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IRRADIATION OF 3- SUBSTITUTED-2-PHENYLOXAZIRIDINES

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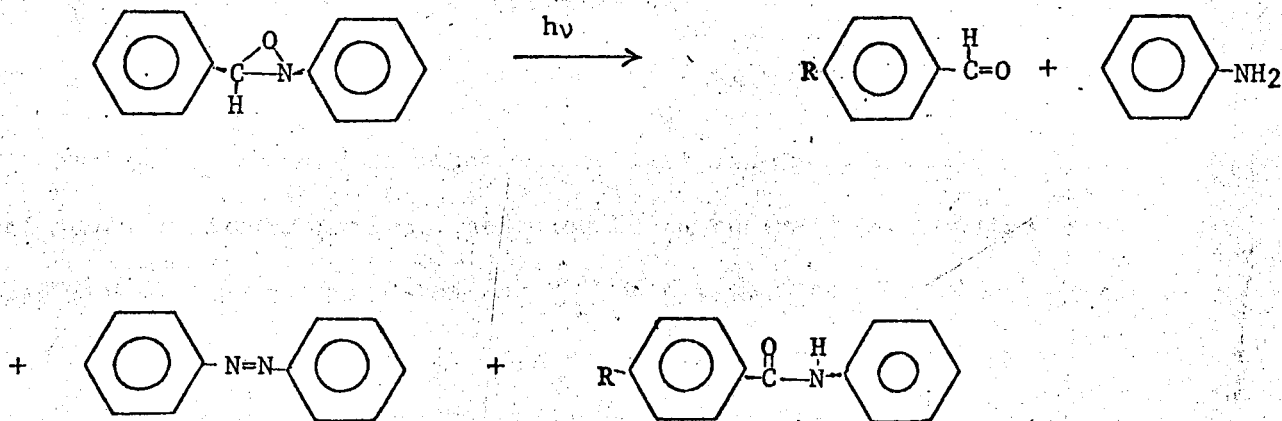
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University of California, Berkeley, California

August 30, 1967

It was noted previously that 3-(p-dimethylamino)-2-phenyloxaziridine (I) and 3-(p-dimethylamino)-2-(m-nitrophenyl)oxaziridine were photosensitive.¹ Further study on the irradiation (in a variety of solvents under nitrogen) of (I), 2,3-diphenyloxaziridine (II), and 3-(p-nitrophenyl)-2-phenyloxaziridine (III)² indicates the major photo-reaction to be cleavage to the aldehyde and an intermediate which forms



aniline and azobenzene. There is also formed in the photolysis varying amounts of the corresponding anilide.³ The following table gives the yields in three different solvents.

