Tetrahedron Letters,Vol.25,No.30,pp 3187-3190,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

THE STEREOSPECIFIC EPOXIDATION OF OLEFINS CATALYSED BY RUTHENIUM

G. Balavoine*, C. Eskenazi, F. Meunier et H. Rivière

Laboratoire de Chimie Organique des Eléments de Transition, LA-CNRS n° 255
Institut de Chimie Moléculaire d'Orsay, Bât. 420 91405 Orsay Cédex (France)

Summary : Epoxidation of olefins by sodium periodate is effected by the catalysis of $RuCl_3,(H_2O)_n$ *associated with bipyridyl. The reaction is stereospecific for both cis and trans alkenes.*

Ruthenium oxides are extremely powerful oxidising reagents which have been extensively used in oxidative transformations in organic chemistry[1]. These reactions involve the use either of a stoechiometric amount of ruthenium tetroxide, or more conveniently of a ruthenium compound in a catalytic quantity with a stoechiometric amount of a readily available oxidant. Many different catalyst-oxidant systems have been described, the most common of which involve $RuCl_3,(H_2O)_n$ as catalyst and hypochlorite or periodate as oxidant. Generally, the reactions are conducted in a two-phase solvent system such as CCl_4-H_2O Recently it has been shown by Sharpless that addition of acetonitrile as a cosolvent gives greatly improved results[2].

The behavior of inorganic transition metal oxidising agents can be modified by the introduction of ligands. Electron rich ligands which increase the basicity of the metal and moderate its oxidising power have been used to improve the selectivity of oxidations. Thus unlike chromium(VI) reagents such as CrO_3 or $HCrO_3Cl$, the corresponding pyridine[3] or bipyridyl complexes[4] are able to convert allylic or benzylic alcohols to the aldehydes and do not react with thioethers and olefins.

To our knowledge, in all reported catalyzed oxidations of olefins with the $RuCl_3(H_2O)_n$ hypochlorite or periodate system, the double bonds undergo the well known oxidative cleavage to ketones or carboxylic acids. However, as we observed, the oxidative cleavage is in some cases accompanied by the formation of a small amount of epoxides (< 1 %). On the other hand, some other oxidation and, in particular epoxidation reactions (all with low yields) have been described which involve ruthenium(II) complexes such as $RuCl_2(PPh_3)_3$ as catalyst with molecular oxygen[5-7] or terbutylhydroperoxide[7,8] as oxidant. This suggests that the use of a good electron donating ligand able to resist to a strongly oxidising environment might moderate the oxidising power of the $RuCl_3,(H_2O)_n/NaIO_4$ system and favour the epoxidation reaction at the expense of the oxidative cleavage of double bonds. In this paper, we report our initial results in the area of olefin epoxidation which confirm that the above postulate is indeed correct.

By employing bipyridyl as a ligand with the $RuCl_3,(H_2O)_n$ catalyst and $NaIO_4$ as oxidant in the solvent system CH_2Cl_2-H_2O we have found that, with the exception of compounds with a terminal double bond, the oxidation of olefinsleads to epoxides rather than to ketones or carboxylic acids (Table I).

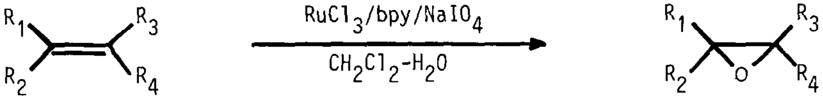
This method provides a convenient and efficient new synthesis of epoxides (yields up to 83 %). In a typical experiment, a flask is charged with a magnetic stirrer, 4 ml of water, 7 mg (0.027 mmol) of ruthenium trichloride hydrate (calculations based on $n = 3$ for $RuCl_3(H_2O)_n$) and 25 mg (0.16 mmol) of bipyridyl. The mixture was stirred vigorously at 0-5°C for 5 min. Then, a solution of 250 mg (1.4 mmol) of *trans*-stilbene in 6 ml of CH_2Cl_2 was added, followed by 600 mg (2.8 mmol) (2 equiv.) of sodium metaperiodate and, the resulting reaction mixture was stirred for 15 h at 0-5°C. Then, a solution of sodium hydroxide (1 M) was added to adjust the pH of the aqueous phase to 12. The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (4 x 10 ml). The combined organic extracts were washed with saturated sodium chloride, dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography on silica (pentane/ether (1:1) as eluent) to give *trans*-stilbene epoxide (228 mg, 83 %). In table I the yields are for isolated products which were identified by comparison with authentic samples, by GC/MS and NMR spectroscopy.

