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Epoxidation of allylic alcohols by hydrogen peroxide in the presence of complexed peroxotungstic species

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Abstract

Peroxotungstic acid and quaternary ammonium peroxotungstic salts when complexed to organophosphorus(V) ligands exhibit enhanced reactivity and selectivity in the epoxidation of unsaturated alcohols with hydrogen peroxide. The organophosphorus ligands contain the phosphoryl O=P≡ subunit as complexing moiety and are related to phosphine oxide, arylphosphonic acid and acidic phosphate ester. Allylic and cinnamic alcohols were examined under homogeneous and biphasic liquid–liquid conditions.

Keywords: Allylic alcohols; Amine oxide; Epoxidation; Hydrogen peroxide; Peroxotungstic; Phosphine oxide; Phosphonic acid; Tungsten

1. Introduction

The epoxidation of olefins with molybdenum, vanadium and titanium based catalysts with organic hydroperoxides as external oxidant is a well documented area [1].

However, hydrogen peroxide is a valuable reagent due to its low cost and the absence of effluents problems; in that particular case, tungsten-based catalysts appeared as most convenient [2,3] but their uses as catalysts in the epoxidation of allylic alcohols is quite unusual; this appeared to be mainly due to extensive hydrolysis to the corresponding diols.

To improve the selectivity of peroxotungstic-based catalysts, we first devised catalytic systems for the epoxidation of simple olefins where the tungstic species are complexed with organophosphorus ligands [4]. These ligands are organophosphorus(V) derivatives containing the phosphoryl moiety, O=P≡, as a general substructure. They are related to phosphine oxides, phosphoramides and phosphonic acids.

The corresponding complexes formed with peroxotungstic species proved to be excellent catalysts: they exhibit high efficiency in terms

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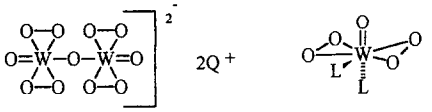


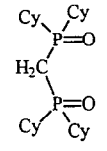
1 Q = H^+ $AliQ^+$

2 Q = $(AliQ^+)_2$

3 Q = $(PhCH_2PPh_3^+)_2$

4b L = OPOct3

7b L,L'= **5a, 6a, 7a,** H_2O



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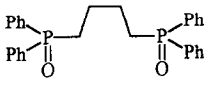

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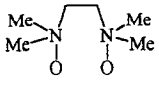

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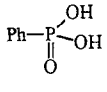

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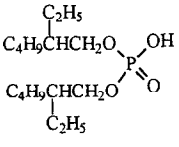

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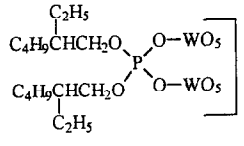

9b

Fig. 1. Ligands and related peroxotungstic salts and complexes.

of kinetics and selectivity [4,5]. The solubility of the catalysts in organic media was ensured by the use of Aliquat™, a lipophilic quaternary ammonium salt [1]. In some instances, it was possible to isolate and characterize the ammonium peroxo salts.

[1] Trioctylmethylammonium chloride, or Aliquat™, is referred to as $AliQ^+Cl^-$ throughout this paper; tetrabutyl ammonium chloride gave $(NBu_4)_2W_2O_{11}$ or $NBu_4HW_2O_{11}$ crystals through procedures modified from that given [6] for the triphenylbenzyl phosphonium salt **3**. All these salts are soluble in the solvent systems reported here.

On the other hand, the efficiency of the asymmetric epoxidation of allylic alcohols according to the Sharpless method [6,7] opened new synthetic pathways for the preparation of homochiral synthons useful to obtain biologically active compounds. We found, in a preliminary experiment, a very fast and clean reaction in the epoxidation of geraniol to its 2,3-epoxide with a turnover frequency = 286 h^{-1} [4].

This prompted us to examine our catalytic systems with unsaturated alcohols in order to perform the reaction later on with chiral ligands. *N'N"*dioxides of diamines have also been examined as potential ligands as chiral amines and diamines are widely used as inductors in several asymmetric procedures.

