

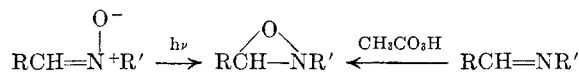
# Communications TO THE EDITOR

## Preparation of Oxaziranes by Irradiation of Nitrones

Sir:

In previous work,<sup>1</sup>  $\alpha$ -(*p*-dimethylaminophenyl)-*N*-phenylnitron (I) had been prepared and found to be very photosensitive in solution. When irradiated in absolute ethanol, *N*-(*p*-dimethylaminophenyl)formanilide was obtained in good yield (m.p. 74–75°;  $\lambda_{\max}$  268 m $\mu$ ,  $\epsilon_{\max}$  21,800 in ethanol. Found: C, 75.06; H, 6.58; N, 11.60; mol. wt. 232). When  $\alpha$ -(*p*-dimethylaminophenyl)-*N*-(*m*-nitrophenyl)nitron (II) is irradiated in benzene to complete disappearance of the nitron spectrum, it will reform nitron to the extent of 60% after 24 hr. in the dark at room temperature. A hydrolytic reaction leading to 4-dimethylaminobenzaldehyde accounts for the remainder.

violet spectrum, 95% active oxygen;<sup>4,5</sup> Va, ultra-violet spectrum, almost quantitative isomerization to the nitron V, 90% active oxygen.



Although the oxazirane (Ia), as well as other 2,3-diaryloxaziranes, could not be synthesized by the oxidation of the imine, the properties and reactions of the products of the irradiation of several *N*, $\alpha$ -diarylnitrones are consistent with the oxazirane structure. The irradiation product of  $\alpha$ -(*p*-nitrophenyl)-*N*-phenylnitron rapidly rearranged to 4-nitrobenzanilide. This anilide also was formed in the oxidation of *p*-nitrobenzylideneaniline with peracetic acid, presumably the oxazirane being formed first. *N*, $\alpha$ -Diphenylnitron on irradiation gave a product which rearranged, depending on

TABLE I  
OXAZIRANES FROM THE IRRADIATION OF NITRONES

R	R'	Nitron, Mg.	Solvent, Ml.	Irrad. Time	Oxazirane, % Yield
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	Et	III, 10	CH <sub>3</sub> CN, 70	1 hr. <sup>a</sup>	IIIa, 35 <sup>b</sup>
<i>p</i> -NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>	<i>t</i> -Bu	IV, 10	EtOH, 70	25 min. <sup>a</sup>	IVa, 40 <sup>b</sup>
C <sub>6</sub> H <sub>5</sub>	<i>t</i> -Bu	V, 10	CH <sub>3</sub> CN, 50	2 hr. <sup>c</sup>	Va, 95 <sup>d</sup>

<sup>a</sup> Between two RSP2 photospots, 20 in. apart; solution thickness, 8 mm. <sup>b</sup> Isolated. <sup>c</sup> In quartz flask, 14 in. above a Hanovia mercury arc lamp, type 16200; solution thickness, 2 cm. <sup>d</sup> From active oxygen content and reversion to nitron.

Recently the oxazirane structure has been suggested as the first product of the irradiation of nitrones.<sup>2,3</sup> Since Emmons<sup>4</sup> has reported that certain oxaziranes can, by peracetic acid oxidation, be prepared from imines, it is now possible to show that the products of the irradiation of some of the corresponding nitrones (Table I) are the same oxaziranes.

To establish the oxazirane structure for IIIa, IVa, and Va, comparison was made in each case with the oxazirane obtained by oxidation of the corresponding imine.<sup>4</sup> The properties used for identification of each are as follows: IIIa, ultraviolet and infrared (in CCl<sub>4</sub>) spectra; IVa, m.p. 58–60°, mixture m.p. 59.5–61.5° with oxazirane of m.p. 61–62°, ultra-

conditions, to give either benzanilide or *N*, *N*-diphenylformamide. These reactions together with the return of the irradiation product of nitron II to the nitron are analogous to the reactions of the oxaziranes described by Emmons.<sup>4</sup>

Thus, it seems evident that the initial product in the irradiation of nitrones is an oxazirane. Since, as is clear from the reversion, the oxazirane is, in general, at a higher energy level than the nitron, this photochemical reaction constitutes a conversion and storage of electromagnetic energy as chemical energy. Further details and discussion will appear in a forthcoming publication.

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