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Synthesis of dipyroromethanes in water and investigation of electronic and steric effects in efficiency of olefin epoxidation by sodium periodate catalyzed by manganese tetraaryl and *trans* disubstituted porphyrin complexes

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ABSTRACT: Condensation of pyrrole with various aldehydes in the presence of BF_3·etherate as an acid catalyst in water provides good yield of some dipyrromethanes. Prolongation of the reaction time with aldehydes substituted by electron-donating (mesityl) or electron-withdrawing (2,6-dichlorophenyl) groups on the *ortho* positions of the phenyl did not lead to decomposition or scrambling. Manganese *trans* disubstituted porphyrin complexes which derive from various dipyrromethanes and manganese tetraaryl porphyrin complexes including various substituents with different steric and electronic properties show good catalytic activity in epoxidation of alkenes by $NaIO_4$ in the presence of imidazole (ImH). The study of steric and electronic effects of the catalysts on the epoxidation of olefins shows that Mn-porphyrin complexes with more bulky and electron-releasing groups on *meso* phenyls could increase the epoxidation yield of most alkenes.

KEYWORDS: dipyrromethanes, porphyrin, manganese, epoxidation.

INTRODUCTION

Meso or 5-substituted dipyrromethanes are important precursors for synthesis of *meso*-substituted porphyrins, expanded porphyrins and porphyrin analogues [1–3]. *Meso*-substituted *trans*-porphyrins are key structural components found in a wide range of system models in biomimetic and material chemistry from [2 + 2] condensation between dipyrromethane and aldehyde which imply preparation of pure *trans*-porphyrins [4–6].

Several methods have been reported for synthesis of 5-substituted dipyrromethanes by condensation of aldehyde and pyrrole using various combinations of acids and solvents. All these reports claim moderate yields of *meso*-substituted dipyrromethanes. Thus, aldehyde and pyrrole readily undergo condensation using homogeneous acid catalysts such as BF_3·etherate, trifluoroacetic acid (TFA) and propionic acid at room temperature to yield *meso*-substituted dipyrromethanes along with oligomeric byproducts. The yields are reduced due to the formation of oligomers and stringent purification methods are needed to remove the byproducts [7–9].

The formation of N-confused dipyrromethanes and tripyrromethanes [10–13], difficulty in controlling the time to stop the reaction when the dipyrromethane concentration is at its maximum, large excess of pyrrole and the distillation of the excess pyrrole [14], decomposition of the dipyrromethane on silica, purification problems and acidolysis of dipyrromethanes [8, 15] are important problems in the reaction conditions as mentioned above.

In this paper, we prepared some *meso*-substituted dipyrromethanes by dropwise addition of pyrrole to an aqueous solution of aldehyde [16] in the presence of

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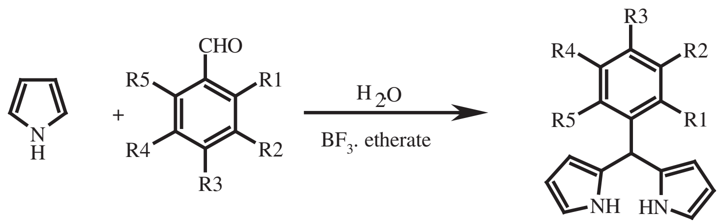


1(a-g)

Fig. 1. Synthesis of dipyrromethanes in water

BF_3·etherate as the acid catalyst and at temperature of 70–80 °C in argon atmosphere after 30–70 min (Fig. 1). The reactions with electron-withdrawing and bulky substituents on the phenyl group in dipyrromethanes prevent the acidolysis and scrambling of these compounds.

