Clean and highly selective oxidation of alcohols by the $PhI(OAc)_2$/ Mn(TPP)CN/Im catalytic system

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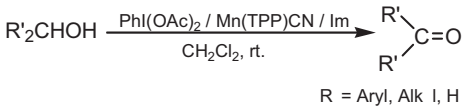
An efficient method for the oxidation of alcohols is presented. Using catalytic amounts of manganese porphyrin [Mn(TPP)CN] in combination with (diacetoxyiodo)benzene ($PhI(OAc)_2$) allows the conversion of benzylic and primary aliphatic and aromatic alcohols into the corresponding aldehydes, and secondary alcohols to ketones as the sole products. This method provides a cost-effective and environmentally friendly oxidation procedure due to the utilisation of less toxic $PhI(OAc)_2$ and biologically relevant manganese porphyrins. The amounts of the products (%) and the selectivities are very dependent upon the nature of the metalloporphyrin catalysts and also upon the electronic and steric properties of the starting alcohols.

Keywords: alcohols, aldehydes, ketones, catalytic oxidation, manganese porphyrin, (diacetoxyiodo)benzene

The oxidation of alcohols to the corresponding aldehydes and ketones is one of the most important functional group transformations in organic synthesis.[1] So far, many methods such as enzymatic[2] and metal-free[3] oxidations have been developed for this purpose. Hypervalent iodine reagents have also received a great deal of attention due to their versatility in oxidation processes.[4] In general, pentavalent iodine reagents such as Dess–Martin periodinane and *o*-iodoxybenzoic acid have been widely used for efficient oxidation of alcohols to the carbonyl compounds.[4,5]

However, the reported methods for the oxidation of alcohols mediated by trivalent iodine reagents have been quite limited. Furthermore, most methods commonly suffer from disadvantages, such as difficulty in manipulation, long reaction times, low selectivities, and the utilisation of toxic reagents. Therefore, it is still desirable to develop a new and efficient oxidant with properties of high stability, low toxicity, and ready availability for alcohol oxidations. While alcohol dehydrogenases often perform this task very efficiently,[6] mild homogeneous catalysts are scarce. Biomimetic processes based on oxygenation by cytochrome P-450 enzymes using synthetic metalloporphyrin catalysts seem to offer a promising route to this goal.[7] However, to the best of our knowledge, there has been no example of the utilisation of $PhI(OAc)_2$ in the presence of metalloporphyrins for the oxidation of alcohols. We present herein a catalytic method for the oxidation of alcohols with $PhI(OAc)_2$ as the oxidant and manganese *meso*-tetrakis(phenylporphyrin) cyanid [Mn(TPP)CN] as the catalyst (Equation).



R = Aryl, Alk l, H

Using this system, benzylic and primary alcohols are converted into the corresponding aldehydes, and secondary alcohols can be easily oxidised to ketones.

Results and discussion

Using metalloporphyrin complexes, epoxidation of alkenes and hydroxylation of alkanes can be achieved by a variety of oxidants.[8] Recently, much attention has been paid to hypervalent iodine(III) reagents due to their low toxicity, ready availability, easy handling and reactivities similar to those of heavy metal reagents. For example, λ^3-iodosylarenes are most commonly used today in oxidation reactions in association with metalloporphyrin catalysts.[8f,9] Several papers describe the use of $PhI(OAc)_2$ as a terminal oxidant in different reactions; competitive hydroxylation of alkanes catalysed by Fe(TPFPP)Cl,[10] chemoselective oxidation of alcohols by Cr(salen)X[11] and oxidation of olefins catalysed by Fe-porphyrin in wet organic solvents.[12] However, most of the mentioned procedures suffer from the disadvantages that besides oxygenated products, stoichiometric amounts of waste products are formed which have to be separated from the major products. Encouraged by the results obtained in our previous work on the oxidative decarboxylation of diphenylacetic acid by tetrabutylammonium periodate (n-Bu_4NIO_4) and Mn(TPP)X catalyst,[13] we next investigated the $PhI(OAc)_2$/ Mn(TPP)CN catalytic system for alcohol oxidation and were pleased to realise that it was more effective in terms of yield and reaction time than the other related catalytic methods. To optimise the oxidations, three complementary approaches can be pursued. Our first attempts focused on the use of a mild and robust catalyst to prevent the overoxidation of alcohols to form the carboxylic acids. Several solvents including CH_2Cl_2, $CHCl_3$, CH_3CN, EtOH, DMF and selected mixtures of these were examined to obtain high carbonyl yield in a short period of time. Among them, CH_2Cl_2 was chosen as an expedient solvent. Oxidation of benzyl alcohol by $PhI(OAc)_2$ in the presence of different molar ratios of Mn(TPP)OAc in a period of 60 minutes shows the dependence of product (benzaldehyde) formation on the concentration of the catalyst. We have found that 0.003 M of Mn(TPP)OAc in the presence of imidazole was the best choice for this conversion (Fig. 1).