The complexing ligands which were examined are mono- and diphosphine oxides: trioctylphosphine oxide **4a**, methylene bis(dihexylphosphine oxide) **5a**, 1,4-bis (diphenylphosphino)butane dioxide **6a**. The phosphonic acid **8a**, the di(2-ethylhexyl) phosphoric acid **9a**, and the diamine–dioxide **7a**, were also examined (Fig. 1).

These ligands are either commercial products or were obtained by oxidation of the corresponding free phosphine or amine with hydrogen peroxide.

2. Experimental

The epoxidations of cinnamyl- and 2-propenyl alcohols were examined in homogeneous conditions in dioxane or in a biphasic system under phase transfer conditions with dichloromethane or 1,2-dichloroethane as solvents. To avoid side reactions, the olefinic compound was generally introduced in a 5/1 excess versus 30% or 70% aqueous solutions of hydrogen peroxide. There is no known report of a possible influence in the epoxidation process of the 0.005% of sodium stannate used as a stabilizer; the W/Sn ratio is higher than 20.

IRFT data were obtained with a IFS48 Brucker spectrometer; ^1H and ^{31}P NMR spectra

were obtained at room temperature in 5 mm o.d. tubes, either on an AM300 (300 and 121.5 MHz, respectively) or an AC200 (200 and 80 MHz, respectively) Bruker spectrometer. Chemical shifts, in ppm, are referred to TMS or external 85% H_3PO_4.

^{183}W spectra have been obtained at room temperature either on an AC300 (12.5 MHz) or an AM 500 (20.8 MHz) Bruker spectrometers. Concentrated solutions in 1-2-dichloroethane/CD_3CN(90/10, v/v) or 1-2-dichloroethane/CD_2Cl_2(90/10, v/v) were examined in 10 mm o.d. tubes. Chemical shifts in ppm are referred to an external aqueous solution of Na_2WO_4 in D_2O; negative δ values correspond to resonances at low frequency to the reference. All spectrometers operate in the Fourier mode.

2.1. Reference compounds

Glycidol (1,2-epoxypropan-3-ol) is commercially available; phenylglycidol (1-phenyl 1,2-epoxypropan-3-ol) was obtained as follows: 4 g (30 mmol) of cinnamic alcohol in 30 mL chloroform were stirred with 100 mL of 10% $NaHCO_3$; a solution of 8.14 g (33 mmol) of metachloroperbenzoic acid in 70 mL chloroform was added dropwise under efficient stirring with an external cooling. The mixture was allowed to stand at room temperature for 45 min then decanted, washed with water and finally dried over $MgSO_4$. The filtrate was evaporated and the residual oil was purified by flash chromatography on silicagel with a 85/15 cyclohexane/ethyl acetate mixture as solvent. Yield 2.78 g (62%, oil). ^1H NMR ($CDCl_3$, ppm): 7.28 (s, 5H, arom); 3.88 (m, 3H, CH_2–O, epoxyde); 3.17 (m, 1 H); 1.41 (s, 1H, OH).

The usual source of tungsten was a 0.9 M (in g/atom of W) aqueous solution of peroxotungstic acid, $H_2W_2O_{11}$, obtained by dissolving 25 g of tungstic acid ('light' acid from Eurotungstene) in 100 mL of 30% H_2O_2: the suspension was gently heated for three hours at 40°C, the cloudy solution was centrifuged and the content of W was determined by colorimetry [8] or elemental analysis.

2.2. Preparation of the ligands

The phosphorus ligands **4a**, **5a** and **8a** are commercial products, **9a** is a gift from Mobil Chemicals, the others were obtained as follows:

1,4-bis(diphenylphosphino)butane P,P'dioxide **6a**: 3 mL (30 mmol) of 30% H_2O_2 are added to a suspension of 2.13 g (5 mmol) of 1,4-bis(diphenylphosphino)butane in 70 mL of toluene. The well stirred mixture was refluxed for 2 h and allowed to cool in a refrigerator; the crystals were collected and rinsed with water and pentane; yield 90%; mp > 265°C; elemental analysis, calc. for $C_{28}H_{28}O_2P_2$ (MW = 458.5); C 73.35, P 13.51; found C 73.36, P 13.24. IR(KBr pellet, cm^{-1}) 1185, 1175 ν(P–O); ^{31}P NMR (dioxane, ppm/ext. 85% H_3PO_4) + 32.6.

