

EPOXIDATION OF ISOLATED DOUBLE BONDS WITH 30% HYDROGEN PEROXIDE CATALYZED  
BY PERTUNGSTATE SALTS

J. Prandi, H. B. Kagan  
Laboratoire de Synthèse Asymétrique associé au CNRS, Bt 420  
Université Paris-Sud, 91405-Orsay Cédex, France.

H. Mimoun  
Institut Français du Pétrole BP 311, 1 Avenue de Bois Préau  
92500 Rueil-Malmaison, France.

**Abstract :** A practical procedure for the epoxidation of alkenes is described. The reaction is performed between 30 and 50°C in 1,2-dichloroethane with 30% hydrogen peroxide and a catalytic amount of a quaternary phosphonium or ammonium pertungstate. Allylic alcohols are very reactive and require lower temperatures for their epoxidation.

Epoxidation of isolated double bonds is classically achieved by the use of peracids<sup>1</sup> or hydroperoxides<sup>2</sup>. Epoxidation by cheap oxidants remains an important problem. Hydrogen peroxide in water solution, especially the cheap and easily available 30% hydrogen peroxide, seems the ideal reagent since it gives no by-products except water. It was used for epoxidation when combined with stoichiometric amounts of some nitriles<sup>3-5</sup> or under phase-transfer conditions with a catalyst formed by the  $WO_4^{2-}/PO_4^{3-}$  association<sup>6</sup>. This last system requires an excess of olefin. Some iron or manganese porphyrins were found to be excellent catalysts for the epoxidation of some representative olefins in the presence of imidazole<sup>7</sup>. Conjugated acids<sup>8</sup> or allylic alcohols<sup>9</sup> were epoxidized in the presence of sodium tungstate as catalyst. Very recently, the scope of allylic alcohols epoxidation was investigated by Prat and Lett<sup>10</sup>. These authors catalyzed the reaction by tungstic acid in buffered media. We wish to report that a simple modification of the procedure using tungsten complexes allows the epoxidation of a number of olefins by 30% hydrogen peroxide.

### Results

The catalyst is prepared as follows : tungstic acid (7.5 g) is dissolved in 30 mL  $H_2O_2$  30% at 40°C. The solution is filtered and cooled to 0°C. A solution of  $Ph_3PCH_2Ph^+Cl^-$  (11.7 g) in 75 mL water is then added dropwise at 0°C. After stirring at 0°C for 15 min., the white precipitate is filtered, washed with water (3x10 mL, 0°C) and dried in vacuo. The catalyst is obtained (12.7 g, 68%), as a white powder mp = 150°C (decomp.).

Analysis :  $C_{50}H_{44}O_{11}P_2W_2$  (M=1250,53)

Calc. % : C = 48.02 H = 3.54 P = 4.95 O = 14.07

Found % : 47.5 3.6 4.97 13.95

The catalyst, formulated as a pertungstate salt  $W_2O_{11}^{2-}$ ,  $2 Ph_3PCH_2Ph^+$ , is very stable and can be stored for a long time. Its use is exemplified in the epoxidation of cis-cyclooctene at 2 mmol or 100 mmol scale :

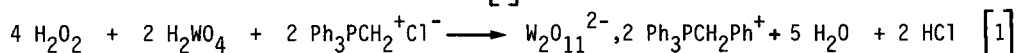
a) 0.2 mmol catalyst was dissolved in 2 mL 1,2-dichloroethane, then were added 2 mmol cyclooctene and 1 mL  $H_2O_2$  30%. The mixture was stirred at 50°C for 15 h. Dichloromethane (10 mL) and water (5 mL) were added. The organic phase was separated, the aqueous phase was extracted twice with dichloromethane. Work-up of the organic phases and short path distillation afford cis-epoxycyclooctane in 88% yield.

b) A 500 mL flask was charged with 1 mmol catalyst, 100 mL 1,2-dichloroethane and 100 mmol cis-cyclooctene. The mixture was brought to 50°C, 20 mL 30%  $H_2O_2$  were added dropwise over two hours, under strong stirring. The mixture was kept at 50°C until completion of the reaction (18h). Work-up as above afforded pure cis-epoxycyclooctane in 89% yield.

Some representative results are listed in Table 1.