Metal complexes of various ligands such as oxazolines [17, 18], Schiff bases [19–22] and porphyrins [23–25] are recognized as catalysts for epoxidation of alkenes. Among these catalysts, porphyrins are efficient catalysts for epoxidation purposes as models of cytochrome P-450 enzymes [26–30]. *Meso*-substituted porphyrins are key structural components found in a wide range of system models in biomimetic and material chemistry from [2 + 2] condensation between a dipyrromethane and an aldehyde derivative for preparation of pure *trans*-porphyrins. At first, we prepared a number of porphyrins from [2 + 2] condensation between dipyrromethane and aldehyde which were used for preparing manganese porphyrin complexes including: *meso*-tetrakis(2,6-dichlorophenyl) porphyrinato manganese(III) acetate, Mn(TDCPP)OAc, *meso*-tetra(mesityl)porphyrinato manganese(III) acetate, Mn(TMP)OAc, 5,15-bis(2,6-dichlorophenyl)-10,20-di-(phenyl)porphyrinato manganese(III) acetate, Mn(BDCPDPP)OAc and 5,15-di(mesityl)-10,20-di(phenyl)porphyrinato manganese(III) acetate and Mn(DMDPP)OAc (Fig. 2).

The complexes were used in a catalytic system for epoxidation of various olefins which were carried out in the presence of imidazole as the best axial ligand, tetra-*n*-butylammonium bromide, Bu_4NBr, as the phase transfer agent in a CH_2Cl_2/H_2O solvent system at ambient temperature and $NaIO_4$ as an oxidation agent. Steric and electronic properties of metalloporphyrins and alkenes substantially affect the yield of the product and the rate of oxygenation [27, 31–36].

The effects of various axial ligands as co-catalysts such as piperidine, pyridine, imidazole and lutidine were investigated in the epoxidation of cyclooctene by Mn(BDCPDPP)OAc. Among the co-catalysts listed above, strong π-donor ImH is the best co-catalyst.

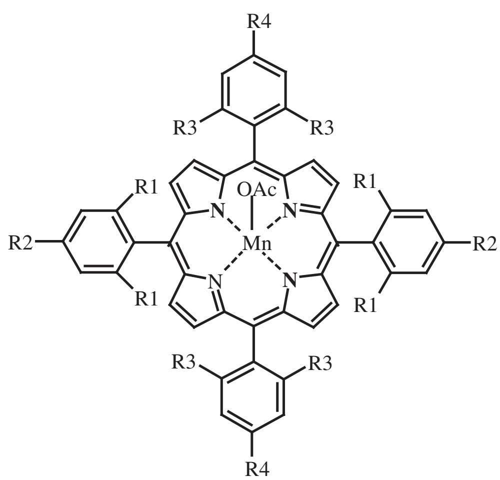
RESULT AND DISCUSSION

Synthesis of *meso*-substituted dipyrromethanes

One step synthesis of dipyrromethanes in water was reported [16]. Success of this approach resides on the fact that the reaction between the pyrrole and the carbonyl compound occurs at the interface between the pyrrole and the acidic aqueous aldehyde or ketone solution. The release of the dipyrromethane from the aqueous layer when it is formed forces the reaction to be completed and protects the product from further reactions.

This method provides the corresponding dipyrromethanes in good to excellent yield with dropwise addition of pyrrole to the aqueous solution of the required aldehyde in the presence of hydrochloric acid after 30–45 min at 90 °C.

In the above-mentioned method, use of aqueous HCl as acid catalyst and a temperature of 90 °C produces tripyrromethane and other oligomers. In the present



Mn(Por)OAc	R_1	R_2	R_3	R_4
Mn(TPP)OAc	H	H	H	H
Mn(TMP)OAc	CH_3	CH_3	CH_3	CH_3
Mn(TDCPP)OAc	Cl	H	Cl	H
Mn(DMDPP)OAc	CH_3	CH_3	Cl	Cl
Mn(BDCPDPP)OAc	Cl	H	H	H

Fig. 2. *Meso*-tetraaryl porphyrinato manganese(III) acetate and *meso-trans* disubstituted porphyrinato manganese(III) acetate used as catalysts in this work

Table 1. Synthesis of various dipyrromethanes in water in the presence of BF_3·etherate

Entry	Aldehyde	Total yield of dipyrromethane (%)
1a	Benzaldehyde	65
1b	Mesitaldehye	85
1c	2,6-dichlorobenzaldehyde	80
1d	4-bromobenzaldehyde	70
1e	4-chlorobenzaldehyde	65
1f	2-hydroxy 4-methoxybenzaldehyde	75
1g	2,3,4,5,6-pentaflourobenzaldehyde	60

study, we have used the same method for the synthesis of dipyrromethanes in water but in the presence of the BF_3·etherate as the acid catalyst at temperature of 70 °C in nitrogen or argon atmosphere after 30–70 min (Fig. 1).

