Studies on Polyoxo- and Polyperoxo-metalates. Part 1. Tetrameric Heteropolyperoxotungstates and Heteropolyperoxomolybdates

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New heteropolyperoxometalates of the type $R_3[XO_4\{MO(O_2)_2\}_4]$ [R = $N(C_6H_{13})_4^+$, $N(PPh_3)_2^+$ or $\frac{1}{3}[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine); X = P or As; M = Mo or W] have been characterized by IR, Raman and where appropriate ^{31}P NMR spectroscopy. Epoxidation of cyclic and linear alkenes by these species with H_2O_2 as co-oxidant has been studied; $[AsO_4\{WO(O_2)_2\}_4]^{3-}$ was found to be the most effective. The oxidation of alcohols by $[PO_4\{WO(O_2)_2\}_4]^{3-}$ with H_2O_2 has been investigated.

Polyoxometalates are currently of considerable interest and have been used in catalytic, medicinal and solid-state chemistry.[1–4] Many of their oxidations involve H_2O_2 or Bu^tO_2H as co-oxidants and may well involve heteropolyperoxo complexes, in which some of the O^{2-} ligands have been replaced by peroxo (O_2^{2-}) or hydroperoxo ligands. Stomberg and co-workers have isolated a few such species, *e.g.* $[NH_4]_4[Mo_3O_7(O_2)_4]\cdot 2H_2O$,[5] $K_6[Mo_5O_{10}(O_2)_8]\cdot 5H_2O$[6] and $K_6[W_4O_8(O_2)_6(CO)_3]\cdot 6H_2O$,[7] but there is no evidence that these function as oxidation catalysts. In 1985, however, Venturello *et al.*[8] isolated and characterized the heteropolyperoxo species, $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ **1** and it was shown that $[PO_4\{WO(O_2)_2\}_4]^{3-}$ is an active catalyst for the epoxidation[9] and *cis*-hydroxylation[10] of unactivated alkenes by H_2O_2 under phase-transfer conditions with salts containing large lipophilic quaternary ammonium cations. Catalysis by the related complex $[CH_3(CH_2)_{15}N(C_5H_5)]_3[PO_4\{WO(O_2)_2\}_4]$ has been shown for oxidation of internal alkynes to the corresponding α,β-epoxy ketones[11,12] and it was also found to catalyse the oxidation of a wide variety of amines to oximes, nitrones and nitrobenzenes.[13] Recent work suggests that the Keggin heteropoly salts $[NBu^n_4]_3[PM_{12}O_{40}]$ (M = Mo or W) react with H_2O_2 to give $[NBu^n_4]_3[PO_4\{MO(O_2)_2\}_4]$.[14]

Here we report the synthesis of heteropolyperoxo compounds of the type $R_3[XO_4\{MO(O_2)_2\}_4]$ {R = $N(C_6H_{13})_4^+$, $N(PPh_3)_2^+$ or $\frac{1}{3}[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine); X = P or As; M = Mo or W}. These have been characterized by IR, Raman and where appropriate ^{31}P NMR spectroscopy. Species of this type have been briefly reported by Csányi and Jáhy[15] but with no analytical data; there are recent reports of $R_3[PO_4\{MoO(O_2)_2\}_4]$ [R = NBu^n_4,[14,15] $N(PPh_3)_2$[16] or $N(C_6H_{13})_4$[16,17]]. The structures of these species in solution have been studied, and a comparison of their ability, under phase-transfer conditions, to catalyse the epoxidation of cyclic and linear alkenes by H_2O_2 has been made. A brief survey of oxidation of primary and secondary alcohols by **1** has also been made.

Results and Discussion

(*a*) *Synthesis.*—The heteropolyperoxo anion $[PO_4\{WO(O_2)_2\}_4]^{3-}$ may be conveniently isolated as the tetra-*n*-hexylammonium salt **1**.[8] We have developed an improved preparation by reaction of an aqueous solution of WO_3, H_2O_2 and Na_2HPO_4, with addition of $N(C_6H_{13})_4Cl$ in benzene to give **1** as a white microcrystalline solid. The analogous new arsenic salt $[N(C_6H_{13})_4]_3[AsO_4\{WO(O_2)_2\}_4]$ **2** may be prepared by adding Na_2HAsO_4 to WO_3 in place of Na_2HPO_4, and by using analogous procedures the molybdenum salts $[N(C_6H_{13})_4]_3[PO_4\{MoO(O_2)_2\}_4]$ **3** and $[N(C_6H_{13})_4]_3[AsO_4\{MoO(O_2)_2\}_4]$ **4** can be isolated. The corresponding bis(triphenylphosphoranylidene)ammonium salts are obtained by adding an ethanolic solution of $[N(PPh_3)_2]Cl$ to $[XO_4\{MO(O_2)_2\}_4]^{3-}$ (X = P or As, M = Mo or W), and the corresponding amber-coloured salts $[Co(en)_3][XO_4\{MO(O_2)_2\}_4]$ were made by adding an aqueous solution of $[Co(en)_3]Cl_3$ to a solution containing $[XO_4\{MO(O_2)_2\}_4]^{3-}$.

