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Nonradical tetrabutylammonium monopersulfate oxidation of hydrocarbons catalyzed by $[Mn_3O_4bipy_4(H_2O)_2](ClO_4)_4$

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Abstract

Tetrabutylammonium monopersulfate ($2NBu_4HSO_5 \cdot NBu_4HSO_4 \cdot (NBu_4)_2SO_4$) is an effective primary oxidant with a high tendency to promote oxo transfer rather than radical pathways in catalysis. Nonradical hydrocarbon oxidation is seen with the complex $[Mn_3O_4bipy_4(H_2O)_2](ClO_4)_4$ as catalyst as indicated by mechanistic studies; this contrasts with the radical pathways found for the same catalyst with t-BuOOH as the primary oxidant. The catalyst is robust, giving up to 15000 catalytic turnovers, and very efficient, the rate of 1-alkene epoxidation being 4000 turnovers/h.

Keywords: Manganese; Alkanes; Oxidation

1. Introduction

Mechanism in oxidation catalysis [1] is a difficult area in which there is still much disagreement. Non-porphyrin catalysts [2–5] are less well studied than their porphyrin counterparts [6] but have taken on added interest with the discovery of increasing numbers of non heme monoxygenases [7]. Efficient catalysis requires that the ligands employed be oxidation resistant, so dipyridyls, carboxylates, aqua, hydroxo- and oxo-groups have proved to be popular in the area. Fish et al. [8] showed that a bipyridyl-stabilized manganese oxo cluster is active for peroxide oxidation of hydrocarbons, for example.

Some years ago we reported that a related cluster $[Mn_3O_4bipy_4(OH_2)_2]^{4+}$ (**1**) catalyzes t-butyl hydroperoxide (TBHP) oxidation of hydrocarbons [9]. In the preliminary note, we suggested that a nonradical mechanism might be operating, but a number of more recent findings [10], have led us to abandon this suggestion: (i) the presence of dioxygen greatly enhances the yield of oxidation products, suggesting an autoxidation pathway is involved and (ii) the oxidation of *cis*-decalin gives *trans*-9-decalol, suggesting a radical intermediate.

Since a radical chain mechanism is usually undesirable in giving low selectivity, we looked for a primary oxidant which would be less likely to undergo homolytic cleavage. Oxone®, or potassium peroxomonosulfate, is commercially available as the triple salt $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Although not a common primary oxidant, it has been used for hydrocarbon

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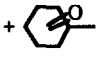
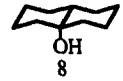
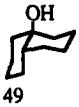
epoxidation and hydroxylation with metalloporphyrin catalysts [6] in two-phase systems as well as with platinum catalysts [11]. As a peracid, it is not as likely to form radicals as a peroxide and usually acts as a single oxygen atom donor like iodosylbenzene. If heterolytic cleavage of the O–OX bond is considered as departure of an XO^- group to leave an 'O^+' group, it can be seen that peroxomonosulfate, with sulfate as the leaving group, would much more readily undergo nonradical, heterolytic cleavage than a peroxide, where hydroxide or alkoxide are expected to be less effective leaving groups.

In preliminary studies with Oxone®, we encountered two problems. We saw some hydrocarbon oxidation in control reactions in the absence of catalyst and Oxone® showed no solubility in organic solvents. Although the commercial potassium salt of Oxone® is not soluble in organic solvents, the corresponding salt, tetrabutylammonium monopersulfate ($2NBu_4HSO_5 \cdot NBu_4HSO_4 \cdot (NBu_4)_2SO_4$) (TBAO) is easily prepared and soluble in many organic solvents [12]. Moving to TBAO was also advantageous in giving no hydrocarbon oxidation in controls without catalyst. In this paper we report our results with TBAO as the primary oxidant. TBAO has previously been used with porphyrin catalysts, but was found to cause rapid catalyst deactivation, [13] and in acetone without a catalyst, where dimethyldioxirane is presumed to be the active oxidant [14].

