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Benzyltributylammonium periodate as a novel and safe oxygen source for Mn-porphyrin catalyzed practical and highly selective oxygenation of hydrocarbons

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ABSTRACT

Benzyltributylammonium periodate ($BzBu_3NIO_4$) was prepared easily in high yield in neat water. The compound crystallized with two cations and two anions per asymmetric unit and a space group of $Pna2_1$ was determined by single-crystal X-ray diffraction. It was used practically in the clean and selective epoxidation of olefins and oxygenation of saturated hydrocarbons catalyzed by manganese (III) porphyrins in water/ethanol as a green media. The catalyst could be reused without noticeable loss of activity, and the oxidant's by-product ($BzBu_3NIO_3$) could also be reused. The efficiency of the oxidation system depends critically upon the steric hindrances and electronic structures of both the nitrogen donors and Mn-catalysts. Some evidences suggest the involvement of a high valent Mn-oxo species as well as a six-coordinate [(L)(Por)Mn–OIO_3] complex in the oxidation reactions.

1. Introduction

The development of selective hydrocarbon oxidation, which is of fundamental importance in both nature and organic synthesis, is a goal that has long been pursued [1,2]. Metalloporphyrins mimicking cytochrome P-450 monooxygenase enzymes have been vastly employed for this invaluable transformation, using a variety of oxygen donors during the past decades [3,4].

Periodates have drawn considerable attention as mild and efficient single oxygen donors for Mn-porphyrin, and salens catalyzed various oxidation reactions in recent decades [5–9]. Nevertheless, the extensive use of toxic and volatile organic solvents in many oxidation systems, including periodates [5–9], mediated by metalloporphyrins has reduced considerably the importance of biologically inspired oxidation catalysis [3]. Furthermore, during recent years, increasingly demanding legislation as well as public and economic pressure has led to increased interest in new, "clean" methods for the production of chemical compounds. Discarding of harmful organic solvents is the major problem in chemical industries, which accounts for around 80% of their wastes. Thus, a new challenge is to make such processes cleaner by using non-toxic solvents, in particularly aqueous media [10–12]. Additionally, the accessibility of the oxidant in terms of their price and availability at a large scale alongside the stability of the catalyst under oxidizing conditions, providing recycling of the reaction, play important roles for economical viability of the processes [10].

In continuation of our ongoing research on the development of new biomimetic methods for the oxidation of organic compounds [13–22], we explored that benzyltributylammonium periodate ($BzBu_3NIO_4$), which is synthesized easily in high yield in water without recourse to any organic solvents for isolation, is a safe and efficient oxygen source for the clean and selective epoxidation of olefins and oxygenation of saturated hydrocarbons to the related alcohols and ketones, catalyzed by Mn(TPP)OAc in H_2O/EtOH as a sustainable media (Scheme 1). Moreover, the catalyst could be reused without noticeable loss of activity. We also report the crystal structure of this novel oxidant, as determined by single-crystal X-ray diffraction.

2. Experimental

2.1. General remarks

All chemicals were purchased from Merck or Fluka. The free base porphyrins: $TPPH_2$ [23], T(4-OMeP)PH_2 [23], T(4-NO_2P)PH_2 [24], $TMPH_2$ [25] and $TDCPPH_2$ [25] were prepared and purified

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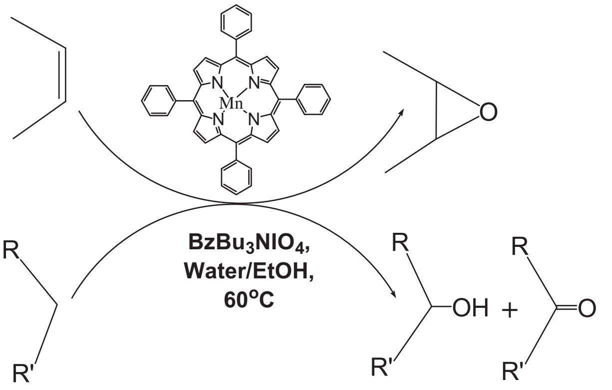


Scheme 1. Oxygenation of hydrocarbons with $BzBu_3NIO_4$ catalyzed by Mn-porphyrins in H_2O/EtOH.

by the methods reported previously. The Mn(Por)OAc complexes were obtained using $Mn(OAc)_2{\cdot}4H_2O$, according to the procedure of Adler et al. [26].

