1) CH ₂ Cl ₂ (0.1)	78 (43) ^c
PhCH ₂ NH ₂	H ₂ O (1) MeOH (1.1) CH ₂ Cl ₂ (0.1)	70 (37)
(PhCH ₂) ₂ O	H ₂ O (1) MeOH (2)	96 (32)
PhCH ₂ OPr ⁱ	H ₂ O (1) MeOH (1)	89 (27)
PhCH ₂ OMe	H ₂ O (1) MeOH (2)	81 (21)
PhCH ₂ COCO ₂ H	H ₂ O (1) MeOH (2)	q.Y. ^d (—)
PhCH ₂ CH(NH ₂)CO ₂ H	H ₂ O	11 (—)
		PhCH ₂ CHO
		29 (—)

^aApparent pH was adjusted to 8.4 (reading of a pH meter) by use of a pH meter.

^bYield based on the starting material consumed.

^cYield based on the oxidant used (in parentheses).

^dAppreciable decomposition of the starting material accompanied.

Thus, in a sealed flask equipped with a gas inlet and outlet, a dropping funnel and a pH electrode was placed a solution of 100 mg (0.15 mmol) of HmMn-(III)OH dissolved in a mixture of 5 ml of 0.05 N NaOH and 5 ml of methanol.

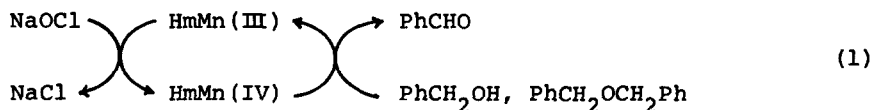
Into the stirred solution, 0.5 ml of 0.16 M aqueous NaOCl was added through the use of a syringe and the solution was stirred for a few minutes for complete consumption of NaOCl. The spectroscopic determination of HmMn(IV) and HmMn(III) concentration was carried out based on their characteristic absorptions in electronic spectra (at 402 for HmMn(IV) and at 350, 460 nm for HmMn(III)). Under the condition, the amount of HmMn(IV) formed was 1.4×10^{-4} mol (93 % based on NaOCl used).

The HmMn(IV) solution was similarly prepared from 1.26 g (1.9 mmol) of the corresponding Mn(III) complex dissolved in 5 ml of methanol and 1 ml of 0.5 N NaOH aqueous solution followed by the treatment with 3 ml of 0.32 M NaOCl aqueous solution (0.96 mmol). Into the HmMn(IV) solution thus obtained was added 63 mg (0.42 mmol) of benzyl isopropyl ether dissolved in 1 ml of methanol and 2 ml of conc. HCl was further added into the mixture with stirring. The reaction was over *instantaneously*.³ The mixture, after pouring into 30 ml of water, was extracted with 5 portions of 30 ml chloroform. The combined organic layer was dried and very carefully condensed to 5 ml through fractional distillation. The residue was analyzed by glpc (using anisol as an internal standard) and glpc-mass spectrum, demonstrating that 25 mg of benzaldehyde (0.24 mmol, 89 % based on the ether consumed and 27 % on HmMn(IV)) was obtained and 23 mg of the starting material was recovered.

Similarly, quantitative analysis of the product from dibenzyl ether demonstrates that single dibenzyl ether molecule was oxidatively cleaved to yield *two* molecules of benzaldehyde in 96 % yield (192 mol % based on the consumed ether). The results are summarized in Table I. Yield of benzaldehyde (Scheme 1) based on a benzyl derivative consumed was satisfactorily high while that on HmMn(IV) used was low, suggesting that the considerable oxidative decomposition of water by HmMn(IV) still took place.

Another significant and interesting characteristics of the HmMn(IV) was its very effective "turn over" as a catalyst. Thus, into a solution of 136 mg of benzyl alcohol (1.26×10^{-3} mol) in 10 ml mixed solvent (MeOH : 0.05 N NaOH - 0.1 M KH_2PO_4 : CH_2Cl_2 = 1.1 : 1.0 : 0.1) was added dropwise 1 ml of aqueous NaOCl solution (3.9×10^{-4} mol) during 3 minutes in the presence of 50 mg of HmMn(IV) (7.9

$\times 10^{-5}$ mol) under Ar afforded benzaldehyde in a yield of 773 % based on HmMn(IV) used (96 % of the benzyl alcohol consumed) where most of the catalyst was still kept unchanged, while under the condition without HmMn(IV), benzaldehyde was formed only in 5 % yield. These observations demonstrate that HmMn(IV) can oxidize the substrate by ca. 760 ($155 \times 39/8$) fold faster than NaOCl, and in return it is very easily regenerated from HmMn(III) by NaOCl (eq. 1).



This potent and unique oxidizing (catalytic) properties are not restricted to HmMn but such porphyrin-Mn complexes as TPPMn also showed similar characteristics, details of which will appear soon.

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