



## Short Communication

Manganese(III) corrole catalyzed selective oxidation of alcohols to carbonyl compounds by *tert*-butyl hydroperoxide under mild condition

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## ABSTRACT

Mild oxidation of alcohols has been achieved with *tert*-butylhydroperoxide catalyzed by electron deficient manganese(III) corroles at room temperature. The catalysts used in this study showed high activity in the oxidation of benzylic alcohols to the corresponding carbonyl compounds.

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## 1. Introduction

Oxidation of alcohols to aldehydes or ketones is an important functional group transformation in organic synthesis [1–3]. The carbonyl compounds represent an important group of products and intermediates in the fine chemicals [4]. Thus, several methods have been explored to accomplish selective oxidation of alcohols to more valuable carbonyl compounds. Most notable among the various processes developed so far are the Oppenauer and Swern oxidation and the reactions utilizing high valent metal compounds such as MnO<sub>2</sub>, ammonium perruthenates and pyridinium chlorochromate [5–10]. These methods suffer from one or more limitations like the use of expensive chemicals, prolonged reaction time, strongly acidic condition and tedious work-up procedure. Sometimes a large amount of toxic waste is also generated [11–13]. The reports of metal complex catalyzed oxidation of alcohols to carbonyl compounds especially with benign oxidants are much less than those involving stoichiometric amount of metallo-oxidants [14]. Thus the development of a catalytic method for selective oxidation of alcohol using safe, economic, and environmentally benign oxidizing agents remains a critical challenge in organic synthesis [15].

During the last decade the metallo-derivatives of corroles have generated intense interest in the field of catalysis [16–18]. Various metallo-corroles have been successfully employed as catalysts in oxygenation of organic compounds [16–24], cyclopropanation [19,25], aziridination [26] and decomposition of reactive oxygen and nitrogen

species (ROS and RNS respectively) [27,28]. The iron(III) and manganese(III) corroles have emerged as efficient decomposition catalysts for peroxy-nitrite to benign products in *in vitro* and *in vivo* studies [27,28], which has far reaching consequence in biological chemistry. There is no known biological defence system against peroxy-nitrite which is involved in the damage of a variety of biomolecules, especially those of vital importance for normal cardiovascular function [29,30]. Recent work has shown that iron complex of corroles activates *tert*-butyl hydroperoxide and successfully oxidizes alkanes, alkenes and alkylbenzenes at ambient condition [24]. So far, no report of metallo-corrole catalyzed oxidation of alcohols to carbonyl compounds is available in the literature.

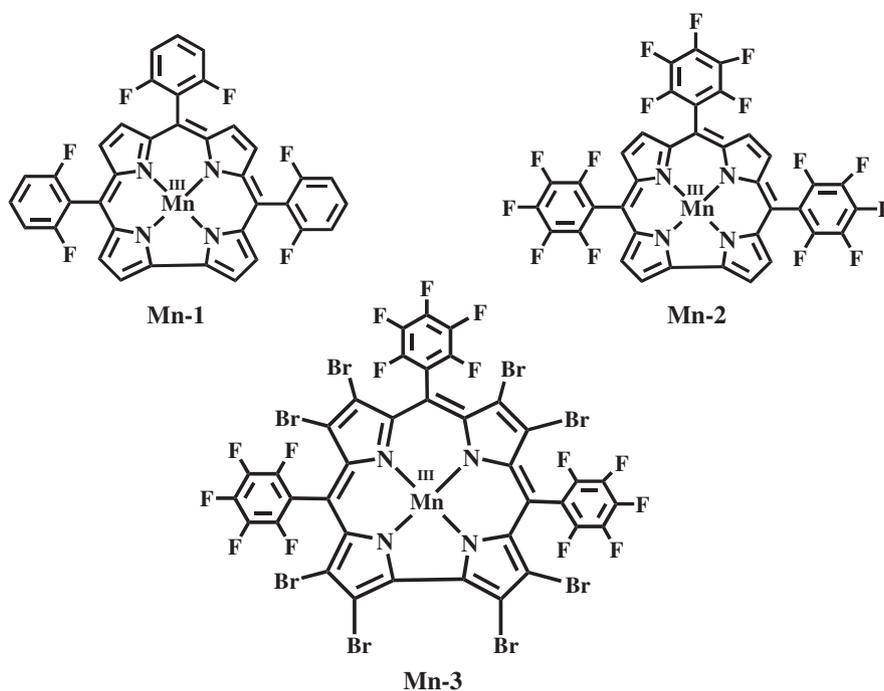
Herein, we wish to report the selective and efficient oxidation of alcohols at ambient condition catalyzed by manganese(III) corroles with an environmentally benign oxidizing agent *tert*-butyl hydroperoxide. The effect of substitution at the corrole ligands on the catalytic activity of manganese(III) corroles has also been examined in this study.