2.2. Instrumentation

Purity determinations of the products were accomplished by GC on a Shimadzu GC-16A instrument equipped with a 25 m CBP1-S25 (0.32 mm ID, 0.5 μm coating) capillary column and a flame ionization detector. IR spectra were recorded on a Perkin Elmer 780 instrument. UV–vis spectra were recorded on a 160 Shimadzu spectrophotometer. NMR spectra were recorded in $CDCl_3$ solutions with a Brucker Avance DPX FT-NMR 250 MHz instrument. The residual $CHCl_3$ in conventional 99.8 atom% $CDCl_3$ gives a signal at $\delta = 7.26$ ppm, which was used for calibration of the chemical shift scale. Mass spectra were recorded on a Shimadzu GC–MS-QP5050A.

2.3. Synthesis of benzyltributylammonium periodate

Benzyltributylammonium periodate was prepared by addition of an aqueous solution of benzyltributylammonium chloride (10 mmol, 3.12 g in 30 mL distilled water) to a solution of $NaIO_4$ (10 mmol, 2.14 g) in distilled water (50 mL), followed by simple filtration. The white solid was eluted by distilled water and dried under air. A solid colorless powder was obtained in 90% yield (4.2 g). M.p. 106.6 °C, IR (KBr) 2956, 2865, 1474, 1372, 839, 725 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$, 25 °C) δ_{ppm}: 0.87 (t, $J = 7.25$ Hz 9H, alkyl protons), 1.23 (m, 6H, alkyl protons), 1.66 (m, 6H, alkyl protons), 3.01 (t, $J = 8$ Hz, 6H, alkyl protons), 4.33 (s, 2H, benzyl protons), 7.29–7.36 (m, 5H, aromatic protons); ^{13}C NMR (63 MHz, CDCl3, 25 °C) δ_{ppm}: 13.56, 19.55, 24.02, 58.25, 62.37, 126.62, 129.48, 130.95, 132.15. *Anal.* Calc. for $C_{19}H_{34}INO_4$ (467): C, 48.83; H, 7.33; N, 3.0. Found: C, 48.80; H, 7.35; N, 3.00%.

2.4. General oxidation procedure and recycling

To a mixture of olefin (1 mmol), Mn(por)OAc (0.01 mmol) and nitrogen donors (0.1 mmol) in H_2O/EtOH (2 mL/3 mL) was added $BzBu_3NIO_4$ (2 mmol, 0.93 g). The reaction mixture was stirred at 60 °C for the appropriate reaction time, which was monitored by GC. After completion of the reaction, ethanol was removed from the mixture and then petroleum ether (3 × 2 mL) was added to the aqueous phase and cooled. The $BzBu_3NIO_3$ from the oxidant was precipitated and removed by filtration. The organic phase containing product was separated and evaporated. If the conversion was not complete, further purification was achieved by silica chromatography eluting with *n*-hexane/ethyl acetate (10/2). Then, the aqueous phase was centrifuged and the solid catalyst was separated, dried under air and reused for a similar reaction [22].

2.5. Crystallographic data collection and structure refinement

Suitable X-ray quality crystals of $BzBu_3NIO_4$ were obtained as colorless plates by slow evaporation of solvent from a 1:2 methanol/acetonitrile solution of the compound at room temperature. The intensity data were collected at 173 K with a Stoe Image Plate Diffraction System [27] using Mo $K\alpha$ graphite monochromated radiation. The image plate distance was 70 mm, ω oscillation scans 0–200°, step $\Delta\omega = 1.0°$, exposures of 3 min, 2θ range 3.27–52.1°, *d*min–*d*max = 12.45–0.81 Å. The structure was solved by direct methods using SHELXS-97 [28]. The refinement and all further calculations were carried out using SHELXL-97 [28]. The H atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. A semi-empirical absorption correction was applied using the MULscanABS routine in PLATON [29]. The compound crystallized in the non-centrosymmetric orthorhombic space group $Pna2_1$, with two cations and two anions per asymmetric unit ($Z = 8$). The structure was refined as an inversion twin and gave as the final refined Flack parameter, or BASF, a value of 0.11(3). Two of the alkyl chains are disordered; they were refined with restraints on the C–C bond distances, given as values close to those found in the non-disordered alkyl chains, with large standard uncertainties and with PARTs. Their occupancies were also refined. Data collection and refinement processes are summarized in Table 1.

Table 1
Crystal data and structure refinement for $BzBu_3NIO_4$.

