

is 0. The nuclear magnetic resonance for the aromatic hydrogen is at τ 3.23.

O. W. Webster

Contribution No. 1051, Central Research Department
Experimental Station

E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

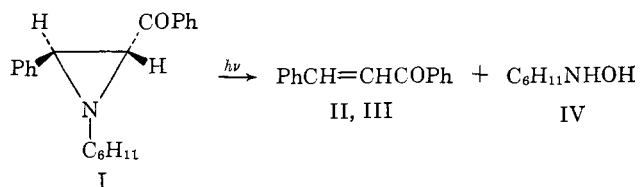
Received December 25, 1964

The Photochemical Deamination of a 2-Benzoylaziridine

Sir:

In view of the structural relationship between the ethylenimine ketones and the epoxy ketones¹ and as a logical extension of our photochemical studies of small-ring carbonyl compounds² it was of interest to determine if the photochemical properties of 2-benzoylaziridines would parallel those of benzoyl epoxides. We now wish to describe the photochemistry of the 2-benzoylaziridine system, in which the relative position of the substituents on the three-membered ring influences the mode of reaction.

trans-1-Cyclohexyl-2-phenyl-3-benzoyl ethylenimine (I) was prepared by treating a mixture of *trans*-benzalacetophenone (II) and cyclohexylamine with iodine in methanol.³ This isomer was initially prepared by Cromwell and co-workers from α,β -dibromobenzylacetophenone and cyclohexylamine.⁴ Irradiation of I in aqueous ethanol at 25° with ultraviolet light of wave length above 305 m μ ⁵ afforded a mixture of *trans*- and *cis*-benzalacetophenone (II and III) and N-cyclohexylhydroxylamine (IV) in high yield. N-Cyclohexylhydroxylamine was identified by its reaction with



benzaldehyde to give the known N-cyclohexyl nitron of benzaldehyde, m.p. 80–82°, in high yield.⁶

A striking feature of this photochemical reaction is the deamination to a mixture of *cis*- and *trans*-benzalacetophenone.⁷ Particular interest is attached to the mechanism of formation of the olefinic mixture.⁸ A conceivable pathway could involve rapid *cis*-*trans* photoisomerization of the 2-benzoylaziridine followed

(1) N. H. Cromwell, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **19**, 214 (1958).

(2) A. Padwa, *Tetrahedron Letters*, No. 15, 813 (1964).

(3) P. L. Southwick and D. R. Christman, *J. Am. Chem. Soc.*, **74**, 1886 (1952).

(4) N. H. Cromwell, N. G. Barker, R. A. Wankel, P. G. Vanderhorst, F. W. Olson, and J. H. Anglin, *ibid.*, **73**, 1044 (1951).

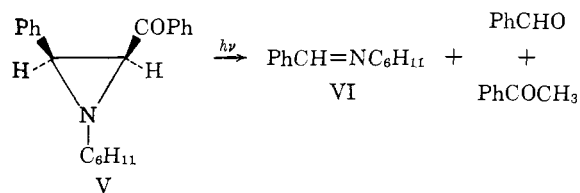
(5) The photolysis was conducted using an internal water-cooled mercury arc lamp (Hanovia, Type L-450 watts) with a soft glass filter to eliminate wave lengths below 305 m μ .

(6) J. Thesing and W. Sirrenberg, *Chem. Ber.*, **91**, 1978 (1958).

(7) The deamination of saturated aziridines with nitrosyl chloride has been reported to give nitrous oxide and the corresponding olefin with greater than 99% stereoselectivity [R. D. Clark and G. K. Helmkamp, *J. Org. Chem.*, **29**, 1316 (1964)].