Prolonging of the reaction time for the aldehydes **1a**, **1d**, **1e**, **1f** and **1g** shows no improvement in the yield of dipyrromethane production and finally leads to production of byproducts. For aldehydes are **1b** or **1c**, yields of the reactions were high and prolongation of the reaction time for a few minutes does not produce any byproduct(s). Thus, it is obvious that higher yields of dipyrromethanes were obtained in the presence of both electron-withdrawing (2,6-dichlorophenyl) and electron-releasing (2,4,6 trimethylphenyl; mesityl) bulky substituents in the *meso* positions (Table. 1).

The bulky substituents on the *ortho* positions of phenyl groups on the *meso* or 5-position of dipyrromethanes suppress the acidolysis of dipyrromethanes. Reaction time for dipyrromethenes including electron-withdrawing substituents on the phenyl groups of these compounds (1g) is low.

Effect of various axial ligands as co-catalysts on the epoxidation of cyclooctene by Mn(BDCPDPP)OAc

Most metal-catalyzed oxidation systems require the addition of a base which acts as an axial ligand and remarkably improves both the rate and the selectivity of the reaction (proximal effect) [37, 38]. In these catalytic systems, similar to other biomimetic catalysts based on synthetic metalloporphyrins, presence of axial ligands remarkably improves the rate of epoxidation [24, 39]. The effect of a number of axial ligands is examined for the epoxidation of cyclooctene in the Mn(BDCPDPP)OAc catalytic system (Table 2).

In the absence of an axial ligand, 12% of cyclooctene oxide is produced. Pure σ-donor amines do not have a co-catalytic effect. Piperidine with σ-donating ability and with low steric effect, shows great co-catalytic activity with this Mn(Por)OAc catalyst. Sterically hindered amines such as 2-metylpiperidine and tertbuthylamine have no co-catalytic effect.

Table 2. Effect of different axial ligands in the epoxidation of cyclooctene by Mn(BDCPDPP)OAc/$NaIO_4$[a]

Entry	Axial ligand	The yield of epoxide (%)[b]
1	None	12
2	Piperidine	14
3	*Tert*-buthylamine	5
4	Pyridine	8
5	4-Methylpyridine	16
6	4-Cyanopyridin	2
7	4-Aminopyridine	20
8	2,6-Dimethylpyridine	7
9	*N*,*N*-dimethylaminopyridine	28
10	Imidazole	78
11	2-Methylimidazole	4
12	2-Ethylimidazole	3
13	1-Methylimidazole	5
14	Benzimidazole	30
15	4-Nitroimidazole	18
16	Pyridine-*N*-Oxide	17
17	2-Methylpyridine	6

[a]The molar ratio for Mn(Por)OAc: axial ligand:cyclooctene:oxidant:phase transfer catalyst are 1:10:10:83:167. [b]Determined by GC at 60 min.

Pyridine or 4-substituted pyridines with weak π-donor abilities or with electron-donor groups show better co-catalytic effects than σ-donor amines. The epoxidation rate decreases in the following order:

N,*N*-Dimethylaminopyridine > 4-Aminopyridine
> 4-Methylpyridine > Pyridine > 4-Cyanopyridine

High co-catalytic activity of 4-aminopyridine results in a π-resonance effect of its *p*-NH_2 group. 4-Cyanopyridine with an electron-withdrawing CN substituent displays no co-catalytic activity. 2-Methylpyridine and 2, 6-dimethylpyridine with one or two group(s) near the nitrogen donor atom prevent the coordination of the Mn(Por)OAc. Therefore, they have no co-catalytic activity.

Among the nitrogenous bases, which are used as co-catalysts, imidazole is the best co-catalyst of the nitrogen donors (Table 2, entry 10). Binding of 2-metylimidazole and 2-ethylimidazole are shown in Fig. 3.

Binding of 2-metylimidazole and 2-ethylimidazole to the central metal would more severely restrict displacement of the central metal toward the strong oxo ligand because of steric repulsion between the 2-methyl and 2-ethyl substituents and the porphyrin ring.