	Compound ($BzBu_3NIO_4$)
Empirical formula	$C_{19}H_{34}NIO_4$
Formula weight	467.37
T (K)	173
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	
a (Å)	16.5662(10)
b (Å)	10.0028(6)
c (Å)	25.5308(17)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V ($Å^3$)	4230.7(5)
Z	8
D_{calc} (Mg/m^3)	1.468
Absorption coefficient (mm^{-1})	1.535
F(0 0 0)	1920
Crystal size (mm^3)	0.19 × 0.30 × 0.38
θ range for data collection (°)	2.19–26.04
Index ranges	$-20 \le h \le 20$
	$-12 \le k \le 12$
	$-31 \le l \le 31$
Reflections collected	32,084
Independent reflections	8300 [$R_{int} = 0.044$]
Observed reflections	*Nnnn* [$I > 2\sigma$ (I)]
Absorption correction	multi-scan
Maximum and minimum transmission	1.000 and 0.9049
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	8300/25/453
Goodness-of-fit (GOF) on F^2	0.924
Final *R* indices [$I > 2\sigma$ (I)]	6079 (R_1[a] = 0.0399, wR_2[b] = 0.0953)
R indices (all data)	R_1[a] = 0.0586, wR_2[b] = 0.1031
Flack parameter	0.11(3)

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[b] $wR_2 = \sum w[(F_o^2 - F_c^2)^2/\sum w[(F_c^{22})^2]]^{1/2}$.

3. Results and discussion

3.1. Properties and structural discussion of $BzBu_3NIO_4$

$BzBu_3NIO_4$ was prepared immediately by mixing aqueous solutions of $NaIO_4$ and $BzBu_3NCl$ at room temperature in 90% yield, without recourse to any organic solvents for isolation. When we carried out this procedure by using *n*-tetrabutylammonium hydrogensulfate or bromide in place of $BzBu_3NCl$, the yield of the precipitated product (n-Bu_4NIO_4) was only 40–43%. The solubility properties of $BzBu_3NCl$ in some traditional solvents were first investigated. It is completely soluble in methanol, ethanol, acetone, dichloromethane, chloroform, acetonitrile, nitromethane, tetrahydrofuran, *N*,*N*-dimethylformamide and dimethylsulfoxide. Other solvents such as ethylacetate, benzene, CCl_4, *n*-hexane, toluene, ether and water are not able to dissolve $BzBu_3NIO_4$.

The compound was characterized by elemental analysis, IR, NMR and single-crystal X-ray diffraction. The ORTEP plot of $BzBu_3NIO_4$ is given in Fig. 1. The compound crystallized with two cations and two anions per asymmetric unit ($Z = 8$) and a space group of $Pna2_1$ was determined by single-crystal X-ray diffraction. Two of the alkyl chains are disordered. The O–I–O angles are 105.9–111.9° and the I–O distances are 1.693–1.764 Å. The C–N–C angles are 106.2–111.5° and the N–C distances are 1.508–1.538 Å for the alkyl chains and 1.540–1.543 Å for the benzyl groups.

3.2. Oxidation activity of $BzBu_3NIO_4$

To evaluate the oxidation activity of $BzBu_3NIO_4$, blank experiments were performed using α-methylstyrene as a model substrate. In the absence of Mn(TPP)OAc as a catalyst and also imidazole (Im) as a co-catalyst in different organic solvents, no oxidation of the substrate was observed, indicating the use of both catalyst and co-catalyst are essential. The addition of $BzBu_3NIO_4$ (2 mmol) to the solution of Mn(TPP)OAc (0.01 mmol) in CH_2Cl_2 containing Im (0.1 mmol) and α-methylstyrene (1 mmol) afforded to the related epoxide in 87% yield after 5 h at room temperature. Also, the full conversion of cyclooctene was observed using this catalytic system. A comparison of these results with those obtained using n-Bu_4NIO_4 as an oxidant under the same conditions indicates the same oxidation activity of both oxidants under the catalytic influence of Mn(TPP)OAc [8]. Nevertheless, the high yielding and safe procedure for the preparation of $BzBu_3NIO_4$ by using $BzBu_3NCl$ as a cheap compound with respect to *n*-tetrabutylammonium salts make it potentially useful for oxidation reactions and therefore an expedient substitute for n-Bu_4NIO_4. However, the reaction media should be sustainable for practical goals requiring scale-up procedures. Accordingly, we tried to carry out our oxidation method in a clean media. Initially, water and ethanol as neat solvents have been examined as green media for the oxidation of α-methylstyrene, which led to the isolation of the starting olefin at room temperature (Table 2, entries 1 and 2). Nevertheless, the reaction was triggered by using a mixture of H_2O/EtOH at room temperature (entry 3) and a quantitative yield of epoxide product was obtained with a 2:3 ratio of H_2O/EtOH within 2.5 h under these conditions (entry 5). It was observed that the reaction proceeded most rapidly and gave the optimal yield of epoxide (92%/5 min) at 60 °C (entry 8). Our results also showed that for complete conversion of the starting olefin in the desired time, a 2:1 M ratio of oxidant to substrate (Fig. 2) and 1 mol% of the catalyst are sufficient (Fig. 3). It is worthy to mention that under these conditions a poorer oxidation activity was observed for $NaIO_4$ and n-Bu_4NIO_4 than that of $BzBu_3NIO_4$ (Fig. 4).