1,2-bis(dimethylamino)ethane N,N'-dioxide **7a**: 3 g (2.59 mmol) of *N,N,N',N'*-tetramethyl ethylenediamine in 3 mL methanol were slowly added with stirring to 10 mL (100 mmol) of 30% H_2O_2 and the mixture was refluxed for 3 h. After cooling, about 200 mg of ground manganese dioxide was added and the mixture was stirred at RT overnight to ensure a complete decomposition of the excess of H_2O_2. The filtrate was evaporated, the residual oil was dissolved in absolute ethanol and ethyl acetate was carefully added as an upper phase. The hygroscopic crystals were collected and dried under vacuum; yield 4.25 g (75%). Elemental analysis for $C_6H_{16}N_2O_2 \cdot 4H_2O$ (MW = 220.2); calc. C 32.72 N 12.72 O 43.58 found C 33.71 N 12.65 O 42.50; IRFT(KBr pellet, cm^{-1}) 1700, 1653, 1636 (H_2O), 1484, 1467, 1459, 1446, 1400, 1385, 1290, 1180, 971 ν(NO), 945, 820, 754; ^1H NMR (D_2O) 3.74 (s, 4H, CH_2–N) 3.12 (s, 12H, CH_3–N).

2.3. Preparation of the catalysts

The ammonium salts **1** and **2** were obtained in solutions as described [4], the phosphonium

salt **3** was prepared according to Ref. [9]. Catalysts from ligands **5a** and **6a** were formed in-situ.

*2.3.1. Trioctylphosphine oxide–peroxotungstic oxide **4b***

To a solution of 2.2 mmol (850 mg) of trioctylphosphine oxide (TOPO) **4a** in 5 mL of dioxane, 1 mL (1 mmol) of a solution of peroxotungstic acid was added with efficient stirring. The oily phase was separated and washed with small amounts of water and then with methanol. Residual solvents were eliminated by prolongated heating at 50°C under the vacuum of an oil pump. Solidification occurred after storing in a refrigerator (660 mg, 73% yield). Elemental analysis for $C_{24}H_{51}PO \cdot WO_5 \cdot 2C_{24}H_{51}PO$ (MW = 1423.7); calc P 6.53; W 12.91; found C, P 6.40, W 13.08; iodometry: 1.95 active oxygen per mole; ^{31}P NMR ($CDCl_3$, ppm) + 81 (1P, complexed ligand, tungstem satellites; $^2J_{W-P} = 11$ Hz), +55 (2P, free ligand). ^{183}W NMR(1,2-dichloroethane/CD_3CN, ppm) −544 (d, $J = 11$ Hz).

*2.3.2. N,N,N′,N′-tetramethyl ethylenediamine N,N′-dioxide-peroxotungstic oxide **7b***

To a solution of 780 mg (5 mmol) of the ligand **7a** in 2 mL water, was added 5.5 mL (5 mmol) of a solution of $H_2W_2O_{11}$; then dioxane (15 mL) was carefully added as an upper phase and was allowed to crystallize for several days. The solid **7b** (yield 25%), was collected and dried under vacuum at 45°C; elemental analysis for $C_6H_{16}N_2O_7W$, $2H_2O$ (MW = 448.1); calc, C 16.08; N 6.25; W 41.04; found C 16.11; N 6.14; W 40.1; iodometry: 1.92 active oxygen per mole; IRFT(KBr pellet, cm^{-1}) 1632(H_2O), 1476, 1462, 915 ν(N–O), 965 ν(W=O), 834 ν(O–O), 733, 698, 627 and 603 ν(W < OO sym), 552 and 513 ν(W < OO sym); ^{1}H NMR (D_2O) 4.30 (s, 4H, CH_2–N) 3.44 (s, 12H, CH_3–N).

*2.3.3. Tetrabutylammonium phenylphosphonatoperoxoditungstate **8b***

13 mL (20 mmol) of a 40% solution of tetrabutylammonium hydroxyde were diluted to 100 mL with water and 1.58 g (10 mmol) of phenylphosphonic acid **8a** were added; then 20 mL (20 mmol of W) of a solution of $H_2W_2O_{11}$ were added dropwise to the clear solution. The flaky solid which formed was collected, rinsed with cold water and dried under vacuum at 45°C; yield 7.23 g, 62%.

