Tetrahedron Letters No. 12, pp 1151 - 1153, 1972. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF OXIMES IV. OXAZIRANES AS INTERMEDIATES IN THE FORMATION OF AMIDES.

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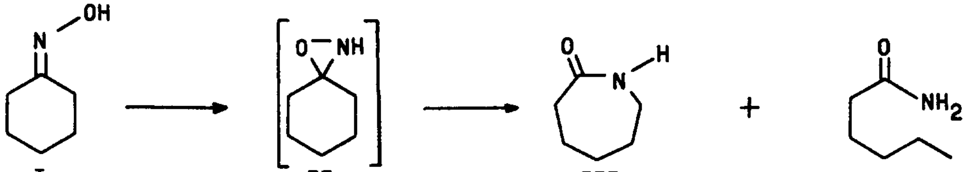
(Received in USA 7 February 1972; received in UK for publication 15 February 1972)

Several recent publications (1a-g) have dealt with the photoreactions of oximes. In many cases (1a, 1d-h), oxaziranes (II) have been postulated to be intermediates in the photodecomposition which leads to Beckmann-type rearrangement products (III) in methanol and dilute (0.1%) aqueous solutions, and amides (IV) derived from reductive α-cleavage in iso-propanol (Table I).

Table I



I II III IV

Ratio of III/IV obtained from			
irradiation^{3} of Oxime I in methanol	9	:	1
Oxazirane II in methanol	2	:	1
Oxime I in iso-propanol	1	:	50
Oxazirane II in iso-propanol	1	:	4

It was not known if the products were formed by thermolysis or photolysis of the hypothetical intermediate oxaziranes. We have therefore prepared several oxaziranes by known methods (2) and studied their photo- and thermal reactions.

Oxaziranes were found to be both thermally and photochemically unstable in alcoholic solvents. The decomposition half-lives of 3,3-pentamethyleneoxazirane (II) (0.2% solutions) are summarized below.

Solvent	Thermal decomposition (25°) $\tau_{1/2}$ (mins)	Photodecomposition[3] $\tau_{1/2}$ (mins)
water	ca. 3	ca. 1
methanol	63	10
ethanol	253	
isopropanol	320	
t-butanol	900	51

For comparison, $\tau_{1/2}$ for cyclohexanone oxime under the same conditions in methanol is 65 minutes.

The products obtained from the photochemical decomposition of oxazirane II and oxime I are identical, but the ratio of lactam to amide produced is different (Table I). The products from the thermal decomposition of oxazirane are cyclohexanone, oxygen and ammonia in water, 1,1-dimethoxycyclohexane in methanol and isopropoxycyclohexene in isopropanol.

In contrast, the oxazirane corresponding to 2-methylcyclohexanone oxime underwent rearrangement to oxime under both photolytic and thermal conditions, showing the (hypothetical) oxime to oxazirane conversion to be reversible.

Comparison of $\tau_{1/2}$ for oxazirane in methanol with $\tau_{1/2}$ for decomposition of the oxime shows that the intermediate can only be present in fairly low steady state concentrations.

It has been reported that the products formed by photolysis of cyclohexanone oxime in water are concentration dependent (1d), cyclohexanone, ammonia and oxygen being the major products at high (1%) concentration and caprolactam at low (0.1%) concentration, using a constant light-source. The simplest explanation for this striking change is that at low concentration, the photo process predominates (see Table I). At high concentration, $\tau_{1/2}$ for the photorearrangement would increase, since the light source remained constant, whereas $\tau_{1/2}$ for the thermal decomposition would remain constant, since the latter process is unimolecular or pseudo-unimolecular. The net result would then be the predominant formation of products of thermal decomposition.

In conclusion, the data presented are qualitatively consistent with oxaziranes being intermediates in the photolysis of oximes, but do not exclude other, perhaps more direct pathways for the phototransformation of oximes to amides.

REFERENCES

1.a. J.H. Amin and P. de Mayo, Tetrahedron Letters, 1585 (1963).
  b. R. T. Taylor, M. Douek and G. Just, Tetrahedron Letters, 4143 (1966).
  c. T. Sato and H. Obase, Tetrahedron Letters, 1633 (1967).
  d. G. Just and L.S. Ng, Canad. J. Chem., 46, 3381 (1968).
  e. T. Oine and T. Mukai, Tetrahedron Letters, 157, (1969).
  f. H. Izawa, P. de Mayo and T. Tabata, Canad. J. Chem., 47, 51 (1969).
  g. B. Fox and N. Rosenberg, Chem. Commun., 1115, (1969).
  h. H. Suguinome and H. Takahashi, Tetrahedron Letters, 5119, (1970).
2.a. E. Schmitz, R. Ohme and D. Murawski, Angew, Chem., 73, 708, (1961).
  b. E. Schmitz, R. Ohme and S. Schramm, Chem. Ber., 97, 2521, (1964).
  c. E. Schmitz and D. Murawski, Chem. Ber., 98, 2525, (1965).
3. All irradiations were carried out in quartz cells in a Rayonet Photochemical Reactor model 1061, with lamps having peak emission at the 253.7 nm line.

ACKNOWLEDGEMENTS

We wish to thank the National Research Council of Canada for generous financial support.