(8) Stereospecific deamination of I to II followed by rapid photoisomerization of the olefin is an alternate possibility. A detailed study of the stereospecificity of the photodeamination is in progress.

by deamination of the mixture to give equal amounts of the isomeric olefins. The *cis*-*trans* photoconversion of the three-ring nitrogen compound was considered a likely possibility since similar isomerizations have been reported for related small ring carbonyl compounds.^{9,10} This sequence however is eliminated by the finding that irradiation of *cis*-1-cyclohexyl-2-phenyl-3-benzoyl ethylenimine (V) does not afford I. Further, the course of the over-all photoreaction is altered drastically for the *cis* isomer. Irradiation of V in aqueous ethanol gave the Schiff's base of benzaldehyde (VI) as the major product (25%), together with a number of minor components. Careful examination of the photolysis mixture revealed the presence of benzaldehyde (6%) and acetophenone (8%), but showed that no detectable amounts of II, III, phenacyl alcohol, or phenacyl ethyl ether were present.¹¹



The low-energy $n-\pi^*$ bands in the spectra of I and V are undoubtedly the significant absorption bands, since light above 310 m μ was employed. The light absorbed by I and V possesses sufficient energy to effect a bond cleavage. The energy corresponding to 316 m μ radiation (90.8 kcal./mole) is substantially greater than the maximum energy required for bond dissociation in aziridine itself, which in turn is higher than that required for bond rupture in I and V. Despite the fact that $n-\pi^*$ excitation would be expected to develop appreciable charge density on nitrogen as a result of a heterolytic cleavage of the aziridine carbon-nitrogen bond, the products obtained from the irradiation of I seem to be those characteristic of an electron deficient nitrogen.¹² A related situation has been noted for the $n-\pi^*$ photochemical transformations of cyclohexadienones.¹³ An electron demotion process was suggested for these cases in order to resolve the enigma of carbonium ion type reactions occurring from an $n-\pi^*$ state.¹³ It is tempting to hypothesize that the aziridine system is behaving analogously and that a related electron demotion from the already weakened C-N bond occurs. This mechanism allows for free rotation of the zwitterion about the central carbon-carbon single bond and consequently is in accord with the formation of a mixture of *cis*- and *trans*-benzalacetophenone.

The molecular changes involved in the photochemistry of the 2-benzoylaziridine system are markedly dependent on the initial stereochemistry. From the results we conclude that the relative positions of the substituents influence the mode of ring opening. To account for

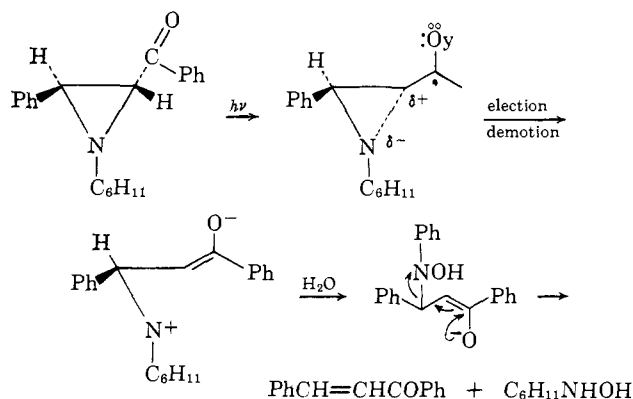
(9) G. W. Griffin, W. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963).

(10) H. E. Zimmerman, Abstracts, Seventeenth National Organic Chemistry Symposium, Bloomington, Ind., June 1961, p. 31.

(11) The low yields found can be attributed to a competing dark reaction. The thermal and solvolytic reactions of 2-benzoylaziridines will be the subject of a future publication.

(12) It remains to be established whether the cleavage reaction involves an electronically excited species or is a thermal reaction of the molecule in the ground state formed by isoenergetic crossing from an electronically excited state.

(13) H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962).



the products obtained from the *cis* isomer we suggest that fission of the carbon-carbon bond of the heterocyclic ring is occurring first. Measurements of the bond distances and bond angles for ethylene oxide can probably be used without introducing any important error in this qualitative discussion of the ethylenimine ring. Cunningham has pointed out that the carbon-oxygen distance is near normal but the carbon-carbon distance is considerably shortened, and consequently most of the ring strain must be accounted for in the carbon-carbon bond.¹⁴ It is suggested that the crowded *cis*-ethylenimine relieves its strain in the excited state by the initial cleavage of the carbon-carbon bond.¹⁵

Experiments designed to provide further information on the identity of the excited states and other transients responsible for these reactions are in progress.

Acknowledgment. We gratefully acknowledge support of this work by the National Science Foundation (Grant GP-3972).

(14) G. L. Cunningham, A. W. Boyd, and W. D. Gwinn, *J. Chem. Phys.*, **17**, 211 (1949).