## 2. Experimental

## 2.1. Materials

All substrates, reaction products, dodecane (internal standard) and *t*-BuOOH (as ~70% solution in water) were purchased from Sigma Aldrich Inc. and were used as received. The exact active oxygen content of the oxidant was determined iodometrically prior to use. The syntheses of the free base corroles, 5,10,15-tris(2,6-difluorophenyl)corrole (tdfc) and 5,10,15-tris(pentafluorophenyl)corrole (tpfc) were carried out by using the 'solvent free' condensation of pyrrole and the respective aldehydes described by Gross et al. [31]. The respective

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Scheme 1. Manganese(III) corroles employed in the study.

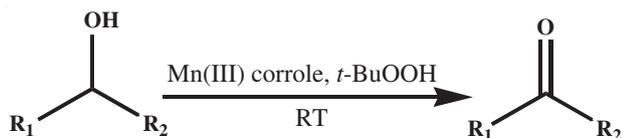
manganese(III) corroles were prepared by refluxing the free base corrole with  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  in DMF [20]. The new complex  $[\text{Mn}^{\text{III}}(\text{tdfc})]$  was prepared from  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  and the corresponding ligand in refluxing DMF (10 ml) and the green product was purified by preparative TLC on a silica gel plate using 1:1 dichloromethane/hexane as the eluant.  $[\text{Mn}^{\text{III}}(\text{tdfc})]$ : yield: 85%; anal.: calcd for  $\text{C}_{37}\text{H}_{17}\text{N}_4\text{F}_6\text{Mn}$ : C, 64.73; H, 2.50; N, 8.16. Found: C, 64.81; H, 2.37; N, 8.25; MS ( $\text{Cl}^+$ , isobutane):  $m/z$  (%): 686 (100)  $[\text{M}^+]$ ; UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  [nm] ( $\log \epsilon$ ) = 400 (4.55), 416 (4.53), 487 (4.14), 622 (4.01).

Perbrominated manganese(III) corrole  $[\text{Br}_8\text{Mn}^{\text{III}}(\text{tpfc})]$  was prepared and characterized following the reported procedure [21]. These three manganese corrole complexes  $[\text{Mn}(\text{tdfc})]$ ,  $[\text{Mn}(\text{tpfc})]$  and  $[\text{Br}_8\text{Mn}^{\text{III}}(\text{tpfc})]$  were designated as **Mn-1**, **Mn-2** and **Mn-3** respectively and shown in Scheme 1.

The product analysis was done by Perkin Elmer Clarus-500 GC equipped with a FID detector using 15 m capillary column (Elite-I, Polysiloxane). The identification and quantification of the products were done from the response factors of standard product samples.

## 2.2. Catalytic oxidation

Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction the catalyst and the substrate were dissolved in benzene. The oxidation reaction was initiated by adding *t*-BuOOH and the contents were magnetically stirred. After periodic time intervals standard solution of dodecane was added to this reaction mixture and an aliquot was analysed by GC. A detailed outline of the catalytic oxidation of benzyl alcohol is given in the later discussion as a representative case.



Scheme 2.

To a mixture of  $\text{PhCH}_2\text{OH}$  (5 mM) and the catalyst (25  $\mu\text{M}$ ) in benzene medium (2 mL) was added *t*-BuOOH (2 mM) at 25 °C for an appropriate reaction time, and the reaction was followed by GC. After completion of the reaction, the reaction mixture was directly injected into a capillary column (elite 1, 15 m) of a preheated GC. The quantitative identification was made from the predetermined response factor of the pure sample of benzaldehyde (internal standard: dodecane, 2 mM) and the yield of the product (benzaldehyde) was calculated.