Table 1
Oxidation of alkanes and alkylarenes with $[Mn_3O_4bipy_4(H_2O)_2](ClO_4)_4$/TBAO

	Compound	Solvent	time(hrs)	[catalyst]	TON(total)	Products (selectivity %)
1		10 CH_3COCH_3 : 1 CH_3CN	17	0.09 mM	230	 >99
2	C_2H_6	CH_3CN	5	*	0	no oxidation products observed
3		CH_3CN	8	0.1 mM	400	 +  1-ol (30) 2-ol (<1) 2-one (22) 3-ol (2.5) 3-one (32) 4-ol not detec 4-one (12)
4		CH_3CN	3.75	0.1 mM	630	 +  8 49  +  14 17
5		CH_3CN	17			
				0.1 mM	1320	>99
				0.02 mM	4700	>99

Standard conditions: 0.4 M substrate, 0.8 M TBAO, 0°C under air. Turnovers in mol. products per mol. catalyst.

2. Results

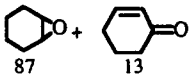
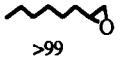
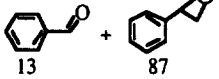
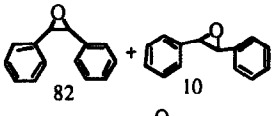
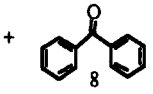
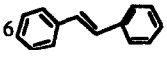
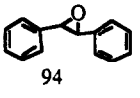
2.1. Product studies

The $[Mn_3O_4bipy_4(OH_2)_2]^{4+}$/TBAO system gave the results shown in Tables 1 and 2. The catalyst is very robust, giving up to 15000 catalytic turnovers (run 4, Table 2). Rates can also be very high, reaching 4000 turnovers per hour for the epoxidation of 1-alkenes (run 2, Table 2).

2.1.1. Alkanes

Alkanes are oxidized directly to the ketone with very little alcohol being formed, except at tertiary positions. A competitive experiment with cyclohexane and cyclopentanol gave cyclopentanone but no cyclohexanol or cyclohexanone, so the ketone we see from alkane may well arise from preferential oxidation of the initially formed alcohol. As we saw with **1**/TBHP, no oxidation of ethane is observed, so only secondary and tertiary C–H groups can be oxidized

Table 2
Oxidation of alkenes with $[Mn_3O_4bipy_4(H_2O)_2](ClO_4)_4$/TBAO

	Compound	Solvent	Time(hrs)	[catalyst]	TON(total)	Products (selectivity %)
1		9 CH_3COCH_3:1 CH_3CN	17	0.02 mM	8740	 87 13
		9 CH_2Cl_2: 1 CH_3CN	3.5	0.01 mM	3270	70 30
2		9 CH_2Cl_2 : 1 CH_3CN	3.5	0.01 mM	13,900	 >99
3		9 CH_2Cl_2 : 1 CH_3CN	3.5	0.01 mM	12,700	 >99
4		CH_3CN	15	0.1 mM	3550	 13 87
		49 CH_2Cl_2 : 1 CH_3CN	13	0.02 mM	15,500	>99
5		1 C_6H_6* : 1 CH_3CN	7	0.05 mM	1410	 82 10  8
6		1 C_6H_6* : 1 CH_3CN	7	0.05 mM	3100	 94
7		CH_3CN	* *	0.05 mM	3900	 >99

Standard conditions: 0.4 M substrate, 0.2 M TBAO, 0°C under air.
* 0.2 M substrate, 0.1 M TBAO.
* * 0.8 M propene, 0.09 M TBAO. Turnovers in mol. products per mol. catalyst.

efficiently in alkanes. The results for methylcyclohexane show a 3-one/3-ol ratio of 13:1 versus 6:1 with **1**/TBHP. The methylcyclohexane data also allows comparison of the relative reactivities of the secondary and tertiary positions. The relative per-bond 3°/2° reactivity ratio is 4.2 compared with 1.6 obtained with TBHP.

Oxidation of *cis*-decalin gives largely *cis*-tertiary alcohol. This contrasts with the TBHP system, in which more *trans*-alcohol is found, strongly suggesting a nonradical pathway. Almost exclusive retention is also seen by Meunier in Oxone® oxidations with manganese porphyrins [15].

2.1.2. Alkenes

Oxidation of propene gives a quantitative yield of the epoxide. Alkenes in general gave mainly epoxide with some allylic oxidation. Some cleavage of styrenes to the corresponding benzaldehyde is found, but the amount of cleavage strongly depends on the solvent: aldehyde is the sole product in dichloromethane, but in acetonitrile the product is largely epoxide. *Cis*-stilbene gives mostly *cis*-epoxide with some *trans*, along with some benzophenone. *Cis*-epoxide is also the major product in Oxone® epoxidations catalyzed by manganese porphyrins [6].