### Discussion

The catalyst is prepared according to reaction [1] :




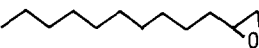

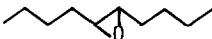
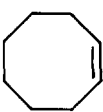
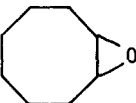
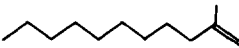
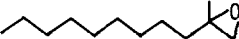
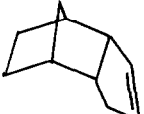
It can be generated in situ by the addition of tungstic acid and  $Ph_3PCH_2Ph^+Cl^-$  to 30% hydrogen peroxide. The results are the same (entries 2 and 4, Table 1) as with the isolated catalyst. However, we prefer to use the latter system because HCl generated in the catalyst preparation is removed from the solid. The reaction is thus run in nearly neutral conditions (the pH remains close to 5 - 6) and there is no need to buffer the aqueous solution. The epoxidation proceeds in the organic phase where the phosphonium pertungstate enters because of the lipophilicity of the phosphonium moiety.  $Ph_3PCH_2Ph^+Cl^-$  can be replaced by  $Bu_4N^+Cl^-$  or  $Ph_3NCH_2Ph^+Cl^-$ , but the corresponding complexes are more difficult to isolate. Internal or terminal olefins react as well as cyclenes, giving epoxides by a cis addition. Allylic alcohols are very rapidly epoxidized. For example geraniol requires only 1% to 0.2% mol. eq. of catalyst, and a reaction temperature around 0°C.

Conjugated double bonds (entry 11) are not very reactive<sup>12</sup>, in contrast to catalysis by sodium tungstate<sup>8</sup>. We are currently investigating the nature of the catalytic species and the scope of the reaction.

### Acknowledgements

We thank CNRS for financial support and ENSET for a fellowship (to J.P.).

TABLE 1

Entry	Alkene	Cat. <sup>a</sup> mol%	Temp. °C	Time h	Product	Yield <sup>d</sup> %
1		10	40	22		65
2	"	10 <sup>b</sup>	40	24	"	70
3		10	20	96		68
4	"	10 <sup>b</sup>	40	22	"	72
5	"	10 <sup>c</sup>	30	45	"	69
6		10	50	15		88
7	"	1	50	18	"	89 <sup>h</sup>
8		10	50	19		65
9		10	40	24	<u>1</u>	76
10	Limonene	10	40	20	<u>2</u> cis/trans = 1/1 <sup>e</sup>	60
11	Carvone	10	50	24	<u>3</u> erythro/threo = 1/1 <sup>e</sup>	63
12	Cholesteryl acetate	10	50	24	<u>4</u> β/α = 0.65 <sup>f</sup>	72
13	Geraniol	1	0	8	<u>5</u>	84
14	"	0.2	0	24	<u>5</u>	98 <sup>g,h</sup>
15	Nerol	1	20	15	<u>6</u>	70

a) Catalyst : isolated  $W_2O_{11}^{2-}$ , 2  $Ph_3PCH_2Ph^+$ , unless stated.

b) Catalyst as in a) but prepared in situ.

c)  $W_2O_{11}^{2-}$ , 2  $NBu_4^+$  prepared in situ.

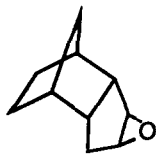
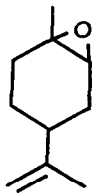
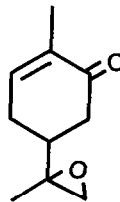
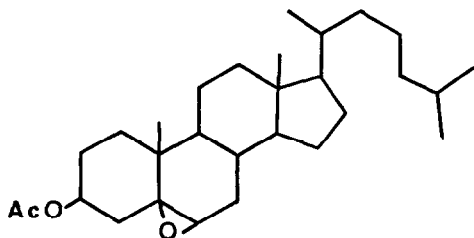
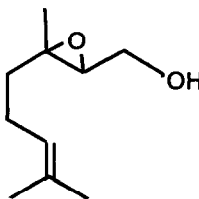
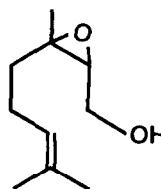
d) Isolated yields, reactions performed at 2 mmol scale as described for cyclooctene.

e) Determined by GLC.

f) Determined by  $^1H$  NMR.

g)  $^1H$  NMR yield on the crude product. Acetylation gives pure acetate in 86% yield.

h) 100 mmol scale.

12 (cis/trans:1/1)3 (erythro/threo:1/1)4  $\alpha/\beta = 0.65$ 56

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- (11) Some sensitive epoxides (from styrene,  $\alpha$ -pinene,  $\beta$ -pinene) could not be isolated; a modified procedure for these cases is under investigation.
- (12) Crotonic acid can be epoxidized in 53% yield at 75% conversion, (24h, 40°C, 10% cat.) provided that the pH is maintained around 6 by addition of 2N NaOH.

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