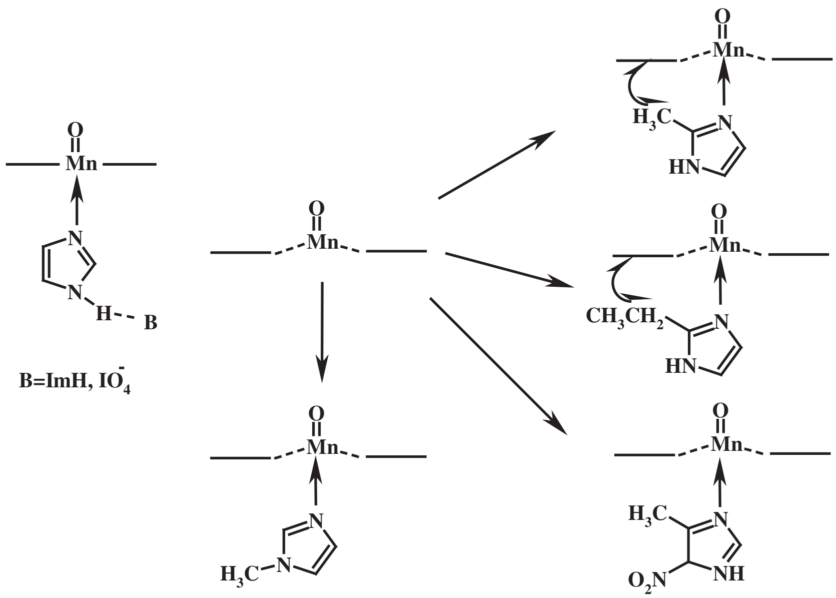


Fig. 3. A comparison between co-catalytic effects of various imidazole axial ligands

1-methylimidazole is coordinated to the metal center without steric effects like 2-alkyl imidazole but it cannot form a N–H···B hydrogen bond with nitrogen which has a methyl group (Fig. 3), so it has no distal effect [39, 40]. The low co-catalyst effect of 4-nitroimidazole which is related to its electron-withdrawing NO_2 substituent is unable to accelerate electron releasing through its imidazole group. Thus, imidazole as a strong π donor for its proximal and distal effects is the best axial ligand in this catalytic porphyrin system.

Catalytic epoxidation of alkenes by various Mn(Por)OAc/ImH/NaIO$_4$ systems

The epoxidation of alkenes and hydroxylation of alkanes catalyzed by metalloporphyrin complexes is the subject of many investigations. The epoxidation of alkenes has been examined with a variety of manganese porphyrins containing different phenyl groups [30]. Comparison of the catalytic properties of five different *meso*-substituted manganese porphyrins in the epoxidation of various alkenes with $NaIO_4$ and in the presence of imidazole is presented in Table 3.

Comparison and investigation of epoxidation of various alkenes with different porphyrin catalysts

In the presence of Mn(TPP)OAc, 1-methylcyclohexene is more reactive than cyclohexene, and for styrene derivatives, 4-methoxystyrene is more reactive than 4-methylestyrene and styrene. Epoxidation of limonene produces only 1,2-epoxide. All of these observations indicate that the electronic properties of alkenes substantially affect the rate of oxygenation. Sterically demanding *trans*-stilbene shows less reactivity than the *cis* isomer. Compared with the *cis* isomer, *trans*-stilbene oxide is formed with higher yield and greater stability, which indicates that there is low-hindered Mn(TPP)OAc complex for rotation about the alkene C–C bond at some intermediate step. In Mn(DMDPP)OAc catalysts, two groups of *trans* phenyls of porphyrin have substituents in contrast to Mn(TPP)OAc, thus steric effect is less only for two sides of Mn(DMDPP)OAc.

Greater reactivity of 1-methylcyclohexene than cyclohexene and styrene derivatives than styrene, clearly demonstrates an electronic effect of alkenes in a Mn(DMDPP)OAc catalyst. The long reaction time for Mn(DMDPP)OAc reflects high steric properties of Mn(DMDPP)OAc due to the methyl groups in *ortho* positions of two *trans* phenyls of Mn(DMDPP)OAc.