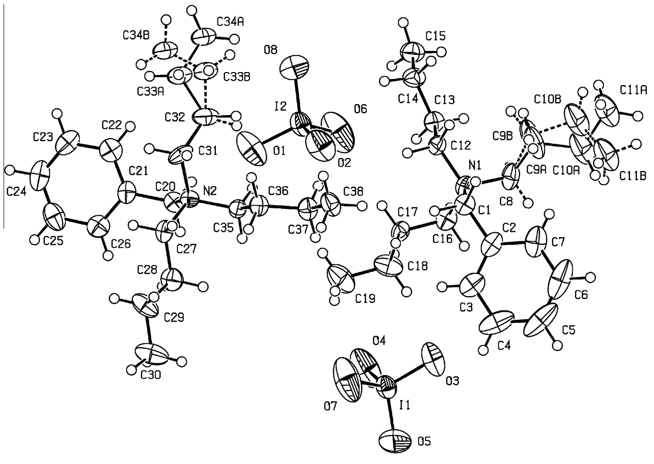


Fig. 1. The molecular structure of $BzBu_3NIO_4$, with the atomic numbering and displacement ellipsoids drawn at the 50% probability level. (The disordered parts of the alkyl chains are drawn with dashed lines.)

3.3. Co-catalytic effect of the nitrogen donors

The efficient catalytic epoxidation, which takes place only when both catalyst and nitrogen base are present, may be taken as an indication of that a nitrogen donor coordinates to the manganese center and makes it prone to oxidation by the periodate [30]. Initially we investigated the effect of the co-catalyst concentration on the oxidation of α-methylstyrene (Fig. 5). An increase in the Im/Mn(TPP)OAc molar ratio up to 10:1 improved the yield of epoxide. However a further increase in this ratio led to a decrease in the

Table 2
The effect of the H_2O/EtOH ratio and temperature on the epoxidation of α-methylstyrene with $BzBu_3NIO_4$ catalyzed by Mn(TPP)OAc in the presence of Im.[a]

Entry	Solvent	Temperature (°C)	Epoxide yield %[b] (time/min)	
1	H_2O	25	–	4.5 (300)
2	EtOH	25	–	7 (300)
3	H_2O/EtOH (1:1)	25	30(60)	76(180)
4	H_2O/EtOH (1:1)	60	75(5)	100(30)
5	H_2O/EtOH (2:3)	25	45(60)	100(150)
6	H_2O/EtOH (2:3)	40	20(5)	25(15)
7	H_2O/EtOH (2:3)	50	40(5)	81(15)
8	H_2O/EtOH (2:3)	60	92(5)	100(15)

[a] The reactions were run under air with the molar ratio of 100:200:10:1 for α-methylstyrene:$BzBu_3NIO_4$:Im:Mn(TPP)OAc.

[b] GC yield based on the starting olefin.

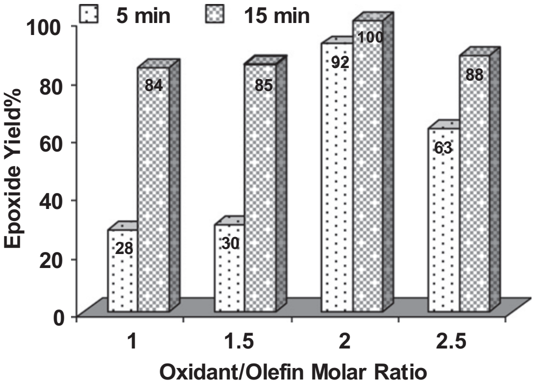


Fig. 2. The effect of various oxidant/olefin molar ratios on the epoxidation of α-Me-styrene by $BzBu_3NIO_4$ in H_2O/EtOH (2:3) at 60 °C after 5 min.

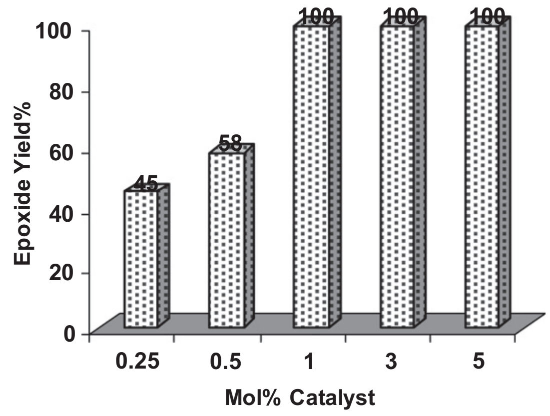


Fig. 3. The effect of the catalyst concentration on the epoxidation of α-methylstyrene with $BzBu_3NIO_4$ in H_2O/EtOH (2:3) at 60 °C after 5 min.