(*b*) *Infrared and Raman Spectra; Structures of the Complexes.*—Infrared and Raman data for $R_3[XO_4\{MO(O_2)_2\}_4]$ are given in Table 1. The phosphate-containing complexes show, as well as several bands due to the quaternary cations, strong bands near 970 cm^{-1} due to ν(M=O) of the terminal oxo group and near 870 cm^{-1} due to ν(O–O) of the peroxo ligands, while bands at about 590 and 520 cm^{-1} are probably due to asymmetric and symmetric stretches of the $M(O_2)$ units. These bands from the $MO(O_2)_2$ units appear in approximately the same positions as those observed in the infrared spectra of the dimeric species $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ (M = Mo or W);[18] such assignments are well established for η^2-peroxo ligands.[19] Strong bands at approximately 575 and 550 cm^{-1} may be assigned to vibrations of the metal–oxygen heteropoly framework and the three bands observed in the region 1100–1030 cm^{-1} to phosphorus–oxygen stretches. The Raman spectra also show strong bands near 975 [ν(M=O)], 880 [ν(O–O)], 590 {$\nu_{asym}[M(O_2)]$} and 525cm^{-1} {$\nu_{sym}[M(O_2)]$}, and weak bands in the 1080–1030 cm^{-1} region due to P=O stretches. The polyperoxometalloarsenates show bands similar to their phosphorus counterparts, with M=O, O–O and $M(O_2)$ stretches in much the same positions in the infrared and Raman spectra. Bands close to 900 and 875 cm^{-1} in the infrared and near 905 and 895 cm^{-1} in the Raman spectra are tentatively assigned to As=O stretches. Attempts to measure the Raman spectra of compounds **1**–**4** in benzene solution were unsuccessful.

The crystal structure of compound **1**, reported by Venturello *et al.*,[8] shows the anion to be composed of four distorted $WO(O_2)_2$ pentagonal bipyramids in edge-shared pairs, linked by a central tetrahedral PO_4 moiety (Fig. 1): a similar structure has recently been reported for **3**.[16] The general similarity of the infrared and Raman spectra of **1**–**4** suggests a similar structure for all four anions.

(*c*) ^{31}P-{^1H} *NMR Spectra.*—The ^{31}P-{^1H} NMR spectrum of compound **1** in C^2HCl_3 appears as a 1 : 8 : 27 : 8 : 1 'quintet' at

Table 1 Spectroscopic data for $[R]_3[XO_4\{MO(O_2)_2\}_4]$

	Vibrational spectroscopic data (cm^{-1})[a]						
Complex	ν(M=O)	ν(O–O)	ν_{asym}[M(O$_2$)]	ν_{sym}[M(O$_2$)]	ν(XO$_4$)	Other bands[a]	^{31}P NMR[b] (δ)
1 $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$	976vs	843vs	591s	526s	1095s 1057s 1037s	575s 549s	3.47 [^2J(P–W) = 22.3 Hz]
	983 (10)	*857 (8)*	*590 (5)*	*536 (3)*	*1065 (4)* *1036 (5)*	*574 (7)*	
2 $[N(C_6H_{13})_4]_3[AsO_4\{WO(O_2)_2\}_4]$	978vs	846vs	590s	521s	893s 876s	647s 574s	
	985 (10)	*862 (7)*	*589 (5)*	*534 (3)*	*914 (5)* *901 (6)*	*557 (8)*	
3 $[N(C_6H_{13})_4]_3[PO_4\{MoO(O_2)_2\}_4]$	968vs	868vs	588s	519s	1073s 1045s 1032s	560m	7.35
	975 (10)	*878 (8)*	*584 (3)*	*527 (4)*	*1076 (2)* *1043 (3)*	*593 (sh) (2)* *556 (5)*	
4 $[N(C_6H_{13})_4]_3[AsO_4\{MoO(O_2)_2\}_4]$	968vs	853vs 831s	589s	517s	899s 868s	654s 555m	
	973 (10)	*875 (8)* *830 (2)*	*588 (4)*	*523 (4)*	*906 (2)*	*554 (5)*	
$[N(PPh_3)_2]_3[PO_4\{MoO(O_2)_2\}_4]$	968vs	874s	584s	537vs	1121s 1074s	698vs 557s	7.29 21.99
	973 (6)	*869 (4)*	*589 (3)*	*525 (2)*	*1109 (6)* *1029 (10)*	*554 (2)*	
$[N(PPh_3)_2]_3[AsO_4\{MoO(O_2)_2\}_4]$	964s	874s	583s	537vs	894s 858s 823s	698vs 557vs	21.89
	961 (7)	*869 (4)*	*589 (3)*	*529 (3)*	*916 (6)*	*555 (2)*	
$[N(PPh_3)_2]_3[PO_4\{WO(O_2)_2\}_4]$	976vs	850s	581s	541vs	1121s 1089s 1058s	698vs 553s	3.53 [^2J(P–W) = 20 Hz]
	981 (6)	*859 (4)*	*575 (3)*	*532 (2)*	*1109 (9)* *1028 (10)*	*557 (2)*	21.99
$[N(PPh_3)_2]_3[AsO_4\{WO(O_2)_2\}_4]$	969s	844s	587vs	534vs	913s 871s	548s	22.02
	967 (10)	*851 (8)*	*565 (5)*	*529 (4)*	*895 (8)*	*555 (3)*	

[a] Raman data in italics (relative intensities in parentheses); bands due to the ligand are not listed. [b] In C^2HCl_3 solution.