Cis-stilbene gives only 7% *trans*-stilbene oxide with Mn(DMDPP)OAc and 14% *trans*-stilbene with Mn(TPP)OAc. These results imply that free rotation about the alkene C–C bond at some intermediate step for Mn(DMDPP)OAc, due to steric methyl groups, is more difficult than for low hindered Mn(TPP)OAc complexes.

Mn(TMP)OAc with bulky substituents at *ortho* and *para* positions of the aryl rings require a long reaction time (18–24 h) for epoxidation of different alkenes. Most alkenes are completely converted to corresponding epoxides with Mn(TMP)OAc after a long reaction time compared to Mn(TPP)OAc (3 h) and Mn(DMDPP)OAc (12 h) catalysts. These observations indicate that the electronic properties of the phenyl substituents have an important role in the epoxidation of most of alkenes and electron-releasing groups increase the reaction times of the catalysts.

Epoxidation of *cis*- and *trans*-stilbene in the presence of bulky Mn(TMP)OAc is 100% stereoselective and leads to formation of the corresponding epoxides. The epoxidation yield of alkenes in the presence of Mn(BDCDPP)OAc with Cl substituents on the *ortho*

Table 3. Epoxidation of alkenes with Mn(Por)OAc/$NaIO_4$/imidazole at room temperature[a]

Alkene	Epoxide yield (%)[b]							
	Mn(TPP)OAc	Mn(DMDPP)OAc		Mn(BDCPDPP)OAc		Mn(TDCPP)OAc	Mn(TMP)OAc	
	3 h	3 h	12 h	3 h	6 h	24 h	3 h	24 h
Cyclooctene	100	40	90	100[h]	—	86	24	99
Cyclohexene	70	54	76	93	—	84	40	100
1-Methylcyclohexene	85[c]	51	92	70	85[i]	82	34	100
Styrene	100	40	75	73	93	85	35	100
α-Methylstyrene	100	60	84	55	72	49	25	100[n]
4-Methylstyrene	100	20	90	72	86[j]	82	22	100
4-Methoxystyrene	100[d]	24	100	79	87[k]	94	25	100
Indene	100	30	100	60	100	95	57	100[n]
Limonene	59[e]	15	72 (20)[g]	52	54 (23)[g]	87[m]	19	100[n]
cis-Stilbene	76 (14)[f]	20	63 (7)[f]	65	95	85	25	96[n]
trans-Stilbene	65	10	46	32	82[l]	36	3	46
1-Octene	70	49	82	70	—	98	12	60
trans-2-Octene	60	25	40	54	71	94	4	54

[a]The molar ratios of Mn(Por)OAc:imidazole:olefin:$NaIO_4$:n-Bu_4NBr were 1:10:10:83:167. [b]GLC yield based on starting alkene. [c]2 h. [d]150 min. [e]1,2-epoxide is sole product. [f]*Trans*-stilbene oxide. [g]8,9-epoxide. [h]110 min. [i]5 h. [j]3.5 h. [k]4 h. [l]4 h. [m]Products:25% 1,2-epoxide, 42% 8,9-epoxide and 20% limonene dioxide. [n]18 h.

positions of phenyl groups as a catalyst is higher than for Mn(DMDPP)OAc.

Low epoxidation yields more electron-rich and sterically hindered alkenes such as 1-methylcyclohexene, *trans*-2-octene and α-methylstyrene demonstrate that electronic properties of alkenes are not important in the presence of Mn(BDCDPP)OAc. In fact, electronic effects of the catalyst are efficient for epoxidation. Epoxidation of *cis*- and *trans*-stilbene with Mn(BDCDPP)OAc is 100% stereoselective.

The long reaction time required for the Mn(TDCPP)OAc catalyst compared to Mn(TPP)OAc, Mn(BDCDPP)OAc and Mn(DMDPP)OAc indicates that the steric properties of Mn(TDCPP)OAc and low epoxide yield for alkenes in the presence of Mn(TDCPP)OAc compared with Mn(TMP)OAc are related to electronic effects. Low epoxide yield for *trans*-stilbene in the presence of Mn(TDCPP)OAc obviously demonstrates the effect of steric properties of catalyst and alkenes. The Mn(TDCPP)OAc catalyst is more active than Mn(TMP)OAc and epoxidation of unfunctionalized alkenes was performed by Mn(TDCPP)OAc in excellent yield. It should be mentioned that the electronic effect of catalyst has a key role in the epoxidation intermediate.

