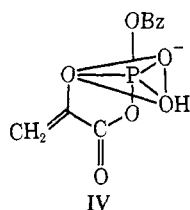


In the case of II the experiments with hydroxylamine also indicate cyclization but do not require intermediates analogous to IIIa and IIIb. This is in accord with the decreased stability of a monoanionic pentacovalent intermediate (IV) whose zwitterion possesses a greater potential driving force for expulsion of BzOH than the neutral species. The successful trapping with hydroxyl-



amine in the case of I may indicate a higher concentration of IIIa and/or IIIb relative to IV if the latter exists other than as a transition state species. A second consideration influencing the hydroxylamine results is the relative magnitude of the proton-transfer steps leading to the product forming zwitterion from the respective initial species.⁹

Consideration of the recently reviewed^{13,14} chemistry of pentacovalent phosphorus indicates that IIIa will be formed by axial attack of the carboxyl with a benzyl group axial and the ring spanning basal and axial positions. The experiments of Dennis and Westheimer¹⁵ and Frank and Usher¹² suggest that the phosphoryl oxygen initially occupies a basal position. Given a pentacovalent intermediate in the hydrolysis of the monobenzyl ester, it is possible that rate of pseudorotation and/or proton transfer to yield the acyl phosphate is competitive with the rate of loss of benzyl alcohol from IV. Consequently, if trapping by hydroxylamine occurs only at the acyl phosphate, the lack of monobenzyl phosphate in the products is explained.

Our observation provides direct verification for the hypotheses of Westheimer¹³ and Ramirez¹⁴ and is in accord with the calculations of Boyd,¹⁶ although there is some question as to the distribution of charge in the pentacovalent species.

In view of the observation that monobenzyl PEP monoanion forms a cyclic intermediate we are examining the possibility that an unproductive cyclic phosphate may form with phosphoenolpyruvic acid itself, although as we have shown previously¹⁷ the carboxyl group has no kinetically important role in PEP hydrolysis. Complete details of the mechanism of this reaction system will be published shortly.

(9) That the ionized hydroxyl group prefers an equatorial position is based on the conclusion of Muettterties¹⁰ that the more electronegative groups are axial, the product distribution of methyl ethylenephosphate as a function of pH,¹¹ and the products of dimethylphosphoacetoin hydrolysis.¹²

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(14) F. Ramirez, *ibid.*, **1**, 168 (1968).

(15) E. A. Dennis and F. H. Westheimer, *J. Amer. Chem. Soc.*, **88**, 3431, 3432 (1966).

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Acknowledgment. We wish to acknowledge support of this work by the National Institutes of Health and the constructive comments of Dr. D. Usher.

(18) Alfred P. Sloan Fellow, 1968–1970; National Institutes of Health Career Development Awardee.

(19) National Institutes of Health Predoctoral Fellow, 1967–1969.

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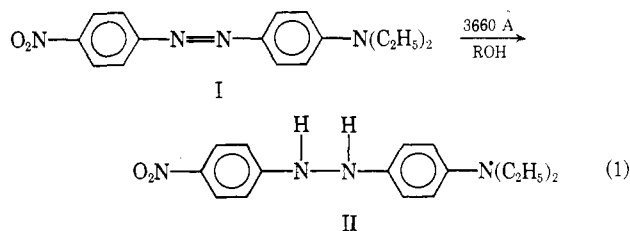
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Received April 7, 1969

Photochemistry of Azo Compounds. III. Evidence for an Electron-Transfer Process in Amine Solvents

Sir:

We wish to report our finding that both the products and the kinetics of the photoreduction of 4-(diethylamino)-4'-nitroazobenzene¹ (I) are markedly influenced by the nature of the solvent used. The results from photolyses in alcohols and in butylamine allow a distinction to be made between a mechanism involving hydrogen abstraction from an excited state of I and electron transfer to an excited state of I. We recently found^{2,3} that photoreduction of I in alcoholic media occurred with low quantum efficiency to produce 4-(diethylamino)-4'-nitrohydrazobenzene (II) (reaction 1). Sensitizers such as naphthalene were inefficient, thus dem-



onstrating that the low quantum yields for reaction I were not a result of inefficient intersystem crossing to a photoreducible triplet.² However, benzophenone efficiently sensitized the photoreduction by a mechanism involving transfer of a hydrogen atom from the photochemically generated benzophenone ketyl radical to the azo linkage of I.³

Photolyses^{4,5} of degassed solutions of I in butylamine (ca. 10^{-4} M) with 3660-Å light, both with and without ketonic sensitizers present, yielded a product absorbing at 420 nm ($\epsilon \sim 2.6 \times 10^4$) with a shoulder at 460 nm. This product was not formed during photolyses in isopropyl alcohol. When air was admitted to the solution, this product was rapidly converted to a new absorbing species (λ_{\max} 507 nm). The second product was identified as 4,4'-bis[[p-(diethylamino)phenyl]azo]azoxybenzene (IV): mp 295–298° dec; ir (KBr) 1303 cm^{-1} (s, NO); mass spectrum⁶ (70 eV) m/e (rel intensity) 548 (25), 532 (100), 148 (38), 44 (27); visible spectrum $\lambda_{\max}^{\text{butylamine}}$ 507 nm ($\epsilon 5.2 \times 10^4$).

(1) E. Baumberger, *Ber.*, **28**, 843 (1895); E. Ziegler and G. Snatzke, *Monatsh. Chem.*, **84**, 610 (1953).