It is important to note that the Mn(TPP)OAc catalyst shows little activity in the absence of the imidazole co-catalyst. It is now accepted that nitrogenous bases improve the catalytic activity of metalloporphyrin-mediated oxidation reactions by improving the selectivities, reactivities and turnover

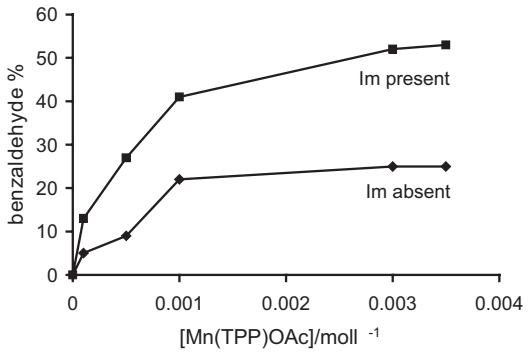


Fig. 1 Oxidation of benzyl alcohol by $PhI(OAc)_2$ with different concentrations of Mn(TPP)OAc in the absence and the presence of imidazole.

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numbers.[14] Accordingly, the oxidation of benzyl alcohol by the $PhI(OAc)_2$/Mn(TPP)OAc catalytic system was studied in the presence of imidazole (Im) nitrogenous base. We found that this nitrogenous base dramatically increases the efficiency of Mn(TPP)OAc catalyst (Fig. 1). Study of some other Im derivatives showed that the catalytic efficiency of Mn(TPP)OAc increased in the order of: Im> 4(5)-MeIm> BzIm>1-MeIm > 1,2-MeIm. This trend is nicely consistent with the electronic and steric effects of imidazole derivatives in alkene epoxidations by the *n*-Bu_4NIO_4/Mn-porphyrin catalytic system described in our previous work.[15] Moreover, under the reaction conditions, these nitrogenous bases were stable, and not oxidised. By similar experiments, we have studied the catalytic activities of various Mn(TPP)X complexes (X^- = F^-, Cl^-, Br^-,I^-, OAc^-, ClO_4^-, SCN^-, OCN^-, N_3^-, CN^-) and found that Mn(TPP)CN (in the presence of imidazole) is among the best in this class. Chemoselectivity of the catalytic system was checked by employing equimolar amounts of 4-nitrobenzyl alcohol and 4-methoxybenzyl alcohol. The results showed that only 4-nitrobenzylalcol was selectively converted into 4-nitrobenzaldehyde, whereas 4-methoxybenzyl alcohol gave only 7% of 4-methoxybenzaldehyde. Similar results were also obtained by competitive oxidation of pentan-1-ol and 3-phenyl propan-1-ol in terms of the formation of the 3-phenyl-propanal as the sole product. Another finding was that manganese porphyrins bearing a tightly coordinated ligand (*i.e*. SCN^-, OCN^-, $N_3^-$and CN^-) with a capability of both σ and π-bonding with the Mn centre[13] show the higher efficiency with the $PhI(OAc)_2$ oxidant. Therefore, the nature of axial anionic ligands in Mn(TPP)X complexes play a crucial role in this catalytic oxidising system, leading to the differentiation of catalytic activities of the Mn complexes.

After establishing the optimal conditions for oxidation of benzyl alcohol, we next examined the oxidation of different benzylic, primary aliphatic and aromatic, and secondary alcohols as substrates by the $PhI(OAc)_2$/Mn(TPP)CN/Im catalytic system. The results are summarised in Table 1. Inspection of the results, clearly show that benzylic alcohols were converted into the corresponding aldehydes (runs 1–9) and secondary and cyclic alcohols were oxidised to their ketone derivatives (runs 18–21) with a moderate to high yield and >90% selectivity.

