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A new and highly effective method for catalytic oxidation of alcohols to the corresponding carbonyl compounds using the tris[(2-oxazolinyl)phenolato]manganese(III)/Oxone®/*n*-Bu_4NBr oxidation system

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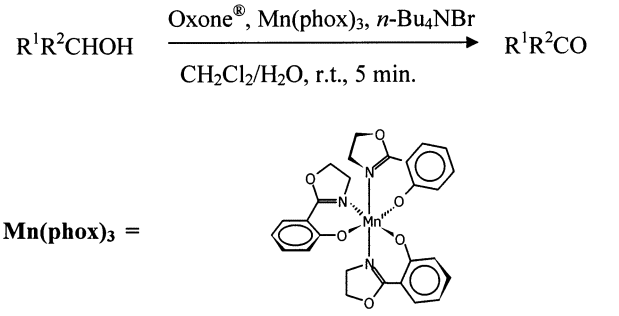
Abstract—Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) in the presence of *mer*-tris[(2-oxazolinyl)phenolato]manganese(III), $Mn(phox)_3$, as catalyst under biphasic reaction conditions (CH_2Cl_2/H_2O) and tetra-*n*-butylammonium bromide as phase transfer agent efficiently oxidises alcohols to their corresponding aldehydes and ketones at room temperature with very short reaction times (5 min) and good to quantitative yields.

The oxidation of alcohols to the corresponding aldehydes and ketones is a key reaction in synthetic organic chemistry and numerous oxidizing reagents are available to effect this important reaction.[1] Many of these oxidation systems require stoichiometric amounts of metal compounds with concomitant environmental problems, for example the chromium oxidants which are used in vast amounts in both the laboratory and industry.[2] Recent efforts have focused on systems which employ metal compounds only in catalytic amounts together with a stoichiometric oxidant.[3]

Oxone® which contains potassium peroxymonosulfate, $KHSO_5$ as the oxidizing species, is commercially available as the triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. There are reports in the literature where Oxone® is used for the oxidation of sulfides, amines, and alkenes.[4] It can also be used for the oxidation of alcohols to aldehydes and ketones[5] and benzaldehyde to benzoic acid.[6] TEMPO/Oxone®/*n*-Bu_4NBr is effective for the oxidation of alcohols.[7] In preceding papers, we reported that Oxone® as an oxidant and a source of protons, promotes the nitration of phenols,[8] *N*-nitrosation of amines[9] and the oxidation of urazoles to their corresponding triazolidines.[10]

In this paper we demonstrate the efficient oxidation of alcohols to their corresponding aldehydes and ketones under mild and biphasic conditions (CH_2Cl_2/H_2O) at room temperature with Oxone® catalysed by *mer*-tris[(2-oxazolinyl)phenolato]manganese(III), $Mn(phox)_3$, a complex previously used in the epoxidation of styrene with H_2O_2 (Scheme 1).[11]

In a typical experiment, a solution of Oxone® (0.25 mmol) in H_2O (5 mL) at room temperature was added to a solution of alcohol (0.25 mmol), tetra-*n*-butylammonium bromide, (0.1 mmol), and tris[(2-oxazolinyl)phenolato]manganese(III) (0.025 mmol), in CH_2Cl_2 (1 mL), and the biphasic mixture stirred vigorously. Formation of products and consumption of substrates were monitored by GLC. The identity of



Scheme 1.

Keywords: Mn-oxazoline complex; alcohol; catalytic oxidation; Oxone®.

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products was determined by IR and ^{1}H NMR spectral data and by comparison with authentic samples using gas–liquid chromatography.

In order to choose a suitable solvent, the oxidation of benzyl alcohol was carried out in dichloromethane, chloroform, acetonitrile, benzene, and ethyl acetate. Our findings showed that CH_2Cl_2 was generally the best of the solvents tested in terms of yields (Table 1).

Important effects of a nitrogen base acting as the axial ligand to the metal in manganese complex-catalysed oxidation is well-known in some systems.[11,12] In the present oxidation method, however, the same yields were obtained for benzyl alcohol oxidation in the presence or in the absence of various nitrogen donor bases such as imidazole and pyridine.