An analytical sample was recrystallized from 1,2-dichloroethane/EtOAc. Elemental analysis for $C_{38}H_{77}N_2O_{13}PW_2$ (MW = 1167.69); calc C 39.05; N 2.4; W 31.46; P 2.65.; found C 38.93; N 2.4; W 31.45; P 2.64; iodometry: 4.1 active oxygen per mole; IR(KBr pellet, cm^{-1}) 960 (νW = O), 835 (νO–O) 645; ^{31}P NMR (1,2-dichloroethane/CD_2Cl_2, ppm): +11.34 (tungsten satellites, $^2J_{P-W} = 10.3$ Hz, 2W, relative area of the doublet 28%); ^{183}W NMR (1,2-dichloroethane/CD_2Cl_2, ppm) −624.6 (d, $^2J_{P-W} = 10.3$ Hz).

*2.3.4. Tetrabutylammonium di(2-ethylhexyl)phosphatodiperoxotungstate **9b***

The ammonium salt of di(2-ethylhexyl)phosphoric acid (DEHPA) **9a** was first obtained from 2.6 g (4 mmol) of tetrabutylammonium hydroxide in 5 mL water and 1.3 g (4 mmol) of DEHPA in 2 mL 1,2-dichloroethane; after efficient stirring, the aqueous solution was discarded; a sample of the organic phase was dried over molecular sieves and evaporated for ^{31}P NMR spectroscopy (+0.6 ppm $CDCl_3$). Then 8 mL (8 mmol) of a solution of $H_2W_2O_{11}$ was added dropwise to the well stirred solution of the ammonium salt; the supernatant aqueous phase was discarded and the organic phase was dried over magnesium sulfate, filtered and evaporated under vacuum to give a fluffy solid **9b**, 2.5 g (77%); elemental analysis for $C_{32}H_{70}NO_{14}PW_2$ (MW = 1091.56) C 35.21; N 1.28; P 2.84; W 33.69; found C 38.80; N 1.26; P 3.20; W 31.89 (presence of traces of free ligand). Iodometry: 3.91 active oxygen per mole; IR (nujol mull, cm^{-1}) 1240 ν(P=O), 960 ν(W=O), 835 ν(O–O), 580 ν(W–O); ^{31}P NMR (CD_3CN, ppm) −6.4 (tungsten satellites); ^{183}W

(1,2-dichloroethane/CD_2Cl_2, ppm) −477.4 (d, $^2J_{P-W}$ = 11 Hz).

2.4. Epoxidation procedure

The reactions were run in a 250 mL glass reactor fitted with a nitrogen inlet and a reflux condenser. The solvent (30 mL), the olefin (100 mmol), the catalytic system (an isolated compound or the mixture of components) at 0.005 mol equivalent versus hydrogen peroxide, and the internal standard were added; the mixture was heated to the required temperature; then 25 mmol of 30% (when biphasic) or 70% (when homogeneous) hydrogen peroxide was slowly added by means of a syringe.

For allylic alcohol, the reactions were monitored by GLC on a Carlo Erba Fractovap apparatus fitted with a 2.5 m 10% Carbowax 20M column at 150°C and anisole as internal standard; for cinnamic alcohol, the reactions were monitored by HPLC on a 5μ Lichrospher-60 column with a L6200 Merck pump, a L4000 Merck UV detector and a 1/1 acetonitrile/water mixture as solvent at 1 mL min^{-1}; neroline was used as internal standard.

3. Results and discussion

3.1. Catalysts

The catalysts were prepared from a solution of the phosphorous ligands (those reported in Fig. 1) and an aqueous solution of peroxotungstic acid '$H_2W_2O_{11}$'; the latter is in fact a mixture of peroxomonotungstic (WO_8^{2-}, WO_7^{2-}) and diperoxoditungstic anions ($W_2O_{11}^{2-}$) in equilibrium as shown by Griffith [10,11]. With non-ionic ligands, the procedures were roughly the same as that given by Mimoun [12]; these ligands cleaved all the W–O–W bounds, when present, to give complexes with separated WO_5 units.