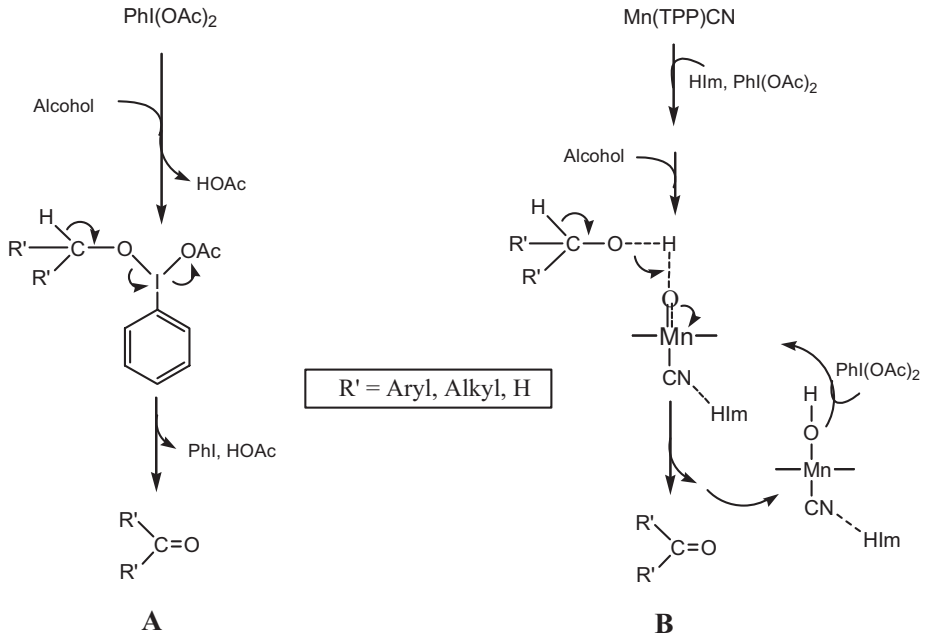
Primary aliphatic and aromatic alcohols are oxidised under the oxidation conditions to the respective aldehydes with lower yields (runs 10–17). In addition, some further oxidation of the produced aldehydes to the respective carboxylic acids was observed. *t*-Butanol remained unchanged by this oxidising system, as expected (run 22). Comparison of the yields and conversions in Table 1, demonstrate the high selectivities (>90%) for alcohol oxidation to carbonyl derivatives by this method.

The second feature of the $PhI(OAc)_2$/Mn(TPP)CN/Im catalytic system is the dependence of conversion (%) and yield (%) upon the alcohol structures. We observed that electron-withdrawing groups on the phenyl ring (i.e. NO_2), highly increase the activity of the corresponding benzyl alcohol (compare runs 1–9). Surprisingly, 4-amino butan-1-ol (run 13) displayed higher activity than *n*-amyl alcohol (run 11). However, comparison of the products (%) in runs 2 and 8 or runs 4 and 7 shows the steric effects of NO_2 and Cl substitutions in the *ortho* position of the phenyl rings, which leads to a dramatic decrease in the reactions times.

It has been shown that both the allylic C=C bond and the phenyl ring in alcohols have an effect on their oxidation reactions.[16]

One can conclude that the C=C bond near the –OH group– causes the corresponding alcohol to be more reactive. This idea comes from the oxidation of cinnamyl alcohol which gives >90% conversion (run 18). The corresponding aliphatic alcohol of cinnamyl alcohol (3-phenyl propan-1-ol) (run 14) had a very low conversion, (~30%) compared to >90% for cinnamyl alcohol, suggesting the need for an allylic C=C bond in the molecule to aid the oxidation. To establish the role of the phenyl ring, the products obtained from 3-phenyl propan-1-ol (run 14) and 2-phenylethanol (run 15), may also be considered. The phenyl ring is near the –OH group in the latter. The better activity observed for 2-phenylethan-1-ol may be attributed the phenyl ring near the –OH group which facilitates the oxidation.

Thus, from all considerations above, it may be concluded that this catalytic functional group transformation by $PhI(OAc)_2$ is a function of axial nitrogenous and anionic ligands in the Mn catalyst and both steric and electronic effects in the starting alcohols.