## 3. Results and discussion

It has been documented that high valent metallocorroles with electron-withdrawing groups at the three *meso* positions are efficient oxidation catalysts [16,17,32]. Three electron deficient manganese(III) corrole complexes (**Mn-1**, **Mn-2** and **Mn-3**) have been utilized in the present study (Scheme 2).

The oxidation of benzyl alcohol ( $\text{PhCH}_2\text{OH}$ ) with *tert*-butyl hydroperoxide (*t*-BuOOH) at room temperature was used as the model reaction.

The influence of different factors like catalyst concentration, solvent nature and ligand structure on the conversion as well as on the selectivity of the oxidation reaction was examined to optimise the reaction conditions. Initially the reaction was carried out with catalyst **Mn-2** in different solvents and the results are summarized in Table 1.

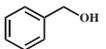
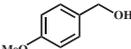
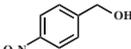
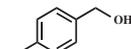
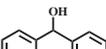
Table 1  
Influence of the solvent on the oxidation of  $\text{PhCH}_2\text{OH}$  using *t*-BuOOH catalyzed by **Mn-2**.<sup>a</sup>

Solvent	PhCHO yield (%) <sup>b</sup>
$\text{CH}_2\text{Cl}_2$	11
MeOH	16
$\text{CH}_3\text{COOC}_2\text{H}_5$	22
$\text{CH}_3\text{CN}$	27
$\text{CH}_3\text{COCH}_3$	41
$\text{C}_6\text{H}_6$	62

<sup>a</sup> The reactions were run under air at room temperature, and the molar ratio of  $\text{PhCH}_2\text{OH}/t\text{-BuOOH}/\text{catalyst}$  was 100:800:1.

<sup>b</sup> Yields are reported with respect to the initial concentration of the substrate.

**Table 2**  
Oxidation of alcohols by *t*-BuOOH catalyzed by manganese(III) corroles.

Substrate	Catalyst	Time	Method A <sup>a</sup>		Method B <sup>b</sup>	
			Conversion (%) <sup>c</sup>	Yield (%) <sup>d</sup>	Conversion (%) <sup>c</sup>	Yield (%) <sup>e</sup>
	Mn-1	12hrs.	56	54 (97)	32	76 (96)
	Mn-2	12hrs.	63	62 (98)	36	87 (97)
	Mn-3	12hrs.	65	64 (98)	38	90 (97)
	Mn-1	12hrs.	60	58 (97)	39	92 (97)
	Mn-2	8hrs.	64	63 (98)	42	100 (98)
	Mn-3	8hrs.	68	66 (98)	42	100 (98)
	Mn-1	12hrs.	52	50 (96)	35	84 (97)
	Mn-2	12hrs.	60	58 (96)	39	94 (97)
	Mn-3	8hrs.	64	62 (97)	40	99 (97)
	Mn-1	12hrs.	38	36 (94)	29	70 (95)
	Mn-2	12hrs.	44	42 (96)	33	78 (96)
	Mn-3	12hrs.	50	48 (96)	34	82 (96)
	Mn-1	12hrs.	50	48 (96)	34	80 (96)
	Mn-2	12hrs.	54	52 (97)	36	85 (97)
	Mn-3	12hrs.	58	56 (97)	38	91 (97)
	Mn-1	12hrs.	39	37 (94)	24	56 (92)
	Mn-2	12hrs.	45	43 (96)	26	61 (93)
	Mn-3	12hrs.	48	46 (96)	29	68 (93)

<sup>a</sup> Method A: the molar ratio of substrate/*t*-BuOOH/catalyst was 100:800:1.

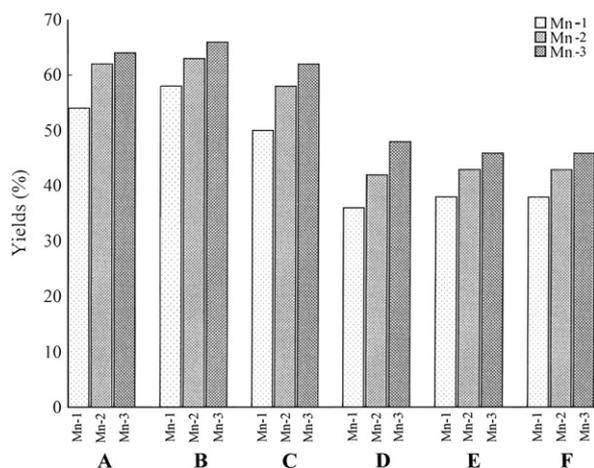
<sup>b</sup> Method B: the molar ratio of substrate/*t*-BuOOH/catalyst was 200:80:1.