Investigation of stability of various Mn porphyrins used in this work

It is well known that metalloporphyrins suffer from oxidation at the *meso*-position which is followed by ring opening [33].

The *ortho* substituents of the *meso*-phenyl rings protect the *meso*-position sterically and electronically from a bimolecular oxidation process. The stability of five different manganese porphyrins was studied for cyclooctene epoxidation with $NaIO_4$ in the presence of imidazole and the results are illustrated in Fig. 3. The obtained results show that the *ortho* substituted catalysts *e.g.* Mn(TDCPP)OAc, Mn(TMP)OAc and to some extent Mn(BDCDPP)OAc were unchanged, but intense degradation of Mn(TPP)OAc and Mn(DMDPP)OAc was observed.

Study of stability of all catalysts in cyclooctene after 24 h by UV-vis spectroscopy illustrates that the simple Mn-porphyrins, *e.g.* Mn(TPP)OAc, Mn(DMDPP)OAc and to some extent Mn(BDCDPP)OAc with low steric protection of both faces of the macrocycle, are more sensitive to destruction through the *meso* position than Mn(TDCPP)OAc and Mn(TMP)OAc catalysts which have substituents on their *ortho* positions of porphyrin phenyls.

We found that Mn(DMDPP)OAc was completely destroyed after 24 h in comparison with Mn(BDCDPP)OAc. This observation indicates that electron-releasing groups in the *ortho* positions of low-hindered Mn(Por)OAc such as Mn(DMDPP)OAc accelerate the degradation of the porphyrin ring after a long time (Fig. 4).

In fact, electron-releasing or electron-withdrawing substituents are known to provide a steric protection to porphyrin rings against the oxidative degradation of the complex during both thermal and photochemical catalytic processes.

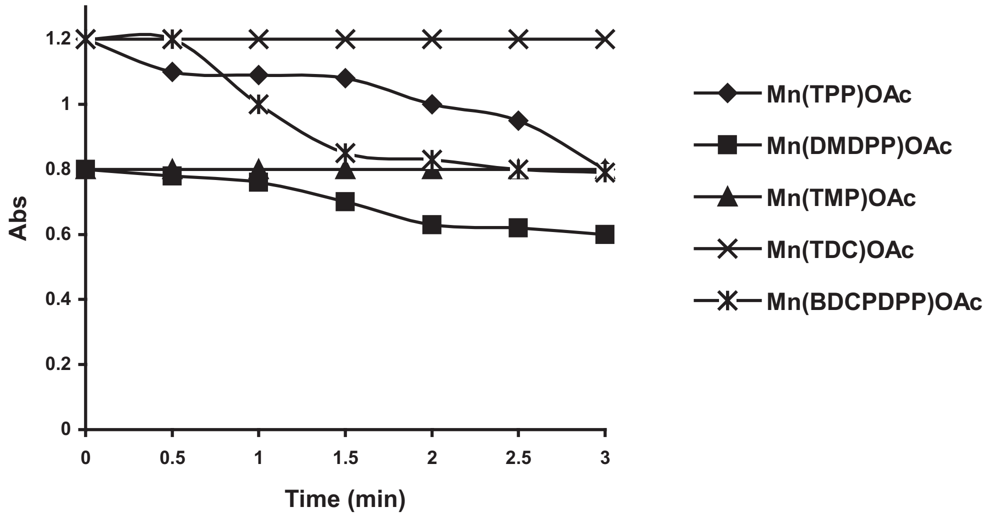


Fig. 4. Mn-(Por)OAc decomposition measured by UV-vis spectroscopy *vs.* time for five Mn-(Por)OAc in the epoxidation of cyclooctene by $NaIO_4$ and in the presence of imidazole

Epoxidation of cyclooctene with $NaIO_4$ catalyzed by Mn(BDCPDPP)OAc in the presence or absence of 2,6-di *tert*-butyl *p*-cresol as an inhibitor

It has been suggested that high valent Mn-oxo species are considered as the active intermediates during olefin epoxidation with various single oxygen donors in biphasic systems [32].

