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EPOXIDATIONS WITH 30% HYDROGEN PEROXIDE CATALYZED BY TUNGSTIC ACID IN BUFFERED MEDIA

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ABSTRACT : The scope of the tungstic acid catalyzed hydrogen peroxide epoxidation of olefinic alcohols is examined, at room temperature, in buffered protic media. Epoxidation occurs with complete retention of configuration for both *cis* and *trans* alkenes. Chemoselectivity is discussed with respect to the olefinic alcohol structure and olefin substituents.

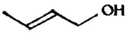
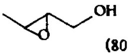
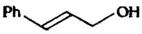
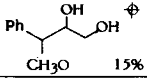
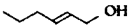
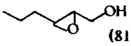
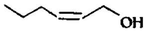
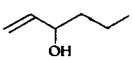
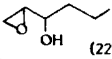
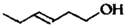
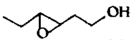
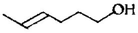
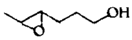
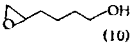
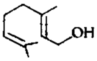
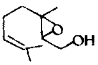
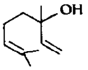
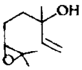
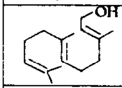
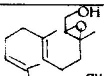
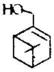
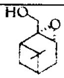
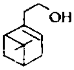
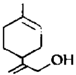
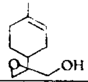
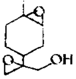
To our knowledge, since the pioneering work of M. MUGDAN and D.P. YOUNG (1), there are only some scarce examples and mechanistic studies of the tungsten-catalyzed epoxidation of simple olefins (2) or allylic alcohols (3), though there are some industrial processes such as the allylic alcohol conversion into glycidol and its derivatives (4). Our own interest in the tungsten-catalyzed process originated from some of its a priori appealing features :

- Tungsten derivatives and 30% hydrogen peroxide are quite cheap and safe reagents. Pertungstic acid or pertungstates are known to give highly stable aqueous solutions. Moreover the tungstate ion has been shown to be quite superior to the molybdate and vanadate ions, since the metal ion induced hydrogen peroxide decomposition is much slower and allows the use of a broader pH range, up to 6-7 (5). Therefore, some large-scale tungstate procedures have been run with much more concentrated hydrogen peroxide, at temperatures up to 50-70° C (1-4).

- Tungstate-catalyzed epoxidations are run in aqueous or protic media in contrast with the vanadium, molybdenum or titanium-catalyzed t-butyl hydroperoxide reactions which are either slowed down or inhibited by water or alcohols (4, 6, 7). Consequently, the tungsten procedure would be highly valuable for compounds which are soluble in water or water-alcohol mixtures, thus avoiding expensive aprotic solvents or anhydrous t-butyl hydroperoxide (8).

The exact mechanism of tungsten-catalyzed aqueous epoxidations, even in the case of PAYNE's original process for α,β-unsaturated acids (9), is still very poorly understood (4, 10). Therefore we felt it might be useful to get a better knowledge concerning the scope, synthetic utility and mechanism of this reaction, and to compare them with other transition metal catalyzed epoxidations with alkyl hydroperoxides or dialkyl peroxides (4, 7, 11).

TABLE I : TUNGSTEN-CATALYZED HYDROGEN PEROXIDE EPOXIDATIONS

Olefin	Temp	Olefin + [M]	Time (h)	Epoxide * (yield)	by-products *
	20° C	1.4	5	 (80)	
	20° C	0.8	16	 (57)	 15%
	20° C	1.4	5	 (81)	
	20° C	1.4	5	 (85)	
	20° C	3.1	40	 (22)	24 % s.m.
	20° C	3.4	16	 (49)	36 % s.m.
	20° C	3.4	17	 (8)	70 % s.m.
	20° C	2.3	64	 (7)	52 % s.m. cyclic ethers : 17%
	20° C	2.2	64	 (10)	75 % s.m.
	0° C	1.5	4	 (98)	
	20° C	2.0	46	 ≠ (9)	49 % s.m. cyclic ethers : 30%
 t,t	0° C	0.7	5	 quant.	
	20° C	1.2	6	 (85)	
	20° C	1.2	20	none	95 % s.m.
	20° C	2.1	16	 ≠ (72)	 ≠ 18 %