The diamine–dioxide **7a** gave the complex **7b** which was labile in water as shown by its ^1H NMR spectra in D_2O: the signals at 4.30 (CH_2–N) and 3.44 (CH_3–N) were shifted to the averaged values at 4.03 and 3.30 ppm, respectively, when a small amount of the free ligand **7a** (signals at 3.74 and 3.12 ppm) was added.

Mono- and bidentate ligands gave complexes which could not be isolated as crystals; their structures are expected to be pentagonal bipyramids (**4b** and **7b**) in analogy with known peroxotungstic structures [13–16]. The complexes were formed in-situ for epoxidation experiments.

Complexing anions behaved differently; with phosphoric acid itself, Venturello [13,17,18] isolated the complex salt $[PW_4O_{24}]^{3-}[Q^+]_3$ from $H_2O_2/Na_2WO_4/H_3PO_4$ mixtures. Epoxidations with this complex were also examined by Brégeault [19]; it was shown that the $[PW_4O_{24}]^{3-}$ anion was not the only catalytic operating species as complexes with lower degree of condensation were detected in solution [20]; some complexes with a P/W = 2 were isolated [21] [22].

The situation was more confusing when non-peroxo tungsten-based heteropolyanions (HPA) such as $[PW_{12}O_{40}]^{3-}$ were used, by Ishii, as catalysts with hydrogen peroxide [23–25]. Brégeault established by spectroscopy the outcoming of several smaller peroxo species [21,22]; this was also shown by electrochemical studies [26]. Khenkin, however, claimed that in some cases, the HPA structure may survive in the presence of hydrogen peroxide [27,28]. Recently, Hill assumed that during an epoxidation process, the PW_4 framework reformed continuously from smaller peroxo and non-peroxo species [29].

Very interestingly, phenyl phosphonic acid **8a** gave the peroxoditungstic complex **8b** which exhibited efficiencies by far higher than those reported for the Venturello and Ishii systems [4,5]. The structure of **8b** has been determined (for full structure of complex **8b**, see Ref. [30]) (Fig. 2).

This structure consists of two distorted $W(O_2)_2O$ pentagonal bipyramids, in edge shared

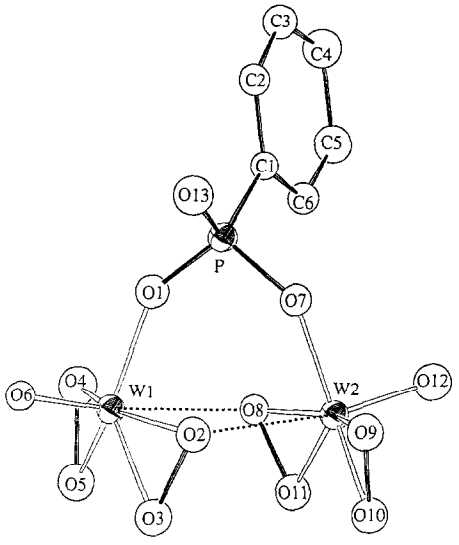

Fig. 2. Structure of complex **8b**.

pairs and bridged by the C_6H_5–PO_3 group. This structure is reminiscent to that of the $[PW_4O_{24}]^{3-}$ anion which contains four $W(O_2)_2O$ units around the P atom [13] and to that of analogous phosphonatomolybdenum [31] and arsenatotungsten [32] peroxoanions.

Like trioctylphosphine oxide, di(2-ethylhexyl) phosphoric acid, DEHPA, **9a** is also a metal cations extractant [33]; it gave the anionic diperoxotungstic complex **9b** in the form of an amorphous powder, the elemental analysis of which revealed small amounts of free ligand.

The ^{31}P NMR chemical shifts of the isolated complexes spectra appeared downfield from that of the corresponding free ligand. The signals of the complexes exhibited tungsten satellites (^{183}W; $I = 1/2$, natural abundance 14.28 atoms %) with $^2J_{P-W}$ couplings in the range of 10 Hz.

For **8b** and **9b**, the integration of the satellite signals confirms unambiguously the W–O–P–O–W substructure; the ^{183}W NMR showed doublets ($^2J_{P-W}$ about 10 Hz) in the -400 -600 ppm range, typical for peroxotungstic species.

These are the first examples of phosphonic and *organo*–phosphoric species complexed to the peroxo form of tungstic acid.