2.1.3. Alkylarenes: Hammett plot

Alkylarenes give the benzylic ketone and competitive oxidation of various *para*-substituted ethylbenzenes leads to the Hammett plot shown in Fig. 1. The slope (ρ) of −0.70 compares to the value of −0.24 obtained for **1**/TBHP system, −0.35 for $RuCl_2(PPh_3)_3$/TBHP [16] and −0.42 for cytochrome P-450 [17].

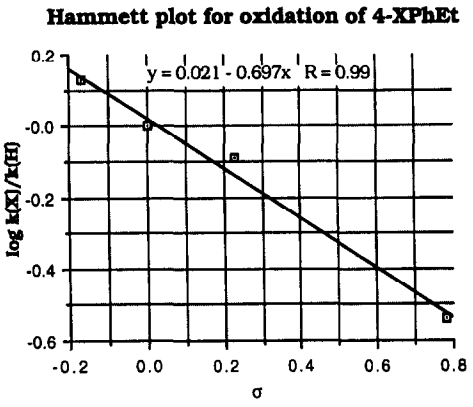


Fig. 1. Hammett plot for $[Mn_3O_4bipy_4(H_2O)_2](ClO_4)_4$/TBAO oxidation of *para*-substituted ethylbenzenes XC_6H_4Et (X = Me, Br, NO_2).

2.2. Mechanistic studies

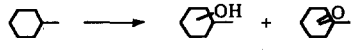
2.2.1. Kinetic isotope effect

Competitive oxidation of C_6H_{12} and C_6D_{12} gave a k_H/k_D of 4.9, the same value found for TBAO hydroxylation catalyzed by $(Br_8TMP)Mn(Cl)$, which gave the highest value found for any manganese porphyrin [18]. Manganese porphyrins generally give kinetic isotope effects in the range 2–3 [15].

2.2.2. Phenylethylcyclopropane oxidation

We used phenylethylcyclopropane as substrate to help confirm the nonradical character of the reaction. Surprisingly, we see a mixture of over 20 oxidation products. The largest single product (19%) is identified by MS as 1-(phenylcyclopropyl)ethanone, an authentic sample of which was prepared by Simmons–Smith methylenation of *trans*-4-phenyl-3-buten-2-one for comparison purposes. The formation of this product clearly did not go via a radical pathway unless collapse of the radical to form product is competitive with ring opening.

Table 3
Oxidation of methylcyclohexane under air and nitrogen.



Product	Turnovers	
	air	nitrogen
1-ol	120	180
2-one	90	110
3-one	130	160
4-one	50	60

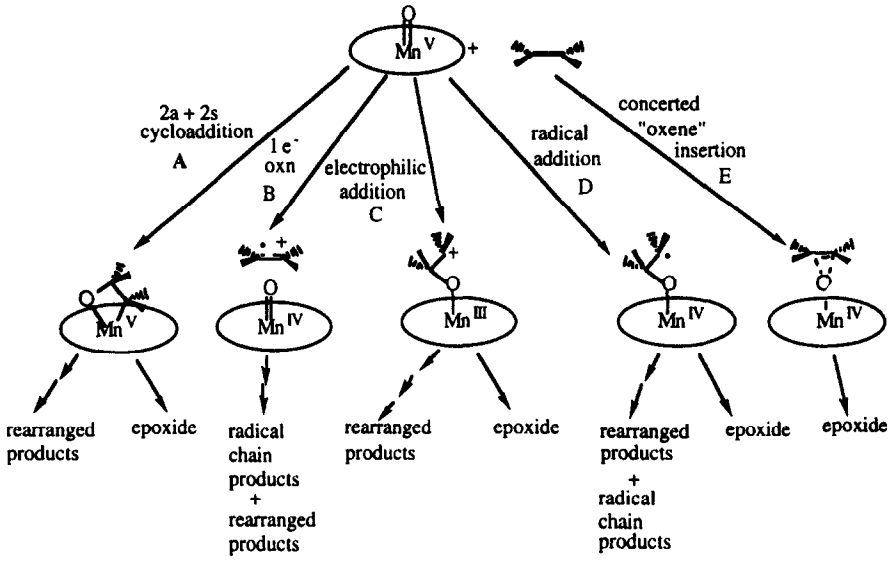


Fig. 2. Possible mechanisms for alkene epoxidation.