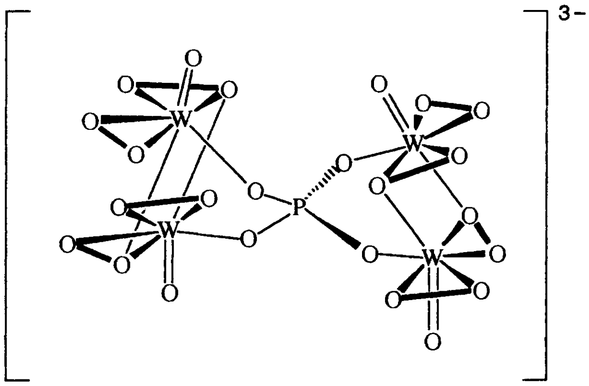

Fig. 1 The anion of compound **1**, $[PO_4\{WO(O_2)_2\}_4]^{3-}$ (ref. 8)

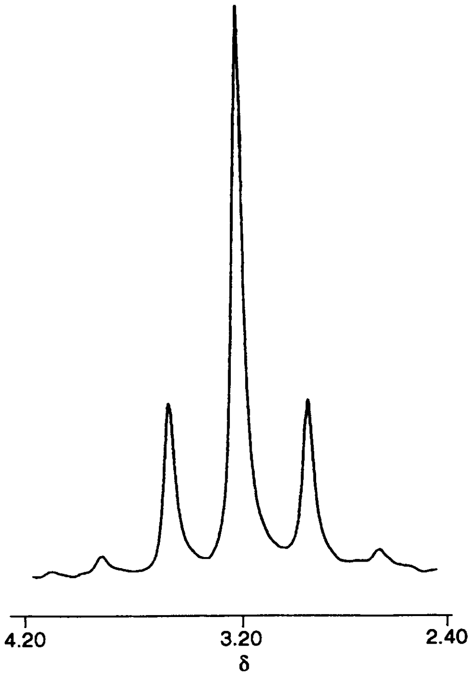

Fig. 2 The 36.21 MHz $^{31}P-\{^1H\}$ NMR spectrum of compound **1** in C^2HCl_3

approximately δ 3.5 (Fig. 2); Brégeault and co-workers[14] observed a similar spectrum. This pattern arises from interactions of the four tungsten nuclei (^{183}W, $I = \frac{1}{2}$, 14% abundant) with the phosphorus nucleus (^{31}P, $I = \frac{1}{2}$, 100% abundant) giving a value of ^2J(P–W) = 22.3 Hz. It may best be explained by considering an amalgamation of five distinct spin systems: *viz.* A = PW_4 (no ^{183}W); AX = $PW_3{}^{183}W$; AX_2 = $PW_2{}^{183}W_2$; AX_3 = $PW^{183}W_3$; AX_4 = $P^{183}W_4$. The theoretical intensity ratios from these would be 1:8:27:8:1, *i.e.* each satellite will have *ca.* 30% of the intensity of the centre peak, in close agreement with our observed spectrum. We conclude from this that $[PO_4\{WO(O_2)_2\}_4]^{3-}$ gives rise to this peak. The salt $[N(PPh_3)_2]_3[PO_4\{WO(O_2)_2\}_4]$, in C^2HCl_3, gave essentially the same spectrum but with an extra phosphorus resonance at δ 21.99, due to the cation. The molybdenum species **3** has a singlet centred at δ 7.35 assigned to $[PO_4\{MoO(O_2)_2\}_4]^{3-}$ while

$[N(PPh_3)_2]_3[PO_4\{MoO(O_2)_2\}_4]$ shows an additional peak at δ 21.99 due to $[N(PPh_3)_2]^+$.

In an attempt to confirm the presence of $[PO_4\{WO(O_2)_2\}_4]^{3-}$ in aqueous solution, the ^{31}P-$\{^1H\}$ NMR spectra of solutions containing PO_4^{3-}, H_2O_2 and $[WO_4]^{2-}$ in a 1:8:4 ratio were measured over a range pH 4.0–1.5, using HCl to adjust the pH. In the range pH 4.0–3.0 the predominant species appears to be $[PO_4\{WO(O_2)_2\}_2]^{3-}$ **A**, since a 'triplet' with intensities 1:6:1 is observed (δ 0.69 at pH 3.2), with each satellite *ca.* 16% of the intensity of the central peak. The theoretical pattern for **A** is a 'quintet' in a 1:24:150:24:1 ratio; if the outermost weak satellites were not observed, however, an apparent 'triplet' of *ca.* 1:6:1 ratio would be expected, similar to the pattern obtained. At lower pH (3.0–2.0) the relative intensity of **A** decreases and a new species **B** appears (δ −0.64 at pH 2.0) thought to be $[PO_4\{WO(O_2)_2\}_3]^{3-}$. This appears as a 'quintet' of relative intensities 1:12:52:12:1 with each satellite *ca.* 23% of the central signal (theoretical pattern for **B** 1:12:52:12:1). At pH < 2.0 the signals from **A** and **B** decrease and a new signal **C** appears (at δ −1.36, pH 1.6), assigned to $[PO_4\{WO(O_2)_2\}_4]^{3-}$, showing a 1:8:27:8:1 'quintet' as described above. In addition, the chemical shifts of all three species were found to be pH dependent but below pH 1.3 the solution decomposes, probably to give $[WO(O_2)Cl_4]^{2-}$. A typical ^{31}P-$\{^1H\}$ NMR spectrum at pH 1.6 is shown in Fig. 3.

