investigating a π-system (15) containing the cyclobutadiene ring.

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Supplementary Material Available: Tables II and III containing calculated $\Delta H_f°$ values and geometries (6 pages). Ordering information is given on any current masthead page.

Metal Catalysis in Oxidation by Peroxides.[1] Sulfide Oxidation and Olefin Epoxidation by Dilute Hydrogen Peroxide Catalyzed by Molybdenum and Tungsten Derivatives under Phase-Transfer Conditions

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A procedure is described which allows the oxidation of nucleophilic substrates such as organic sulfides or alkenes, under phase-transfer conditions, by employing dilute hydrogen peroxide, Mo(VI) and W(VI) catalysts, and a neutral lipophilic monodentate ligand as extracting agent. The yields and selectivities observed are generally rather high, thus establishing the synthetic relevance of the method. The success of this procedure, and particularly the efficiency of monodentate ligands, is also discussed from a mechanistic point of view.

The availability of a vast body of information on the chemistry of peroxo metal species has already made possible remarkable achievements in transition metal-catalyzed oxidations by peroxides.[2] Therefore, very efficient and selective, including chemo-, regio-, and enantioselectivity, synthetic procedures, employing either hydrogen peroxide or alkyl hydroperoxides combined with a variety of metal derivatives, have been reported in recent years.[3]

It is well-known that molybdenum(VI) or tungsten(VI) peroxo complexes, in aqueous solution, are readily formed by addition of hydrogen peroxide to H_2MO_4 acids;[4] the resulting peroxo species are also fairly acidic so that they are largely present as anions in solutions.[4,5] However, by adjusting the acidity of the medium, neutral peroxo compounds may be obtained[6] which, upon addition of an appropriate neutral ligand L (HMPT, DMF, PyO, etc.), precipitate as the sparingly water soluble complexes $MO(O_2)_2L,H_2O$. In these species, the water molecule is only weakly coordinated and may be easily removed whereas the ligand L is strongly bound to the metal.[7] The dehydrated complexes $MO(O_2)_2L$ are soluble in many organic solvents and have been used as effective stoichiometric oxidants of several nucleophilic substrates.[6,8]

Table I. Monodentate Neutral Ligands

	R	R′	abbreviation
$[RR'N]_3P=O$	CH_3	CH_3	HMPT
	CH_3CH_2	CH_3CH_2	HEPT
	$CH_3(CH_2)_3$	$CH_3(CH_2)_3$	HBPT
	cyclohexyl	H	TCyPT
	$CH_3(CH_2)_{11}$	H	TDPT
4-R-pyridine *N*-oxide	$Ph(CH_2)_3$		RPyNO
	$CH_3(CH_2)_8$		R′PyNO

There is now evidence that the displacement of the neutral ligand L by the substrate is not a prerequisite for the occurrence of the oxygen-transfer process.[2b,3a,9] On the other hand, L is continuously released in the reaction medium with the progress of the oxidation, owing to the low affinity of such ligands for the reduced oxo species of Mo(VI) and W(VI).[6]

These observations convinced us of the feasibility of an oxidizing procedure based on a two-phase system.[10]

In such a system, the neutral Mo(VI) or W(VI) peroxo complexes formed in aqueous solution are extracted by a lipophilic, monodentate, neutral ligand in an organic phase, usually dichloroethane, where the oxidation of the substrate takes place.

The experimental results reported in this paper illustrate in a quantitative way the features which make the procedure synthetically valuable. Among these, an obvious

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Table II. Oxidation of Organic Sulfides with H_2O_2 Catalyzed by Mo(VI) or W(VI) Complexes in the Presence of Monodentate Ligands under Phase-Transfer Conditions at 40 °C