2.2.3. *Effect of atmosphere*

To see whether oxygen had any effect on the reaction, we compared the results of oxidation of methylcyclohexane with nitrogen bubbling through the reaction mixture with the results obtained under air. As seen in Table 3, the total number of turnovers obtained after 2.5 h is somewhat larger under nitrogen than under air. This indicates that, unlike the situation for **1**/THBP, an autoxidative mechanism is not operative in this system. The selectivity for tertiary attack is slightly higher under nitrogen, > 5, than in air, 4.2.

2.2.4. *Epoxidation*

A variety of mechanisms (Fig. 2) have been proposed by Bruice [19] for epoxidation by metal-oxo species: (A) 2 + 2 cycloaddition followed by reductive elimination, (B) electron-transfer followed by collapse to the products, (C) electrophilic addition, (D) radical addition, or (E) oxene insertion. Pathway B can also lead to pathways C or D by formation of a C–O bond.

Pathway A, formation of a metallaoxetane or oxametallacyclobutane, has been proposed for metalloporphyrins by Meunier et al. [20] In the octabromo-tetraphenylporphinatoiron(III) chloride ($Br_8TPP)Fe^{III}(Cl)$ case [21], molecular modeling studies on the proposed oxo intermediate in epoxidation have shown that metallaoxetane formation requires unreasonable bond lengths to avoid severe steric interactions. Therefore, metallaoxetane intermediates are not invariably involved as intermediates for epoxidation.

Bruice [22] has used the cyclopropyl substituted alkene shown in Fig. 3 to test for radical intermediates in epoxidation by $(Cl_8TPP)Mn^{IV}(O)$ and found the ring-opened product shown. Pathway B of Fig. 2 was ruled out by comparison of rate constants with ioniza-

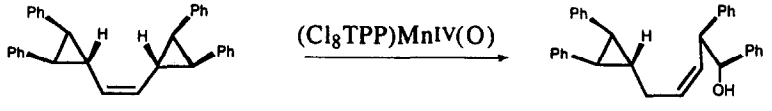


Fig. 3. Reaction of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenyl cyclopropyl)ethene with $(Cl_8TPP)Mn^{IV}(O)$.

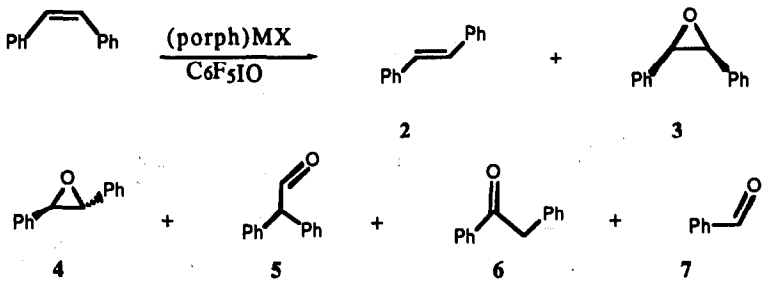


Fig. 4. Typical oxidation products from *cis*-stilbene catalyzed by metalloporphyrins.

tion potentials for other alkene substrates, leaving pathway D as the only reasonable explanation.

A common substrate for probing an epoxidation mechanism is *cis*-stilbene. Being less stable than the *trans*-isomer, any intermediate allowing free rotation would be expected either to give *trans*-stilbene or oxidation products derived from it.

Pentafluoroiodosylbenzene oxidation of *cis*-stilbene with various metalloporphyrins as catalysts, has been found to give any of the range of products shown in Fig. 4, depending on the catalyst [22]. Electrophilic addition to give a cationic species (pathway C in Fig. 2) followed by migration of phenyl or hydride gives products **5** and **6** respectively. Product **5** is always found in larger amounts, reflecting preferential phenyl migration. Formation of *trans*-stilbene (**2**) is thought to go via pathway B: the cation-radical of the alkene can undergo free rotation about what was the C–C double bond. The cation–radical can react with oxygen, ultimately cleaving the C–C bond to form benzaldehyde (**7**). *trans*-Stilbene oxide (**4**) arises from epoxidation of *trans*-stilbene.