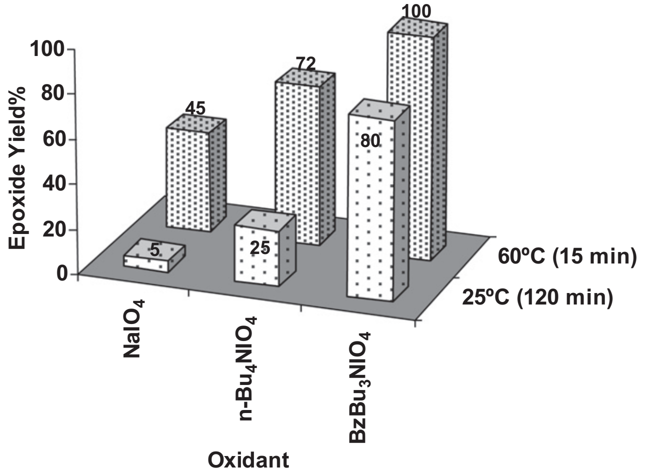


Fig. 4. Comparison of the oxidation activity of NaIO4, *n*-Bu4NIO4, and $BzBu_3NIO_4$ in the epoxidation of α-methylstyrene catalyzed by Mn(TPP)OAc in H_2O/EtOH.

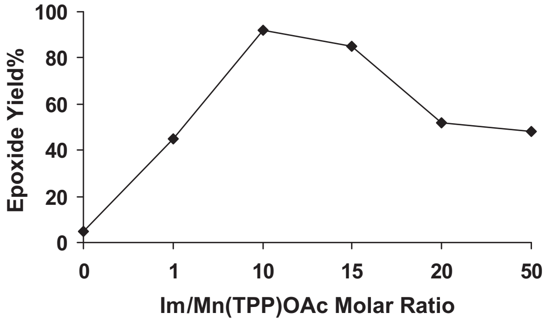


Fig. 5. The effect of various Im/Mn(TPP)OAC molar ratios on the epoxidation of α-methylstyrene by $BzBu_3NIO_4$ in H_2O/EtOH (2:3) at 60 °C after 5 min.

olefin conversion, confirming the formation of catalytically inactive six coordinate species, i.e., $Mn(TPP)(Im)_2$ [21,30].

Table 3
The effect of different axial ligands on the epoxidation of α-methylstyrene with $BzBu_3NIO_4$ catalyzed by Mn(TPP)OAc in H_2O/EtOH.[a]

Entry	Axial ligand	pK_a	Epoxide yield (%)[b]	
			5 min	15 min
1	Im	6.953	92	100
2	BzIm	5.53	45	76
3	1-MeIm	6.95	20	32
4	Py	5.25	45	65
5	4-*t*-BuPy	5.99	39	45
6	4-CNPy	1.86	15	25
7	Piperidine	11.12	14	25
8	Et_3N	10.75	25	38
9	None	–	0	0

ImH, imidazole; 1-MeIm, 1-methylimidazole; BzImH, benzimidazole; Py, pyridine; 4-t-BuPy, 4-*tert*-butylpyridine; 4-CNPy, 4-cyanopyridine; Et_3N, triethylamine.

[a] The reactions were run under air at 60 °C with a molar ratio of 100:200:10:1 for α-methylstyrene:$BzBu_3NIO_4$:Im:Mn(TPP)OAc.

[b] GC yield.

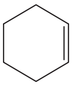
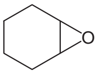
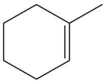
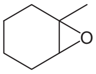
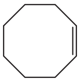
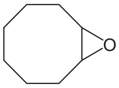
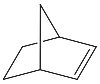
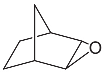
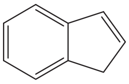
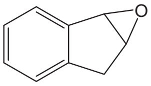
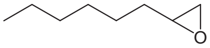
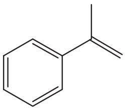
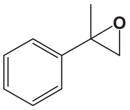
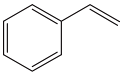
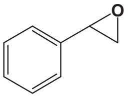
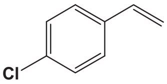
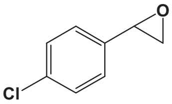
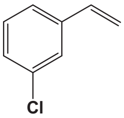
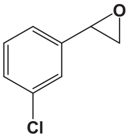
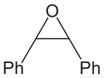
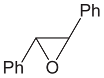
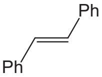
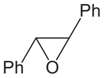
It was also found that the efficiency of the reaction was dramatically dependent upon the nature of the co-catalyst (Table 3). The results for the Mn(TPP)OAc catalyzed oxidation of α-methylstyrene using $BzBu_3NIO_4$ in association with three classes of nitrogen donors as co-catalysts, including the strong pure σ-donor amines (pK_a = 10.75–11.12), the strong π-donor imidazoles (pK_a = 5.53–7.86) and weak π-donor pyridines (pK_a = 1.86–6.65), are given in Table 3. The general order of the co-catalytic activities of the various classes of nitrogen donors was amines < pyridines < imidazoles. Nevertheless, a significant decrease in conversion rates in combination with bulky BzIm and 4-*t*-BuPy indicate that the steric effects are quite pronounced. The sluggish co-catalytic activity of 1-MeIm, lacking the N–H· · ·B (B = nitrogen donor or anionic species) hydrogen bonding, and also the weak base 4-CNPy (pK_a = 1.86), containing an electron-withdrawing CN group, demonstrate the crucial importance of electronic factors upon their donor abilities toward the Mn-por catalyst [21,30]. The much lower co-catalytic activity of pure σ-donor amines (entries 7 and 8) than those of the N–H imidazoles clearly confirm that the π-donation of the axial base is considerably dominant in the present catalytic system.