When well defined complexes could not be isolated, the catalytic systems were formed in-situ by mixing appropriate amounts of peroxotungstic acid and oniums; this was the case of the salts **1** and **2** obtained with $AliQ^+$ [1].

Table 1
Epoxidation [a] of allyl alcohol at room temperature

Entry	Catalytic system	Olefin/H_2O_2	Solvent	Time (h)	Yield (%) (TOF) [b]
1	**2**	2/5	biph. [c]	70	25(0.4)
2	**2**	2/1.3	biph.	24	25(1)
3	**3**	2/1.3	dioxane	72	15(0.2)
4	**2** + **4a**	2/5	biph.	70	84(1.2)
5	**2** + **4a**	2/1.3	biph.	72	20(0.2)
6	**4b**	2/1	biph.	3	12(4)
7	**7b**	2/1	biph.	1	53(53)
8	**8b**	2/1	dioxane	24	59(2.5
9	**8b**	2/1	biph.	0.5	40(80)
10	**9b**	2/1	biph.	9	50(5.6)
11	$H_2WO_4 + Et_3N$ [d]	1.1/1	H_2O	21	55(5.8)
12	$NaHWO_4$ [e]	1/2	H_2O	5	78(4.4)
13	$H2WO_4 + Et_3NO$ [f]	1/5	H_2O	5	80(4)
14	$PW_{12}O_{40}(Q^+)_3$ [g]	2/3	biph.	4	96(5)

[a] In dioxane with 70% H_2O_2 or in a biphasic system with 30% H_2O_2.
[b] Yield in epoxide calculated from consumed H_2O_2, TOF = turnover frequency = moles of epoxide formed per mole of catalyst per hour.
[c] Biph. = biphasic system: 1,2-dichloroethane/water.
[d] Ref. [34].
[e] Ref. [35].
[f] Ref. [36].
[g] Ref. [24].

3.2. Epoxidations

The results on the epoxidation of allylic alcohol with hydrogen peroxide are given in Table 1, and compared to the epoxidations reported with other catalytic systems of allylic alcohol (entries 11 and 12), crotyl (entries 12 and 13) and *iso*butenyl alcohols (entry 14).

Moderate yields were obtained with the onium salt **2** and **3** (entries 1–3) whatever the solvent system used; due to the basicity of these salts, hydrogen peroxide decomposed to some extent. But addition of *one* equivalent of the phosphine oxide **4a** gave a very reactive catalytic system (entry 4) if an excess of olefin was provided.

The amine oxide derived complex **7b** (entry 7) is significantly more reactive (turnover frequency, TOF = 53) than the phosphine oxide **4b** (entry 6, TOF = 4); this is promising for the use of chiral diamines as precursors of chiral complexes for the asymmetric epoxidation.

It should be noted that when triethylamine *N*-oxide was used to buffer the acidity of the reaction mixture [36,37], it was possible that the true catalyst involved was a *N*-oxide complex similar to **7b**. The same event might have occurred in the original tungstic acid system of Raciszewski with triethylamine as a base [34], as *N*-oxides are readily formed in the acidic conditions provided by the free peroxotungstic acid. A menthol derivated *N*-oxide has been checked as a chiral ligand in the stoichiometric epoxidation with peroxomolybden compounds [38].

Even higher TOF were obtained with the phosphato- and phosphonatoperoxotungstate salts **8b** and **9b** in biphasic systems (entries 8–10).

These results seem related to the high lipophilic character of these salts where both the anionic *and* the cationic part of the complex are organic. During the reaction they are essentially concentrated in the organic phase and the transfer of the mono- or non-peroxo form back from

Table 2
Epoxidation [a] of cinnamyl alcohol at 70°C [b]

