

Mn (Br₈TPPS) Supported on Amberlite IRA-400 as a Robust and Efficient Catalyst for Alkene Epoxidation and Alkane Hydroxylation

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Abstract: Manganese (III) *meso-tetrakis(p-sulfonatophenyl)-β*-octabromoporphyrin supported on Amberlite IRA-400 [Mn(Br₈TPPS)-Ad-400] is a robust and efficient catalyst for epoxidation of alkenes and hydroxylation of alkanes with sodium periodate at room temperature.

Keywords: Octabromoporphyrin, epoxidation, hydroxylation, sodium periodate

Introduction

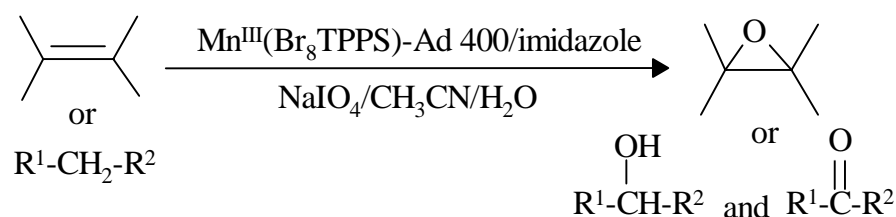
Epoxidation of alkenes and hydroxylation of alkanes catalyzed by metalloporphyrin catalysts is a subject of much investigation. A variety of oxygen donors like iodosylarenes, hypochlorites, alkylhydroperoxides, hydrogen peroxide and periodates have been used these transformations [1]. In fact, the majority of the studies are directed toward understanding the mechanism of the catalytic activity of heme-containing enzymes such as cytochrome P-450. Homogeneous metalloporphyrin catalysts with steric hindrance, and those containing sophisticated chiral auxiliaries, or strongly electron-withdrawing groups can exhibit high regio- [2-5], shape- [4-6] and enantioselectivity [7], and high catalyst turnovers [8,9]. However, difficulty in recovery and the high cost of the catalysts outweigh these appealing features and so far have made their applications to synthesis impractical. A

potential approach to prepare commercial metalloporphyrin catalysts is to immobilize them onto solid supports. Such immobilization makes the catalysts separable from reaction mixtures and reusable, enhance the catalyst stability towards oxidation and allow preparation of environmentally friendly catalysts. Many heterogenized metalloporphyrin catalysts have been reported for alkene epoxidation and alkane hydroxylation [10-23].

Results and Discussion

This report describes the use of Mn(Br₈TPPS) supported on Amberlite IRA-400 for epoxidation of alkenes and hydroxylation of alkanes with sodium periodate in a CH₃CN/H₂O mixture at room temperature. Mn(Br₈TPPS) is a sulfonated hindered metalloporphyrin with electron withdrawing substituents at the β-positions of the pyrroles. The electronegative groups on the pyrrole moieties enhance the reactivity of the metal oxo species and immobilization of the metalloporphyrin on ion-exchange resin (Amberlite IRA-400) and avoid μ-oxo formation. The catalyst exhibits a high activity and stability in alkene epoxidation and alkane hydroxylation by NaIO₄. Scheme 1 shows the reaction conditions:

Scheme 1



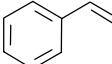
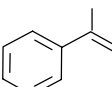
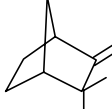
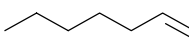
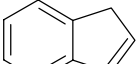
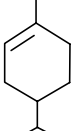
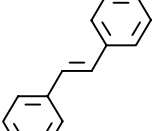
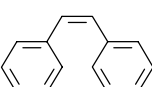


It is found that addition of a heterocyclic nitrogen base such as imidazole or 1-methylimidazole to this catalytic system improves the activity of the catalyst. In the presence of imidazole, the Mn(Br₈TPPS) –Ad-400 system converts different olefins efficiently to their corresponding epoxides (Table 1). Epoxidation of *trans*-stilbene proceeds in a stereospecific manner with complete retention of configuration. In contrast, epoxidation of *cis*-stilbene is associated with some loss of stereochemistry and affords 80% *cis*- and 10% *trans*-stilbene oxides, respectively. This catalytic system exhibits a good regioselectivity for epoxidation of R-(+)-limonene. The ratio among 1,2- and 8,9-epoxides was found to be 2.3:1.