TABLE I

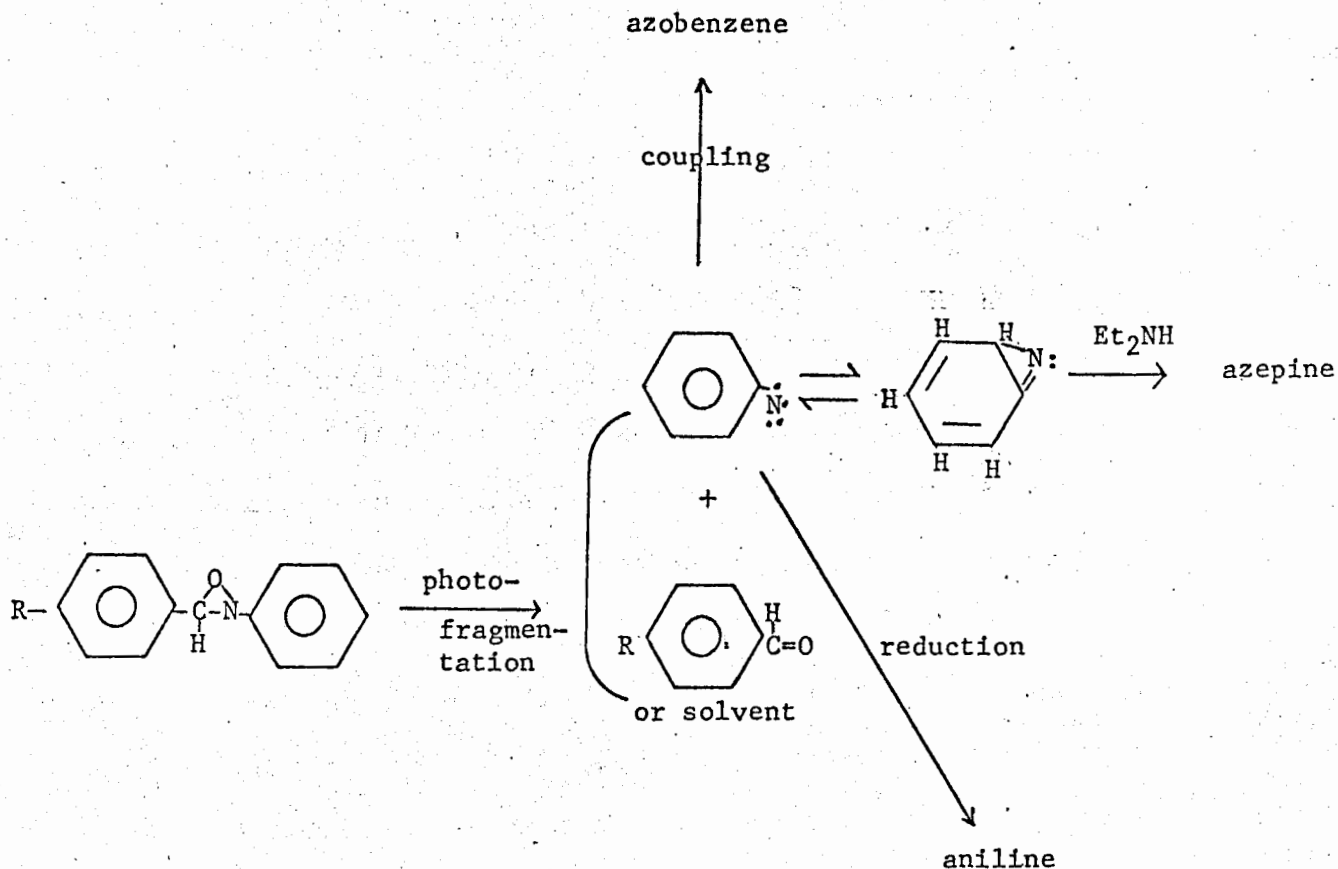
Products from the Irradiation of Oxaziridines^a

Oxaziridine	Solvent	% Yield			
		Aldehyde	Aniline	Azobenzene	Anilide
I	CH ₃ COCH ₃	54	15	15	12
I	C ₆ H ₅	45	7	15	32
I	(C ₂ H ₅) ₂ NH	18	50	--	16
II	CH ₃ COCH ₃	50	15	3	7
II	C ₆ H ₅	55	15	7	25
II	(C ₂ H ₅) ₂ NH	40	35	3	13
III	CH ₃ COCH ₃	75	16	17	7
III	C ₆ H ₅	75	4	8	8
III	(C ₂ H ₅) ₂ NH	40	45	2	2

a) Irradiations were carried out under nitrogen in a water-cooled quartz jacket around a 450 watt Hanovia Type L mercury vapor lamp. Concentrations were 1×10^{-3} M in starting nitrene. II was irradiated for 3-1/2 min., III for 4 min. I was irradiated with a pyrex filter for 6-1/2 min. Products were separated on an Aerograph A-90-P preparative gas chromatograph with a 10 ft. x 1/4in. column of 4.8% SE30 on Aeropak. Product analysis was by GLC retention times on an F & M Research Chromatograph 5750 with a 6 ft. x 1/8 in. column of 10% SE30 on Chrome W, ultraviolet absorption spectroscopy on a Cary 14 Spectrophotometer, and mass spectroscopy on a Consolidated Electroynamics Type 21-103C Mass Spectrograph. The yields of anilide were corrected for anilide resulting from a small amount of unirradiated oxaziridine.

