Tetrahedron Letters No.12, pp. 1445-1448, 1968. Pergamon Press. Printed in Great Britain.

IRRADIATION OF 3-SUBSTITUTED-2-PHENYLOXAZIRIDINES--DIRECT EVIDENCE FOR PHENYLNITRENE

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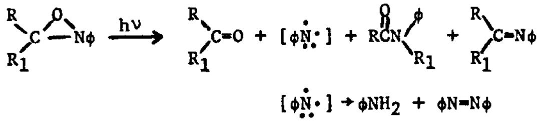
(Received in USA 15 September 1967)

It was noted previously that 3-(p-dimethylaminophenyl)-2-phenyloxaziridine (I) was photosensitive.[1] Further study on the irradiation of I[2] and 2,3,3-triphenyloxaziridine (II)[3] indicates the major photoreaction to be cleavage to the aldehyde from I, ketone from II, and phenylnitrene.[4] Phenylnitrene was demonstrated in the photolysis of II at 77°K in acetophenone and in methylene chloride-Fluorolube solution.[5] Its EPR absorption spectrum at 6701 gauss was identical in all characteristics to that of the ground state triplet phenylnitrene produced from the photolysis of phenylazide in Fluorolube.[6] There was no indication of the presence of diphenylmethylene.[7]



I, R = p-$(CH_3)_2NC_6H_4$; R_1 = H   II, R = R_1 = φ

In Table I are given the results of the photolyses of I and II under various conditions. Diethylamine was used as a solvent with the intention of trapping the intermediate phenylnitrene.[8] However, only a trace of 2-diethylamino-3H-azepine was detected although the yield of aniline was greatly increased in the photolysis of I.[9] Varying amounts of anilide and imine[10] were also formed.

The photolysis of I (see Table I) under oxygen shows quenching of the photofragmentation but little quenching of the rearrangement to anilide. Oxaziridine II has little absorption above 280 mμ,[3] and so with direct irradiation in diethylamine and benzene very little photofragmentation occurs. However, under nitrogen in acetone or with p-dimethylaminobenzaldehyde added to the diethylamine solution, a considerable increase in photofragmentation results. Since oxygen is known to be an efficient triplet state quencher and acetone a triplet state photosensitizer, the results indicate that it is the oxaziridine triplet state that undergoes photofragmentation and the singlet state that undergoes rearrangement. Since the major

Table I

PRODUCTS FROM THE IRRADIATION OF TWO OXAZIRIDINES(a)

Oxaziridine	Solvent	Photolysis Conditions(b)	% Yield(c) Unchanged oxaziridine	Aldehyde or ketone	Aniline	Azobenzene	Anilide	Imine
I	CH_3COCH_3	N,6-1/2	4	54	15	15	12	2
I	C_6H_6	N,6-1/2	2	45	7	15	24	4
I	$(C_2H_5)_2NH$	N,6-1/2	2	27	50	-	10	6
I	CH_3COCH_3	0,6-1/2	25	30	9	6	12	-
I	C_6H_6	0,6-1/2	15	19	7	4	18	-
II	$(C_2H_5)_2NH$	0,10	88	-	-	-	-	-
II	CH_3COCH_3	0,10	80	6	-	-	5	-
II	$(C_2H_5)_2NH$	N,10	67	11	3	-	-	7
II	CH_3COCH_3	N,10	21	55	-	2	5	5
II	C_6H_6	N,10	81	8	-	-	5	-
II	$(C_2H_5)_2NH$	0,4-1/2 N,8 (d)	32	36	46	-	-	3
II	$(C_2H_5)_2NH$	0,4-1/2 N,4 (e)	18	47	7	2	-	22

(a) Irradiations (100 ml) were carried out at room temperature with a 450 watt Hanovia type L mercury vapor lamp equipped with a Pyrex filter. Concentrations were 1×10^{-3} M in starting nitrone.

(b) $O=O_2$; $N=N_2$; time of irradiation in minutes including about 2-minute warm-up time of the lamp and including 3 minutes' irradiation of the nitrone to I and 4 minutes to II.

(c) Unchanged oxaziridine II was determined by active O determination, and oxaziridine I by amount of formanilide formed on concentration compared to the control. After concentration to 5 ml, products were separated on an Aerograph A-90-P preparative gas chromatograph with a 10 ft x 1/4 inch column of 4.8% SE30 on Aeropak. Product analysis was by GLC retention time on an F&M Research Chromatograph 5750 with a 6 ft x 1/8 inch column of 10% SE30 on Chrom W, ultraviolet absorption spectroscopy, and mass spectrometry. At an injection temperature of 300°C in the chromatograph, oxaziridine II yielded 60% anilide, 28% benzophenone, and 10% imine. The yields of the products from oxaziridine II determined by GLC were corrected for the products from the thermal reaction of the unchanged oxaziridine.

(d) p-Dimethylaminobenzaldehyde was added after the irradiation to oxaziridine so that the resulting solution was 0.001 M in aldehyde. The aldehyde absorbed practically all the light above 280 mμ.

