

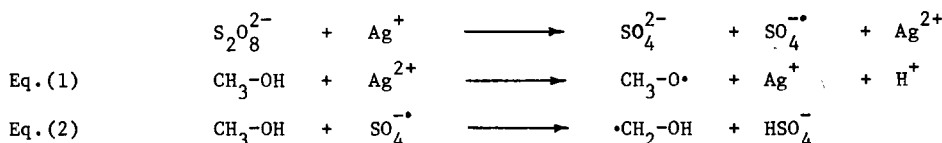
INTRA- AND INTERMOLECULAR FREE RADICAL REACTIONS OF ALCOHOLS AND OLEFINS  
WITH PEROXYDISULPHATE. NEW HOMOLYTIC AROMATIC ALKYLATIONS.

A. Clerici\*, F. Minisci and K. Ogawa. Istituto di Chimica del Politecnico,  
P.zza L. da Vinci 32, 20133 Milan.

J-M. Surzur. Laboratoire Chimie Organique B, Université d'Aix-Marseille III,  
Rue H. Poincaré, 13397 Marseille Cedex 4.

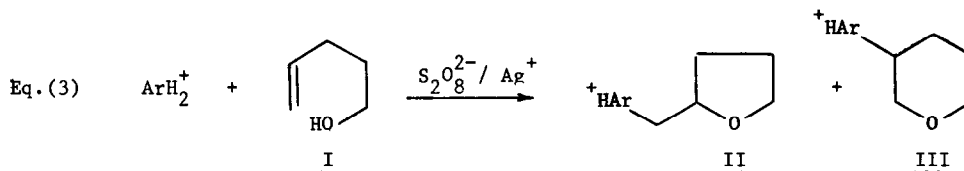
(Received in UK 23 January 1978; accepted for publication 3 February 1978)

We<sup>1</sup> have recently reported evidence concerning the debated<sup>2</sup> mechanism of the oxidation of alcohols by peroxydisulphate. We suggested different reaction pathways in the presence or absence of silver salt. In the first case an alkoxy radical is formed by  $\text{Ag}^{2+}$  [Eq.(1)], while in the latter an hydrogen abstraction occurs at C-H bonds by  $\text{SO}_4^{\cdot-}$  [Eq.(2)]:



Now we wish to report further conclusive evidence with regard to Eq.(1) and, at the same time, new types of selective homolytic aromatic substitutions. We have taken advantage of the great trapping effectiveness of protonated heteroaromatic bases towards alkyl radicals (absolute rate constants in the range of  $10^5\text{-}10^7 \text{ l M}^{-1} \text{ sec}^{-1}$  were determined for the addition of alkyl radicals to protonated bases<sup>3</sup>).

A) Oxidation of alcohol I (4-penten-1-ol) by  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{Ag}^+$  in presence of protonated heteroaromatic bases leads to formation of cyclic tetrahydrofuran- and tetrahydropyran-type alcohols (II and III) in good yields [Eq.(3)]:  $\text{ArH}_2^+$  = protonated heteroaromatic base

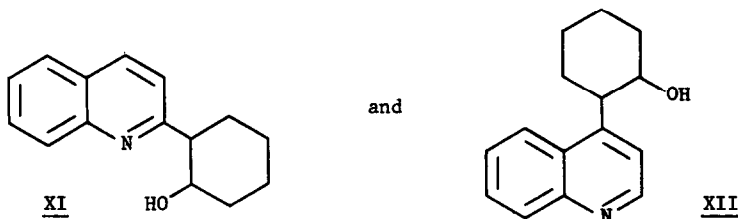


The substitution takes place at positions  $\alpha$  and  $\gamma$  to the protonated nitrogen.

A typical example is offered by the alkylation of lepidine: heteroaromatic base (0.025 mol),  $\text{H}_2\text{SO}_4$  conc. (0.0125 mol), alcohol I (0.125 mol) and  $\text{AgNO}_3$  (0.00125 mol) in 20 ml of  $\text{H}_2\text{O}$  and 5 ml of  $\text{CH}_3\text{-CN}$  were refluxed for 4 hours, adding  $\text{Na}_2\text{S}_2\text{O}_8$  (0.025 mol) into the solution. The alcohols IV (90%) and V (10%) were obtained in 95% yields based on converted base (38%), analyzed by G.L.C. and characterized by N.M.R., I.R. and Mass Spectra:



