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EPOXIDATION WITH THE H_2O_2/VILSMEIER REAGENT SYSTEM

By Jean-Pierre DULCERE and Jean RODRIGUEZ

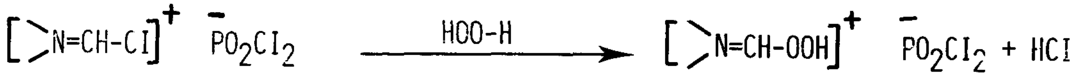
Laboratoire Associé au C.N.R.S. n° 109 - Faculté des Sciences et Techniques - Rue Henri Poincaré - F. 13397 MARSEILLE CEDEX 13.

SUMMARY : Alkenes 1 a-d interact at -80°C in 15 min. with the Vilsmeier reagent I $(Me_2N{=}CHCl)^+PO_2Cl_2^-$ *in presence of 30%* H_2O_2 *to yield the corresponding epoxides 3 a-d. The reaction could involve the formation of the highly reactive hydroperoxymethylenedimethylammonium salt* $(Me_2N{=}CH{-}OOH)^+PO_2Cl_2^-$ *II.*

The ability of the Vilsmeier reagent I to give rise to products of substitution with substrates bearing a labile hydrogen atom received interesting applications for the preparation of alkyl halides (1) esters (2) or nitriles (3) from alcohols, acids or aldoximes, respectively.

We expected such a reaction of substitution to occur between Vilsmeier reagent I (7) and hydrogen peroxide, to afford hydroperoxymethylenedimethylammonium salt II (Scheme I).

The aim of our investigations in this work will particularly concern the behaviour of II towards alkenes 1 a-d.



I

SCHEME I

II

Attempts to isolate the highly electrophilic hydroperoxymethylenedimethylammonium salt II were unsuccessful. Therefore, we investigated oxygen atom transfer reactions of this unstable peroxide, by adding an alkene in the medium.

According to the Scheme II, one can observe that when II is generated in presence of an olefin in MeOH it whether acts as an oxidant of HCl (path A) or a powerful epoxidizing reagent (pàth B), depending on reaction temperature.

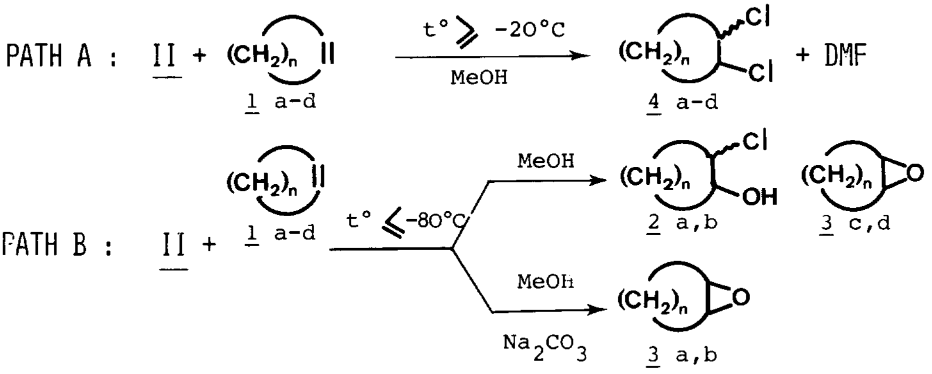
Path A : When t° $\geq$ -20°C, addition of chlorine on the double bond constitutes the exclusive reaction and results in trans 1,2-dichlorocompounds 4a, b, c, d (95-98 %) (4).

Path B : When t° $\leq$ -80°C, the epoxidation reaction affords in 15 min. 3c, d (95-97%) (5) whereas 1a, b are converted whether to the trans chlorhydrins 2a, b (50-85%) or the alkene oxides 3a, b (55-60 %) by addition of sodium carbonate.

Yields are given for recovered products by GC or silica gel column.

All compounds gave satisfactory microanalyses and spectral data.

1a : n = 4 ; 1b : n = 5 ; 1c : n = 6 ; 1d : n = 10.



SCHEME II

The strongly electrophilic character of hydroperoxymethylenedimethylammonium salt, together with the substantial driving force from the formation of the stable DMF molecule can account of the reactivity of this new H_2O_2/Vilsmeier reagent system.

Because of the very low temperature (-80°C) and the short reaction time (15 min.) required to effect the oxygen tranfer, our data indicate that the cheap hydrogen peroxide / Vilsmeier reagent system can be a highly efficient epoxidative reagent. For these reasons, our method competes advantageously other ones recently published (6).

We are currently investigating synthesis and properties of various hydroperoxymethyleneалkylammonium salts, including optically active derivatives.

REFERENCES

1 - D.R. HEPBURN, H.R. HUDSON, Chem. and Ind., 1974, 664 and J.C.S. Perkin I, 1976, 754.

2 - P.A. STADLER, Helv. Chim. Acta, 1978, 61, 1675.

3 - J.P. DULCERE, Tetrahedron Letters, 1981, 22, 1599.

4 - If a mixture of 1c in DMF, 30% H_2O_2 and 2 equivalents of HCl is stirred for 1 hr at -20°C, 1c is quantitatively recovered, leading to the assumption that the system II is essential to provide chlorine from HCl.

5 - Typical experiment : At -80°C, I (30 mmol) in CH_2Cl_2 (20 ml) is added dropwise in 15 min. to a mixture of 1b (30 mmol) in CH_3OH (30 ml) and 30 % H_2O_2 (4 ml). Then addition of H_2O (40 ml) is followed by ether extraction. The organic extracts are carefully washed with an ammonium-iron (II) sulfate solution.

6 - J. REBEK and R. Mc CREADY, Tetrahedron Letters, 1979, 1001 and 4337.
J. REBEK and R. Mc CREADY, Tetrahedron Letters, 1980, 2491.
A.L. BAUMSTARK, D.R. CHRISOPE, M.E. LANDIS, J. Org. Chem., 1981, 46, 1964.
C.J. STARK, Tetrahedron Letters, 1981, 22, 2089.

7 - L.A. PAQUETTE, B.A. JOHNSON and F.M. HINGA, Org. Synth., 1966, 46, 18.

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