Phenylazide on irradiation in hydrocarbon solvents forms aniline and azobenzene in small amounts from the intermediate phenylnitrene.⁴ By analogy the intermediate in the oxaziridine irradiation may be phenylnitrene.⁵ Recently, oxiranes have been reported to undergo photofragmentation to the aldehyde or ketone and the substituted carbene.⁶

Oxaziridine photolysis was done in diethylamine with the intention of trapping the intermediate phenylnitrene.⁷ However, only a trace of 2-diethylamino-3H-azepine was detected by gas-liquid chromatography, although the yield of aniline was greatly increased. When phenylazide was irradiated in diethylamine in the presence of approximately equal molar amounts of p-dimethylaminobenzaldehyde, just a small amount of the azepine (> 7%) was found but a high yield (> 80%) of aniline was produced. Since all three of our oxaziridines would yield an aldehyde alone with the nitrene on photofragmentation we can understand the suppression of azepine formation in terms of the competitive reduction of the nitrene to aniline either directly by the aldehyde or catalytically influenced by it. Since the diethylamine solvent normally promotes the formation of azepine which is almost completely suppressed by the external presence of aldehyde, we suggest that the azacyclopropene may be in equilibrium with the nitrene.



Along with the photofragmentation reaction, there was photorearrangement to the corresponding anilide. When (I) was irradiated in acetone or benzene in air, the fragmentation reaction was greatly quenched but the photorearrangement was not. When the irradiation time in air was the same as in the nitrogen atmosphere, at least 30% of the oxaziridine was unchanged with the yield of anilide remaining the same as in nitrogen. This suggests that it is the triplet state of the oxaziridine that undergoes photofragmentation and the singlet state that undergoes rearrangement.

The photolysis of oxaziridines with substituents other than phenyl in the 2-position is being studied.

References and Footnotes

- (1) J. S. Splitter and M. Calvin, *J. Org. Chem.* 30, 3427 (1965),
Footnote 11.
- (2) These oxaziridines from irradiation of the corresponding nitron are thermally unstable, but in the solvents used have half-lives of many hours (Ref. 1). A complication in the irradiation of the oxaziridines is the photosensitivity of the aldehydes and to a lesser extent the other products.
- (3) There was a small amount of imine formed in the irradiation of the oxaziridines.
- (4) (a) R. A. Abramovitch and B. A. Davis, *Chem. Rev.* 64, 149 (1964).
(b) J. H. Hall, J. W. Hill and H. Tsai, *Tetrahedron Letters*, 1965, 2211.
(c) G. Smolinsky, E. Wasserman and W. A. Yager, *J. Am. Chem. Soc.* 84, 3220 (1962).
- (5) C. J. Pedersen, *J. Am. Chem. Soc.* 79, 5014 (1957) obtained azo compounds (some in high yields) from the photolysis of N,N'-disubstituted p-quinonediimine-N,N'-dioxides. This is suggestive of photofragmentation of the intermediate oxaziridine.
- (6) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.* 88, 1579 (1966); A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson and I. Sarkar, 153rd meeting of the American Chemical Society, Miami, Florida, April 10-14, 1967, Abstract O-160.
- (7) W. v. E. Doering and R. A. Odum, *Tetrahedron*, 22, 81 (1966); at the time this communication was prepared, E. Meyer and G. W. Griffin, *Angew. Chem.* 79, 648 (1967) reported a 10% yield 2-diethylamino-3H-azepine from the irradiation of a 2-phenyl spirooxaziridine in diethylamine and postulated photofragmentation to phenylnitrene.