+ molarity (M) in H_2O_2 30% -CH_3OH : s.m. = starting material

* isolated yield ; ⊕ : one diastereoisomer ; ≠ : no stereoselectivity

Since tungstic and pertungstic acids are very strong acids (5), the earlier experiments only led to glycols or glycol derivatives (1, 2a, 2b, 4) ; on the other hand, some epoxides were obtained with tungstate-catalyzed reactions, or when tungstic acid was neutralized with an alkali or a tertiary amine (3, 4). However, these last procedures have the drawback that a slight base excess leads to basic conditions which favour hydrogen peroxide decomposition (12). Therefore, we looked for buffered conditions in order to avoid the epoxide cleavage and found that olefinic alcohols epoxidations can be achieved in high yields, in buffered water-alcohol mixtures around pH 4.5 at room temperature or 0°, with 1.5 eq 30% hydrogen peroxide, 1% molar tungstic acid, 2-3% molar sodium acetate or trimethylamine N-oxide (Table I).

The reactivity of non allylic olefinic alcohols, as well as the stereochemistry of allylic alcohols tungsten-catalyzed epoxidations, have not at all been previously investigated (3,4). Our results clearly show that the epoxidation occurs with complete retention of configuration for both *cis* and *trans* alkenes; furthermore, no isomerization or cleavage of the olefinic bond occurs in our conditions, in contrast with some other transition metal-catalyzed epoxidations (4, 13). Strikingly, traces of conjugated enone are at most observed in the acyclic compounds, whereas oxidation of the allylic alcohol can be a competitive reaction in some cyclic compounds (14).

The olefinic bond reacts faster in *cis* and *trans* allylic than in *cis* homoallylic alcohols; *trans*-homoallylic, bis-homoallylic alcohols or isolated olefins are almost unreactive at room temperature, when comparing compounds which have almost the same degree of substitution and steric hindrance of the olefinic bond. These results,in water-methanol or other protic media, are quite surprising since they show quite a different reactivity, due to the proximity of the olefinic bond and the hydroxyl group which may favour the coordination of the substrate to the reactive tungsten epoxidizing species.

Quite consistently with the previous tungstate-catalyzed epoxidations of some allylic alcohols (3b) and with SHARPLESS' results concerning α,β-unsaturated acids (10), reactivity increases with the nucleophilicity of the double bond : terminal double bonds are much less reactive than disubstituted at room temperature, and more substituted olefinic alcohols are epoxidized even at 0° (Table I) (14). With respect to this point, the results with allylic alcohols are particularly significant for showing the probable coordination of the hydroxyl group to the catalytic species, since an allylic hydroxyl group decreases the nucleophilicity of the olefinic bond (15). Moreover, consistently, tertiary allylic alcohols such as 2-methyl 3-buten-2-ol are almost unreactive (3b). Therefore, the limonen-10-ol, geraniol, t,t-farnesol and linalool results are particularly significant (Table I).

It is also noteworthy that neutral sodium tungstate-catalyzed reactions are not much slower than those with tungstic acid buffered at pH 4.5 with sodium acetate or trimethyl amine N-oxide : the epoxidation rate is only decreased by a factor 2 to 3 at pH 7, which is quite surprising if a pertungstate ester is involved (3b).

The chemoselectivity of tungstic acid-catalyzed epoxidations is also an interesting feature : ^{1}HNMR kinetics of the reaction mixture show quite different rates [olefin 0.67 M in 30% H_2O_2 (5 eq.) -CH_3OH; 4% mol H_2WO_4; 12% mol Me_3NO; r.tp.; pH 4.8]. Crotyl alcohol is much more reactive (87% epoxide after 1.1 h) since, after 23 h, no epoxide is observed for crotonic acid methyl ester, cyclohexenone and isophorone, whereas epoxides are formed in only 26% for 4-methyl-3 penten-2- one in the above conditions and 14% for crotonic acid sodium salt at pH 5.6. Furthermore, competitive experiments between crotyl alcohol and each of these substrates, in equimolecular amounts, result in an almost quantitative conversion into crotyl alcohol epoxide, with at most traces (< 5%) of the other epoxide as shown by the NMR of the crude reaction mixture.

In the accompanying paper (14), we also examine the threo/erythro selectivity obtained in the epoxidation of some allylic and homoallylic alcohols, and discuss them with respect to other epoxidation procedures.

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