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Organic carbonates as solvents in macrocyclic Mn(III) salen catalyzed asymmetric epoxidation of non-functionalized olefins

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ABSTRACT

Organic carbonates, e.g., dimethyl carbonate and propylene carbonate were used as reaction media in enantioselective epoxidation of non-functionalized alkenes by using a series of chiral macrocyclic Mn(III) salen complexes (5 mol%) as catalyst with pyridine *N*-oxide as an axial base. This protocol worked effectively with urea hydrogen peroxide, as well as sodium hypochlorite as oxidants to give respective epoxides in high yields and ee (up to >91% in selected cases). Furthermore kinetic studies of the catalytic epoxidation reaction in dimethyl carbonate:methanol (optimized solvent mixture) with urea hydrogen peroxide as an oxidant showed first order dependence on catalyst and oxidant whereas it is zero order for the substrate, styrene.

1. Introduction

The correct choice of solvent is one of the central problems in the synthetic chemistry, for in many cases the physical and toxicological properties of a solvent have a pivotal influence on its use both in the laboratory and industrial scale [1]. A case in study here is the classic chiral Mn(III) salen catalyst that has shown high enantioselectivity for the asymmetric epoxidation of prochiral alkenes under homogeneous condition. Invariably, dichloromethane is used as preferred solvent for this reaction particularly with the oxidant NaOCl [2]. Notwithstanding environmental implications; very high catalyst solubility in this solvent also poses challenges in catalyst recyclability [2–4]. To make Mn(III) salen catalyst recyclable, strategies like its immobilization on organic polymers [5], inorganic supports [6–8], encapsulation in zeolite cavities [9], physical entrapment in siloxane membranes [10], tuneable solubility and multiphase methods have been reported. In the past, the ecologically sensible media have been used, notable among these are water [11–13], fluorinated hydrocarbons [14], supercritical CO_2 [15–18], and ionic liquids [19,20]. To our best knowledge there are no reports on the use of organic carbonates as solvent in asymmetric epoxidation reaction. Organic carbonates are polar aprotic solvents, which are noncorrosive, nontoxic and biodegradable, hence are safer, and environment friendly alternatives to conventionally used CH_2Cl_2 (DCM), tetrahydrofuran (THF) and other hazardous aromatic solvents [21,22]. For the present study we have employed our earlier reported macrocyclic Mn(III) salen complexes **1**, **2** [23] and two new but closely related complexes **3** and **4** for the epoxidation of several prochiral olefins in organic carbonates as reaction media using pyridine *N*-oxide (Py*N*O) as an axial ligand. This protocol worked equally well with sodium hypochlorite (NaOCl) and urea hydrogen peroxide (UHP) as oxidants in our initial exploratory experiment. However, due to the environment friendly nature of UHP, it was studied in detail. The present study revealed that dimethyl carbonate (DMC) could be a suitable replacement for chlorinated solvents like CH_2Cl_2 and gave comparable conversions (>99%) and enantioselectivities (ee, up to 91%) in the epoxidation of styrene, *cis*-β-methyl styrene, Indene and chromenes. Additionally, the use of DMC over DCM has allowed easy catalyst separation due to relatively lower catalyst solubility in the former solvent.

2. Experimental

2.1. Materials and methods

Indene and styrene (both from Fluka) were passed through a pad of neutral alumina before use. (1*R*,2*R*)-(+)-1,2-diphenyl-1,2-ethanediamine, (1*S*,2*S*)-(+)-1,2-diaminocyclohexane and 1-butyl-3-methylimidazolium hexaflurophosphate (BMIM-PF_6) were procured from Sigma–Aldrich. All chromenes [24,25] and

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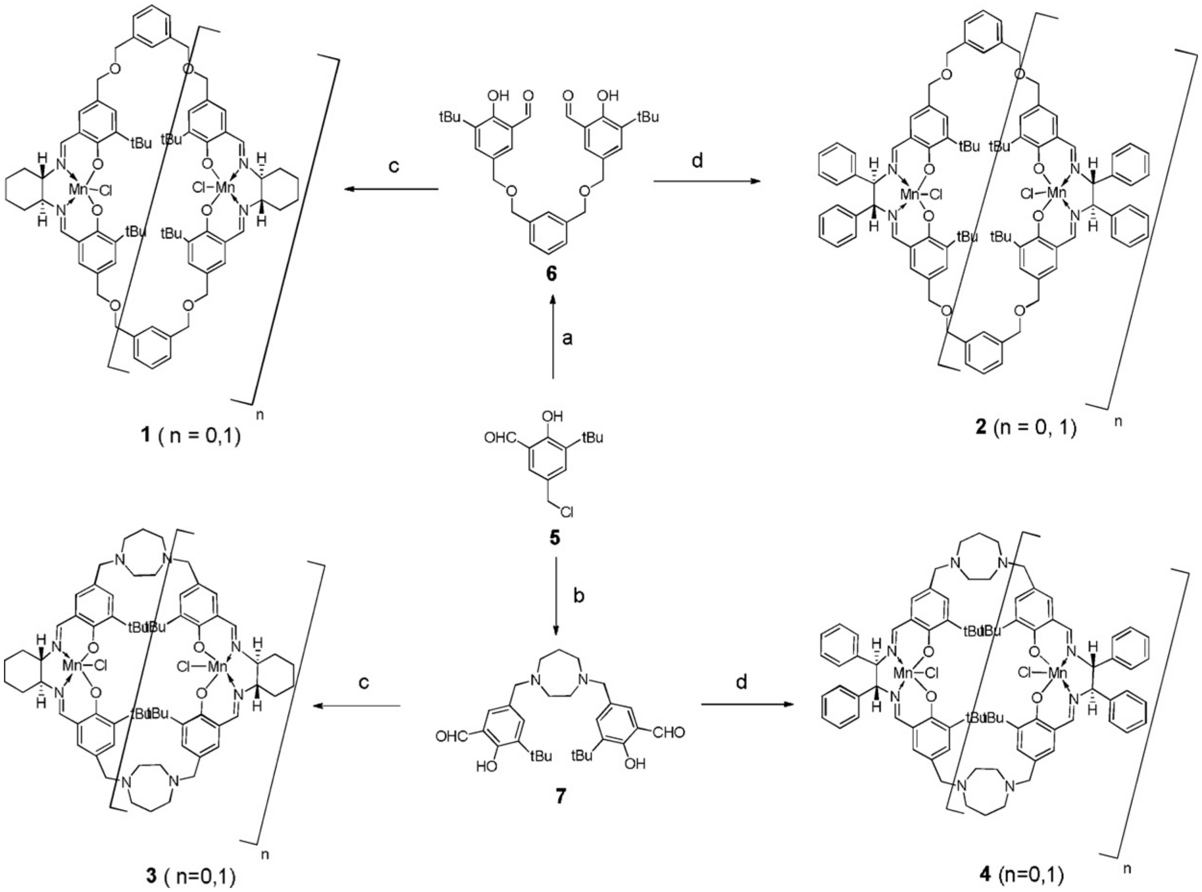