<sup>c</sup> Percentage conversion of the substrate.

<sup>d</sup> Yields are reported with respect to the initial concentration of the substrate. Yields in parentheses are reported with respect to the consumed substrate.

<sup>e</sup> Yields are reported with respect to the concentration of the oxidant. Yields in parentheses are reported with respect to the consumed substrate.

The previously mentioned results (Table 1) reveal that a non-polar medium like benzene is most effective in terms of selectivity and yield of benzaldehyde. The molar ratio of benzyl alcohol, *t*-BuOOH and the catalyst was 100:800:1 and the yields were reported with respect to the substrate concentration. Hereafter, this reaction condition is described as 'Method A'. However, it has been found that using benzyl alcohol 2.5 times more than the oxidant results in almost a quantitative conversion of the substrate to benzaldehyde based on the concentration of the oxidant. Thus the molar ratio of benzyl alcohol, *t*-BuOOH and the catalyst has been optimized to 200:80:1 for further reactions (Method B). Oxidation of different alcohols under both condition A and condition B has been performed and the results are summarized in Table 2.



**Fig. 1.** Relative yields of ketones for different alcohols; where A, B, C, D, E and F stand for benzyl alcohol, *p*-methoxy benzyl alcohol, *p*-nitro benzyl alcohol, *p*-hydroxy benzyl alcohol, diphenyl methanol and cyclohexenol respectively.

It is observed from Table 2 that substituted benzyl alcohols are transformed into the corresponding benzaldehyde derivatives (entries 1–4) with good yields and 100% selectivity. The secondary alcohols gave the corresponding ketones (entries 5–6). No over oxidation by-products, carboxylic acids, were detected in the present work. The presence of an electron-donating or an electron-withdrawing group in the substrates has no appreciable effect on the reaction time or yield.

The influence of electronegative substituents on the catalytic activity of the manganese(III) corroles has been examined. The performances of the manganese(III) corrole catalysts towards the oxidation of different alcohols have been shown in Fig. 1. Manganese(III) corroles used in the present oxidizing system steadily maintain the catalytic efficiency in the order of Mn-3 > Mn-2 > Mn-1 for each substrate (Table 2), although the effect is not so dramatic. Therefore, manganese(III) corroles with greater electron-withdrawing substituents have been found to be better catalysts in oxidizing alcohols. However, complete bleaching of all the three catalysts has been observed at the end of the reactions.

#### 4. Conclusion

To the best of our knowledge, this is the first report on manganese(III) corrole catalyzed selective and efficient oxidation of alcohols at room temperature with *t*-BuOOH as terminal oxidant. In conclusion, the present work demonstrates that manganese(III) corroles together with environmentally benign *t*-BuOOH are an efficient, safe and low-cost system for the oxidation of benzylic alcohols. Electron-withdrawing groups on the *meso*-phenyl rings of the corrole ligands enhance the catalytic activity of the manganese catalysts. The mild and room temperature oxidation of various electron rich alcohols seems promising for practical purposes.

