

AZIRIDINES XIX. THE PHOTOLYSIS OF 1-(2,4,6-TRINITROPHENYL)-2,3-DIPHENYL-AZIRIDINE AND 1-(2,4-DINITROPHENYL)-2-PHENYL-3-BENZOYL-AZIRIDINE

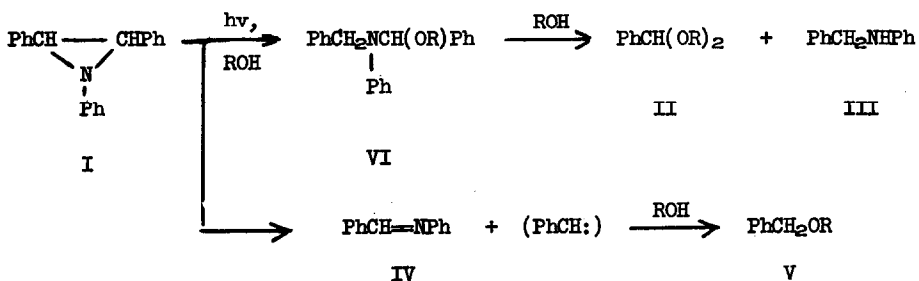
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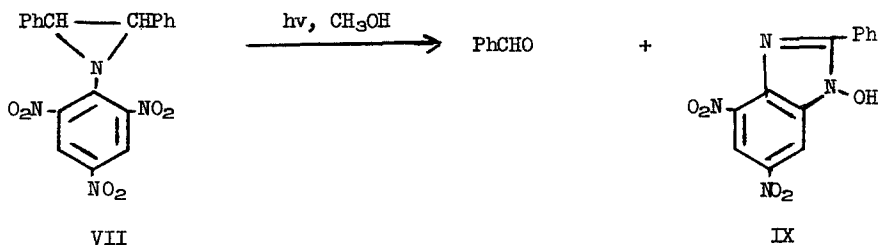
The photochemistry of 1,2,3-triphenylaziridine(I) has recently been investigated(1). Irradiation of I in alcoholic solvents gave benzaldehyde acetals(II), N-benzylaniline(III), benzalaniline(IV) and alkyl benzyl ethers(V). Conversion of I to the intermediate VI and subsequent reaction of VI with the 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.

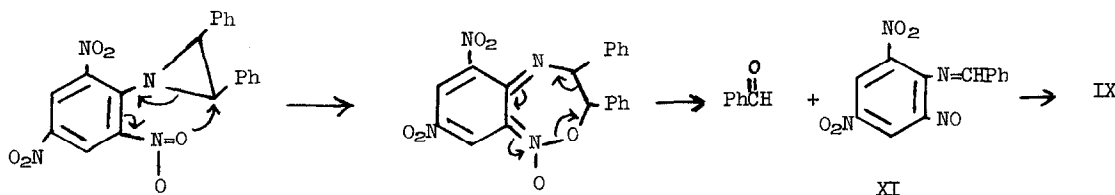
Irradiation of a methanolic solution of VII by a Hanovia mercury arc Type 16106 for an hour caused deposition of 1-hydroxy-2-phenyl-4,6-dinitrobenzimidazole (IX, mp 281-2°) on the walls of the reaction flask in 95% yield. Benzaldehyde was also formed and was isolated as its 2,4-dinitrophenylhydrazone.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



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.



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References

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