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Chiral Mn(III) salen catalyzed oxidation of hydrocarbons

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Abstract Four chiral manganese(III)-salen complexes (**1**–**4**) were employed as catalysts in the oxidation of hydrocarbons at room temperature using pentafluoroiodosylbenzene as terminal oxidant. The reactions were carried out in acetonitrile and dichloromethane. Norbornene has been selectively oxidized to *exo*-epoxynorborane in 85% yield. At room temperature, oxygenation of cyclohexane up to 14% in acetonitrile medium has also been achieved.

Introduction

The oxidative functionalization of hydrocarbons under mild conditions is an important area of contemporary chemical research [1–3]. Transition metal complexes have been extensively studied as catalysts for hydroxylation of alkanes and epoxidation of alkenes [4–9]. The epoxidation of alkenes offers a convenient and important synthetic route for transformation into variety of compounds *via* highly regio- and stereoselective ring opening reactions [10]. Manganese(III) and iron(III) complexes of porphyrins, phthalocyanines, chlorins, triazacylononanes and Schiff bases have been used as alkene oxidation catalysts [9, 11–14]. Kochi et al. introduced a group of manganese(III) complexes with Schiff bases of N_2O_2 donor set, commonly known as salen complexes, as catalysts for the oxidation of alkenes [14]. Subsequently, the groups of Jacobsen and Katsuki independently developed several manganese(III) salen complexes with Schiff bases having chiral centers in the diammine bridge. These chiral manganese(III) salen complexes find their best application as catalysts in enantioselective epoxidation of unfunctionalized olefins with different terminal oxidants [12, 15–19]. In contrast, chiral manganese(III) salen complexes catalyzed oxidation of hydrocarbons, where prochirality is absent, is a less explored area [14, 20, 21]. Herein, we wish to report the catalytic properties of a group of chiral manganese(III) complexes toward hydrocarbon oxidation by pentafluoroiodosylbenzene (C_6F_5IO). The steric and electronic properties of the catalysts have been tuned by the substitution pattern at the aldehyde moiety and the chiral diamine fragment, respectively.

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Experimental

Instruments and reagents

IR spectra were recorded in KBr palate with Nicolet 460 protégé IR spectrophotometer. Reactions were monitored with a Perkin-Elmer Autosystem XL Gas Chromatograph. Mass spectra were recorded with a Jeol SX-102 (FAB). Elemental analyses were carried out with a Perkin-Elmer Series II, CHNS/O Analyzer.

All chemicals used for the synthesis of the ligands and metal complexes were reagent grade. From Aldrich, 3,5-dinitrosalicylaldehyde, (1R, 2R)-(+)-1,2-diaminocyclohexane, (1R,2R)-(+)-1,2-diphenylethylenediamine, 2-tert butyl-4-methylphenol, Tin(IV) chloride and triethylamine were obtained and used as received. Cyclohexene and the solvents used for the catalytic experiments were distilled under argon prior to use.

Synthesis of the ligands and the catalysts

Nitro-substituted and alkyl-substituted salen ligands and the Mn(III) complexes were prepared by literature methods [17]. Catalysts **1** and **2** were characterized by mass, spectral and analytical data that corresponded to the reported data [17]. For the other metallosalen catalysts, the characterization data are given below.

3. MS(FAB): 591 (M^+). Anal.: Calcd for $C_{20}H_{16}N_6O_{10}MnCl.\ H_2O$: C, 39.4; H, 2.9; N, 13.8. Found: C, 39.8; H, 3.1; N, 14.0. IR (KBr) ν (C=N)/cm^{-1}: 1643.

4. MS(FAB): 689 (M^+). Anal.: Calcd for $C_{28}H_{18}N_6O_{10}MnCl.$: C, 48.80; H, 2.6; N, 12.2. Found: C, 48.9; H, 2.8; N, 12.2. IR (KBr) ν (C=N)/cm^{-1}: 1635.