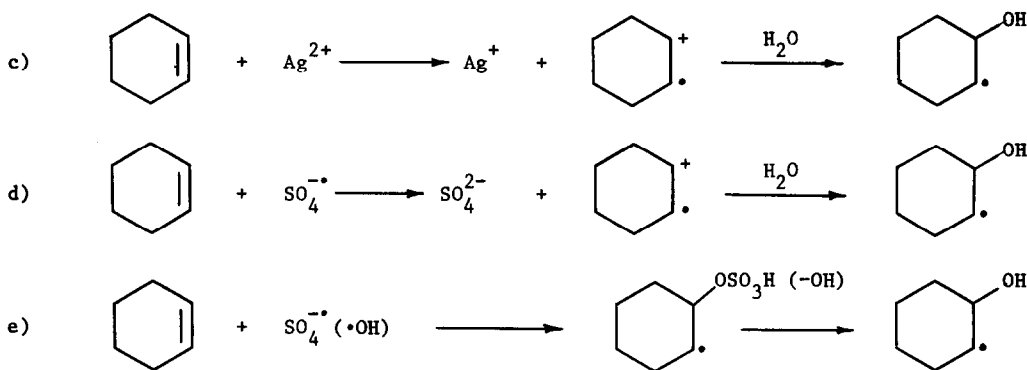
A typical example is the reaction of cyclohexene with quinoline: heteroaromatic base (0.02 mol),  $H_2SO_4$  conc. (0.01 mol), olefin IX (0.2 mol) and  $AgNO_3$  (0.004 mol) in 20 ml of  $H_2O$  and 10 ml of  $CH_3-CN$  were refluxed for 4 hours, adding  $Na_2S_2O_8$  (0.02 mol) into the solution. The alcohols XI (35%) and XII (65%) were obtained in quantitative yields based on converted base (36%):



XI and XII represent mixtures of cis and trans isomers (the latter prevailing) and were characterized by N.M.R., I.R. and Mass Spectral analysis.

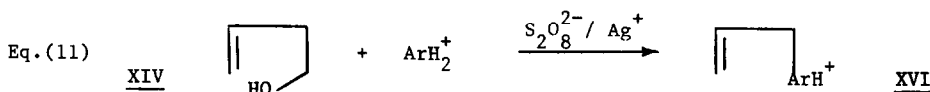
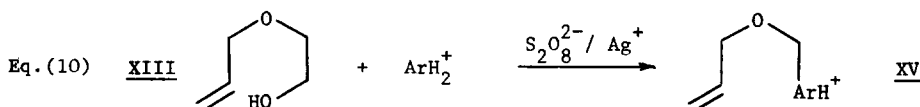
The reaction also occurs in the absence of silver salt but in lower yield.

In this case three different reaction pathways might be considered:

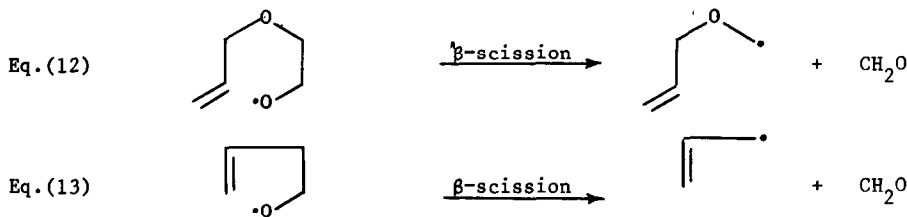


At present our opinion is more consistent with pathway d) on the ground of the intermediate radical cation formation between  $SO_4^-$  and alkybenzenes<sup>1,4</sup> having ionization potentials similar in magnitude of that of cyclohexene. However further studies are in progress to find out other significant evidence supporting such interpretation.

C) Oxidation of alcohol XIII (2-allyloxyethanol) and alcohol XIV (3-buten-1-ol) by  $Na_2S_2O_8$  and  $Ag^+$  in presence of protonated heteroaromatic bases leads to products of structure XV and XVI [Eq.(10) and (11)] :



These results clearly indicate that formation of alkoxy radicals is the favoured process with unsaturated alcohols [Eq.(12) and (13)] :



Furthermore they support mechanism a) in the formation of tetrahydrofuran-type ethers and are in agreement with previous studies<sup>5</sup> concerning the intramolecular addition of alkoxy radicals to a double bond, though oxidation of an olefinic bond by peroxydisulphate remains a real possibility as we have shown in the oxidation of cyclohexene. We do not even rule out that tetrahydropyran-type ethers might arise by a competitive reaction according to Eq.(7).

To conclude, in our point of view, the results of this work offer evidence that alkoxy radicals are formed in silver-catalyzed oxidation of alcohols by peroxydisulphate according to Eq.(1) and show new types of aromatic substitution in the heterocyclic series.

Further studies along this line are in progress in our laboratories.

ACKNOWLEDGMENT: We are grateful to the French D.G.R.S.T. for the postdoctoral fellowship to one of the authors ( A. Clerici ) who has performed most of this work at the Université d'Aix-Marseille III, Laboratoire Chimie Organique B.

#### REFERENCES

- 1) T. Caronna, A. Citterio, L. Grossi and K. Ogawa. *Tetrahedron* **32**, 2741 (1976).
- 2) A. Ledwith, P.J. Russel and L.H. Sutcliffe. *J. Chem. Soc. Perkin II*, 630 (1973).
- 3) A. Citterio, F. Minisci, O. Porta and G. Sesana. *J. Am. Chem. Soc.* **99**, 7960 (1977).
- 4) A. Clerici, F. Minisci and O. Porta. *Tetrahedron Letters* **48**, 4183 (1974).  
P. Maggioni and F. Minisci. *La Chimica e l'Industria*, in the press.
- 5) J-M. Surzur and M-P. Bertrand. *Bull. Soc. Chim.*, 2393 (1973).