run[a]	sulfides (mmol)	catalyst (mmol)	ligand (mmol)	time, min	H_2O_2 concn, %	product(s) yield, %[b]
1	p-$ClC_6H_4SCH_3$ (20.5)	Mo(VI) (0.1)		10	c	c
2	p-$ClC_6H_4SCH_3$ (20.5)	Mo(VI) (0.1)	HMPT (1.0)	10	54	52 (96)
3	p-$ClC_6H_4SCH_3$ (20.5)	W(VI) (0.1)	HMPT (1.0)	10	24	24 (100)
4	p-$ClC_6H_4SCH_3$ (20.5)	Mo(VI) (0.1)	HMPT (1.0)	30	77	77 (94)
5	p-$ClC_6H_4SCH_3$ (20.5)	Mo(VI) (0.1)	HBPT (1.0)	10	77	77 (94)
6	p-$ClC_6H_4SCH_3$ (20.5)	W(VI) (0.1)	HBPT (1.0)	10	17	16 (100)
7	p-$ClC_6H_4SCH_3$ (20.5)	Mo(VI) (0.5)	HMPT (1.0)	10	97	97 (87)
8	p-$ClC_6H_4SCH_3$ (20.5)	W(VI) (0.5)	HMPT (1.0)	10	81	81 (92)
9	p-$ClC_6H_4SCH_3$ (20.5)	Mo(VI) (0.5)	HBPT (1.0)	10	100	100 (88)
10	p-$ClC_6H_4SCH_3$ (20.5)	W(VI) (0.5)	HBPT (1.0)	10	75	75 (92)
11	p-$ClC_6H_4SCH_3$ (40.5)	Mo(VI) (0.5)	HBPT (1.0)	10	100	100 (97)
12	DBTP[d] (20.5)	Mo(VI) (0.5)	HBPT (1.0)	60	78	75 (69)

[a] The oxidations are carried out in a two-phase system consisting of 1,2-dichloroethane (25 mL) and aqueous (2 mL) H_2O_2 (20.5 mmol). Added acid (H_2SO_4) in the ratio M(VI):H^+ = 1:1.2. [b] Numbers given in parentheses are percentage of sulfoxide based on the total oxidized products, i.e., sulfoxide + sulfone. [c] No detectable consumption of H_2O_2 is observed. [d] DBTP = dibenzothiophene.

Table III. Oxidation of Various Olefins with H_2O_2 Catalyzed by Mo(VI) Complexes in the Presence of Monodentate Ligands under Phase-Transfer Conditions at 50 °C

run[a]	olefin (mmol)	ligand (mmol)	H^+, mmol	time, h	H_2O_2 concn, %	product(s) yield %[b]
1	cyclohexene (100)		0.6	24	37	
2	cyclohexene (100)	HMPT (1.0)	0.6	5	44	14 (86)
3	cyclohexene (100)	HMPT (1.0)	2.5	5	82	35 (14)
4	cyclohexene (100)	HEPT (1.0)	0.6	5	81	21 (95)
5	cyclohexene (100)	HEPT (1.0)	2.5	5	100	80 (10)
6	cyclohexene (100)	HBPT (1.0)	0.6	5	35	21 (91)
7	cyclohexene (100)	HBPT (1.0)	2.5	5	100	74 (15)
8	*trans*-2-octene (100)	HBPT (1.0)	0.6	14	92	29 (100)
9	*trans*-2-octene (100)	HBPT (1.0)	2.5	14	100	98 (80)
10	cyclohexene (100)	TCyPT (1.0)	0.8	5	78	33 (100)
11	cyclohexene (100)	TCyPT (1.0)	2.5	5	95	55 (16)
12	cyclohexene (100)	TDPT (1.0)	0.6	5	96	51 (67)
13	cyclohexene (100)	TDPT (1.0)	2.5	5	100	90 (32)
14	*trans*-2-octene (100)	TDPT (1.0)	2.5	14	100	70 (63)
15	cyclohexene (100)	R-PyN→O (1.0)	0.8	5	100	64 (98)
16	cyclohexene (100)	R-PyN→O (1.0)	2.5	5	100	80 (27)
17	*trans*-2-octene (100)	R-PyN→O (1.0)	2.5	14	100	76 (85)
18	cyclohexene (100)	R′-PyN→O (1.0)	0.8	5	97	65 (93)
19	cyclohexene (100)	R′-PyN→O (1.0)	2.5	5	99	74 (25)
20	*trans*-2-octene (100)	R′-PyN→O (1.0)	2.5	14	100	77 (82)

[a] The oxidations are carried out in a two-phase system consisting of 1,2-dichloroethane (25 mL) and aqueous (2 mL) H_2O_2 (20.5 mmol)–Mo(VI) (0.5 mmol). [b] Numbers given in parentheses are percentage of epoxide based on the total products, i.e., epoxide + diol.

advantage is the use of dilute hydrogen peroxide under relatively mild conditions.