In our TBAO system, a significant amount of *trans*-epoxide is formed, but no dehydrobenzoin (**6**), diphenylacetaldehyde (**5**), or benzaldehyde (**7**). However significant quantities of benzophenone are also found. The most plausible explanation for these products is over-oxidation of **5**. Analysis of the recovered starting material shows significant quantities of *trans*-stilbene.

2.2.5. Hydrogen peroxide

Several other compounds were investigated as primary oxidants with **1** as a catalyst. Hydrogen peroxide is commonly used in metalloporphyrin systems [6] as well as some of the Gif systems [5]. It is desirable in that it is relatively cheap and gives no byproducts for disposal. In our system, however, no oxidation products were observed with hydrogen peroxide.

3. Discussion

3.1. Mechanism

The catalyst (**1**) is unusual for a Mn(IV) compound in having aqua ligands and therefore providing potential sites for coordination of the primary oxidant after dissociation of water. This first step is probably the same for THBP and TBAO, but numerous clues indicate that the subsequent steps are very different for these two oxidants. For TBAO, the almost exclusive formation of ketone from alkanes, the higher 3°/2° selectivity for alkanes, the greater degree of stereochemical retention in the oxidation of *cis*-decalin, the higher ρ value in oxidation of substituted ethylbenzenes, and the formation of epoxides from alkenes all contrast with the THBP case and point to a different intermediate as the oxidizing species.

The fact that product formation from methylcyclohexane with **1**/TBAO is not diminished and is even slightly enhanced under nitrogen

versus air indicates that dioxygen does not play a significant role in the oxidation. This rules out a radical-chain autoxidation like that proposed for **1**/TBHP.

Monopersulfate can in principle undergo heterolytic or homolytic cleavage, although the former is preferred with metalloporphyrins [23]. The formation of epoxides is generally taken to indicate the involvement of a metal-oxo species as intermediate, although non-redox-active metals have also been shown to catalyze the epoxidation of alkenes with iodosylbenzene presumably via formation of a Lewis acid–base adduct [24]. Metal–oxidant adducts have also been proposed for oxidations with peroxides [1] (e.g. the Sharpless epoxidation) as well as with Oxone® [15]. In our case, the Mn seems most likely to be redox active.

The negative slope of the Hammett plot shows that the reaction is disfavored by electron-withdrawing groups to a much greater extent than is the case with **1**/TBHP. This indicates an electrophilic species is involved in the rate-determining step, presumably the C–H bond-breaking. Since radical reactions, as in the **1**/TBHP case, usually have a small ρ value, the larger value found for **1**/TBAO is consistent with a nonradical mechanism.

The oxidation of *cis*-decalin by nonradical oxidants gives almost exclusive retention of configuration, so the formation of any *trans*-9-decalol from *cis*-decalin is usually interpreted as requiring the formation of a radical intermediate. The high degree of retention found in the **1**/TBAO case is consistent with a nonradical mechanism or, less likely, with a radical mechanism having very short-lived radical intermediates.

In the phenylethylcyclopropane oxidation, our observation of oxidation at the position adjacent to the cyclopropane ring without rearrangement strongly suggests a nonradical insertion or very fast rebound [25]. Since the rate of 2-phenylcyclopropylcarbinyl ring opening is estimated to be about 4×10^{11} s^{-1}, around a hundred times faster than inversion of the decalyl radical, one would expect that a rebound faster than the cyclopropylcarbinyl ring-opening would give complete retention in the oxidation of *cis*-decalin. However, since the other oxidation products of 2-phenylethylcyclopropane could not be readily identified, it is possible that ring opening did occur and that a radical mechanism is involved, but collapse to product is competitive with ring-opening, so that some product with the ring intact is seen.

We cannot completely exclude a radical hydroxylation mechanism in which monopersulfate first reacts with the catalyst to generate a $Mn^{V}(O)_2Mn^{V}=O$ species which in turn abstracts a substrate hydrogen atom to give the corresponding alkyl radical. Rapid recombination of this alkyl radical with the metal bound OH group could give the alcohol before the radical has time to rearrange.

