

Selective and efficient C–H oxidation of alkanes with hydrogen peroxide catalyzed by a manganese(III) Schiff base complex

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Abstract

A variety of hydrocarbons were efficiently oxidized to the corresponding carbonyl compounds in good yields at the ambient temperature with a Schiff base Mn(III) complex as catalyst in the presence of 30% hydrogen peroxide. The oxidation took place selectively at the benzylic C–H bond through a Mn(V)-oxo intermediate. The influence of product yield as a function of solvent, temperature, catalyst concentration and reaction time was evaluated. The reaction is simple, clean and moderately high yield and generates water as the only by-product.

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Keywords: Monosubstituted arenes; Disubstituted arenes; Oxidation; Hydrogen peroxide; Catalyst; Selective oxidation; Mn(III) complex

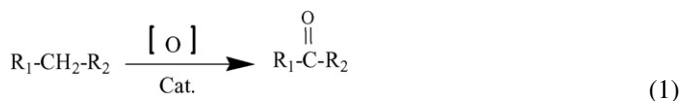
1. Introduction

Oxidative activation of C–H bonds in alkanes is often regarded as one of the Holy Grails of organic chemistry [1,2]. Whereas in nature such oxidations are efficiently carried out by enzymes, there exists no single general laboratory or industrial method, despite the undoubted commercial importance of such a process. Nevertheless, a number of methods have been developed which do affect the oxidation of unactivated C–H bonds [3,4]. Much of the current work in this area focuses on the use of transition-metal catalyzed processes [5–17]. Recent studies have demonstrated that manganese complexes in combination with various oxidizing reagents catalyze a range of oxidation reactions, oxygenation of saturated [18–23] and aromatic hydrocarbons [24–27].

Although many studies performed on the oxidation of hydrocarbons by using Mn(III) complexes [28–35] and various peroxide substances as oxidant, there are few which used H₂O₂ as source of oxygen in the C–H oxidation of alkanes [36]. Hydrogen peroxide is considered as an ideal “green” oxidant due to its strength and lack of toxic by-products.

In continuation of our research on the selective oxidation of hydrocarbons [37], herein, we report an oxidation procedure

using a Schiff base Mn(III) complex **1** (Chart 1), LMn, that convert a wide range of hydrocarbons to the corresponding oxidized products as shown in Eq. (1).



2. Experimental

All chemicals were of reagent grade. Hydrogen peroxide was used without further purification. All the isolated carbonyl compounds are commercially available and were identified through comparison of their GLC (retention time), IR and NMR (with literature known data) with those of authentic samples. GLC analyses were performed on a Perkin-Elmer 5500 instrument using a 2 m column packed with silicon OV₁ or Carbowax 20M with a FID detector under helium as a carrier gas. GC parameters were quantified by the authentic product samples prior to the analysis.

3. General procedure for oxidation

In a typical experiment, 0.1 mol% of catalyst complex, 2 mmol substrate and 20 mmol hydrogen peroxide (30%) in 2 ml of acetonitrile was stirred at the ambient temperature for the period indicated in Table 1. The progress of the reaction

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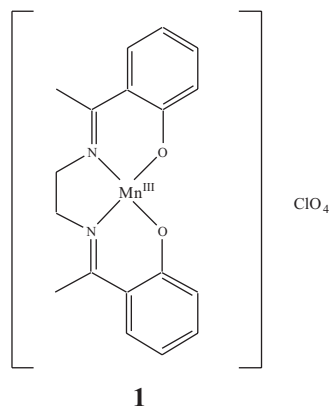


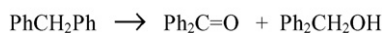
Chart 1.

was followed by TLC (solvent, *n*-hexane:ethyl acetate 9:2, v/v). After the completion of the reaction 50 μ L dimethyl sulfide was added to the resulting mixture. The aqueous acetonitrile solution was then removed on a rotary evaporator and the residue was treated with 15 mL diethyl ether. The organic solution was washed with saturated brine. Drying (Na_2SO_4) and evaporation of the solvent on a rotary evaporator afforded a residue which was passed through a short pad of silica gel or a silica gel plate using hexane and ethyl acetate (9:2, v/v) as eluent to result the analytical pure products. The oxidation products were identified by comparisons with authentic samples (retention time in GC; IR; NMR).