Scheme 1

Table 1 Oxidation of various alcohols with the $PhI(OAc)_2$/Mn(TPP)CN/Im catalytic system in CH_2Cl_2 at room temperature[a]

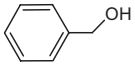
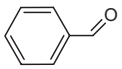
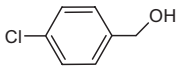
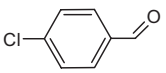
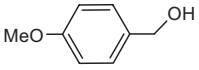
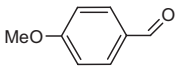
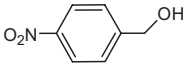
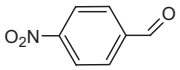
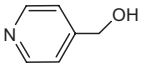
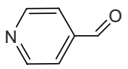
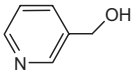
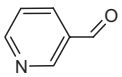
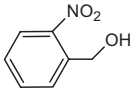
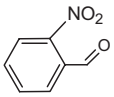
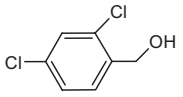
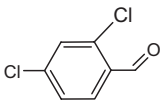
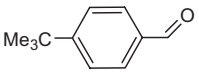
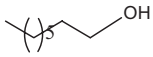
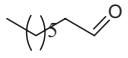
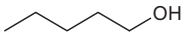
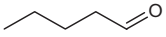
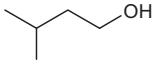
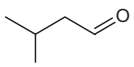
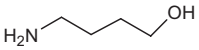
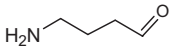
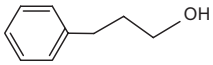
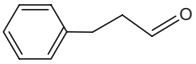
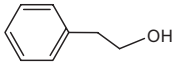
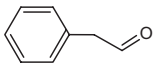
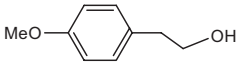
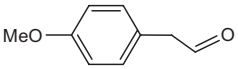
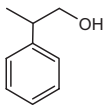
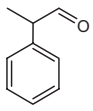
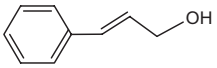
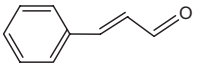
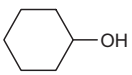
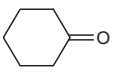
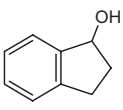
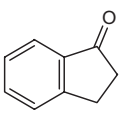
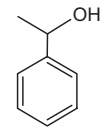
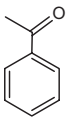
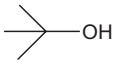
Run	Alcohol	Product	Conversion /%[b]	Yield /%[c]	Time/min	M.p./°C Found (Lit.)
1			55	52	60	Oil (oil)[d]
2			72	69	60	46–47(47.5)[d]
3			72	70	60	Oil(oil)[d]
4			100	100	10	106 (107) [d]
5			100	99	10	Oil(oil)[e]
6			94	90	60	Oil(oil)[e]
7			100	100	120	42 (43.5)[d]
8			74	73	120	71(68-71)[e]
9			76	75	60	Oil(oil)[d]
10			13	7 (~3[g])	120	Oil(oil)[d]
11			15	10 (~3[g])	120	Oil(oil)[d]
12			17	15 (~2[g])	60	Oil(oil)[d]
13			47	39 (~4[g])	60	Oil(oil)[f]
14			29	25 (~2[g])	60	Oil(oil)[d]
15			38	37 (~2[g])	60	Oil(oil)[d]
16			32	29	60	Oil(oil)
17			38	33	60	Oil(oil)[e]
18			91	84	120	Oil(oil)[e]
19			100	100	30	Oil(oil)[d]
20			77	72	60	37(37–40)[e]

Table 1 *Continued*

Run	Alcohol	Product	Conversion /%[b]	Yield /%[c]	Time/min	M.p./°C Found (Lit.)
21			100	98	60	Oil(oil)[e]
22			0.0	0.0	120	–

[a]See experimental section for details. All reactions were run in duplicate and data represent the average of these reactions. [b]Amount of the starting alcohol consumed during the reaction based on the starting alcohols. [c]Amount of the carbonyl product formed during the reaction based on the starting alcohols. [d]R. L David, *Handbook of Chemistry and Physics*, 81st edn.; CRC Press: New York, 2000–2001, 3-3 to 3- 330. [e]Merck Chemicals and Reagents Catalog, 2005–2007. [f]P.L. Wood, A.K. Khan, J.K. Moskal, K.G. Todd, V. Tanay and G. Baker, *Brain Res.*, 2006, 1122; 184. [g]Yields of the corresponding carboxylic acids.