Selective partial alkane hydroxylation is a particularly challenging problem in organic chemistry. Mn(Br₈TPPS)-Ad-400 catalytic system oxidizes different alkanes to corresponding alcohols and ketones with sodium periodate in CH₃CN/H₂O mixture at room temperature (Table 2). Overoxidation of the alkane hydroxylation product is highly dependent on the nature of the hydrocarbon itself. In the case of benzylic hydroxylation the main products detected were ketones due to the subsequent transformation of alcohols to ketones in the reaction mixtures. The hydroxylation of *cis*-decaline gives the *cis*-9-decanol and *cis*-1-decalone in yield 20 and 36%, respectively. In the case of




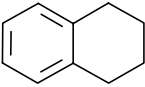
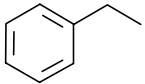
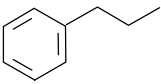
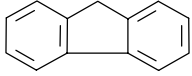
tetrahydronaphthalene and propylbenzene only α -tetralone and ethylphenylketone have been identified in the reaction mixtures, respectively.

Table 1: Epoxidation of alkenes with NaIO_4 catalyzed by $\text{Mn}(\text{Br}_8\text{TPPS})\text{-Ad-400}$ in the presence of imidazole at room temperature

Entry	Alkene	Conversion(%) ^a	Epoxide yield(%) ^a	Reaction time/h
1		92	92	6
2		93	78	6
3		90	67	6
4		90	65	4
5		70	70	6
6		55	55	10
7		88	88	6
8		86	60(1,2-epoxide) ^b 26(8,9-epoxide) ^b	6
9		60	60(trans-epoxide) ^b	6
10		90	80(cis-epoxide) ^b 10(trans-epoxide) ^b	6

^a GLC yield based on starting alkene; ^b Both ¹H-NMR and GLC data confirmed the reported yields.

Table 2: Hydroxylation of alkanes with NaIO_4 catalyzed by $\text{Mn}(\text{Br}_8\text{TPPS})\text{-Ad-400}$ in presence of imidazole at room temperature

Entry	Alkane	Ketone(%) ^a	Alcohol(%) ^a	Reaction time/h
1		28	17	10
2		50	4	10
3		36	20	10
4		57	-	10
5		39	-	10
6		27	-	10
7		90	-	10

a: GLC yield based on starting alkane.

Conclusions

This robust and stable catalytic system is a convenient and efficient system that expands the scope of utilization of metalloporphyrins in useful organic transformations.

Acknowledgements

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Experimental

General

Alkenes, alkanes and alkylaromatic compounds were obtained from Merck and Fluka and purified prior to use by passing through a column containing active alumina to remove peroxidic impurities.

The porphyrin ligand H₂TPPS was prepared, brominated and metallated according to literature procedures [24-26].

Immobilization of Mn(Br₈TPPS) on Amberlite IRA-400

Mn(Br₈TPPS) (0.5 g) was dissolved in a 1:1 mixture of acetone-water and Amberlite IRA-400 (5 g) was added to the solution. The mixture was stirred at 80 °C for 8 h. The mixture was cooled to room temperature, filtered, washed with water and acetone and dried. The polymer supported porphyrin is insoluble in common organic solvents. The reflectance spectrum clearly indicates a Soret band at 488 nm and a Q band at 566 nm. IR spectrum of the solid supported manganese porphyrin shows $\nu(\text{S}=\text{O})$ at 1400 and 1180 cm⁻¹. The degree of manganese porphyrin incorporation into the polymer was determined by neutron activation analysis (NAA), which gave a value of about 0.29% w/w.

Typical procedure for oxidation reactions catalyzed by Mn(Br₈TPPS)-Ad-400

All of the reactions were carried out at room temperature under air in a 25 mL flask equipped with a magnetic stirring bar. A solution of NaIO₄ (2 mmol) in H₂O (10 mL) was added to a mixture of alkene or alkane (1 mmol), Mn(Br₈TPPS)-Ad 400 (11 μmol) and imidazole (0.2 mmol) in CH₃CN (10 mL). The progress of reaction was monitored by GLC. The reaction mixture was diluted with CH₂Cl₂ (20 mL) and filtered. The resin was thoroughly washed with CH₂Cl₂ and combined washings and filtrates were purified on silica-gel plates or a silica-gel column. IR and ¹H-NMR spectral data confirmed the identities of the products.

Catalyst reuse and stability

The stability of Mn(Br₈TPPS)-Ad 400 was studied in repeated epoxidation reactions. The epoxidation of α -methylstyrene was chosen as a model substrate for studying of catalyst reuse and stability. The reaction was carried out as described above. At the end of the reaction, the catalyst was removed by filtration and washed with water and acetonitrile and reused. The dried catalyst was consecutively reused four times. After the use of catalyst for four consecutive times, the conversion yield was 88%. The amount of leached Mn (1.0 %) was determined by atomic absorption.

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Sample availability: Samples of the catalyst Mn(Br₈TPPS) are available from MDPI.