Catalytic oxidations

Catalytic reactions were carried out in small screw capped vials fitted with PTFE septa. In a typical reaction, catalyst and substrate were dissolved in 2 mL of argon saturated solvent. The final concentrations of the catalyst and the substrate were 100 μM and 100–200 mM, respectively. The oxidation reaction was initiated by adding C_6F_5IO (final concentration 2 mM), and the contents were magnetically stirred for 1 h. The standard solution of dodecane was added to this reaction mixture, and an aliquot was injected into a capillary column (carbowax, 30 m) of a preheated GC. The identification and the quantitation of the products were done from the response factors of standard product samples as usual (Internal standard: Dodecane, 2 mM).

Results and discussion

Four tetradentate chiral salen ligands were synthesized according to reported methods [17]. Manganese(III) complexes (**1**–**4**) (Fig. 1) were prepared from $Mn(OAc)_2.\ 4H_2O$ and the corresponding ligands in the presence of LiCl. The spectral (MS and IR) and elemental analysis data of two known complexes (**1, 2**) are in agreement with the reported values [17]. The two complexes (**3**, **4**) were characterized on the basis of by MS, IR and elemental analysis data.

Initially, the efficacy of the catalysts (**1**–**4**) was investigated with norbornene under a standard set of conditions. The rationale behind the choice of norbornene as substrate is based on the wide applicability of norbornene and its derivatives like epoxy norborane, diol etc., in polymer synthesis, pharmaceutical intermediates and general organic synthesis [22]. The probable products during the oxidation of norbornene include 2,3-epoxynorborane, 2-norbornanone and *exo*, *endo*-norborneols. Oxidations of norbornene were carried out by a number of catalytic systems [23–26] but the selectivity and yield of epoxide are moderate in most of the cases [27]. The present oxidizing system selectively oxidizes norbornene to *exo*-epoxynorborane at room temperature. Mn(III)-salen complexes (**1** & **2**) have emerged as more efficient catalysts, affording the *exo*-epoxide in 72–85% yield, than the catalysts, **3** & **4** (Table 1). The introduction of electron donating groups (*tert*-butyl and methyl) in the 3 and 5 positions of the aldehyde fragment of the Schiff base increases significantly the yield of norbornene epoxidation but the presence of electron withdrawing nitro groups decreases the yield. Our