Thus, it appears that a number of species related to $[PO_4\{WO(O_2)_2\}_4]^{3-}$ exist in aqueous solution. We have not so far succeeded in separating these. Nevertheless, we believe that these findings may explain the observations of Venturello *et al.*[20] that, at pH 1.6, mixtures of $[WO_4]^{2-}$, H_2O_2 and PO_4^{3-} are more effective than $[WO_4]^{2-}$–H_2O_2 mixtures alone for epoxidations of linear alkenes (in water–dichloroethane using the phase-transfer agent, Aliquat, at 40–70 °C). In addition such mixtures are effective reagents for the oxidative cleavage of 1,2-diols to carboxylic acids at pH 2.[21]

(*d*) *Oxidation Studies.—Alkenes.* Venturello and co-workers[8,9] have shown that quaternary ammonium salts of $[PO_4\{WO(O_2)_2\}_4]^{3-}$ are effective catalysts for the epoxidation by H_2O_2 of a range of alkenes, using phase-transfer conditions and temperatures ranging from 40 to 70 °C, typically for 24 h. Conversions of 7–94% and catalytic turnovers of up to 500 were obtained for a series of unactivated alkenes, *e.g.* hex-1-ene, oct-1-ene and cyclooctene.

We find that compounds **1**–**4** are active catalysts for the epoxidation of both cyclic and linear alkenes by H_2O_2 (Table 2). In a typical catalytic experiment a biphasic mixture of **1** dissolved in benzene, cyclooctene and 15% aqueous H_2O_2 was stirred vigorously at 70 °C for 3 h. Proton NMR and GC analysis of the organic layer revealed the presence of 1,2-epoxycyclooctane (99% yield). For cycloalkenes, the percentage conversion into epoxide (in each of the catalytic systems studied) varied with the ring size of the substrate, excepting cyclohexene, the larger the cycloalkene ring the greater being the conversion into the epoxide. Attempted epoxidations of cycloalkenes by **1** in the presence of Bu^tO_2H as the co-oxidant resulted in the reprecipitation of **1**. The order of increasing catalytic activity **1**–**4** towards epoxidation of cycloalkenes was determined to be $[PO_4\{MoO(O_2)_2\}_4]^{3-} < [AsO_4\{MoO(O_2)_2\}_4]^{3-} \ll [PO_4\{WO(O_2)_2\}_4]^{3-} < [AsO_4\{WO(O_2)_2\}_4]^{3-}$. In the case of $[XO_4\{MoO(O_2)_2\}_4]^{3-}$ (X = P or As), the conversion of cyclododecene into cyclododecene oxide was substantially lower than expected. This may be the result of steric constraints about the $MO(O_2)_2$ core, which does not allow sufficient approach of the substrate to the active sites on the metal centre.

Epoxidation of secondary linear alkenes generally gave better yields of epoxide than of the corresponding terminal alkenes. It was also noted that small terminal alkenes such as pent-1-ene, hex-1-ene and hept-1-ene underwent ring opening, forming a 1,2-diol, which was subsequently oxidized to a carboxylic acid.

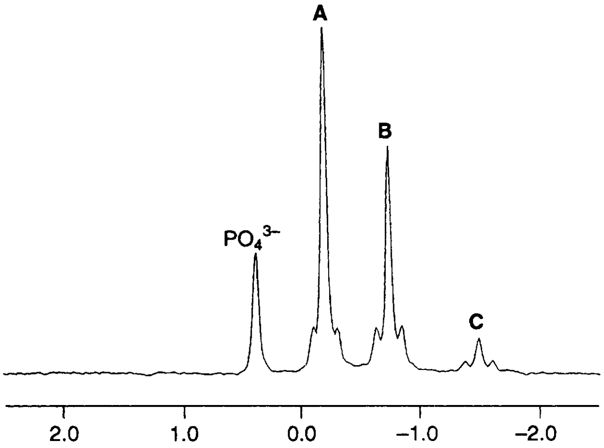

Fig. 3 The 109.25 MHz ^{31}P-$\{^1H\}$ NMR spectrum showing species **A**, **B** and **C** in H_2O–^2H_2O solution at pH 1.6

In general the tungsten complexes **1** and **2** are far superior to their molybdenum analogues **3** and **4** in catalysing the epoxidation of alkenes with H_2O_2 as co-oxidant. The epoxidation of cycloalkenes by **1** and **2** is markedly more successful than that of their linear counterparts (Table 2). In all cases the purity of the products was checked by ^1H NMR spectroscopy and in many cases by gas chromatography–mass spectrometry (GC–MS).

