Tetrahedron Letters No.46, pp. 4801–4802, 1968. Pergamon Press. Printed in Great Britain.

AZIRIDINES XIX. THE PHOTOLYSIS OF 1-(2,4,6-TRINITROPHENYL)-2,3-DIPHENYLAZIRIDINE AND 1-(2,4-DINITROPHENYL)-2-PHENYL-3-BENZOYLAZIRIDINE

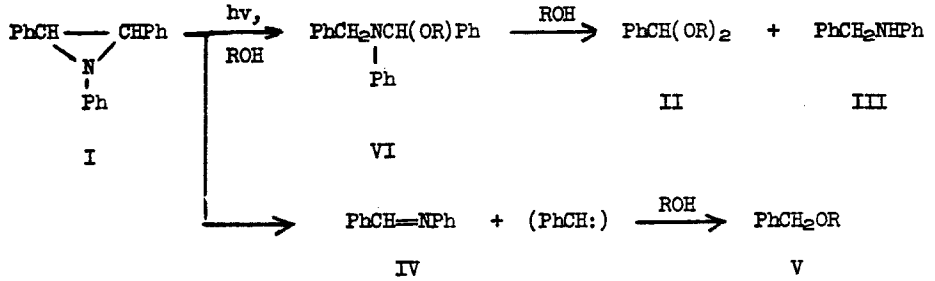
Harold W. Heine, Gregory J. Blosick and George B. Lowrie III

Department of Chemistry, Bucknell University

Lewisburg, Pennsylvania 17837

(Received in USA 12 June 1968; received in UK for publication 16 August 1968)

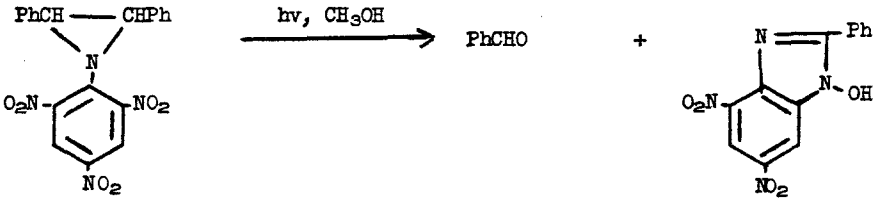
The photochemistry of 1,2,3-triphenylaziridine(I) has recently been investigated(1). Irradiation of I in alcoholic solvents gave benzaldehyde acetals(II), N-benzylaniline(III), benzalaniline(IV) and alkyl benzyl ethers(V). Conversion of I to the intermediate VI and subsequent reaction of VI with the solvent is presumed to form II and III. Fragmentation of I to IV and phenylcarbene is also suggested to occur. Interaction of phenylcarbene with the solvent affords V.



We have studied the photolysis of cis-1-(2,4,6-trinitrophenyl)-2,3-diphenylaziridine(VII) and 1-(2,4-dinitrophenyl)-2-phenyl-3-benzoylaziridine(VIII). The photolytic products in alcohols are quite different from those observed with I due to the interaction of a nitro group with the aziridine ring. Compound VII (mp 189-90°) was prepared by reaction of cis 2,3-diphenylaziridine with 2,4,6-trinitroanisole in methanol. Compound VIII (mp 156-8°) was synthesized by the slow addition of an ethereal solution of 1-fluoro-2,4-dinitrobenzene and triethylamine to an ethereal

solution of 2-phenyl-3-benzoylaziridine (mp 97-8°) and allowing the reaction mixture to stand at room temperature for one day.

Irradiation of a methanolic solution of VII by a Hanovia mercury arc Type 16106 for an hour caused deposition of 1-hydroxy-2-phenyl-4,6-dinitrobenzimidazole (IX, mp 281-2°) on the walls of the reaction flask in 95% yield. Benzaldehyde was also formed and was isolated as its 2,4-dinitrophenylhydrazone. If an ethanolic solution of VIII is irradiated under similar conditions and the

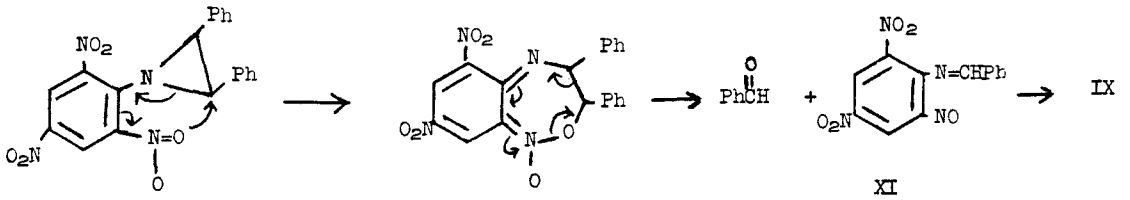


VII IX

solvent evaporated a 96% yield of 1-hydroxy-2-phenyl-6-nitrobenzimidazole(X, mp 264-5°) is obtained.

Compounds IX and X were also synthesized by refluxing N-benzyl-2,4,6-trinitroaniline and N-benzyl-2,4-dinitroaniline respectively in methanol containing sodium hydroxide. The base-catalyzed cyclization of N-benzyl-o-nitroanilines is a general method for the preparation of 1-hydroxybenzimidazoles(2).

A possible reaction sequence to account for the products of irradiation involves conversion of VII to the nitroso intermediate XI.



XI

Acknowledgement: We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work.

References

(1) H. Nozaki, S. Fujita and R. Noyori, Tetrahedron 24, 2193(1968).

(2) G. W. Stacy, B. V. Ettling and A. J. Papa, J. Org. Chem. 29, 1537(1964).