It has been suggested that metal-oxo species which oxidize C–H bonds via radical mechanisms have some radical character at oxygen. However, in important recent studies on CrO_2Cl_2 oxidation of hydrocarbons, Mayer has shown that the important factor is the strength of the O–H bond formed on H atom transfer to the oxo group, rather than any radical character in the initial oxo group [26]. Chromate and permanganate ion are both diamagnetic and lack any O radical character yet they are effective H atom abstractors from a variety of hydrocarbons.

We prefer the nonradical pathway for our alkane oxidation shown in Fig. 5 in which monopersulfate first reacts with the catalyst to form a $Mn^{V}(\mu\text{-}O)_2Mn^{V}=O$ species which then transfers the oxygen atom to the C–H bond. We cannot exclude the adduct of the catalyst with

$$Mn^{IV}O_2Mn^{IV}\text{-}S + {}^{\cdot}OOSO_3H = Mn^{IV}O_2Mn^{IV}\text{-}OOSO_3H$$

$$Mn^{IV}O_2Mn^{IV}\text{-}OOSO_3H = Mn^{V}O_2Mn^{V}{=}O + {}^{\cdot}OSO_3H$$

$$Mn^{V}O_2Mn^{V}{=}O + RCH_2R' = Mn^{IV}O_2Mn^{IV}\text{-}S + RCHOHR'$$

Fig. 5. Proposed non-radical mechanism for oxidation of alkanes by $[Mn_3O_4bipy_4(OH_2)_2]^{4+}$/TBAO. S = solvent. In this diagram, we assume a binuclear di-μ-oxo dimer is the true active species.

peroxomonosulfate, being the active species, as suggested by Meunier for manganese porphyrins [15]. Work is in progress to try to isolate the active species and determine the nuclearity of the cluster and oxidation level of the Mn ions.

The epoxidation of *cis*-stilbene gives largely the *cis*-epoxide, but a small amount of isomerization occurs by un unknown process to give *trans*-stilbene and its epoxide. Benzophenone, another minor product, may arise from phenyl migration to a carbocation formed in epoxide ring opening and further oxidation of the resulting diphenylacetaldehyde intermediate.

3.2. Related Studies

Zhu and Ford [27] have shown that Oxone® alone is able to epoxidize olefins in the absence of organic solvent, while Bloch and coworkers also epoxidized olefins with Oxone® in aqueous methanol [28]. In addition, Oxone® is also known to react with acetone to give dimethyldioxirane, which is also capable of epoxidizing olefins without a metal catalyst [29]. However, Trost reports that TBAO does not react with acetone under mild conditions. Our control experiments show no product formation with non-aromatic alkenes and little product formation with styrene (3% conversion to benzaldehyde, 1% to styrene oxide under the same conditions) in the absence of catalyst under our conditions. This indicates that the metal complex is required for the reaction to occur and is indeed acting as a catalyst.

4. Conclusions

TBAO is likely to be a generally useful primary oxidant with convenient solubility in organic solvents and with a high tendency to promote oxo transfer, rather than radical oxidation pathways in catalysis. It is likely to be especially effective in the case of a cationic catalyst, as is the case here. In marked contrast with the radical pathways found for the **1**/TBHP system investigated earlier, we now find oxo transfer chemistry for the **1**/TBAO system. In the oxidation of alkanes, **1**/TBAO gives a much higher selectivity for ketone, as well as higher 3°/2° selectivity. The **1**/TBHP system gives allylic oxidation or C=C cleavage products, while **1**/TBAO gives mainly epoxides. While the **1**/TBHP system probably has a radical chain mechanism, the **1**/TBAO system is non-radical and probably goes via a metal-oxo intermediate.

5. Experimental section

5.1. General

Gas chromatographic analyses were performed on a Varian 3700 or 3300 instrument (flame-ionization detection) equipped with an SP4270 integrator. Mass spectral analyses were carried out using an HP 5890 gas chromatograph equipped with a 5971A MSD mass-selective detector. NMR spectra were recorded on a Bruker WM 250 spectrometer. TBAO [12] and $[Mn_3O_4bipy_4(H_2O)_2](ClO_4)_4$ [9] were prepared by published methods.

5.2. Materials

All solvents used were reagent grade from Baker.