Results and Discussion

In the present study, after some preliminary experiments,[11] two classes of neutral monodentate ligands have been selected, i.e., phosphoric amides and pyridine *N*-oxides. The individual ligands are presented in Table I.

Also, two classes of substrates have been employed, namely organic sulfides and alkenes. It is well-known that the oxidation of sulfides to sulfoxides is usually much faster than the epoxidation of olefins, reflecting the higher nucleophilicity of the sulfur atoms as compared with that of the carbon–carbon double bond.[2b] Thus, the fast and clean sulfide–sulfoxide transformation has been used as a model reaction to establish the best experimental conditions to be adopted in the more synthetically significant olefins epoxidation.

As shown in Table II the selectivities observed in p-$ClC_6H_4SCH_3$ oxidation are usually very high: values of about 90% for equimolar amounts of substrate and oxidant are observed which become about 100%, in the case of Mo(VI) catalysis, when a 2-fold excess of sulfide is used; W(VI), though an effective catalyst, appears to be less efficient under otherwise identical conditions.

As expected, the reaction rates depend on the concentration of the catalyst so that a 5-fold increase of the metal leads to higher conversions in shorter reaction times.

It was also confirmed that addition of H_2O_2 at the end of the reaction fully restores the oxidizing ability of the system, thus indicating little or no degradation of either the metal complex or the ligand.

The procedure is also effective for much less nucleophilic sulfides, such as DBTP.

Other experiments, not included in the Table II, indicate that, under the same experimental conditions, the oxidation of other organic compounds containing heteroatoms, such as Ph_3P or Ph_3As, is equally feasible providing high yields and selectivities.

Turning now to the epoxidation of alkenes, the pertinent results are collected in Table III. It is confirmed that the addition of the ligand is crucial. In the absence of an extracting agent only decomposition of hydrogen peroxide is observed. Moreover, the efficiency of the system depends on the lipophilicity of the ligand. In fact, decomposition of the oxidant decreases and product yields in-

(11) It has been observed that ligands such as amides or phosphine oxides are also capable of extracting peroxo complexes but less efficiently. On the other hand, aliphatic trialkylamine *N*-oxides, though rather efficient extracting agents, undergo decomposition under the experimental conditions adopted.

crease in the order HBPT > HEPT > HMPT for hexaalkylphosphoric triamides and TDPT > TCyPT for trialkylphosphoric triamides. Also the nature of the ligand plays a role, probably in connection with its coordinating ability; thus, pyridine *N*-oxides appear to be more effective than phosphoric amides.

As anticipated above, the acidity of the aqueous phase is another important parameter to be considered. In fact, an increase of the H_2SO_4: catalyst ratio produces a remarkable increase of the overall yields, likely as a result of neutralization of anionic peroxo complexes in the aqueous phase making the extraction by the ligand more effective. At the same time, however, the selectivities in epoxide tend to drop, owing to the acid-catalyzed hydrolytic cleavage of the oxirane ring to diol.[12] This is particularly severe for cyclohexene oxide, whereas *trans*-2-octene oxide appears to be more resistant to ring-opening reactions.

Conclusions

The data reported in the preceding section clearly demonstrate the synthetic value of the two-phase system. In fact, a viable procedure has been established which may be employed for many other oxidative transformations. Moreover, in such a simple system, where the nature of the oxidizing species is fairly well understood, it should be possible to improve the efficiency by acting on the characteristics of the extracting agents. Indeed, a relevant point worthy of further studies is connected with the relative importance of the two salient features of the ligands employed, i.e., their lipophilicity and their coordinating ability, respectively, in determining the most effective oxidizing conditions.

