Tetrahedron Letters,Vol.29,No.23,pp 2817-2818,1988 0040-4039/88 $3.00 + .00
Printed in Great Britain Pergamon Press plc

ACID CATALYZED OXYGEN TRANSFER FROM AN OXAZIRIDINE TO A THIOETHER

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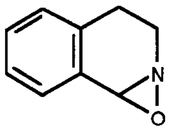
Summary : Oxygen can be transferred from the oxaziridine derived from 3,4-dihydroisoquinoline to a thio-ether. As shown by the different pathways followed on various conditions, the oxygen transfer depends on acid catalysis and on the nucleophilicity and basicity of the substrate.

We have found that the transfer of the oxygen atom of an oxaziridine on a thioether, previously achieved by substitution of an electron attracting group on the nitrogen of the oxaziridine[1], may be also obtained by acid catalysis .

Oxaziridine 1[2] is stable in deuteriochloroform or methylene chloride. In the presence of one equivalent of trifluoroacetic acid it transfers its oxygen atom to dimethylsulfide, to give dimethylsulfoxide (quantitative, by NMR). In the same acidic conditions methyl-phenyl sulfoxide, diphenylsulfoxide and phenyl-vinyl sulfoxide have been prepared (85%, 73% and 72%, isolated), but trimethylamine, N-methyl morpholine, dimethylsulfoxide and norbornene do not react. This reaction of the oxaziridine requires the simultaneous presence of acid and sulfide. Other reactions take place if one of the two is absent : isomerisation to nitrone 5[2] (quantitative by NMR) in the absence of sulfide, formation of lactam 2[3] and isoquinoline 3 (38% and 41% isolated) in the absence of acid.



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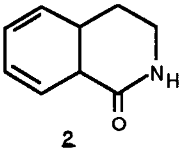

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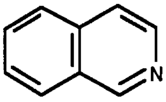

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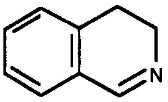

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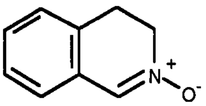

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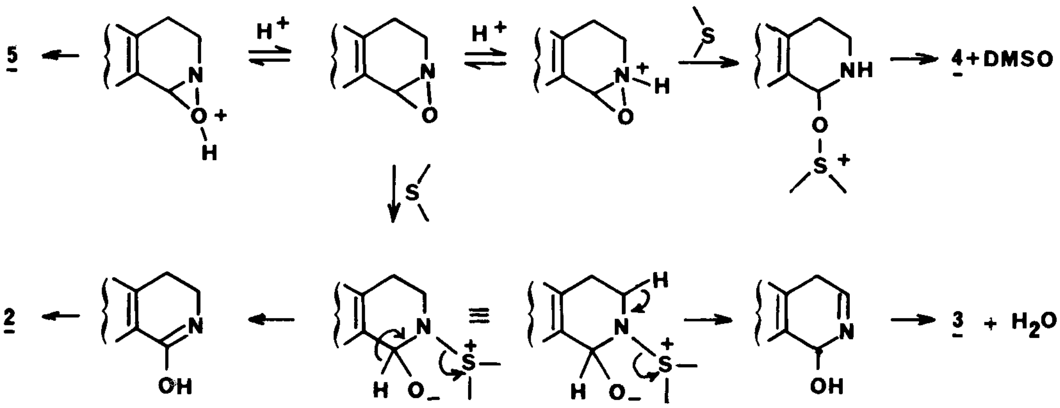
These results can be rationalized according to scheme 1. In the presence of acid, the two protonated oxaziridines, at oxygen or at nitrogen, are in equilibrium and one or the other reacts according to the nucleophilicity of the substrate, no reaction taking place if the substrate is a relative strong base. In absence of acid a weakly basic strong nucleophile reacts at the nitrogen[4]. A more basic substrate, as trimethylamine, abstracts a proton on carbon 3, leading directly to an imino-carbinol[5] and then to isoquinoline without formation of the lactam.



SCHEME 1

In conclusion, acid catalyzed transfer of oxygen from an oxaziridine is feasible but seems limited to weakly basic, relatively strong, nucleophiles. This results may have some biochemical implications. Flavoproteine-monooxygenases transfer an oxygen atom on thioethers and amines ; an oxaziridine has been proposed as the active intermediate[6]. Activation by protonation, or some equivalent, without deactivating the substrate, such an amine, seems required.

BIBLIOGRAPHY

1 - F.A. DAVIS, J.P. McCAULEY Jr. and M.E. HARAKAL, J. Org. Chem., 49, 1465 (1984).

2 - Y. OGATA and Y. SAWAKI, J. Am. Chem. Soc., 95, 4692 (1973).

3 - E. BAMBERGER and W. DIECKMANN, Ber., 26, 1205 (1893).

4 - Y. HATA and M. WATANABE, J. Am. Chem. Soc., 101, 6671 (1979).

5 - W.D. EMMONS, J. Am. Chem. Soc., 79, 5739 (1957) ; P. MILLIET and X. LUSINCHI-Tetrahedron, 30, 2825 (1974).

6 - H.W. ORF and D. DOLPHIN, Proc. Natl. Acad. Sci., U.S.A., 71, 2646 (1974).

(Received in France 15 April 1988)