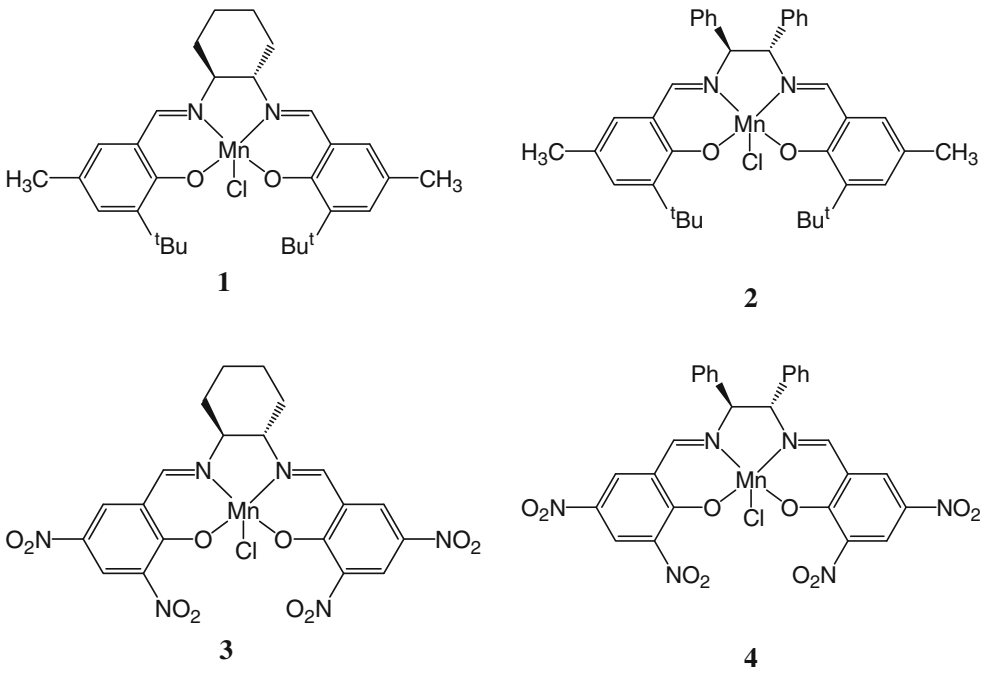

Fig. 1 Manganese (III)-salen catalysts used in the study

Table 1 Mn(III) salen catalyzed oxidation of Norbornene by C_6F_5IO at 25 °C

Entry	Catalyst	Solvent	% Yield of epoxide[a]
1	**1**	CH_3CN	77
2	**1**	CH_2Cl_2	72
3	**2**	CH_3CN	80
4	**2**	CH_2Cl_2	85
5	**3**	CH_3CN	45
6	**3**	CH_2Cl_2	45
7	**4**	CH_3CN	52
8	**4**	CH_2Cl_2	52

[a] Yields are with respect to total oxidant concentration

results are in agreement with the view that oxidized species are stabilized by the introduction of the electron donating substituents in the aldehyde fragment and destabilized by electron withdrawing groups in Mn(III)-salen complexes [20, 28].

The effect of chiral diamine fragment on the catalytic activity of the Mn(III)-salen complexes can be appreciated by the fact that catalysts **2** & **4** with (1R, 2R)-(+)-diphenyl moiety afford better conversions than those (**1** & **3**) with (1R, 2R)-(+)-cyclohexyl moiety. The catalytic reactions were carried out separately in acetonitrile and dichloromethane but no solvent effect was observed. This suggests the involvement of similar type of intermediates in both the solvents. It is reasonable to believe that the active species is [O=Mn(V)(salen)Cl] that transfers the oxygen to the alkenes by a stepwise radical mechanism with C_6F_5IO [29].

High selectivity and conversion in epoxidation of norbornene by the catalysts (**1–4**) encouraged us to extend our study on oxidation of other hydrocarbons. At room temperature, Mn(III)-salen complexes (**1–4**) catalyze the oxygenation of cyclohexene to epoxide as major product with C_6F_5IO (Table 2). Interestingly, Mn(III)-salen catalyzed oxygenation of cyclohexene does not show much dependence on the substituents at the salicylidine moiety or on reaction medium; the percentage conversion of cyclohexene by C_6F_5IO remained almost same in both acetonitrile and dichloromethane (Table 2). Another distinct feature of these reactions is that epoxidation is favoured over allylic oxidation (Table 2) although appreciable amount of allylic oxidation is observed in case of catalyst **2** (entry 4, Table 2). Thus, conversions obtained are modest but the formation of cyclohexene oxide without serious competition from the production of cyclohexenol and cyclohexenone is noteworthy as it is known that cyclohexene is prone to allylic oxidation. This result is in contrast with the chiral iron(III)-salen catalyzed oxidation [30] of cyclohexene, where allylic oxidation dominates over epoxidation with much lower selectivity.

The Mn(III) salen complexes were also effective in epoxidation of cyclooctene and 1-octene, the results are summarized in Tables 3 and 4, respectively. For cyclooctene, alkyl-substituted Mn(III) salen complexes appear to be better catalysts. The conversion of cyclooctene to cyclooctene oxide with catalysts **1** and **2** was observed up to 60%, whereas the epoxidation with catalysts **3** and **4** was much lower (43 and 48%, respectively) (Table 3). Here also, no allylic oxidation was observed. No distinct solvent effect was observed for the nitro-substituted Mn(III)-complexes (**3** and **4**), although the epoxidation of cyclooctene with catalysts **1** & **2** was found to be facilitated in acetonitrile medium than in dichloromethane. In metal-catalyzed epoxidations, terminal alkenes are known to be least reactive among the olefins [14], yet 1-octene is readily oxidized by C_6F_5IO in the presence of chiral Mn(III)-salen catalysts (Table 4). Here, the nitro-substituted catalysts (**3** & **4**) appear more efficient than alkyl substituted catalysts (**1** & **2**) unlike the epoxidation of cyclooctene. It is well documented that the substitution of nitro groups at 5, 5′ positions of the Mn(III)-salen complexes can modulate the donor properties of the oxomanganese(V) intermediates by