3.4. Catalytic epoxidation and hydroxylation reactions

To establish the general applicability of the method, various olefins were subjected to the oxidation protocol using $BzBu_3NIO_4$ under the catalytic influence of Mn(TPP)OAc at 60 °C (Table 4). As summarized in Table 4, different olefins were generally excellent substrates for this catalyst. It led to high/excellent conversion of cyclohexenes, cyclooctene and norbornene, with the formation of the corresponding epoxides as the sole products (entries 1–4). The conversion and selectivity of indene was 100% (entry 5). The epoxidation of 1-octene as a less reactive terminal olefin proceeded with moderate yield (60%) and excellent selectivity (entry 6). It seems that the efficiency of epoxidation in this catalytic system is very dependent on the electronic and steric requirements of the substrate. Electron-donating and electron-withdrawing substituents on the styrene have a pronounced effect on the rate of oxygenation. The conversion and yield of α-methylstyrene were 100%, whereas the epoxidation yield of electron-deficient 3-Cl and 4-Cl styrenes were 75% and 60%, respectively (entries 6–10). *trans*-Stilbene, having great phenyl–phenyl non-bonded interactions, oxidized slowly (54%) with the catalyst, with absolute stereospecificity (entry 12). Nevertheless, a quantitative conversion occurred for *cis*-stilbene with the formation of a mixture of *cis*- (83%) and *trans*-stilbene oxide (12%) with the same period (entry 11). Formation of *trans*-stilbene oxide in the oxidation of *cis*-stilbene suggests competition between closure of the epoxide ring and rotation around the C–C bond during the oxygen transfer step from the active oxidizing species to the olefin [31].

When we applied the present catalytic system to the oxygenation of C–H bonds, a mixture of alcohols and ketones with combined yields of 21–84% and excellent selectivities in desired times (20 min) were obtained (Table 5).

Table 4
Epoxidation of different olefins with $BzBu_3NIO_4$ catalyzed by Mn(TPP)OAc in the presence of Im in H_2O/EtOH.[a]

Entry	Alkene	Conversion %[b] (isolated yield %)[c]	Product	Selectivity %[b]
1		100		100
2		100		100
3		98 (90)		100
4		97 (89)		100
5		100 (92)		100
6		60		100
7		100 (90)		100
8		93 (85)[d]		100
9		63		100
10		75 (64)[d]		100
11		95[e]		87[e]
				13[e]
12		54[e]		100[e]

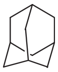
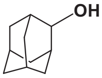
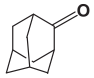
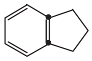
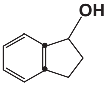
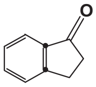
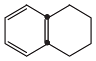
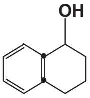
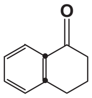
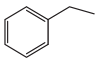
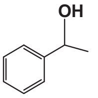
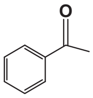
[a] The reactions were run under air at 60 °C with a molar ratio of 100:200:10:1 for Olefin:$BzBu_3NIO_4$:Im:Mn(TPP)OAc.
[b] GC yields based on the starting olefins. All products were identified by authentic samples [19,22].
[c] Yields of isolated products after evaporation of petroleum ether.
[d] Yields of isolated products after plate chromatography.
[e] Determined by ^1H NMR.