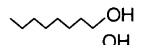
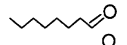
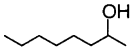
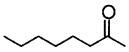
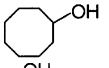
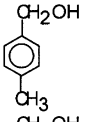
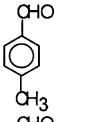
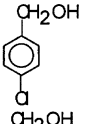
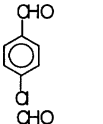
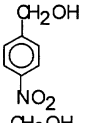
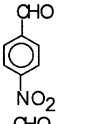
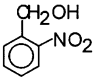
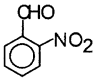
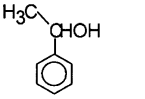
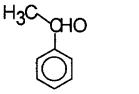
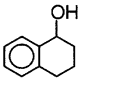
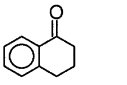
In order to find the optimum conditions for the oxidation, various molar ratios of the catalyst, phase transfer agent, benzyl alcohol, and Oxone® were used. The optimization of the reaction conditions revealed that simple stirring of a solution of the catalyst (1 equiv.), tetra-*n*-butylammonium bromide (10 equiv.), benzyl alcohol (10 equiv.) and Oxone® (10 equiv., which contains 20 equiv. of the oxidizing component of Oxone®, i.e. potassium peroxymonosulfate, $KHSO_5$) in a biphasic medium (CH_2Cl_2/H_2O) effected the formation of benzaldehyde in quantitative yield within 2 min at 0°C to room temperature. However, in the absence of the Mn-complex catalyst, benzaldehyde was only formed in 15% yield. Over-oxidation of aldehydes to their corresponding carboxylic acids which has been observed in the oxidation of aldehydes with Oxone®[6] did not occur in our system.

We showed that this oxidation method could be applied to a wide range of benzylic, allylic, alicyclic, primary and secondary alcohols (Table 2). Oxone® is a poor oxidant for all types of alcohols in the absence of $Mn(phox)_3$ over a period of 5 min. However various alcohols were converted to the corresponding aldehydes or ketones in quantitative yield in the presence of the catalyst (Table 2). While alicyclic alcohols were oxidised in upwards of 80% yields (entries 3–5), the acyclic aliphatic alcohols, 1-octanol and 2-octanol, were less efficiently oxidised (entries 1 and 2). Although, introducing a nitro group to the phenyl ring of benzyl alcohols often reduces the reactivity of the alcohol in oxidation processes, with the $Mn(phox)_3$/Oxone®/*n*-Bu_4NBr oxidation system, both nitro benzyl alcohols were oxidised in good yields (entries 11 and 12).

Table 1. The effect of the nature of solvent on the oxidation of benzyl alcohol by $Mn(phox)_3$/Oxone®/*n*-Bu_4NBr catalytic system

Solvent	Benzaldehyde (%)
CH_2Cl_2	100
CH_3Cl	90
C_6H_6	80
$CH_3COOC_2H_5$	78
CH_3CN	71

Table 2. Oxidation of alcohols by the $Mn(phox)_3$/Oxone®/*n*-Bu_4NBr catalytic system[a]

Entry	Substrate	Product	Yield %[b]	Yield %[c]
1			60	6
2			68	7
3			93	12
4			82	18
5			90	14
6			98	12
7			100	15
8			100	15
9			100	21
10			100[d]	14
11			67[d]	11
12			81[d]	10
13			81	10
14			99	23

[a]The reactions were run for 5 min at room temperature. The oxidation of benzyl alcohol was complete after 2 min. The yields are based on GC data. [b]The oxidation was carried out in the presence of catalyst. [c]Without catalyst. [d]The yield is based on ^{1}H NMR data.

The marked reduction of the benzaldehyde yield (41%) when the benzyl alcohol oxidation reaction is carried out in the presence of 2,6-di-*tert*-butyl-*p*-cresol as an inhibitor, suggests that a radical intermediate is formed during the oxidation reaction. A radical intermediate could be formed via a one-electron transfer process between the Mn-complex and substrate as Oakes et al. have reported in Calmagite dye oxidation catalysed by manganese(II) ions.[13]

In conclusion, the results obtained in this research show that tris[(2-oxazolinyl)phenolato]manganese(III), $Mn(phox)_3$, is an excellent catalyst for the simple, selective and very fast oxidation of alcohols to the corresponding carbonyl compounds with Oxone® under mild conditions in CH_2Cl_2/H_2O.

Acknowledgements

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