(e) This experiment was done in quartz under nitrogen after the irradiation in Pyrex under oxygen.

reaction is photofragmentation, intersystem crossing from the singlet oxaziridine to the triplet oxaziridine must be faster than the formation of products from singlet oxaziridine.

When phenylazide was irradiated (Pyrex filter) in diethylamine in the presence of an equimolar amount of p-dimethylaminobenzaldehyde, the yield of azepine was decreased to about 7% and the yield of aniline increased to about 70-80%.[11] The reduction to aniline is consistent with the aldehyde, which absorbed 99% of the light, acting as a photosensitizer to give triplet phenylazide which by spin conservation results in triplet phenylnitrene.[12] Then by hydrogen abstraction from the solvent[13] triplet phenylnitrene yields aniline. Azepine formation was found not to be quenched by oxygen, indicative of reaction from an excited singlet state. Benzophenone in equimolar amount (absorbing only 60-70% of the light) either in Pyrex or in quartz did not cause a reduction in the yield of azepine from phenylazide. However, there was only a trace of azepine formation in both the unsensitized photofragmentation in quartz and the sensitized photofragmentation in Pyrex of oxaziridine II in diethylamine to give benzophenone and phenylnitrene. Since the photofragmentation presumably occurs via the triplet state to give triplet phenylnitrene, azepine formation appears not to be *via* the triplet state. Also, it is the singlet nitrene that most easily undergoes insertion in carbon hydrogen bonds and addition to aromatic double bonds.[14] Thus, 2-diethylamino-3H-azepine is most likely formed from singlet phenylnitrene *via* the azacyclopropene, 7-azabicyclo (4.1.0) hepta-2,4,6-triene.[8]

The results reported in this study are in accord with oxaziridine photofragmentation occurring mainly *via* the triplet oxaziridine to give triplet phenylnitrene, and azepine being formed from the irradiation of phenylazide in diethylamine *via* the singlet phenylazide and singlet phenylnitrene.

A detailed account of this work will be submitted for publication.

References and Footnotes

*This work was supported, in part, by the U. S. Atomic Energy Commission.

1. J. S. Splitter and M. Calvin, J. Org. Chem., 30, 3427 (1965), footnote 11.

2. 2,3-Diphenyloxaziridine and 3(p-nitrophenyl)-2-phenyloxaziridine gave similar results with irradiation in quartz. These oxaziridines from the irradiation of the corresponding nitrone are thermally unstable, but in the solvents used have half-lives of several hours (Ref. 1). A complication in the irradiation of these oxaziridines is the photosensitivity of the aldehydes and to a lesser extent the other products.

3. This oxaziridine was found to be quite stable; to be published by Howard Ono and M. Calvin.

4. At the time this communication was prepared, E. Meyer and G. W. Griffin, Angew. Chem., 79, 648 (1967), reported as the only products a 10% yield of 2-diethylamino-3H-azepine and a 9% yield of aniline from the irradiation of a 2-phenyl spiro-oxaziridine in diethylamine and postulated photofragmentation to phenylnitrene.

5. We are indebted to James Chang for determining the EPR absorption spectra.

6. G. Smolinsky, E. Wasserman, and W. A. Yager, J. Am. Chem. Soc., 84, 3220 (1962).

7. A. M. Trozzolo, W. A. Yager, G. W. Griffin, H. Kristinsson and I. Sarkar, J. Am. Chem. Soc., 89, 3357 (1967), report the EPR absorption spectrum of diphenylmethylene in the photolysis of triphenyl- and tetraphenyloxiranes at 77°K.

8. W. v. E. Doering and K. A. Odum, Tetrahedron, 22, 81 (1966). The spin state responsible for the reaction was not investigated.

9. In the photolysis of II there is evidence that benzophenone reacted with aniline but imine was not formed as a result.

10. The irradiation of the nitrone corresponding to the oxaziridine II in diethylamine in quartz under N_2, gave about 40% imine in addition to II which was further irradiated. Oxaziridine II irradiated under the same conditions gave 22% imine. The 7% yield of imine reported for oxaziridine II irradiated in Pyrex probably results from nitrone deoxygenation rather than imine deoxygenation.

11. Most of the aldehyde was transformed (presumably to the pinacol) as it is when irradiated alone in diethylamine. The aldehyde is more photosensitive in diethylamine than it is in acetone or benzene.

12. Photosensitization of azides is known to occur: W. Lwowski and T. W. Mattingly, Jr., J. Am. Chem. Soc., 87, 1947 (1965); J. S. McConaghy, Jr. and W. Lwowski, J. Am. Chem. Soc., 89, 4450 (1967); L. Barash, E. Wasserman, W. A. Yager, J. Am. Chem. Soc., 89, 3931 (1967).

13. Diethylamine is a good hydrogen atom source; J. G. Hadley and D. H. Volman, J. Am. Chem. Soc., 89, 1053 (1967).

14. W. Lwowski and R. L. Johnson, Tetrahedron Letters, 1967, 891.