In a typical experiment, addition of an inhibitor in different molar ratios to cyclooctene was performed. Figure 5 shows the results of this experiment by use of radical trapping experiments (with a radical scavenger, 2,6-di *tert*-butyl *p*-cresol). It was established that intermediates with radical character are probably involved in the epoxidation reactions.

The production of *trans*-stilbene oxide from *cis*-stilbene with low hindered catalysts such as Mn(TPP)OAc and Mn(DMDPP)OAc requires an intermediate which leads to its direct formation with a *cis*/*trans* inversion. This may be accounted for by a mechanism involving radical intermediates.

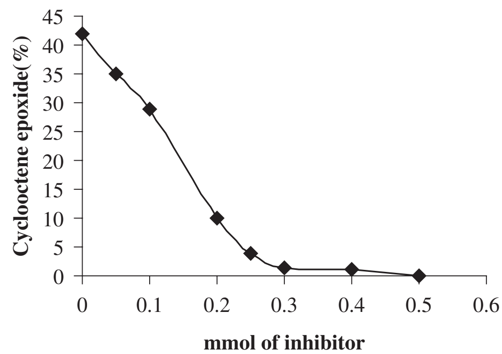


Fig. 5. Addition of inhibitor in different molar ratio to cyclooctene in epoxidation reaction with Mn(BDCDPP)OAc/$NaIO_4$/ImH for 30 min

EXPERIMENTAL

Materials

All used compounds were purchased from Merck or Fluka in analytical grade. Dichloromethane, chloroform, pyrrole, benzaldehyde and ethyl acetate were distilled before reactions.

Physical measurement

^{1}H NMR spectra were collected by a Bruker FT-NMR 500 MHZ spectrometer using $CDCl_3$ as solvent at ambient temperature. UV-vis spectra were obtained with a CARY 100 Bio spectrophotometer. The reaction products of oxidation reactions were determined and analyzed by an HP Agilent 6890 gas chromatograph equipped with a HP-5 capillary column (5% phenyl methyl siloxane 60.0 m × 250 μm × 1.00 μm) and a flame-ionization detector.

Synthesis of dipyrromethanes

In a typical experiment, a solution of 3.6 mmol of mesitaldehyde was added to 80 mL boiling water and stirred under nitrogen or argon atmosphere for 15 min at room temperature. Then 0.5 mmol BF_3·etherate was added, followed by the dropwise addition of 18 mmol of pyrrole. After refluxing for 30–70 min, at which point no aldehyde was detected by TLC analysis (cyclohexane/ethyl acetate/triethylamine; 80:20:1), the suspension was\ left to cool at 40–50 °C and then the reaction mixture was diluted with CH_2Cl_2 (50 mL) and 50 mL NaOH (0.1 N) in order to quench the reaction. Afterwards, the mixture was extracted with CH_2Cl_2 and the organic layer was dried over Na_2SO_4. The solvent was then removed under reduced pressure and the resulting green dipyrromethane product was washed with a small volume of *n*-hexane. Finally, the hexane/residual pyrrole mixture was removed under vacuum. Recrystallization (water: ethanol 4:1) gave the dipyrromethane as white crystals (Table1).

***Meso*-(2,4,6 *trimethylphenyl)dipyrromethane* (1*b*).** mp: 160 °C, Yield (80–85%), ^{1}H NMR (solvent: $CDCl_3$ internal standard: TMS): δ ppm): 2.1 (s, 6H), 2.31 (s, 3H), 5.94 (s, 1H, *meso*-H), 5.99 (m, 2H), 6.15 (m, 2H), 6.64 (m, 2H), 6.87 (s, 2H), 7.89 (brs, 2H, NH).

***Meso*-(2,6-*dichlorophenyl)dipyrromethene* (1*c*).** mp: 98–99 °C, Yellowish solid, Yield (80%), ^{1}H NMR: δ ppm): 6.05–6.10 (m, 2H), 6.20 (m, 2H), 6.52 (s, 1H, *meso*-H), 6.73–6.77 (m, 2H), 7.13–7.15 (m, 1H), 7.36–7.37 (d, 2H), 8.28 (bs, 2H, 2NH).