5.3. Standard procedure for oxidations

5.3.1. Alkanes and arylalkanes

To a solution of substrate (4 mmol) in CH_3CN or CH_3COCH_3 (10 ml) was added 1.4–1.5 mg (1 μmol) catalyst in CH_3CN. The solution was cooled in an ice bath and TBAO (2 mmol) added. The reaction was allowed to run for 3.5 h, 5% $NaHSO_3$ added to quench any remaining oxidant, and the solution extracted with ether. Solutions were analyzed by GC or GC/MS, using chlorobenzene or mesitylene as an internal standard.

5.3.2. Alkenes

As above except the catalyst was dissolved in 10 ml CH_3CN and 1 ml of this solution (0.1 μmol catalyst) was added to the substrate solution.

5.4. Oxidation of propene

TBAO (3.0 g, 1.8 mmol) was measured into a thick-walled glass pressure vessel equipped with a Teflon stopcock. The flask was evacuated and 0.704 g propene (16.7 mmol) introduced while cooling with liquid nitrogen to freeze the propene. A solution of 1.5 mg of **1** in 20 ml of CH_3CN was then added. The flask was then sealed, allowed to warm to about −25°C ($Ca(NO_3)$/NaCl/ice bath) and stirred at that temperature for 10 h. The vessel was then allowed to warm to room temperature, and the mixture stirred overnight.

5.5. Synthesis of organic oxidation products for comparison

Trans-1-ethyl-2-phenylcyclopropane [30] was prepared from *trans*-1-phenyl-1-butene according to the Rawson and Harrison modification [31] of the Simmons–Smith procedure [32] for cyclopropanation of olefins with the further modification that 0.15 eq iodine was added together with the starting material in ether. ^{1}H NMR δ 7.03–7.36 (m, 5 H, C_6H_5), 1.57 (m, 1 H PhC*H*), 1.40 (m, 2 H CH_3CH_2), 1.26 (m, 1 H), 1.01 (t, $J = 7$ Hz, 3 H CH_3), 0.88 (m, 1 H), 0.75 (m,1 H); EI-MS *m/z* 146 (M^+,38), 117 ($M - CH_2CH_3$, 100), 115 (79), 104 (64), 91 (50), 78 (25). 1-(Phenylcyclopropyl)ethanone and 2-ethyl-1-methyl-1-phenylcyclopropane were prepared by the same method.

1-(2-Phenylcyclopropyl)ethanol. To a solution of 1-(phenylcyclopropyl) ethanone (0.542 g, 3.38 mmol) in 10 ml MeOH was added sodium borohydride (1.079 g, 28.5 mmol). The reaction was stirred overnight, quenched by pouring on ice, extracted with ether, dried, evaporated. Yield 0.264 g (48%). ^{1}H NMR δ 7.05–7.42 (m, 5 H C_6H_5); 3.39 (m, 1 H CH_3CH OH); 1.86 (m, 1 H); 1.55 (d, 4 H CH_3 + OH); 1.33 (m, 2 H); 1.95 (m, 1 H); EI-MS *m/z* 162 (M^+, 3) 144 ($M - H_2O$, 4), 129 (25), 117 (95), 107 (100), 104 (71), 91 (36), 79 (9).

1-Phenyl-3-penten-1-ol. To a mixture of magnesium turnings (0.188 g, 7.73 mmol) and benzaldehyde (0.316 g, 2.98 mmol) in 10 ml ether is added crotyl bromide (0.542 g, 4.01 mmol) in 2 ml ether. After stirring 4 h, reaction is quenched with aqueous ammonium chloride, extracted, dried, evaporated. Yield 0.190 g (crude) (39%). EI-MS *m/z* 107 ($PhCHOH^+$, 100), 105(9), 79 (42), 77 (25).

1-Phenyl-3-penten-1-one. Chromium trioxide (0.083, 0.83 mmol) is added to 1.2 ml pyridine in an ice bath, allowed to warm to room temperature, stirred 2 h. 1-Phenyl-3-penten-1-ol (0.090 g, 0.55 mmol) in 1 ml pyridine is added and the solution stirred for 0.5 h. Water added, solution extracted with ether, dried, evaporated. Compound was not purified as we were only interested in determining GC retention time and mass spectrum for comparison purposes. EI-MS *m/z* 105 (100), 77 (79), 51 (29).

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