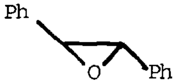
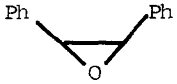
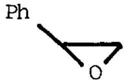
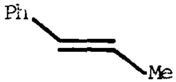
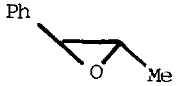
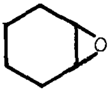
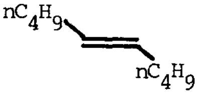
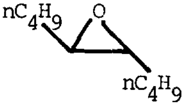
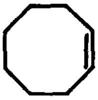
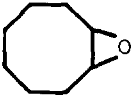
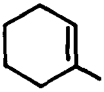
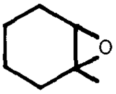
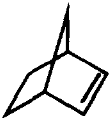
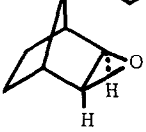
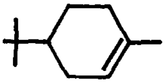
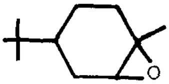
Examination of table I reveals that the results are variable although in all cases the conversion of olefins is total. The side products result from oxidative cleavage of the double bond or of rearrangement of the epoxide. Control experiment run on cyclohexene and styrene showed that the corresponding epoxides are not stable in the reaction medium.

The epoxidation is syn and stereospecific for both *cis* and *trans* alkenes[9] (runs 1, 2, 4, 6) ; furthermore no isomerisation of olefins occurs during the course of the reaction, in contrast to some other systems[10]. This observation rules out a mechanism involving radical intermediates[10,11]. It seems likely that periodate transfers an oxygen atom to a ruthenium bipyridyl complex to form a metal oxo intermediate[12] from which the transfer of "oxene" to the carbon-carbon double bond could take place. The mechanism of this process could well be similar to that proposed by Sharpless involving an oxo metallacycle intermediate[13-15]. Preliminary experiments showed that ruthenium(II) bipyridyl complexes such as *cis*-$[(bpy)_2RuCO_3]$ or *cis*-$[(bpy)_2RuCl_2]$ can be used as catalyst precursors whereas $[(bpy)_3Ru]^{2+}$ is inactive. Further investigations are necessary to clarify the mechanism of the reaction and the nature of the reactive species. However, to the best of our knowledge, we have reported here the first example of high yield epoxidation catalysed by ruthenium. We are presently exploring the possibility of using other ligands and oxygen donors.

Aknowledgements : The authors wish to thank the Centre National de la Recherche Scientifique for financial support and for a scholar fellowship (F.M.).

Table I : Epoxidation of olefins



	Substrate	reaction time a)	Product	Yield b)
1)		15 h		83 %
2)		15 h		45 %
3)		15 h		24 %
4)		18 h		48 %
5)		15 h		10 %
6)		15 h		68 %
7)		15 h		70 %
8)		15 h		55 %
9)		4 h		56 %
10)		4 h		65 % c)

a) Reaction time at 0-5°C, for total conversion of olefins. At room temperature, reactions are about three times faster, but yields in epoxides are lower, and cleavage products more abondants.

b) Yields of isolated products.

c) *cis/trans* ratio = 60/40.

REFERENCES

1) a- D.G. LEE and M. Van den ENGH, in "Oxidation in Organic Chemistry", W.S. TRAHANOVSKY ed., Academic Press, N.Y. 1973.

   b- E.S. GORE, Platinum Metal Reviews (Johnson Matthey ed.) 27, 111 (1983).

2) P.H.O. CARLSEN, T. TATSUKI, V.S. MARTIN and K.B. SHARPLESS, J. Org. Chem., 46, 3936 (1981).

3) a- G.I. POOS, G.E. ARTH, R.E. BEYLER and L.H. SARETT, J. Amer. Chem. Soc., 75, 422 (1953).

   b- R.W. RATCLIFFE, Org. Syn., 55, 84 (1976).

4) F.S. GUZIEC, Jr., and F.A. LUZZIO, Synthesis, 9, 691 (1980).

5) M.E. PUDEL, L.G. PRIVALOVA, Z.H. MAIZUS, L.U. REVENKO, M.L. KHIDEKEL and I.V. KALECHITS, Neftekhimiya, 13, 64 (1973).

6) S. CENISI, A. FUSI and F. PORTA, Gazz. Chim. Ital., 108, 109 (1978).

7) J.O. TURNER and J.E. LYONS, Tetrahedron Lett., 29, 2903 (1972).

8) J.O. TURNER and J.E. LYONS, German Patent 2,231,678 (1973).

9) *Cis* and *trans* stilbenes are epoxidized at approximatively equal rates, but *cis* stilbene undergoes undesired oxidative cleavage of the double bond to give benzaldehyde faster than *trans* stilbene. These observations are consistent with the yields reported in table I for *cis* and *trans* stilbenes oxides (runs 1 and 2).

10) C.C. FRANKLIN, R.B. Van ATTA, A. FANTAI and S.S. VALENTINE, J. Amer. Chem. Soc., 106, 814 (1984).

11) J.T. GROVES, W.J. KRUPER, Jr., R.C. HAUSHALTER, J. Amer. Chem. Soc., 102, 6375 (1980).

12) B.A. MOYER and J.J. MEYER, Inorg. Chem., 20, 436 (1981).

13) H.B. SHARPLESS, A.Y. TERANISHI and J.E. BACKWALL, J. Amer. Chem. Soc., 99, 3120 (1977).

14) H. MIMOUN, I. SERREE de ROCH and L. SAJUS, Tetrahedron, 26, 37 (1970).

15) M. SCHRÖDER and E.C.CONSTABLE, J. Chem. Soc., Chem. Commun., 734 (1982)

(Received in France 10 April 1984)