(15) A steric interaction between two groups attached to the carbon atoms of a number of related ethylenimine ketones has been suggested by Cromwell to account for the lower polarity and less single bond character of the carbonyl group for the *cis* isomer in contrast with the *trans* isomer (N. H. Cromwell, R. E. Bambury, and J. L. Adelfang, *J. Am. Chem. Soc.*, **82**, 4241 (1960), for leading references).

(16) National Institute of Health Predoctoral Fellow; 1964-present.

Albert Padwa, Lewis Hamilton¹⁶

*Department of Chemistry, The Ohio State University
Columbus, Ohio*

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The Photochemical Splitting of Water by Riboflavin

Sir:

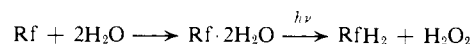
When air-free aqueous solutions of riboflavin are exposed to visible light, the yellow color slowly fades. Subsequent admission of air partly restores the yellow color and the solution is found to contain a complex mixture including riboflavin, lumichrome, lumiflavin, and aldehydes.¹⁻³ If, however, certain tertiary amines or sulfur compounds (*e.g.*, EDTA or methionine) are present in solution, fading is rapid and it is possible by admitting air to restore completely the yellow color and recover all of the riboflavin.^{4,5} To account for

(1) R. Brdicka, *Collection Czech. Chem. Commun.*, **14**, 130 (1949).
(2) G. Oster, J. S. Bellin, and B. Holmstrom, *Experientia*, **18**, 249 (1962).

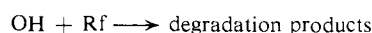
(3) E. C. Smith and D. E. Metzler, *J. Am. Chem. Soc.*, **85**, 3285 (1963).

(4) J. R. Merkel and W. J. Nickerson, *Biochim. Biophys. Acta*, **14**, 303 (1954).

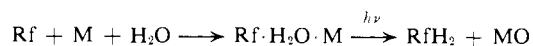
these and other observations, Nickerson, *et al.*,^{5,6} have proposed a reaction scheme that postulates the splitting of water.



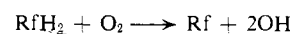
On addition of air



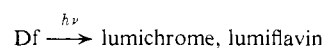
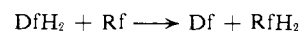
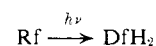
In the presence of a suitable nitrogen- or sulfur-containing compound (M)



On addition of air



On the other hand, Oster, *et al.*,^{2,7} have suggested a reaction scheme in which water plays no direct role but which, in the absence of M, postulates the existence of a light-sensitive intermediate deuterioflavin (Df).



In the presence of M



In this investigation air-free solutions of riboflavin were irradiated in a Pyrex polarographic cell with a General Electric H100 SP38-4 mercury arc lamp. With this arrangement it is possible to carry out polarographic analysis at any time during or after irradiation without exposing the solution to air. Polarographic analysis is especially suited for studying the photochemistry of riboflavin because it is capable of detecting and determining quantitatively such pertinent compounds as riboflavin, reduced riboflavin, lumichrome, aldehydes, oxygen, and hydrogen peroxide.¹ The solutions were 0.2 mM in riboflavin, 0.1 M in KCl and in phosphate buffer, and at pH 7.8. The values of the absorption maxima and $E_{1\%}^{1\text{cm}}$ of the riboflavin, Eastman White Label grade, agreed with those reported in the literature. Therefore the riboflavin was used without further purification. The solutions were deaerated by flushing with nitrogen which had been passed through a train consisting of three flasks containing acidified chromous chloride and amalgamated zinc and two flasks containing distilled water.

Polarograms of riboflavin solutions, which had been irradiated in the absence of nitrogen- or sulfur-containing compounds and to which no air had been admitted, showed the presence of riboflavin, reduced riboflavin, lumichrome, an aldehyde, and possibly other products. There was no evidence of hydrogen peroxide. These results agree with those of Brdicka¹ and Smith, *et al.*,³ and tend to support Oster's reaction scheme. The Nickerson scheme requires the formation of hydrogen

(5) W. J. Nickerson and G. Strauss, *J. Am. Chem. Soc.*, **82**, 5007 (1960).

(6) G. Strauss and W. J. Nickerson, *ibid.*, **83**, 3187 (1961).

(7) B. Holmstrom and G. Oster, *ibid.*, **83**, 1867 (1961).