Entry	Catalytic system	Solvent	Time (h)	Epoxide (%) (aldehyde)	TOF [c]
1	**1**	dioxane	42 [d]	20(nd)	0.5
2	**3**	dioxane	7	24(15)	3.4
3	**1 + 4a**	dioxane	21	30(—)	1.4
4	**1 + 4a**	dioxane	8	21(—)	2.6
5	**3 + 4a**	dioxane	7	35(22)	5
6	**3 + 5**	dioxane	7	40(24)	5.7
7	**2 + 6**	dioxane	4	33(20)	5
8	**2 + 8a**	dioxane	24	15(0)	0.6
9	**7b**	dioxane	24	34(0)	1.4
10	**7b**	iPrOH [e]	5	31(0)	6.2
11	**8b**	dichl. [f]	30 [d]	26(0)	0.9
12	**8b**	dioxane	31 [d]	36(0)	1.2
13	**8b**	dioxane	23	28(0)	1.2
14	**8b**	dichl. [f]	23	55(0)	2.4
15	$H_2WO_4 + Me_3NOg$)	H_2O	16 [d]	57(nd)	1

[a] With a ratio olefin/H_2O_2 = 2/1.
[b] Unless reported.
[c] TOF = turnover frequency as defined in Table 1.
[d] At RT.
[e] iPrOH = 2-propanol.
[f] dichl. = 1,2-dichoroethane.
[g] Ref. [36].

the aqueous hydrogen peroxide phase ensures the regeneration of the diperoxo form. [2]

When compared to similar values reported in the literature (entries 11–14), the yields reported here are in the same range but the TOF are significantly higher by one order of magnitude.

The epoxidation of cinnamyl alcohol was performed in the same conditions with almost the same series of catalysts as above. The results reported in Table 2 showed that the quaternary onium peroxosalts **1** and **3** required heating or prolongated reaction time to give significant amounts of epoxide (entries 1–2).

When making the complexes in-situ with the neutral ligands **4a** and **5a**, the yield and the turnovers were significantly improved even if some benzaldehyde formed as a cleavage product (entries 3–7); an excellent selectivity was found with the acid **8a** though the turnover remained moderate (entry 8).

Interestingly, the isolated complexes **7b** and **8b** gave no cleavage products at all (entries 9–14) and the use of a biphasic system gave even a better yield (entry 14).

Though the yields were in the same range as those obtained by Lett [36,37] in aqueous solution (entry 15), the TOF reported here are much higher.

As no phenylglycerol was detected, it could be assumed that no hydrolysis occurred, due to the low acidity of the reaction medium (pH > 5); but the presence of benzaldehyde, which resulted from cleavage reactions, revealed the transitional formation of phenylglycerol and/or of hydroxyhydroperoxide [40].

4. Conclusions

Phosphorus ligands related to organic derivatives of P(V) are very good complexing species for peroxotungstic acid and its onium salts. The corresponding complexes are better catalysts for the epoxidation of allylic alcohols than those previously reported.

This confirms also the superiority of P(V) derived organic ligands for the preparation of well defined peroxotungstic complexes. A careful choice of phosphoryl containing ligands is expected to afford further tunings of the chemo- and the stereoselectivity in the epoxidation with hydrogen peroxide.

[2] (with very lipophilic species, inverted micelles were involved preferentially to a classical phase-transfer catalysis [39])

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References

[1] R.A. Sheldon, in: Peroxides, S. Patai (Ed.) (J. Wiley, New-York, 1983) p. 161.
[2] R.A. Sheldon, in: Aspects of Homogeneous Catalysis, R. Ugo (Ed.), Vol. 4 (Reidel, Dordrecht, 1991) p. 3.
[3] R.A. Sheldon, J. Mol. Catal. 7 (1980) 107.
[4] M. Quenard, V. Bonmarin and G. Gelbard, Tetrahedron Lett. 28 (1987) 2237.
[5] M. Quenard, V. Bonmarin and G. Gelbard, Nouv. J. Chim. 13 (1989) 183.
[6] B.E. Rossiter, Asymmetric Synthesis, J.D. Morrison (Ed.), Vol. 5 (Academic Press, New-York, 1985) p. 194.
[7] M.G. Finn and K.B. Sharpless, Asymmetric Synthesis, J.D. Morrison (Ed.), Vol. 5 (Academic Press, New-York, 1985) p. 247.
[8] G. Charlot, Les Méthodes de la Chimie Analytique: Analyse Quantitative Minérale (Masson, Paris, 1966) p. 551.
[9] J. Prandi, H.B. Kagan and H. Mimoun, Tetrahedron Lett. 27 (1985) 2617.
[10] W.P. Griffith, J. Chem. Soc. (1963) 5345.
[11] N.J. Campbell, A.C. Dengel, C.J. Edwards and W.P. Griffith, J. Chem. Soc., Dalton Trans. (1989) 1203.
[12] H. Mimoun, I. Serée de Roch and L. Sajus, Bull. Soc. Chim. Fr. (1969) 1491.
[13] C. Venturello, R. D'Aloisio, J.C.J. Bart and M. Ricci, J. Mol. Catal. 32 (1985) 107.