4. Results and discussion

The oxidation of hydrocarbons was carried out by using complex **1** as a catalyst. This complex was prepared by a procedure similar to that used by Karmaker et al. [38] but 1,2-diaminoethane was used instead of 1,3-diaminopropane.

Table 1
Benzyl oxidation of diphenylmethane with 30% H_2O_2



Entry	Catalyst (0.1 mol%)	Time (h)	Conversion (%)	Ratio (2:3) ^a
1 ^b	1	4	69	>99:0
2 ^c	1	4	64	94:6
3 ^d	1	4	47	>99:0
4	None	20	–	–
5	$\text{Mn}(\text{OAc})_3$	4	7	>99:0
6	LH_2^e	4	12	>99:0
7 ^f	1	8	38	>99:0

^a Determined as isolated yield.

^b 0.1 mol% of catalyst complex **1**, 2 mmol diphenylmethane and 20 mmol H_2O_2 (30%) in 2 ml of CH_3CN was stirred in 25 °C.

^c The reaction was carried out at ca. 80 °C.

^d The reaction was performed at 0 °C.

^e LH_2 stands for a free ligand in which two protons are bound to the phenolic oxygens.

^f The reaction was carried out under an atmosphere of O_2 instead of in the presence of 30% H_2O_2 .

Table 2
Effect of solvent on catalyzed oxidation of diphenylmethane with 30% H_2O_2

Solvent	Conversion after 4 h ^a (%)	Ratio (2:3) ^a
CH_3CN	69	>99:0
CH_3NO_2	58	>99:0
Benzene	62	>99:0
CCl_4	51	>99:0
CH_2Cl_2	40	>99:0

0.1 mol% of catalyst complex **1**, 2 mmol diphenylmethane and 20 mmol H_2O_2 (30%) was stirred in 25 °C in 2 ml of solvent.

^a Determined as isolated yield.

The oxidation of diphenylmethane was first examined as a standard substrate with 30% H_2O_2 in the presence of a catalytic amount of **1** in acetonitrile under the ambient conditions (Table 1). As expected the oxidation took place selectively, to afford benzophenone in 69% yield in the presence of **1** and 10 equiv. of 30% H_2O_2 in 4 h (Table 1, entry 1). Alternatively, the reaction was carried out at 80 and 0 °C under the same reaction conditions. The former was carried out by heating the reaction mixture for 4 h which resulted to the formation of a 1:1 mixture of diphenylmethanol and benzophenone in 64% conversion (Table 1, entry 2) and the latter showed benzophenone as the only product with 47% conversion (Table 1, entry 3). A control experiment without catalyst **1** using the same reaction conditions did not show oxidation (Table 1, entry 4). $\text{Mn}(\text{OAc})_3$ and free ligand LH_2 were also examined as catalysts for this reaction. However, they were less effective compound than **1** and afforded benzophenone in 7 and 12% yields, respectively (Table 1, entries 5–6). The large excess of hydrogen peroxide required was a result of its decomposition in the presence of the catalyst **1**. The oxygen released in the decomposition played little role in the oxidation of diphenylmethane. The oxidation occurred, albeit in poor yield, by simply bubbling molecular oxygen through the reaction mixture under similar reaction conditions (Table 1, entry 7).

To evaluate the solvent effect on the oxidation process, the oxidation of diphenylmethane was carried out with different solvents under the similar reaction conditions. These results are presented in Table 2. The comparatively higher yield was observed in case of acetonitrile among the tested solvents and resulted benzophenone as the sole product. As a consequence acetonitrile was chosen as the solvent of reaction.

To determine the catalytic effect of complex **1**, the oxidation of diphenylmethane was carried out with different catalyst concentrations under the similar reaction conditions. These results are presented in Fig. 1. As the results show with increase in catalyst concentration the reaction time decreases. Furthermore, the conversion did not proceed for longer than 4 h. As a result 0.1 mol% of catalyst and 4 h reaction time prove to be the most efficient.

