Manganese Porphyrin-catalysed Oxidation of Olefins to Ketones by Molecular Oxygen

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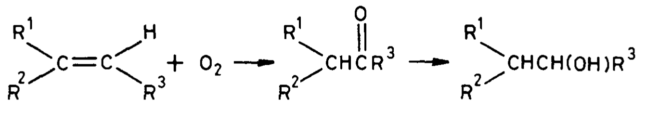
Summary Manganese(III) tetraphenylporphin $Mn^{III}(tpp)Cl$ catalyses the specific oxidation of olefins to ketones by O_2 in the presence of $[NBu_4][BH_4]$; the latter reagent further reduces the ketones to the alcohols.

HOMOGENEOUS oxidation of olefinic compounds by molecular oxygen has been the subject of numerous investigations, but until now, except for radical-chain autoxidations, only very few examples of oxygenation reactions of ethylene derivatives have been reported.[1] Recently, manganese tetraphenylporphins $Mn^{III}(tpp)Cl$[2] and $Mn^{II}(tpp)$,[3] and phthalocyanins $Mn^{II}(pc)$[4] were shown to catalyse dioxygenation of alkyl-substituted indoles. $Mn^{III}(tpp)Cl$ with $NaBH_4$ as reducing agent was also reported to promote the conversion of cyclohexene into a mixture of cyclohexanol and cyclohexenol.[5] Finally, oxidation of $\gamma\delta$-unsaturated ketones by O_2 to give enediones was achieved using catalytic amounts of $Mn^{II}(salen)$ [salen = bis(salicylidene)ethylenediaminato].[6] We report that the use of the system O_2–$Mn^{III}(tpp)Cl$–$[NBu_4][BH_4]$ allows the selective conversion of various olefins into the corresponding ketones which can be reduced *in situ* to alcohols.



In a typical experiment, $Mn^{III}(tpp)Cl$ (0·05 mmol), $[NBu_4][BH_4]$ (2 mmol), and the olefin (5 mmol) were dissolved in dry CH_2Cl_2 (10 ml); the solution was first degassed with a nitrogen stream to allow the reduction of $Mn^{III}(tpp)Cl$ to $Mn^{II}(tpp)$† and the reaction mixture was then stirred at room temperature for 24 h in the presence of either air or pure oxygen. In the latter case the oxidations could be achieved only when pure O_2 and N_2 were alternately bubbled for periods of *ca.* 2 h (6 N_2–O_2 purge cycles in 24 h). The organic products were isolated by column chromatography on alumina and analysed by g.l.c. and n.m.r. Both methods gave very similar results (Table).

TABLE

Olefin	Products [% yields based on $Mn^{III}(tpp)Cl$]
Cyclohexene	Cyclohex-2-en-1-ol (800), Cyclohexanol (1600)
Cyclo-octene	Cyclo-octanone (2000), Cyclo-octanol (800)
Styrene	Acetophenone (700), 1-Phenylethanol (1700)
Oct-1-ene	Octan-2-one (700), Octan-2-ol (900)
(*E*)-1-Phenylprop-1-ene	Propiophenone (1200), 1-Phenylpropan-1-ol (2000)

If the reaction is carried out in the presence of pure oxygen the yields of oxidation products become negligible, indicating that high concentrations of O_2 inhibit the oxidation. Further work is in progress to find the origin of this effect: a possible explanation might be a rapid consumption of the reducing agent $[NBu_4][BH_4]$ in the presence of pure O_2.

In all cases but one (cyclohexene) the olefin was converted into a simple oxidation product, the corresponding ketone. In particular, styrene and (*E*)-1-phenylprop-1-ene were oxidised very cleanly to acetophenone and propiophenone, respectively, showing the high regiospecificity of the reaction. The only other reaction product was the alcohol resulting from the reduction of the ketone by excess of borohydride, this reduction being slow in chlorinated solvents.[7] At the end of the reaction, more than 80% of the catalyst could be re-isolated as Mn^{III} porphyrin. Epoxides were never detected as reaction products.‡ Cyclohexene oxidation led to a 2:1 mixture of cyclohexanol and cyclohexenol, the allylic oxidation product. Though the

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† The reduction of $Mn^{III}(tpp)Cl$ to $Mn^{II}(tpp)$ by $[NBu_4][BH_4]$ can be monitored by u.v.–visible spectroscopy when it is carried out under an inert atmosphere, the Soret band of the former compound (λ_{max} 478 nm) being replaced by that of the latter (λ_{max} 446 nm).

‡ Oxidations carried out with the system O_2–$Mn^{III}(tpp)Cl$–$NaBH_4$ in a water-dichloromethane solvent mixture proved to be less selective but again no epoxides were formed.

mechanism of this oxygenation reaction remains to be established, it is likely that the role of $[NBu_4][BH_4]$ is to reduce $Mn^{III}(tpp)Cl$ to $Mn^{II}(tpp)$ which, by its known ability to bind O_2 reversibly,[8] must be the true catalyst of the reaction.

The oxidation reactions reported here differ markedly from the $Mn^{III}(tpp)Cl$-catalysed epoxidation of olefins using iodosylbenzene as oxygen donor.[9] Our efforts currently concern an investigation of the mechanism of this interesting new reaction, and also attempts to improve the yields of the oxidation products by the use of other metalloporphyrins and reducing agents.

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[1] G. Read and P. J. C. Walker, *J. Chem. Soc., Dalton Trans.*, 1977, 883; G. Read, *J. Mol. Catal.*, 1978, **4**, 83; R. Tang, F. Mares, N. Neary, and D. E. Smith, *J. Chem. Soc., Chem. Commun.*, 1979, 274; H. Mimoun, M. Perez Machirant, and I. Serée de Roch, *J. Am. Chem. Soc.*, 1978, **100**, 5437.

[2] M. N. Dufour, A. L. Crumbliss, G. Johnston, and A. Gaudemer, *J. Mol. Catal.*, 1980, **7**, 277.

[3] M. N. Dufour, G. Johnston, and A. Gaudemer, unpublished results.

[4] K. Ushida, M. Soura, S. Naito, T. Onishi, and K. Tamaru, *Chem. Lett.*, 1978, 471.

[5] I. Tabushi and N. Koga, *J. Am. Chem. Soc.*, 1979, **101**, 6456.

[6] M. Costantini, A. Dromard, M. Jouffret, B. Brossard, and J. Varagnat, *J. Mol. Catal.*, 1980, **7**, 89.

[7] D. J. Raber and W. C. Guida, *J. Org. Chem.*, 1976, **41**, 690.

[8] R. D. Jones, D. A. Summerville, and F. Basolo, *J. Am. Chem. Soc.*, 1978, **100**, 4416; B. M. Hoffman, T. Szymanski, T. G. Brown, and F. Basolo, *ibid.*, p. 7253.

[9] J. T. Groves, W. J. Kruper, Jr., and R. C. Haushalter, *J. Am. Chem. Soc.*, 1980, **102**, 6377.