Tetrahedron Letters,Vol.24,No.34,pp 3621-3624,1983
Printed in Great Britain

0040-4039/83 $3.00 + .00

STEREOCHEMICAL ARGUMENTS AGAINST A POSSIBLE CHLOROHYDRIN ROUTE IN THE CATALYTIC EPOXIDATION OF OLEFINS WITH NaOCl/Mn-porphyrins

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Summary : The stereochemistry of the epoxidation of norbornene and 3-carene with the NaOCl/Mn(TPP)OAc system is the same as that observed with peracids, suggesting that the chlorohydrin route does not occur in this catalytic epoxidation.

Recently, a number of studies have been devoted to the development of metalloporphyrin catalyzed oxidations using different sources of oxygen atom : PhIO,[1] NaOCl,[2], O_2/reductant,[3] or ROOH.[4] We published a modified catalytic system for the epoxidation of non-activated olefins with NaOCl in the presence of manganese porphyrins.[5a] Aliphatic olefins are stereospecifically epoxidized (*cis* olefins lead to *cis* epoxides), while an olefin like stilbene gives a mixture of *cis* and *trans* epoxides.

Different hypotheses on the mechanism of this new catalytic epoxidation can be proposed :

i) possible formation of chlorinated species such as the chlorohydrin.

ii) coordination of the hypochlorite anion on the metal after transfer of $^-$OCl from the aqueous to the organic phase assisted by the phase transfer agent. In this case, the resulting species may present an electrophilic character and consequently behave as an electrophilic epoxidation agent.

The chlorohydrin route is known to give epoxides with a stereochemistry opposite from what was obtained by the peracid method.[6]

In order to establish whether the epoxide formation results from a transfer of an electrophilic oxygen atom to the olefin (*syn* addition) or occurs via a possible formation of a chlorohydrin (*anti* addition), we have studied the stereochemistry of this catalytic epoxidation.

Here we report the results of the epoxidation of norbornene, 3-carene, and α-pinene with the NaOCl/Mn(TPP)OAc*/pyridine method.

In a typical experiment, a solution of 4 mmoles of olefin in 10 mL of dichloromethane with 0.04 mmole of Mn(TPP)(OAc), 0.05 mmole of dimethylbenzyldodecylammonium chloride, and 0.62 mmole of pyridine is stirred with 20 mL of 0.35 M NaOCl under nitrogen at room temperature.

In these conditions, norbornene **1** gives *exo*-2,3 epoxynorbornane **2** (isolated product : 41 %)

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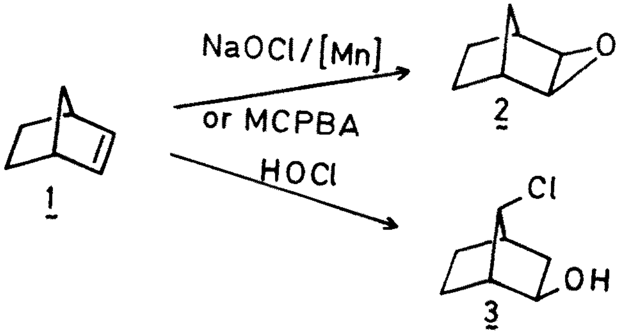
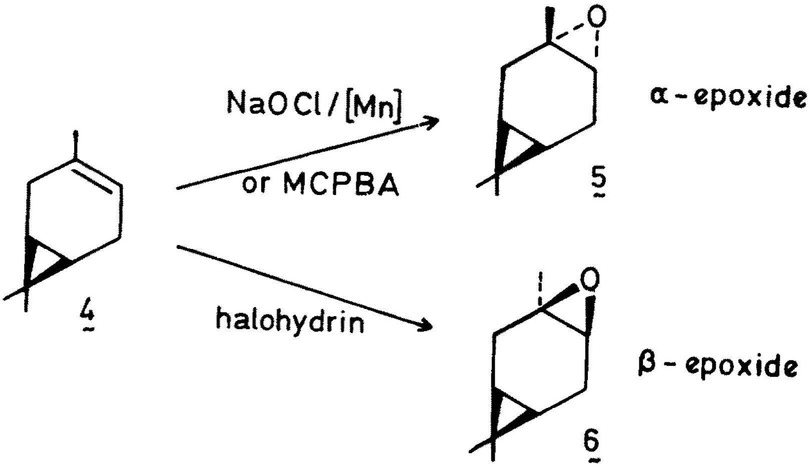
[*] Mn(TPP)OAc = tetraphenylporphyrinatomanganese acetate.