Finally, from a mechanistic point of view, it is evident that the success of monodentate ligands in carrying out these oxidations gives further support to the suggestions of other authors and ourselves for an "external"[2b,3a,9] oxygen transfer from the peroxo metal species rather than an "internal" oxidation of the coordinated nucleophile via preliminary displacement of the originally bound ligand.[13]

Experimental Section

Materials. *p*-Chlorophenyl methyl sulfide was prepared by methylation of the commercially available thiol. Cyclohexene and *trans*-2-octene were purified by distillation. 1,2-Dichloroethane was obtained by standard procedures from highly pure commercial samples.

Hexaalkylphosphoric triamides were synthesized according to literature methods;[14] the products were purified by low pressure (4–5 atm) liquid chromatography on silica gel (>0.063 mm). Trialkylphosphoric triamides were obtained by condensation of the corresponding amines with $Cl_3P(O)$ and the products purified by chromatography. The pyridine *N*-oxide derivatives were synthesized by oxidation of the corresponding pyridines with *m*-chloroperbenzoic acid.

All other chemicals were used as received.

Procedures. In a typical run 1 mL of an aqueous solution of $Na_2MoO_4 \cdot 2H_2O$ (0.5 mmol) and H_2SO_4 (0.3 mmol) was added to a dichloroethane solution (25 mL) containing cyclohexene (100 mmol) and the ligand (1.0 mmol) in a glass reactor mantained at 50 °C. Then 1 mL of H_2O_2 70% w/v (20.5 mmol) was added under vigorous stirring.

After 5 h the two phases were separated and the amount of unreacted H_2O_2 determined by iodometric titration. In all cases comparison of the products in the organic phase with authentic samples confirmed their identity.

The yields were obtained by GLC analysis (internal standard) on an OV-101 3% on Chromosorb WAW-DMCS (1.5 m) column with a Varian 3700 instrument equipped with a Varian CDS 401 or a Perkin-Elmer Sigma 10 integrator.

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Registry No. DBTP, 132-65-0; HMPT, 680-31-9; HBPT, 22421-85-8; HEPT, 2622-07-3; TCyPT, 31160-09-5; TDPT, 7261-34-9; *p*-ClC_6H_4SMe, 123-09-1; *trans*-$CH_3CH{=}CH(CH_2)_4CH_3$, 13389-42-9; *p*-$ClC_6H_4S(O)Me$, 934-73-6; $Na_2Mo(VI)O_4$, 7631-95-0; $Na_2W(VI)O_4$, 13472-45-2; *p*-Cl-C_6H_4-$S(O)_2Me$, 98-57-7; $CH_3(CH_2)_4(CH(OH))_2CH_3$, 20653-90-1; cyclohexene, 110-83-8; dibenzothiophenoxide, 1013-23-6; cyclohexene oxide, 286-20-4; 2,3-epoxyoctane, 3234-26-2; 4-(3-phenylpropyl)pyridine *N*-oxide, 84824-92-0; 4-nonylpyridine *N*-oxide, 96689-75-7; dibenzothiophene dioxide, 1016-05-3; 1,2-cyclohexanediol, 931-17-9.

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Effect of Different Dialkylamino Groups on the Regioselectivity of Lithiation of O-Protected 3-(Dialkylamino)phenols

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The lithiation of 3-(dialkylamino)phenols (dialkylamino = 1-pyrrolidinyl, 1-piperidinyl, 4-morpholinyl, and dimethylamino) O-protected by a methyl, a methoxymethyl, or a carbamoyl group (X) has been studied. The results demonstrate that the site of lithiation depends on the relative ortho-directing capacities of both the dominant OX and the dialkylamino groups. With the moderate ortho-directing methoxy group the lithiation occurs exclusively (**1b** and **1c**) or predominantly (**1a**) ortho to both substituents. The site of lithiation of the *N*,*N*-dialkyl-3-(methoxymethoxy)anilines **4a–c** depends on the solvent used and on the type of dialkylamino group. With a strong ortho-directing group such as carbamoyloxy (**9a,b,d**) the lithiation takes place at the least hindered ortho position. In the absence of an electrophile the lithiated carbamates **9a,d** and **10a,d** rearrange stereospecifically to the corresponding benzamides **13a,d** and **14a,d**, respectively.

Heteroatom-facilitated lithiation of aromatic compounds is a convenient route to polysubstituted aromatics. Because of the high selectivity and the wide range of further transformations the process is often used in organic syn-

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