Table 2 Mn(III) salen catalyzed oxidation of Cyclohexene by C_6F_5IO at 25 °C

Entry	Catalyst	Solvent	Conversion (%)	Product (% yields)[a]		
				1-ol	1-one	Epoxide
1	**1**	CH_3CN	31	7	3	21
2	**1**	CH_2Cl_2	31	7	3	21
3	**2**	CH_3CN	65	16	10	39
4	**2**	CH_2Cl_2	62	20	15	27
5	**3**	CH_3CN	46	6	2	38
6	**3**	CH_2Cl_2	44	7	2	35
7	**4**	CH_3CN	43	5	1	37
8	**4**	CH_2Cl_2	42	7	1	34

[a] Yields are with respect to total oxidant concentration

Table 3 Metallosalen catalyzed oxidation of Cyclooctene by C_6F_5IO at 25 °C

Entry	Catalyst	Solvent	% Yield of epoxide[a]
1	**1**	CH_3CN	55
2	**1**	CH_2Cl_2	39
3	**2**	CH_3CN	59
4	**2**	CH_2Cl_2	43
5	**3**	CH_3CN	42
6	**3**	CH_2Cl_2	43
7	**4**	CH_3CN	44
8	**4**	CH_2Cl_2	48

[a] Yields are with respect to total oxidant concentration

Table 4 Mn(III) salen catalyzed oxidation of 1-octene by C_6F_5IO at 25 °C

Entry	Catalyst	Solvent	% Yield of epoxide[a]
1	**1**	CH_3CN	10
2	**1**	CH_2Cl_2	12
3	**2**	CH_3CN	12
4	**2**	CH_2Cl_2	10
5	**3**	CH_3CN	34
6	**3**	CH_2Cl_2	32
7	**4**	CH_3CN	38
8	**4**	CH_2Cl_2	43

[a] Yields are with respect to total oxidant concentration

decreasing their electron density thereby making them more reactive toward terminal olefins [14]. This prompted us to utilize this enhanced reactivity of oxomanganese(V) to oxidize saturated hydrocarbons such as cyclohexane. Thus under identical conditions, cyclohexane was reacted with C_6F_5IO in presence of the catalysts **1**–**4**. The nitro-substituted catalyst **4** was found to catalyze the oxidation of cyclohexane (14% conversion). The yields of cyclohexanol and cyclohexanone are 6 and 8%, respectively. It is noteworthy that the oxidation of cyclohexane to adipic acid has been achieved with encapsulated complex **3** as catalyst [31]. The alkyl-substituted Mn(III)-salen complexes were found to be ineffective in bringing about cyclohexane oxidation.

Conclusion

In conclusion, we have demonstrated the effectiveness of four chiral Mn(III)-salen complexes (**1**–**4**) as catalysts for hydrocarbon oxidation at room temperature using C_6F_5IO as the terminal oxidant. The pronounced effect of substitution pattern at the aldehyde fragment toward catalytic activity of the Mn(III)-salen complexes has been observed. Alkyl-substituted chiral Mn(III) complexes emerged as better catalysts in epoxidation of olefins than the corresponding nitro-substituted ones. On the other hand, electronegative Mn(III)-salen complexes have been found to be superior catalysts in epoxidation of terminal olefins like 1-octene and oxidizing saturated hydrocarbons like cyclohexane. Further studies on detailed mechanism of the reactions are currently in progress.

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