Tetrahedron Letters,Vol.28,No.20,pp 2237-2238,1987 0040-4039/87 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

EPOXIDATION OF OLEFINS BY HYDROGEN PEROXIDE CATALYZED BY PHOSPHONOTUNGSTIC COMPLEXES

M. QUENARD, V. BONMARIN, G. GELBARD*
Laboratoire des Matériaux Organiques - CNRS
B.P. 24 , F-69390 Vernaison, France.

Abstract : The highest turnovers reported so far in the epoxidation of olefins with hydrogen peroxide are obtained under homogeneous conditions with trioctylmethylammonium tungstate complexed by lipophilic neutral or anionic phosphorus ligands containing the P=O subunit.

The direct epoxidation of olefins is generally performed with alkyl - or benzyl hydroperoxides or more conveniently with hydrogen peroxide in the presence of catalysts made from class IVB,VB and VIB transition metals (1,2). When hydrogen peroxide is chosen for economic reasons, tungsten-based catalysts are found the most efficient (3,4), specially in the epoxidation of allylic alcohols (5,6) ; the reactivity of non-functional olefins however, still remains a stimulating challenge. Recently, biphasic systems (7-9) have been used for the epoxidation of such olefins.

A careful examination of the results obtained with non-functional olefins (2-10) indicates that catalytic systems used exhibit a lack of reactivity even when the selectivity in epoxide is good.

The results we report here show that the efficiency of the tungsten based catalytic systems can be significantly increased by using a lipophilic quaternary ammonium tungstate complexed with the phosphine oxide 1 or with the anionic 2,3 phosphonated ligands. In this case, hydrogen tungstate ($HWO_4^{\ominus}$) is a good catalyst precursor (10, 11) as it ensures a near-neutral medium (pK_2= 4.6).

$O{=}P(Octyl)_3$	$Ph{-}PO_3H_2$	$C_{12}H_{25}PO_3H_2$
1	2	3

Ligands 1 and 2 are known to complex transition metals at high oxidation levels (13) and are widely used in hydrometallurgy as liquid-liquid extractants (12, 14-16). Thus they seemed to us to be good ligand candidates for the tungsten (VI) catalysis.

Results: The epoxidations are run at 70° C in dioxane solution with a 5:1 molar ratio of olefin vs.70% H_2O_2 (24 mmol). The catalyst (0.6 % molar in W) is generated in situ by the addition of trioctylmethylammonium tungstate and the required amount of ligands 1-3. The following olefins are examined cyclohexene, 1-octene, styrene and geraniol. The yields in epoxide (Table) are determined by G.L.C. The turnover is defined as T = mole epoxide/mole W/time.

Table : Epoxidation of olefins with trioctylmethylammonium (Q) tungstate complexed with phosphorus ligands

Entry	Olefin	Catalytic system	time(h)	yield (%)	turnover
1	cyclohexene	$QHWO_4$	2	91	68[a]
2	"	$QHWO_4$+ 1 eq. 1	1.3	88	100
3	"	$QHWO_4$+ 1 eq. 2	0.8	100	162
4	"	Q_2WO_4+ 2 eq. 3	1	84	148
5	1-octene	Q_2WO_4+ 3 eq. 2	8	61	11
6	"	H_2WO_4+ 2 eq. 1	4	70	24[b]
7	styrene	H_2WO_4+ 2 eq. 1	1	70	59
8	"	Q_2WO_4+ 3 eq. 2	4	80	33[c]
9	geraniol	Q_2WO_4+ 2 eq. 2	0.4	87[d]	286[e]

a) turnover values of 42 and 6.6 are respectively reported in ref. (17) and (8).
b) a turnover value 19 is reported in ref. (7)
c) a turnover value of 7.4 is reported in ref. (7)
d) as acetate
e) turnovers of 6.13 and 8.9 are respectively reported in ref. (6) and (9).

In the epoxidation of cyclohexene, the use of a lipophilic ammonium salt (entry 1) gives a high turnover which is further increased in the presence of phosphonated ligands (entries 2-4). With 1-octene, this improvement occurs only with the neutral ligand 1 (entry 6). In the case of styrene, the remaining olefin contains less than 5 % of polymerized products (entry 8).
These are the highest turnovers reported so far in such epoxidations. The most promising result is obtained with geraniol (a typical allylic alcohol) where an exceptionally high turnover is obtained (entry 9). The regioselectivity is 9:1 in favor of the 2,3-epoxide ; no trace of diepoxide is formed.

Acknowledgements : We thank the C.N.R.S. and RHONE-POULENC for financial support and for a fellowship to one of us (M.Q.). We thank Dr L. Krumenacker (RHONE-POULENC) for stimulating discussions.

References : (1) Sheldon R.A., Kochl J.K., Metal Catalyzed Oxidation of Organic Compounds, Academic Press, New-York, 1981 p. 275.-(2) Sheldon R.A., Metal Catalyzed Epoxidation of Olefins with Hydroperoxides, in Aspects of Homogeneous Catalysis, Vol. 4, Ugo R., Ed., D. Reidel, Dordrecht, 1981, p.3.-(13) Schirmann J.P., Delavarenne S.Y., Hydrogen Peroxide in Organic Chemistry, EDI, Paris, 1979.- (4) Kirshenbaum K.S., Sharpless K.B., J. Org. Chem., 1985, 50, 1979.- (5) Stevens H.C., Kaman A.J., J. Amer. Chem. Soc., 1965, 87, 734.-(6) Pratt D., Lett R., Tetrahedron Lett. 1986, 27, 707.- (7) Venturello C., Alneri E., Rici M., J. Org. Chem., 1983, 48, 3831.-(8) Bortolini O., Di Furia F., Modena G., Seraglia R., J. Org. Chem., 1985, 50, 2688.-(9) Prandi J., Kagan H.B., Mimoun H., Tetrahedron Lett., 1986, 27, 2617.-(10) Allen G.G., Neogi A.N., J. Catal., 1970,16, 197, 256.-(11) Quénard M., Thèse de Docteur-Ingénieur, Lyon 1985.-(12) Sekine T., Hasegawa Y., Solvent Extraction Chemistry, M. Dekker, Basle, 1963.-(13) Worms K.H., Schmidt-Dunker M., Organic Phosphorus Compounds, Kosolapoff G.M., Maier L. Ed., Wiley-Interscience, New-York, 1975, Vol. 7, Chap.18.-(14) De Bolster M.W.G., Topics in Phosphorus Chemistry, Vol. 11, J. Wiley, New-York, 1981, p.69.- (15) Shigetomi Y., Kojima T., Kamba H., Yamamoto Y., Anal. Chim. Acta, 1980, 116, 199.-(16) Sato T., Ikoma S., Nakamura T., Hydrometallurgy, 1980, 6, 13.

(Received in France 12 December 1986)