identical to an authentic sample prepared by peracid epoxidation.[7] In the case of the anti-addition of hypochlorous acid, the reaction would lead to the rearranged molecule **3**.[8]



MCPBA = meta-chloroperbenzoic acid

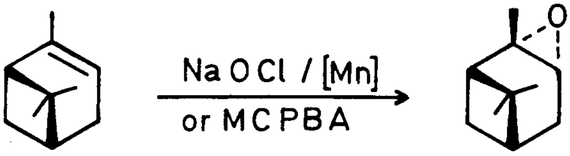
The syn-addition of the oxygen atom with NaOCl/ Mn is also confirmed in the case of 3-carene, **4**. The α-3,4-epoxycarane[9], **5**, is obtained in 60 % yield after 4 hours ($[\alpha]_D^{20} = +19°$, chloroform, c = 0.46).



No trace of the β isomer **6** usually obtained via halohydrin[10] is detected.

For these two olefins, the epoxidation occurs with the same stereochemistry as that observed with peracids. These results are in favour of the syn addition of an electrophilic oxygen atom in the case of aliphatic olefins without intermediate formation of chlorohydrins.

Using this catalytic epoxidation, we have also observed the same stereoselectivity as with peracids on other olefins like α-pinene, **7**, and trans-β-methylstyrene.



7 **8**

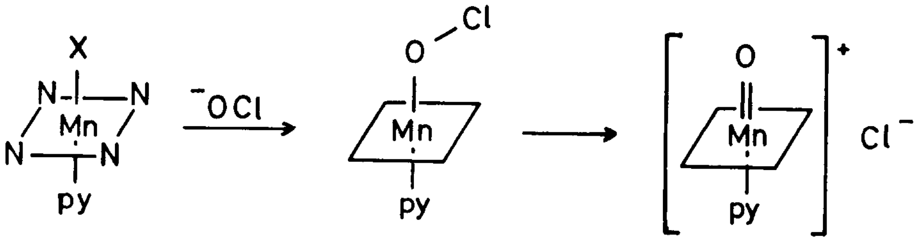
For **7**, the NaOCl/ Mn method affords the same isomer **8**, α-pinene oxide ($[\alpha]_D^{20}$ = -59°, chloroform, c = 1.17; 52 % yield in 4 hours) as with MPCBA,[12] corresponding to the addition of the epoxidizing species on the sterically less hindered side of the olefin.

The only product of the epoxidation of trans-β-methylstyrene is the epoxide[12] (52 % yield). This epoxide is easily isomerized on packed GC columns whereas the phenomenon is not observed on a wall-coated capillary column. It has to be noted that, within two hours, α-methylstyrene gives 95 % of the corresponding epoxide with NaOCl/[Mn].

Furthermore, an additional information is obtained from the epoxidation of 1,3-cyclooctadiene, where the product observed with NaOCl/ Mn is the monoepoxide (47 % yield).[13a] The absence of endoperoxide[13b] suggests that singlet oxygen $^{1}O_2$ is not present during the reaction (If any hydrogen peroxide is produced, the mixture of NaOCl and H_2O_2 can be a chemical source of singlet oxygen[14]).

From these data, it is reasonable to assume that this epoxidation route involves a catalytic transfer of an electrophilic oxygen rather than chlorohydrin intermediates or the presence of singlet oxygen.

Thus, the remaining hypothesis is the formation of a coordinated hypochlorite anion on the metalloporphyrin leading to two possible species as epoxidizing agents : the coordinated hypochlorite ligand itself (complex A) or, after a heterolytic cleavage of the oxygen-chlorine bond, an oxomanganese complex (complex B).



