Communications TO THE EDITOR

Preparation of Oxaziranes by Irradiation of Nitrones

Sir:

In previous work,[1] α-(*p*-dimethylaminophenyl)-*N*-phenylnitrone (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°; λ_{max} 268 mμ, ϵ_{max} 21,800 in ethanol. Found: C, 75.06; H, 6.58; N, 11.60; mol. wt. 232). When α-(*p*-dimethylaminophenyl)-*N*-(*m*-nitrophenyl)nitrone (II) is irradiated in benzene to complete disappearance of the nitrone spectrum, it will reform nitrone 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.

TABLE I

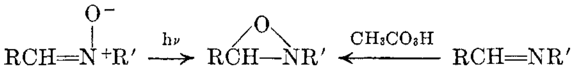
OXAZIRANES FROM THE IRRADIATION OF NITRONES

R	R′	Nitrone, Mg.	Solvent, Ml.	Irrad. Time	Oxazirane, % Yield
p-$NO_2C_6H_4$	Et	III, 10	CH_3CN, 70	1 hr.[a]	IIIa, 35[b]
p-$NO_2C_6H_4$	*t*-Bu	IV, 10	EtOH, 70	25 min.[a]	IVa, 40[b]
C_6H_5	*t*-Bu	V, 10	CH_3CN, 50	2 hr.[c]	Va, 95[d]

[a] Between two RSP2 photospots, 20 in. apart; solution thickness, 8 mm. [b] Isolated. [c] In quartz flask, 14 in. above a Hanovia mercury arc lamp, type 16200; solution thickness, 2 cm. [d] From active oxygen content and reconversion to nitrone.

Recently the oxazirane structure has been suggested as the first product of the irradiation of nitrones.[2,3] Since Emmons[4] 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.[4] The properties used for identification of each are as follows: IIIa, ultraviolet and infrared (in CCl_4) spectra; IVa, m.p. 58–60°, mixture m.p. 59.5–61.5° with oxazirane of m.p. 61–62°, ultraviolet spectrum, 95% active oxygen;[4,5] Va, ultraviolet spectrum, almost quantitative isomerization to the nitrone 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*,α-diarylnitrones are consistent with the oxazirane structure. The irradiation product of α-(*p*-nitrophenyl)-*N*-phenylnitrone 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*,α-Diphenylnitrone on irradiation gave a product which rearranged, depending on conditions, to give either benzanilide or *N*, *N*-diphenylformamide. These reactions together with the return of the irradiation product of nitrone II to the nitrone are analogous to the reactions of the oxaziranes described by Emmons.[4]

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 nitrone, 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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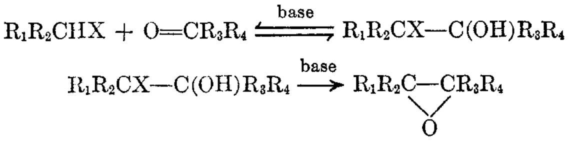
Mechanism of the Darzens Condensation. Isolation of Two Aldol Intermediates

Sir:

It is generally believed[1,2] that a Darzens condensation, *i. e.*, the oxirane-yielding base-catalyzed reaction of a carbonyl compound and a halogenomethylene substance, occurs *via* aldol addition intermediates.

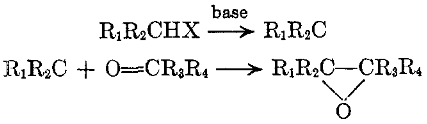


$$R_1R_2CHX + O{=}CR_3R_4 \xrightleftharpoons{\text{base}} R_1R_2CX{-}C(OH)R_3R_4$$

$$R_1R_2CX{-}C(OH)R_3R_4 \xrightarrow{\text{base}} R_1R_2\underset{\diagdown\,O\,\diagup}{C{-}C}R_3R_4$$

Some features of certain Darzens condensations have been recently reasoned from this assumption.[2] However, no such intermediates have ever been isolated under the condensation conditions.

A mechanism involving bivalent radicals formed by 1,1-elimination of hydrogen chloride at the halogenomethylene component has been favored by some authors.[3]



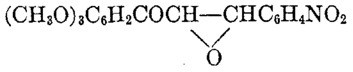
$$R_1R_2CHX \xrightarrow{\text{base}} R_1R_2C$$

$$R_1R_2C + O{=}CR_3R_4 \longrightarrow R_1R_2\underset{\diagdown\,O\,\diagup}{C{-}C}R_3R_4$$

Furthermore, recent kinetic[4a] as well as structural[4b] evidence for bivalent radical formation from certain halogenomethylene substances upon attack by base has given to this mechanism some circumstantial support.

In this connection the authors wish to report that the hydroxyl ion–catalyzed condensation of *m*-nitrobenzaldehyde and 2,4,6-trimethoxyphenacyl chloride at 0°, in aqueous dioxane, gives 98.8% yield of *m*-nitrophenyl-2,4,6-trimethoxybenzoyloxirane, I, m.p. 170–171°. *Anal.* Calcd. for $C_{18}H_{17}NO_7$: C, 60.2; H, 4.8; N, 3.9. Found: C, 60.1; H, 4.8; N, 4.1. When the reaction is run so that only a small fraction of the starting materials are converted into condensation product it is possible to isolate two intermediate chlorohydrins, II, melting at 163.0–164.5° and 111–112°. *Anal.* Calcd. for $C_{18}H_{18}ClNO_7$: C, 54.6; H, 4.6; Cl, 9.0; N, 3.5. Found (m.p. 163–164.5°); C, 54.9; H, 4.7; Cl, 9.0; N, 3.5. Found (m.p. 111–112°): C, 54.7; H, 4.5, Cl, 9.2; N, 3.6. They give almost quantitative yields of I when treated with the base under the usual conditions. The trimethoxyphenacyl chloride is perfectly stable towards hydroxyl ion.

These results are therefore the first compelling evidence ruling out the "bivalent radical" mechanism and showing that *the Darzens condensation is essentially of aldol-addition type.*



$$(CH_3O)_3C_6H_2CO\underset{\diagdown\,O\,\diagup}{CH{-}CH}C_6H_4NO_2$$

(I)

$(CH_3O)_3C_6H_2COCHCl{-}CH(OH)C_6H_4NO_2$

(II)

The details and full discussion of the above-mentioned and other related experimental results will be reported in a forthcoming publication.

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[2] N. H. Cromwell and R. A. Setterquist, *J. Am. Chem. Soc.*, **76**, 5752 (1954); H. Dahn and L. Loewe, *Chimia*, **11**, 98 (1957); H. Kwart and L. G. Kirk, *J. Org. Chem.*, **22**, 116 (1957). See also Kwart's correction to his paper, *J. Org. Chem.*, **22**, 1755 (1957). This correction which concerns one of our previous papers contains an important error: "diastereomerically related intermediates" should be substituted for "diastereomerically related transition states."

[3] S. Bodforss, *Ber.*, **51**, 192 (1918); E. Bergmann and J. Hervey, *Ber.*, 62, 893 (1929).

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