Stoichiometric oxidation of 1 equivalent of cyclooctene in C^2HCl_3 by compound **1** results in formation of cyclooctene oxide within 20 min at room temperature. The ^{31}P-$\{^1H\}$ NMR spectrum of this reaction mixture showed a small peak at δ 2.17, with partially resolved ^{183}W 'satellites'. Addition of further equivalents of cyclooctene gives rise to a series of peaks in the ^{31}P-$\{^1H\}$ NMR spectrum, the most prominent of which are at δ 2.51 with ^2J(P–W) = 16.0 Hz and δ 5.62 with ^2J(P–W) = 14.7 Hz. Addition of a small amount of H_2O_2 to the reaction mixture regenerates **1**; a signal at δ 3.47 is the only resonance observed. These results suggest that complete breakdown of the heteropolyperoxometalate framework does not take place during epoxidation. Similar observations were noted for the molybdenum analogue, although the reaction rate was much slower. Several attempts were made at isolating a metal-containing intermediate from large-scale stoichiometric oxidations of cyclooctene by both **1** and **3**. In a typical experiment, to a stirred solution of **1** in CH_2Cl_2, cyclooctene was added and stirred at room temperature for 2 h. The solution was then either cooled to 4 °C or left to evaporate at room temperature. The colourless crystalline solid obtained was filtered off and air dried. The ^{31}P-$\{^1H\}$ NMR spectrum of C^2HCl_3 solutions of these materials were found to contain both the parent and a new species at δ 2.51 in approximately equal amounts. A similar attempt was made using fumaronitrile (1,2-dicyanoethene). Again a new ^{31}P NMR signal was observed at δ 1.93 with ^2J(P–W) = 17.4 Hz. During the course of the reaction this was the only signal present other than that due to the parent anion. Attempts to obtain crystals of this new species were unsuccessful.

The mechanism of the epoxidation reaction is not clear and we have not attempted to carry out mechanistic studies to determine the likely pathway. It is probably significant, however, that one of the two η^2-peroxo rings co-ordinated to the metal in complex **1** is markedly asymmetric, owing to the formation of a long bond from the peroxidic oxygen atom [O(2)] to an adjacent tungsten atom, unlike the other oxygen atom, O(1), which has no such bond; in this ring, the W–O(1) distance is 1.92 Å and W–O(2) 2.03 Å.[8] It is likely, therefore, that the W–O(2) bond is more readily cleaved to form a peroxometallapentane intermediate, subsequent to initial co-ordination of the alkene, if the mechanism of Mimoun[22] for

Table 2 Epoxidation of linear and cyclo-alkenes by tungsten and molybdenum complexes

		Yield (%) (turnover)[a]			
Substrate	Product	**1**	**2**	**3**	**4**
Cyclopentene	1,2-Epoxycyclopentane	48[b] (258)	69[b] (306)	4[b] (15)	6[b] (21)
Cyclohexene	1.2-Epoxycyclohexane	18[c] (90)	36[c] (195)	1[b] (1)	5[b] (15)
Cycloheptene	1,2-Epoxycycloheptane	62[d] (342)	83[d] (402)	9[d] (45)	28[d] (135)
Cyclooctene	1,2-Epoxycyclooctane	99[e] (1080)	99[e] (1080)	33[d] (180)	40[d] (216)
Cyclododecene	1,2-Epoxycyclododecane	99[d] (1080)	99[e] (1125)	3[b] (6)	11[b] (21)
2,3-Dimethylbut-2-ene	2,3-Dimethyl-2,3-epoxybutane	76[b] (204)	84[b] (216)	—	—
2,4,4-Trimethylpent-2-ene	2,3-Epoxy-2,4,4-trimethylpentane	92[b] (225)	96[b] (228)	—	—
Pent-1-ene[f]	1,2-Epoxypentane	56[c] (140)	76[c] (160)	2[b] (6)	6[b] (16)
Hex-1-ene[f]	1,2-Epoxyhexane	48[c] (145)	66[c] (165)	3[b] (8)	9[b] (22)
trans-Hex-2-ene	*trans*-2,3-Epoxyhexane	73[c] (204)	75[b] (207)	—	—
trans-Hex-3-ene	*trans*-3,4-Epoxyhexane	59[c] (153)	83[b] (216)	—	—
Hept-1-ene[f]	1,2-Epoxyheptane	34[c] (120)	56[c] (140)	4[b] (8)	5[b] (10)
Oct-1-ene[f]	1,2-Epoxyoctane	62[c] (140)	48[c] (145)	2[b] (4)	6[b] (12)
trans-Oct-2-ene	*trans*-2,3-Epoxyoctane	82[c] (183)	93[b] (198)	—	—
trans-Oct-4-ene	*trans*-4,5-Epoxyoctane	73[c] (168)	89[b] (189)	—	—
Non-1-ene[f]	1,2-Epoxynonane	93[c] (180)	94[c] (185)	2[b] (4)	8[b] (14)
Dec-1-ene[f]	1,2-Epoxydecane	89[c] (182)	97[c] (200)	2[b] (2)	6[b] (10)
Undec-1-ene[f]	1,2-Epoxyundecane	85[c] (185)	99[c] (205)	3[b] (4)	11[b] (18)
Dodec-1-ene[f]	1,2-Epoxydodecane	96[c] (200)	99[c] (205)	6[b] (8)	16[b] (20)
cis-1,2-Diphenylethene	*cis*-1,2-Epoxy-1,2-diphenylethane	—	87[b] (207)	—	—
trans-1,2-Diphenylethene	*trans*-1,2-Epoxy-1,2-diphenylethane	—	96[b] (226)	—	—