3.5. Stability and reusability of catalyst

The high/excellent yields of the oxidation products, especially in the oxidation of the less reactive substrates such as 1-octene (Table 1, entry 6) and saturated hydrocarbons (Table 1, entry 9–12), obtained using this new biomimetic method in desired times demonstrate the high catalytic activity and relative stability of the simple Mn(TPP)OAc complex in association with $BzBu_3NIO_4$. More evidences in this matter have been achieved by the impressive turnover numbers obtained in the oxidation of norbornene (6800) and α-methylstyrene (6200) using a 10,000:20,000:1 M ratio for substrate/$BzBu_3NIO_4$/catalyst. This was further supported by the study of the electronic spectra of the complex in the oxidation of α-methylstyrene. The Mn-catalyst decomposition, both under the oxidizing conditions and in the absence of olefin, was followed by measuring the percentage decrease of the absorbance at 478 nm (Soret band of Mn(TPP)OAc, referred to the sample taken at zero time of reaction) (Fig. 6). The slow reduction of the absorption with time is indicative of the stability of the catalyst in this oxidation system. It is noteworthy that Mn-por is reasonably stable even in the absence of any substrate (Fig. 6).

These results encouraged us to evaluate the reusability of the catalyst. After isolation of the products, the solid catalyst was separated from the aqueous solution by centrifuging and was reused for a subsequent reaction under similar reaction conditions. The catalyst has been observed to be reusable for at least three times. Moreover, the oxidant's by-product ($BzBu_3NIO_3$) was separated, which can be reused as a valuable compound. Therefore, from

Table 5
Oxygenation of different hydrocarbons with $BzBu_3NIO_4$ catalyzed by Mn(TPP)OAc in the presence of Im in H_2O/EtOH.[a]

Substrate	Conversion %[b]	Alcohol	Yield %[b]	Ketone	Yield %[b]
	21		14		7
	48		23		25
	66		30		36
	84		70 (65)[c]		14 (12)[c]

[a] The reactions were run under air at 60 °C with a molar ratio of 100:200:10:1 for substrate:$BzBu_3NIO_4$:Im:Mn(TPP)OAc.

[b] GC yields based on the starting materials. All products were identified by authentic samples [22].

[c] Yields of isolated products after plate chromatography.

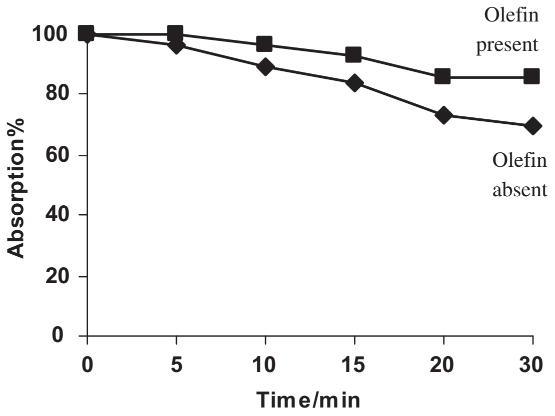
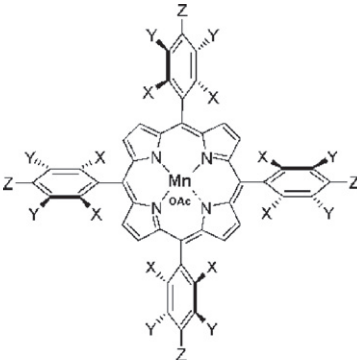


Fig. 6. Change of the percent absorption at 478 nm in the electronic spectra of Mn(TPP)OAc in the presence of Im and $BzBu_3NIO_4$ at 60 °C.



	X	Y	Z
TPP	H	H	H
T(4-OMeP)P	H	H	OMe
$T(4-NO_2P)P$	H	H	NO_2
TMP	Me	H	Me
TDCPP	Cl	H	H

Fig. 7. The Mn-porphyrins utilized in this study.

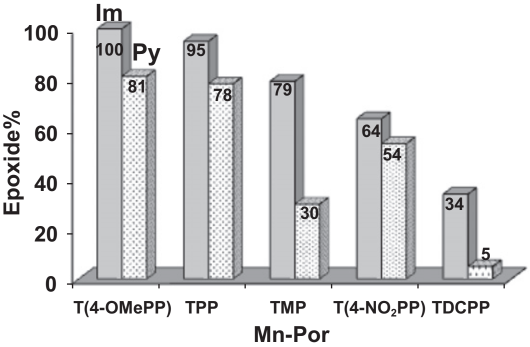


Fig. 8. The effect of the electronic and steric requirements of the porphyrin ligands on the catalytic activity of the Mn-catalysts in the epoxidation of α-methylstyrene with $BzBu_3NIO_4$ in the presence of Im and Py.

the stand point of greener chemical processes, the present method does not lead to the three major sources of waste: toxic organic solvents, catalysts and harmful by-products. These advantages for this high yielding oxidation method offer ready scalability. In the oxidation of α-methylstyrene as a substrate, in a semi scale-up procedure (25 mmol), the related epoxide was secured in 93% yield.