Scheme 1. Reaction conditions: (a) NaH, THF, 0 °C; (b) dry toluene, reflux; 2 h; (c) Step I: (*1S,2S*)-(+)-1,2-cyclohexane diamine, THF, RT, 2 h; Step II: $Mn(CH_3COO)_2 \cdot 4H_2O$, MeOH, LiCl; (d) Step I: (*1R,2R*)-(+)-1,2-diphenylethylene diamine, THF, RT, 2 h; Step II: $Mn(CH_3COO)_2 \cdot 4H_2O$, MeOH, LiCl.

3-*tert*-butyl-5-(chloromethyl)-2-hydroxy benzaldehyde were synthesized according to the reported procedures [26]. All the solvents were purified before use [27]. Analytical reagent grade propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC) (all from Spectrochem Pvt. Ltd., India), manganese acetate (SD Fine Chem. Ltd., India), NaOCl (14% aqueous solution, National Chemicals, India) and UHP (Merck) were used as received. Racemic epoxides were synthesized from their corresponding alkenes by racemic [Mn(III) (salen) Cl] complex and were purified by flash column chromatography. All the melting points reported here were determined on Thermo Scientific MET-TEMP (Model No. 1002D) and were uncorrected. Optical rotations of chiral intermediates and the chiral complexes were recorded on an automatic polarimeter (Digipol 78, Rudolph) instrument. Microanalysis of the products was carried out on a vario MICRO cube (Elementar) CHNS analyzer. The ^1H NMR and ^{13}C NMR spectra were recorded on Bruker 200 MHz or 500 MHz instruments at ambient temperature. The chemical shifts are reported in ppm relative to TMS ($\delta = 0.00$) for ^1H NMR and relative to the central $CDCl_3$ resonance ($\delta = 77.0$) for ^{13}C NMR. FT-IR spectra were recorded on Perkin Elmer Spectrum GX spectrophotometer in KBr window. Electronic spectra of chiral macrocyclic Mn(III) salen complexes were recorded in (1:1) DMC:MeOH on a Shimadzu UV-Vis-NIR spectrophotometer (Serial No. A108446). TOFF mass of the catalysts and intermediates were determined on a Micromass Q-TOF-micro instrument. The purity of the solvents, alkenes and analysis of the epoxide product were determined by gas chromatography (GC) using a Shimadzu GC 2010 instrument with a Bruker Factor four capillary column VF-1ms (15 m long, 0.25 mm inner diameter, 0.25 μm density of film) equipped with an FID detector. Ultrapure nitrogen was the carrier gas (rate 30 ml/min). Injection port and detector temperature were kept at 200 °C. For the product analysis of styrene, *cis*-*β*-methyl styrene and indene the column temperature was programmed at 70–140 °C, while for chromene it was kept at 140 °C (isothermal). Synthetic standard of the products were used to determine the conversions by comparing the peak height and area. Flash column chromatography (FCC) was carried out using neutral alumina (Grade-1). Enantiomeric excesses (ee) of the indene oxide and chromenes were determined by HPLC (Shimadzu SCL-10AVP) using Daicel Chiralpak OD or OB column with 2-propanol/hexane as eluent. Enantiomeric excess of styrene and *cis*-*β*-methyl styrene were determined by gas chromatography using a Shimadzu GC 2010 instrument with a Supelco Astec Chiral DEX^{TM} G-TA column. The following abbreviations were used to designate NMR chemical shift multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad; coupling constants are given in Hertz (Hz). The NMR data of known compounds are in aggrement with literature values [28,29]. Optical rotations are reported as follow: $[\alpha]_D{}^t$ (*c* in g per 100 mL, $CHCl_3$). HPLC and GC traces of product epoxides were compared with their respective racemic samples. The complexes **1**, **2** and **3**, **4** were prepared via intermediate dialdehydes **6** [23] and **7** respectively according to Scheme 1.

2.2. Synthesis of 5,5′-((1,4-diazepane-1,4-diyl)-bis-(methylene))-bis-(3-tert-butyl)-2-hydroxybenzaldehyde ***7***

1,4-Diazacycloheptane (0.88 g, 8.8 mmol) was added to a solution of 3-(*tert*-butyl)-5-(chloromethyl)-2-hydroxybenzaldehyde **5** (4.0 g, 17.6 mmol) in dry toluene (20 mL) at room temperature. The