[a] Turnover = mol product/mol catalyst. [b] By ^{1}H NMR spectroscopy. [c] By GC–MS. [d] by GC. [e] Isolated yield; oxidations carried out at 70 °C for 3 h. [f] Oxidation carried out for 20 h.

alkene epoxidation by molybdenum η^2-peroxo complexes is accepted. The alternative mechanism of nucleophilic attack of the substrate on co-ordinated peroxide proposed by Sharpless and co-workers[23,24] cannot, however, be precluded. In connection with this, we note that epoxidation effected by $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ is less effective than are those of **1**; the crystal structure of $K_2[W_2O_3(O_2)_4(H_2O)_2]$ shows the η^2-peroxo tungsten triangles to be essentially isosceles, with W–O 1.94 and 1.97 Å.[25]

The reason for the superiority of compound **2** compared with **1** for epoxidation reactions is not clear, nor is the much lower efficiency of the molybdenum analogues **3** and **4** though it has been noted that mononuclear tungsten complexes are often superior catalysts to their molybdenum analogues for epoxidation of alkenes by H_2O_2.[26] It may be that in the molybdenum complexes **3** and **4** there is less asymmetry in the $Mo(O_2)$ units, which are presumably involved in bonding to adjacent metal atoms (assuming these to have similar structures to those of **1**). To check this point, we made many attempts to isolate crystals of **3** and **4** with a variety of different cations. We have, however, shown by X-ray diffraction measurements on microcrystalline powders that **1**–**4** are isostructural.

Alcohols.—Oxidation by compound **1** of primary alcohols, such as benzyl alcohol, at room temperature in benzene with H_2O_2 as co-oxidant result in aldehyde yields of 20–40%, with turnovers ranging from 450 to 1450 (Table 3). Yields of ketones, formed by oxidation of secondary alcohols, were lower than those of aldehydes, obtained by oxidation of primary alcohols. Complex product mixtures were obtained from oxidations of cinnamyl alcohol, geraniol and citronellol (3,7-dimethyloct-6-en-1-ol), presumably due to competing oxidations of the alkene and alcohol moieties. All these results are reminiscent of those reported for $[PPh_4]_2[M_2O_3(O_2)_4]$ (M = Mo or W),[18] which are also relatively inefficient catalytic oxidants for alcohols.

We conclude that $[N(C_6H_{13})_4]_3[XO_4\{MO(O_2)_2\}_4]$ (X = P or As) are active catalysts with H_2O_2 for the epoxidation of a variety of alkenes and alcohols; the arsenic-containing species **2** is the most effective. The corresponding molybdenum analogues also catalyse such transformations, although much less efficiently; the arsenate **4** is marginally more effective than **3**. Spectroscopic evidence suggests that the polyperoxometalate framework does not completely break down during the course of the reaction and is restored on addition of more peroxide.

Table 3 Oxidation of alcohols by $[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$

Substrate	Product	Yield (%)	Turnover[a]
Benzyl alcohol	Benzaldehyde[b]	40	1440
4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde[b]	31	880
2-Methylbenzyl alcohol	2-Methylbenzaldehyde[b]	15	480
Piperonyl alcohol	Piperonal[b]	23	600
Cinnamyl alcohol	Cinnamaldehyde[b]	38	1120
Cyclohexanol	Cyclohexanone[c]	18	520
(±)-Menthol	(±)-Menthone[c]	16	500

[a] Turnover = mol product/mol catalyst. [b] Product yield determined by ^1H NMR spectroscopy. [c] Product yield determined by GC–MS.

Experimental

General.—Infrared spectra of the solids were measured over the range 4000–220 cm^{-1} using Nujol mulls on CsI plates on a Perkin Elmer 1720 Fourier-transform spectrometer, Raman spectra of the solids (as powders in melting-point tubes) on a Perkin Elmer 1760X FR-IR instrument fitted with a 1700X NIR FT-Raman accessory using a Nd:YAG laser (1064 nm excitation). The NMR spectra were obtained on a JEOL ESX 270 spectrometer (^1H, 270.05 MHz; ^{31}P, 109.25 MHz) and a JEOL FX 90Q spectrometer (^{31}P, 36.21 MHz) as C^2HCl_3 solutions, using either the residual solvent peak or external H_3PO_4 as reference. The GC data were obtained on a Perkin Elmer Autosystem instrument using a Perkin Elmer stainless-steel column (2 m) packed with 5% Carbowax 20M on Chromasorb WHP AW (DCMS treated), GC–MS data on a Nermag R10-10 instrument linked to a Hewlett-Packard chromatograph. Microanalyses were carried out by the Microanalytical Laboratories at Imperial College and University College. Peroxide analyses were carried out by dissolving the complex in acetone and titrating with a 0.001 mol dm^{-3} $KMnO_4$ solution in 2 mol dm^{-3} H_2SO_4.