3.6. The electronic and steric effects of the porphyrin ligand

The catalytic activity of different electronic and structural Mn-porphyrins (Fig. 7) in combination with both Im and Py have been compared in the oxidation of α-methylstyrene as an electron-deficient olefin with some steric hindrances around the double bond (Fig. 8). The extent of the catalytic activity of the Mn(Por)s was found to follow the order: Mn(TDCPP)OAc < $Mn[T(4-NO_2P)P]OAc$ < Mn(TMP)OAc < Mn(TPP)OAc < Mn[T(4-OMeP)P]OAc. The lower activity of $Mn[T(4-NO_2P)P]OAc$, containing an electron-withdrawing $-NO_2$ group, compared to the simple Mn(TPP)OAc and electron-rich Mn[T(4-OMeP)P]OAc, with very similar steric environments at their Mn centers, reflects the reducing influence of the electron-deficient substituent upon the catalytic activity of the Mn-catalyst in the presence of both co-catalysts. When hindered catalysts such as Mn(TMP)OAc and particularly Mn(TDCPP)OAc, with a large electrophilicity at the Mn center, were employed, the steric factors became dominant in the presence of both co-catalysts. Nevertheless, a more significant steric effect appeared in the presence of Py rather than Im, confirming the involvement of a bulky and weak electrophilic six coordinate adduct $[(Py)(TPP)Mn–OIO_3)]$ during the reaction under the co-catalytic effect of Py [21]. On the other hand, the pronounced catalytic performance of electron-rich porphyrins in the presence of strong π-donor Im is due to the formation of a less hindered and high valent Mn-oxo species.

This was further supported by monitoring the UV–vis spectral changes by addition of $BzBu_3NIO_4$ to a solution of Mn(TMP)OAc (0.1 mM) in water/EtOH containing Im and Py (10 mM). When Py was employed as the co-catalyst, the spectrum displayed no change. In the presence of Im, an intense Soret band, (λ_{max} = 418 nm) appeared after addition of the oxidant (Fig. 9), confirming the formation of MnTMP(Im)(O) species [32]. Addition of an excess amount of α-methylstyrene immediately gave the original Soret

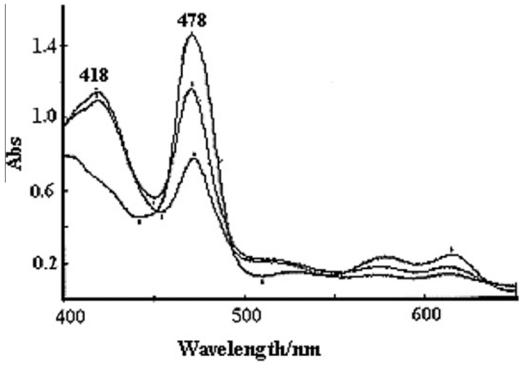


Fig. 9. The UV–vis spectra of Mn(TPP)OAc (0.1 mM) in the presence of Im (10 mM) before (λ_{max} = 478 nm) and after (λ_{max} = 418 nm) the addition of $BzBu_3NIO_4$ (20 mM) in H_2O/EtOH (2:3) at 60 °C.

band (λ_{max} = 478 nm), clearly indicating that the new species formed after addition of the oxidant is kinetically competent for performing substrate oxidation. It is worth mentioning that the spectrum displayed no change when the electron-deficient Mn[T(4-NO_2P)P]OAc and Mn(TDCPP)OAc were used in association with both the Im and Py.

The scope and synthetic and industrial applications of the oxidation procedure using different catalysts are currently under investigation.

4. Conclusion

In conclusion, a biomimetic catalytic method for the selective epoxidation of olefins and oxygenation of saturated hydrocarbons to alcohols and ketones using $BzBu_3NIO_4$ as a novel and safe oxidant in the presence of the Mn(TPP)OAc/Im system in H_2O/EtOH has been developed. The employment of H_2O/EtOH as a 'green' media in this high yielding oxidation method as well as the reusability of the catalyst, providing ready scalability, makes it more attractive for a practical goal. Our findings show that the strong π-donating N–H imidazoles demonstrate higher co-catalytic activity than pyridines and amines. The low activity of the electron-deficient Mn[T(4-NO_2P)P]OAc and Mn(TDCPP)OAc catalysts reflect the diminishing effect of the electron-withdrawing substitute upon the catalytic activity of the Mn-catalyst. The experimental results and spectroscopic evidences suggest the involvement of a high valent Mn-oxo species as well as a six-coordinate $[(L)(Por)Mn–OIO_3]$ complex.

Acknowledgment

Support for this work by the Research Councils of the University of Birjand is highly appreciated.

Appendix A. Supplementary data

CCDC 775581 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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