(A) (B)

We are currently investigating these two different hypotheses. The reactivity of the hypochlorite ligand in coordination chemistry is presently unknown since no example of complexes like A has been reported.

Acknowledgements : The authors are indebted to Prof. R. Poilblanc for this constant interest throughout this work and are grateful to the Produits Chimiques Ugine-Kuhlmann Company and the CNRS (ATP "Chimie Fine") for financial support. One of us (M.E. De Carvalho) thanks the CNPq (Brazil) for a doctoral fellowship.

References

1. a) J.T. Groves, R.E. Nemo and R.S. Myers, J. Amer. Chem. Soc., 1979, 101, 1032.
   b) C.K. Chang and M.S. Kuo, J. Amer. Chem. Soc., 1979, 101, 3413.
   c) J.R. Lindsay-Smith and P.R. Sleath, J. Chem. Soc. Perkin II, 1982, 1009.
2. a) I. Tabushi and N. Koga, Tetrahedron Letters, 1979, 3681.
   b) E. Guilmet and B. Meunier, Tetrahedron Letters, 1980, 4449.
3. a) I. Tabushi and N. Koga, J. Amer. Chem. Soc., 1979, 101, 6456.
   b) M. Perree-Fauvet and A. Gaudemer, J. Chem. Soc. Chem. Comm., 1981, 874.
   c) I. Tabushi and A. Yazaki, J. Amer. Chem. Soc., 1981, 103, 7371.
   d) D. Mansuy, M. Fontecave and J.F. Bartoli, J. Chem. Soc. Chem. Comm., 1983, 253.
4. a) H.J. Ledon, P. Durbut and F. Varescon, J. Amer. Chem. Soc., 1981, 103, 3601.
   b) D. Mansuy, J.F. Bartoli and M. Momenteau, Tetrahedron Letters, 1982, 2781.
5. a) E. Guilmet and B. Meunier, Tetrahedron Letters, 1982, 2449.
   b) E. Guilmet and B. Meunier, Nouv. J. Chim., 1982, 6, 511.
6. G. Berti, Topics in Setreochemistry, 1973, 7, 93.
7. a) H. Kwart and W.G. Vosburgh, J. Amer. Chem. Soc., 1954, 76, 5400.
   b) S.P. Soloway and S.J. Cristol, J. Org. Chem., 1960, 25, 327.
   c) S.P. Acharya and H.C. Brown, J. Org. Chem., 1970, 35, 196.
   d) R.A. Budnick and J.K. Kochi, J. Org. Chem., 1976, 41, 1384.
8. T.G. Traylor, Acc. Chem. Res., 1969, 2, 152.
9. a) K. Gollnick, S. Schroeter, G. Ohloff, G. Shade and G.O. Schenck, Annalen, 1965, 687, 14.
   b) W.D.P. Burns, M.S. Carson, W. Cocker and P.V.R. Shannon, J. Chem. Soc. (C), 1968, 3073.
10. W. Cocker and D.H. Grayson, Tetrahedron Letters, 1969, 4451.
11. V.P. Yurev, I.A. Gailyunas, Z.G. Isaeva and G.A. Tolstikov, Izv. Akad. Nauk. SSSR, Ser. Khim., 1974, 919.
12. a) N. Shimizu and P.D. Bartlett, J. Amer. Chem. Soc., 1976, 98, 4193.
    b) I. Tabushi, Y. Kuroda and Z. Yoshida, Tetrahedron, 1976, 32, 997.
13. a) M. Nee and J.D. Roberts, J. Org. Chem., 1981, 46, 67.
    b) A. Horinaka, R. Nakashima, M. Yoshikawa and T. Matswura, Bull. Soc. Chim. Jap., 1975, 48, 2095.
14. C.S. Foote, S. Wexler, W. Ando and R. Higgins, J. Amer. Chem. Soc., 1968, 90, 975.

(Received in France 26 May 1983)