Postulated mechanism

The third approach to this catalytic system is to offer a well -founded mechanism. Considering the artificial P-450 s, a high valent manganese oxo species (O=Mn(Por)) seem to be the active intermediate responsible for the oxidations by the $PhI(OAc)_2$/Mn(TPP)CN/Im catalytic system.[8,17]

In line with the arguments of Groves and others on high-valent Mn-oxo intermediates[8i,18] and, on the bases of the mechanisms proposed for the oxidation of phenols to benzoquinone derivatives[19] and of alcohols to carbonyl compounds[20] with λ^3-iodine reagents (Scheme 1, path **A**), a plausible mechanism for these catalytic reactions includes the initial attack by the alcohol at the electrophilic oxygen atom of O = Mn(Por) to form a Mn(III) species and the product (Scheme 1, path **B**). The liberated Mn(III) species acts again as a base with resultant formation of the high-valently O = Mn(Por) catalyst again.

Conclusion

We have reported for the first time that (diacetoxyiodo)benzene ($PhI(OAc)_2$) can serve as a mild, fast and efficient oxidising agent for oxidation of alcohols to the respective carbonyl products in the presence of a manganese porphyrin [Mn(TPP)CN] catalyst and axial nitrogenous base (especially imidazole). This procedure exhibits a very high degree of selectivity for the oxidation of benzylic and secondary alcohols to the corresponding carbonyl products. Application of the present method to the oxidation of primary aliphatic and aromatic alcohols gave a moderate conversion, without any noticeable overoxidation to carboxyl compounds.

We propose that the oxidation reactions were achieved by contribution of a high-valent Mn-oxo species and a simple mechanism has been presented.

Having established $PhI(OAc)_2$/Mn(TPP)CN/Im a mild and efficient catalytic system for the conversion of alcohols into the corresponding carbonyl compounds without excessive overoxidation, our next goal is to develop a selective artificial oxidation of organic compounds (i.e. alkanes, alkenes, thiols, sulfides, 1,4-dihydropyridines,…) by this catalytic system.

Experimental

Materials

The free base porphyrin, H_2TPP, and Mn(TPP)OAc complex were prepared by the methods of Adler. [21]

Mn(TPP)X complexes ($X^- = F^-, Cl^-, Br^-, I^-, SCN^-, OCN^-, N_3^-, ClO_4^-$) were obtained using Mn(TPP)OAc and corresponding NaX salts by a ligand exchange reaction according to the procedure of Ogoshi *et al*.[22]

Mn(TPP)CN was synthesised in a manner similar to that described by Scheidt *et al*.[23] Alcohols and nitrogenous bases were obtained from Merk or Fluka and used without further purifications (except for benzimidazole which was recrystallised before use).[24] $PhI(OAc)_2$ was prepared by a modification of the method suggested by Böeseken and Schneider:[25] Hydrogen peroxide (30%, 35 ml) and acetic anhydride (152.5 ml) were stirred together for 4 h at 40°C. Iodobenzene (25 g) was added to the solution, which was then kept overnight. Some di(acetoxyiodo)benzene crystallised and was filtered off; the filtrate was concentrated to a small volume under reduced pressure (~30 ml) and a second crop was obtained. The combined crystals were washed with ether and dried (P_2O_5) in a vacuum desiccator (yield 23 g; m.p. 164°C).

General procedure for alcohol oxidation: Stock solutions of metalloporphyrin catalysts (0.003 M) and nitrogenous base (0.2 M) in CH_2Cl_2 were prepared. In a 10 ml round-bottom flask were added in order: alcohol (0.3 mmol), Mn-porphyrin (0.006 mmol, 2 ml), axial nitrogenous base (0.03 mmol, 150 μL) and $PhI(OAc)_2$ (0.33 mmol, 0.106 g) to achieve the desired ratio. The reaction mixtures (~ 2 ml) were stirred thoroughly for the required time at ambient temperature in the air. At first, the identity of the chromophore containing products was checked by TLC and compared with the authentic samples. Some carbonyl products were also separated by a flash chromatography on a neutral alumina (type 507 C 100–125 mesh, $CHCl_3$/EtOAc; 4 : 1) and their melting points (Barstead/Electrotermal 9300, 45W) were recorded and compared with the corresponding known carbonyl compounds (or with the literature). 250 MHz proton NMR spectra (Bruker) were recorded in $CDCl_3$ at ambient temperature and referenced to TMS or the solvent signal 7.26 ($CHCl_3$). The amounts of products were determined by GLC (6890N Agilent on a 10% *SE-on*, Supelco).

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