Preparations.—$[N(C_6H_{13})_4]_3[PO_4\{WO(O_2)_2\}_4]$ **1**. The following procedure is superior to that reported by Venturello *et al.*[8] To a solution of hydrated WO_3 (2.50 g, 10.0 mmol) in water (15 cm^3) and 30% H_2O_2 (7 cm^3) at 60 °C was added Na_2HPO_4 (0.36 g, 2.5 mmol) dissolved in water (5 cm^3), giving a colourless solution. A solution of $N(C_6H_{13})_4Cl$ (1.56 g, 4.0 mmol) in benzene (20 cm^3) was added dropwise over a period of 2 min. The biphasic mixture was stirred vigorously at room temperature for 2 h, during which time a white precipitate of **1** had formed at the interface. This was collected, washed with water (2 × 10 cm^3), benzene (2 × 10 cm^3) and diethyl ether (3 × 10 cm^3) and air dried. The solid is slightly hygroscopic and should preferably be stored in a vacuum desiccator. Yield: 2.64 g (89%) (Found: C, 38.9; H, 7.1; N, 1.9; P, 2.0; O_2^{2-}, 11.4. Calc. for $C_{72}H_{156}N_3O_{24}PW_4$: C, 39.1; H, 7.1; N, 1.9; P, 1.4; O_2^{2-}, 11.6%).

Prepared similarly were: $[N(PPh_3)_2]_3[PO_4\{WO(O_2)_2\}_4]$ as a white solid, yield 3.36 g (91%) (Found: C, 46.9; H, 3.0; N, 1.5; O_2^{2-}, 9.1. Calc. for $C_{108}H_{90}N_3O_{24}P_7W_4$: C, 46.9; H, 3.3; N, 1.5; O_2^{2-}, 9.3%) and $[Co(en)_3][PO_4\{WO(O_2)_2\}_4]$ as an amber solid, yield 1.57 g (85%) (Found: C, 5.6; H, 1.7; N, 6.7. Calc. for $C_6H_{24}CoN_6PO_{24}PW_4$: C, 5.2; H, 1.7; N, 6.1%).

$[N(C_6H_{13})_4]_3[AsO_4\{WO(O_2)_2\}_4]$ **2**. To a solution of hydrated WO_3 (2.50 g, 10.0 mmol) in water (15 cm^3) and 30% H_2O_2 (7 cm^3) at 60 °C was added $Na_2HAsO_4{\cdot}7H_2O$ (0.78 g, 2.5 mmol) dissolved in water (5 cm^3), giving a colourless solution. A solution of $N(C_6H_{13})_4Cl$ (1.56 g, 4.0 mmol) in benzene (20 cm^3) was added over a period of 2 min. The biphasic mixture was stirred vigorously at ambient temperature for 2 h, during which time a white precipitate of compound **2** formed at the interface. This was filtered off and washed successively with water (2 × 10 cm^3), benzene (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3). The solid was thoroughly air dried and then stored in a vacuum desiccator. Yield 2.97 g (99%) (Found: C, 38.4; H, 7.0; N, 1.8; O_2^{2-}, 11.2. Calc. for $C_{72}H_{156}AsN_3O_{24}W_4$: C, 38.3; H, 7.0; N, 1.9; O_2^{2-}, 11.3%).

Prepared similarly were: $[N(PPh_3)_2]_3[AsO_4\{WO(O_2)_2\}_4]$ as a white solid, yield 3.71 g (99%) (Found: C, 45.9; H, 3.0; N, 1.2; O_2^{2-}, 9.0. Calc. for $C_{108}H_{90}AsN_3O_{24}P_6W_4$: C, 46.2; H, 3.2; N, 1.5; O_2^{2-}, 9.1%) and $[Co(en)_3][AsO_4\{WO(O_2)_2\}_4]$ as an amber solid, yield 1.46 g (76%) (Found: C, 5.6; H, 1.7; N, 6.3. Calc. for $C_6H_{24}AsCoN_6O_{24}W_4$: C, 5.0; H, 1.7; N, 5.9%).

$[N(C_6H_{13})_4]_3[PO_4\{MoO(O_2)_2\}_4]$ **3**. Molybdenum trioxide (1.44 g, 10.0 mmol) was dissolved in water (15 cm^3) and 30% H_2O_2 (7 cm^3) at 60 °C to give a bright yellow solution, which was cooled to ambient temperature and Na_2HPO_4 (0.36 g, 2.5 mmol) dissolved in water (5 cm^3) added. A solution of $N(C_6H_{13})_4Cl$ (1.56 g, 4.0 mmol) in benzene (20 cm^3) was added over a period of 2 min. The biphasic mixture was stirred vigorously at room temperature for 2 h, during which time a pale yellow precipitate of compound **3** had formed at the interface. The solid was collected, washed with water (2 × 10 cm^3), benzene (2 × 10 cm^3) and diethyl ether (2 × 10 cm^3), air dried and stored in a vacuum desiccator. Yield: 2.31 g (93%) (Found: C, 46.1; H, 8.4; N, 2.3; P, 1.9; O_2^{2-}, 13.4. Calc. for $C_{72}H_{156}Mo_4N_3O_{24}P$: C, 46.4; H, 8.4; N, 2.3; P, 1.7; O_2^{2-}, 13.7%).

Prepared similarly were: $[N(PPh_3)_2]_3[PO_4\{MoO(O_2)_2\}_4]$ as a pale yellow solid, yield 2.82 g, (88%) (Found: C, 53.5; H, 3.6; N, 1.8; O_2^{2-}, 10.3. Calc. for $C_{108}H_{90}Mo_4N_3O_{24}P_7$: C, 53.7; H, 3.8; N, 1.7; O_2^{2-}, 10.6%) and $[Co(en)_3][PO_4\{MoO(O_2)_2\}_4]$ as an amber solid, yield 1.11 g, (80%) (Found: C, 6.9; H, 3.0; N, 8.2. Calc. for $C_{72}H_{156}Mo_4N_3O_{24}P$: C, 6.9; H, 2.3; N, 8.1%).