Synthesis of porphyrin ligands and Mn(Por)OAc complexes

Dipyrromethanes **1b** and **1c** were selected for synthesis of desired tetraaryl and *trans* disubstituted porphyrins. The [2 + 2] condensation reaction between dipyrromethane and aldehyde was used for preparing pure tetraaryl and *trans* disubstituted porphyrins. Synthesis and characterization of these complexes have been reported in the literature [37]. We have used literature for synthesis of manganese porphyrins [38].

It has been observed that when the dipyrromethane contains an electron withdrawing substituent such as *meso*-(2,6-dichlorophenyl)dipyrromethane, high yields of porphyrins were obtained.

Epoxidation of alkenes

Typically, for alkene epoxidation, a solution of Mn(Por)OAc (0.003 mmol) in CH_2Cl_2 (2mL), tetra-*n*-buthylammonium bromide (0.03 mmol) as the phase transfer catalyst, imidazole (0.03 mmol) and substrate (0.25 mmol) were successively added and then a solution of $NaIO_4$ (0.5 mmol in 5 mL water) was added to the resulting mixture and the two phases were stirred thoroughly for an appropriate time at room temperature. Formation of products and consumption of substrates were monitored by GC and compared with authentic samples.

CONCLUSIONS

In the present research, we prepared some *meso*-substituted dipyrromethanes by dropwise addition of pyrrole to an aqueous solution of aldehyde. It should be mentioned that high yields of dipyrromethane production in aqueous media were obtained in the presence of electron-donating, electron-withdrawing and sterically bulky substituents on *ortho* positions of phenyls of aldehydes that protect dipyrromethanes from acidolysis or scrambling. In other words, one-step synthesis of dipyrromethanes in water was reported in this study. Unsubstituted aldehyde requires a time control to stop the reaction when the dipyrromethane concentration is at its maximum level.

The steric and electronic effects of various metalloporphyrins, alkenes and axial ligand types affect the yield of the epoxidation of alkenes. Epoxidation of various olefins with Mn(TPP)OAc and Mn(BDCDPP)OAc in this catalytic system shows a high reactivity in a short time compared to other catalysts. Therefore, the most efficient time for epoxidation with Mn(TPP)OAc in this catalytic system is 3 h and the electronic effect of alkenes is effective in improving the yield of epoxidation. Greater reactivity of the Mn(BDCDPP)OAc catalyst is due to its steric effects. Low steric effect and electron density of two groups of *trans* phenyls for Mn(DMDPP)OAc lead to high yield epoxidation in a low reaction time compared to more steric catalysts such as Mn(TDC)OAc and Mn(TMP)OAc.

Epoxidation of *trans*-stilbene by all the catalysts and epoxidation of *cis*-stilbene by Mn(BDCDPP)OAc and the more hindered catalysts, *i.e.* Mn(TMP)OAc and Mn(TDCPP)OAc, are 100% stereospecific It should be mentioned that only pure epoxides of these isomeric forms are obtained. Whereas *cis*-stilbene epoxidation by Mn(DMDPP)OAc and the low hindered catalysts, *i.e.* Mn(TPP)OAc lead to a mixture of *cis*- and *trans*-stilbene oxide. These results and the high reactivity of *cis*- and *trans*-stilbene with respect to the *trans* isomer can be interpreted by the more difficult approach of the *trans* isomer to oxidizing active species. This is due to the unfavorable interactions between the olefin and porphyrin substituents. Furthermore, with the aim of increased catalyst stability, the stability of various Mn porphyrins used in this work were studied. In fact, electron-releasing or electron-withdrawing substituents are known to provide a steric protection to the porphyrin ring against the oxidative degradation of the complex during both thermal and photochemical catalytic processes. More hindered catalysts such as Mn(TMP)OAc and Mn(TDCPP)OAc are more stable than the low hindered catalysts in epoxidation reactions because of the protection of the *meso* positions of porphyrin rings by these hindered groups.

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