[14] Z. Ruzic-Toros, B. Kojic-Prodic, F. Gabela and M. Sljukic, Acta Cryst. 33B (1977) 692.
[15] R. Stomberg, Acta Chem. Scand. 39A (1985) 507.
[16] R. Stomberg, J. Less-Comm. Met. 143 (1988) 363.
[17] C. Venturello, R. D'Aloisio and M. Ricci, European Patent 109.273 (1983).
[18] C. Venturello and R. D'Aloisio, J. Org. Chem. 53 (1988) 1553.
[19] C. Aubry, G. Chottard, N. Platzer, J.M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet and H. Ledon, Inorg. Chem. 30 (1991) 4409.
[20] J.M. Brégeault, C. Aubry, G. Chottard, N. Platzer, F. Chauveau, C. Huet and H. Ledon, in: Dioxygen Activation and Homogeneous Catalytic Oxidation, L.I. Simandi (Ed.) (Elsevier, Amsterdam, 1991) p. 521.
[21] J.M. Brégeault, R. Thouvenot, S. Zoughebi, L. Salles, A. Atlamsani, E. Duprey, C. Aubry, F. Robert and G. Chottard, New Developments in Selective Oxidation II, V. Cortès Corberan and S. Vic Bellon (Eds.) (Elsevier, 1994) pp. 571–581.
[22] L. Salles, C. Aubry, R. Thouvenot, F. Robert, C. Dorémieux-Morin, G. Chottard, H. Ledon, Y. Jeannin and J.M. Brégeault, Inorg. Chem. 33 (1994) 871.
[23] T. Ogushi, Y. Sakata, N. Takeuchi, K. Kaneda, Y. Ishii and M. Ogawa, Chem. Lett. (1989) 2053.
[24] Y. Ishii and Y. Sakata, J. Org. Chem. 55 (1990) 5545; 52 (1987) 1868.
[25] Y. Sakata, Y. Katayama and Y. Ishii, Chem. Lett. (1992) 671.
[26] B. Keita, D. Bouaziz and L. Nadjo, Electroanalysis 3 (1991) 637.
[27] A.M. Khenkin and C.L. Hill, Mendel. Commun. (1993) 140.
[28] R. Neumann, M. Gara and A. Khenkin, Poster C-1, 9th Int. Symp. Homog. Catal., Jerusalem (1994).
[29] D.C. Duncan, R.C. Chambers, E. Hechst and C.L. Hill, J. Am. Chem. Soc. 117 (1995) 681.
[30] G. Gelbard, M. Quenard, F. Raison, L. Ouahab, D. Granjean and R. Thouvenot, in preparation.
[31] W.P. Griffith, B.C. Parkin, A.J.P. White and D.J. Williams, J. Chem. Soc., Dalton Trans. (1995) 313.
[32] J.Y. Piquemal, L. Salles, C. Bois, F. Robert and J.M. Brégeault, C.R. Acad. Sci. Paris, Ser. II, 319 (1994) 1481.
[33] DEHPA Extractant, Mobil Chemical Company, Product Information Bull. No. 081201 (1981).
[34] Z. Raciszewski, J. Am. Chem. Soc. 82 (1960) 1267.
[35] V.N. Sapunov and N.N. Lebedev, J. Org. Chem. USSR 263 (1966) 263.
[36] D. Prat and R. Lett, Tetrahedron Lett. 27 (1986) 707.
[37] D. Prat, B. Delpech and R. Lett, Tetrahedron Lett. 27 (1986) 711.
[38] O. Bortolini, F. Di Furia, G. Modena and A. Schionato, J. Mol. Catal. 35 (1986) 47.
[39] R. Neumann and A.M. Khenkin, J. Org. Chem. 59 (1994) 7577.
[40] W. Adam and A. Rios, J. Chem. Soc., Chem. Commun. (1971) 822.