$[N(C_6H_{13})_4]_3[AsO_4\{MoO(O_2)_2\}_4]$ **4**. Molybdenum trioxide (1.44 g, 10.0 mmol) was dissolved in water (15 cm^3) and 30% H_2O_2 (7 cm^3) at 60 °C to give a bright yellow solution, to which upon cooling was added $Na_2HAsO_4{\cdot}7H_2O$ (0.78 g, 2.5 mmol) dissolved in water (5 cm^3). A solution of $N(C_6H_{13})_4Cl$ (1.56 g, 4.0 mmol) in benzene (20 cm^3) was added over a period of 2 min. The biphasic mixture was stirred vigorously at room temperature for 2 h, during which time a pale yellow precipitate of compound **4** formed at the interface. The solid was filtered off, washed successively with water (2 × 10 cm^3), benzene (2 × 10 cm^3), diethyl ether (2 × 10 cm^3), then air dried and stored in a vacuum desiccator. Yield 2.48 g (98%) (Found: C, 45.3; H, 8.2; N, 2.2; O_2^{2-}, 13.2. Calc. for $C_{72}H_{156}AsMo_4N_3O_{24}$: C, 45.4; H, 8.3; N, 2.2; O_2^{2-}, 13.4%).

Prepared similarly were: $[N(PPh_3)_2]_3[AsO_4\{MoO(O_2)_2\}_4]$ as a pale yellow solid, yield 3.25 g (88%) (Found: C, 53.6; H, 3.3; N, 1.7; O_2^{2-}, 10.2. Calc. for $C_{108}H_{90}AsMo_4N_3O_{24}P_6$: C, 53.1; H, 3.7; N, 1.7; O_2^{2-}, 10.4%) and $[Co(en)_3][AsO_4\{MoO(O_2)_2\}_4]$ as an amber solid, yield 0.94 g (64%) (Found: C, 6.7; H, 2.9; N, 8.0. Calc. for $C_6H_{24}AsCoMo_4N_3O_{24}$: C, 6.7; H, 2.4; N, 7.8%).

Catalytic Epoxidation of Alkenes by Compound **1** *with* H_2O_2.—In a typical experiment, cyclooctene (2.2 g, 20 mmol) and compound **1** (0.15 g, 0.07 mmol) were dissolved in benzene (5 cm^3) and the solution mixed with 15% H_2O_2 (7 cm^3). The two-phase mixture was stirred vigorously for 3 h at 75 °C under reflux conditions. After cooling, a sample from the organic layer was analysed by ^1H NMR spectroscopy and/or injected directly into a Perkin Elmer gas chromatograph.

Large-scale Epoxidations.—*Cyclooctene by compound* **1**. Cyclooctene (5.51 g, 50 mmol) and compound **1** (0.15 g, 0.07 mmol) were dissolved in benzene (8 cm^3) and the solution mixed with 15% H_2O_2 (10 cm^3). The biphasic mixture was stirred vigorously for 3 h at 75 °C under reflux conditions. After cooling the organic layer was separated, washed with benzene (2 × 10 cm^3), dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo* to afford large colourless crystals of cyclooctene oxide. Yield 5.86 g, (93%); m.p. 54–56 °C.

Cyclooctene by compound **2**. Cyclooctene (5.51 g, 50 mmol) and compound **2** (0.15 g, 0.07 mmol) were dissolved in benzene (8 cm^3) and the solution mixed with 15% H_2O_2 (10 cm^3). The biphasic mixture was stirred vigorously for 3 h at 75 °C under reflux conditions. After cooling, the organic layer was separated, washed with benzene (2 × 10 cm^3), dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo* to give large colourless crystals of cyclooctene oxide. Yield 5.89 g (95%); m.p. 54–56 °C.

Cyclododecene by compound **2**. Cyclododecene (mixture of *cis* and *trans* isomers) (8.22 g, 50 mmol) and compound **2** (0.15 g, 0.07 mmol) were dissolved in benzene (8 cm^3) and the solution mixed with 15% H_2O_2 (10 cm^3). The biphasic mixture was stirred vigorously for 3 h at 75 °C under reflux conditions. After cooling, the organic layer was separated, washed with benzene (2 × 10 cm^3) dried over anhydrous $MgSO_4$ and the solvent removed *in vacuo* to give a colourless liquid of cyclododecene oxide (mixture of *cis* and *trans* isomers). Yield 8.56 g (95%).

Catalytic Oxidation of Primary Alcohols by Compound **1** *with* H_2O_2.—In a typical experiment, compound **1** (0.075 g, 0.03 mmol) and benzyl alcohol (2.00 g, 18.5 mmol) were dissolved in benzene (5 cm^3) and the solution mixed with 15% H_2O_2 (4 cm^3). The biphasic mixture was stirred vigorously for 3 h at room temperature, after which time a sample from the organic layer was removed and analysed by ^1H NMR spectroscopy.

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