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#### References

- [1] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidation of Organic Compounds, Academic Press, New York, 1981.
- [2] R.A. Sheldon, I.C.W.E. Arends, A. Dijkman, Catal. Today 57 (2000) 157–166.
- [3] J.-E. Bäckvall, Modern Oxidation Methods, Wiley-VCH, Weinheim, 2004.
- [4] A. Kockritz, M. Sebek, A. Dittmar, J. Radnik, A. Bruckner, U. Bentrup, M.M. Pohl, H. Hugel, W. Magerlein, J. Mol. Catal. A Chem. 246 (2006) 85–99.
- [5] W.J. Mijs, C.R.H.I. De Jonge (Eds.), Organic Synthesis by Oxidation with Metal Compounds, Plenum, New York, 1986.
- [6] J. March, Advanced Organic Chemistry, 4th edn., Wiley, New York, 1992, p. 1167.
- [7] R.J. Highet, W.C. Wildman, J. Am. Soc. Chem. 77 (1955) 4399–4401.
- [8] D.G. Lee, U.A. Spitzer, J. Org. Chem. 35 (1970) 3589–3590.
- [9] R.V. Stevens, K.T. Chapman, H.N. Weller, J. Org. Chem. 45 (1980) 2030–2032.
- [10] F.M. Menger, C. Lee, J. Org. Chem. 44 (1979) 3446–3448.
- [11] S. Zhang, L. Xu, M.L. Trudell, Synthesis 11 (2005) 1757–1760.
- [12] B.Z. Zhan, M.A. White, T.K. Sham, J.A. Pincock, R.J. Doucet, K.V.R. Rao, K.N. Robertson, T.S. Cameron, J. Am. Chem. Soc. 125 (2003) 2195–2199.
- [13] J.N. Moorthy, N. Singhal, P. Venkatakrishnan, Tetrahedron Lett. 45 (2004) 5419–5424.
- [14] R.A. Sheldon, I.W.C.E. Arends, G.-J. Ten Brink, A. Dijkman, Acc. Chem. Res. 35 (2002) 774–781.
- [15] T. Mallat, A. Baiker, Chem. Rev. 104 (2004) 3037–3058.
- [16] Z. Gross, H.B. Gray, Adv. Synth. Catal. 346 (2004) 165–170.
- [17] I. Aviv, Z. Gross, Chem. Commun. (2007) 1987–1999.
- [18] I. Aviv-Harel, Z. Gross, Chem. Eur. J. 15 (2009) 8382–8394.
- [19] Z. Gross, L. Simkhovich, N. Galili, Chem. Commun. (1999) 599–600.
- [20] L. Simkhovich, G. Goluvkov, Z. Gross, Angew. Chem. Int. Ed. 39 (2000) 4045–4047.
- [21] G. Goluvkov, J. Bendix, H.B. Gray, A. Mahammed, I. Goldberg, A.J. DiBilio, Z. Gross, Angew. Chem. Int. Ed Engl. 40 (2001) 2132–2134.
- [22] A. Mahammed, Z. Gross, J. Am. Chem. Soc. 127 (2005) 2883–2887.
- [23] A.N. Biswas, P. Das, A. Agarwala, D. Bandyopadhyay, P. Bandyopadhyay, J. Mol. Catal. A Chem. 326 (2010) 94–98.
- [24] A.N. Biswas, A. Pariyar, S. Bose, P. Das, P. Bandyopadhyay, Catal. Commun. 11 (2010) 1008–1011.
- [25] I. Saltzman, L. Simkhovich, Y.S. Balazs, I. Goldberg, Z. Gross, Inorg. Chim. Acta 357 (2004) 3038–3046.

- [26] L. Simkhovich, Z. Gross, *Tetrahedron Lett.* 42 (2001) 8089–8092.
- [27] Z. Okun, L. Kupersmidt, T. Amit, S. Mandel, O. Bar-Am, M.B.H. Youdim, Z. Gross, *ASC Chem. Biol.* 4 (2009) 910–914.
- [28] L. Kupersmidt, Z. Okun, T. Amit, S. Mandel, I. Saltsman, A. Mahammed, O. Bar-Am, Z. Gross, M.B.H. Youdim, *J. Neurochem.* 113 (2010) 363–373.
- [29] A. Mahammed, Z. Gross, *Angew. Chem.* 118 (2006) 6694–6697.
- [30] A. Haber, A. Mahammed, B. Furhman, N. Volkova, R. Coleman, T. Hayek, M. Aviram, Z. Gross, *Angew. Chem. Int. Ed.* 47 (2008) 7896–7900.
- [31] I. Saltsman, N. Galili, Z. Gross, *Angew. Chem. Int. Ed Engl.* 38 (1999) 1427–1429.
- [32] G.R. Geier III, J.F.B. Chick, J.B. Callinan, C.G. Reid, W.P. Auguscinski, *J. Org. Chem.* 69 (2004) 4159–4169.