To assess the scope of the reaction, the oxidations of mono- and disubstituted alkylarenes as well as tetrahydrofuran, anthracene and acenaphthene were further studied (Table 3). Toluene (entry 2) and six other monosubstituted alkylarenes (entries 1–7) were oxidized with H_2O_2 with efficient yields in the presence of compound **1** to benzaldehyde and ketones,

Table 3

Oxidation of mono- and dialkylbenzene and anthracene to the corresponding carbonyl compounds with catalyst **1** in the presence of 30% H₂O₂

Entry	R	R'	Yield ^a
1	Ph	H	69
2	H	H	58
3	Cl	H	71
4	CH ₃	H	62
5	C(=O)Ph	H	61
6	H	<i>p</i> -OH	69
7	H	<i>o</i> -CH ₃	71
Entry	R		Yield ^a
8	-CH ₂ CH ₂ -		69 ^b
9	-CH ₂ CH ₂ CH ₂ -		62 ^c
10			75
11	-CH=CH-		62
12			54
13			66
14			80

0.1 mol% of catalyst complex **1**, 2 mmol substrate and 20 mmol H₂O₂ (30%) in 2 ml of CH₃CN was stirred at room temperature for 4 h.^a Determined as isolated yield. The oxidation products were identified by comparisons with authentic samples (retention time in GC; IR; NMR).^b 1,3-indandione was also obtained in 17% yield.^c 1,4-tetralendione was also obtained in 17% yield.

respectively. Also, hydrogen peroxide oxidation of four other disubstituted alkylarenes indane, tetralin, fluorine and indene were further studied (entries 8–11 in Table 2). As above, all the substrates consistently underwent oxidation selectively to

the corresponding ketones in 62–75% yields. Tetrahydrofuran, anthracene and acenaphthene were oxidized to succinic anhydride, anthraquinone and acenaphthenequinone in 65, 66 and 80% yield, respectively (entries 12–14).

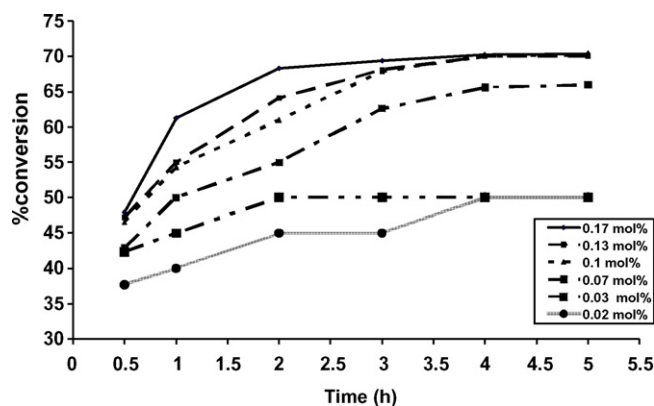


Fig. 1. Progress of the oxidation of diphenylmethane to benzophenone with different concentration of catalyst 1.

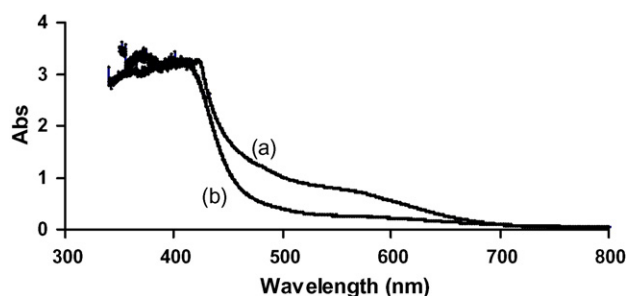


Fig. 2. Spectral changes for the formation of complex that associated with the formation oxomagnesium(V) species: (a) absorption spectrum of LMn^{III} in acetonitrile; (b) spectrum of the resultant solution obtained after addition of H₂O₂ at room temperature.

The spectral changes observed (as shown typically in Fig. 2) upon addition of H₂O₂ to the solution of catalyst complex LMn^{III} in acetonitrile, is probably attributed to the formation of a reactive LMn^V-oxo intermediate. The spectral features noted earlier for Mn(V)-oxo complexes are comparable to those observed in the present case (Fig. 2) [39–41].

Large scale oxidation of diphenylmethane (10 mmol) was also investigated. The results demonstrated that oxidation took place in good yield (typically 5–10% yield was lost).

5. Conclusions

In summary, we have showed the utility of a LMn^{III} complex as the catalyst for the oxidation of mono- and disubstituted alkylarenes to the corresponding carbonyl compounds under mild reaction conditions. The simplicity of the system, non-hazardous nature of the catalyst and oxidizing reagent, easy preparation of catalyst and wide applicability make this system an attractive, environmentally acceptable synthetic tool for the oxidation of variety of hydrocarbons.

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