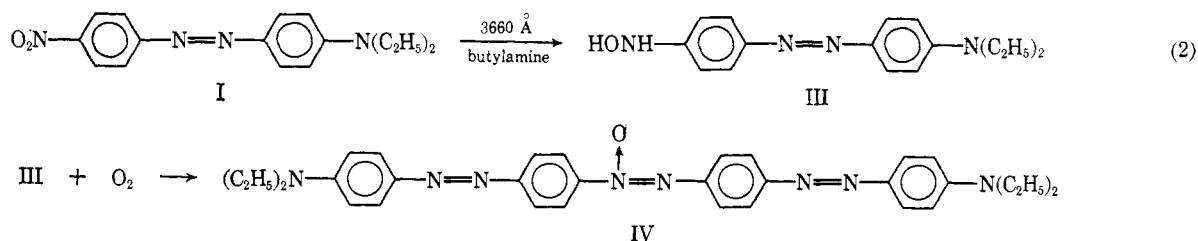
(2) G. Irick, Jr., and J. G. Pacifici, *Tetrahedron Lett.*, 1303 (1969).

(3) J. G. Pacifici and G. Irick, Jr., *ibid.*, 2207 (1969).

(4) Photolyses were followed spectrophotometrically by methods previously described.^{2,3}

(5) $\lambda_{\max}^{\text{butylamine}}$ 483 nm ($\epsilon 3.04 \times 10^4$).

(6) Obtained using a Consolidated Electro Dynamics Corp. Model 21-110B mass spectrometer.



Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{N}_8\text{O}$: C, 70.04; H, 6.61; N, 20.42. Found: C, 69.76; H, 6.56; N, 20.31.

The absorption properties of the initially formed product and its oxidation to azoxy compound IV indicate that it is the hydroxylamine III. These results show that the photoreduction of I in butylamine occurs at the nitro group. The over-all process is shown in reaction 2.

Reduction of an aromatic nitro compound to a hydroxylamine and subsequent condensation to produce an azoxy compound were demonstrated in the photochemical reduction of nitrobenzene.⁷ Oxidation of the initially formed hydroxylamine gave a nitroso compound, which reacted rapidly with the hydroxylamine to give an azoxy compound.⁷⁻⁹ It is interesting to note that IV is readily formed from III by a similar process, even when the concentrations of the reactants are as low as 10^{-4} M. The quantum yields for the photoreduction of I under various conditions are shown in Table I.

Table I. Photoreduction of I^a under Various Conditions with 3660-Å Light^b

Solvent	Additive		Φ_D^c
	Compd	Concn, M	
Isopropyl alcohol	None		1.4×10^{-4}
	Benzophenone	0.27	0.05
	Fluoren-9-one	0.025	$<1 \times 10^{-4}$
Butylamine	None		4.2×10^{-4}
	Benzophenone	0.27	0.14
	Fluoren-9-one	0.025	6.0×10^{-3}

^a Concentration of I was $2.2\text{--}2.4 \times 10^{-4}$ M. ^b A Bausch and Lomb Model 33-86-07 high-intensity grating monochromator was used for these experiments. The light source was an Osram HBO 200-W lamp. The intensity of the incident light as determined by ferroxalate actinometry [C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc. (London)*, **A235**, 518 (1956)] was 3.0×10^{-6} einstein/min for experiments without sensitizers and was 4.8×10^{-1} einstein/min for all others. ^c Over-all quantum yield for the initial 10% degradation of I.

The formation of IV as a product from photolysis of I in butylamine suggests a mechanism different from that for the reaction in alcohol solvent. Recent studies¹⁰⁻¹³ on the photoreduction of aromatic ketones in amine solvents have presented evidence for reduction by a mechanism involving an initial electron transfer from the amine to the excited triplet state of the ketone, followed by a proton transfer and electron redistribution. The over-all process produced the corresponding pinacol in high yield. Selective reduction of the nitro group of I

(7) R. Hurley and A. C. Testa, *J. Amer. Chem. Soc.*, **88**, 4330 (1966).

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(9) G. A. Russell and E. J. Geels, *ibid.*, **87**, 122 (1965).

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in butylamine can be rationalized in terms of a similar electron-transfer process. Since the electron density in the initially formed radical anion of I may be expected to be greater on oxygen than on the azo nitrogen,¹⁴ proton transfer from the amine radical cation to oxygen would follow.

It is interesting to note that a similar process occurred when either benzophenone or fluoren-9-one was used as sensitizer. These results indicate that both the initially formed benzophenone ketyl radical anion and the fluorenone ketyl radical anion transfer an electron rapidly to I before proton transfer from the amine radical cation occurs.¹⁷ Products resulting from interaction of the ketyl radical with I would be formed if proton transfer to the ketyl radical anion competed significantly with electron transfer to I. The photolysis of I (0.01 M) in a 0.5 M solution of benzophenone in butylamine gave a 97% yield of IV (isolated), and photolysis under conditions where the concentration of I was 2.4×10^{-4} M gave a yield of about 96% (determined spectrophotometrically). Thus, at the two extreme concentrations, no appreciable quantity of II was formed.

The low quantum yield obtained for the reduction of I in the presence of benzophenone (lower than 0.9^{13}) may be due in part to reaction 3.



Acknowledgment. We thank Dr. H. L. Browning (esr studies) and Mr. J. C. Gilland (mass spectral analyses), of the Tennessee Eastman Research Laboratories, for their assistance.

(14) The esr spectrum of the radical anion of I in tetrahydrofuran (sodium counterion), although not fully resolved, was similar to spectra reported for *para*-substituted nitrobenzene radical anions ($a_n = 9.8$ G).^{15,16}

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(16) E. G. Janzen and J. L. Gerlock, *J. Org. Chem.*, **32**, 820 (1967).

(17) To show that electron transfer from the benzophenone ketyl radical anion to I was a favorable process, a solution of sodium benzophenone ketyl in tetrahydrofuran (1.0×10^{-4} M) was added to an equivalent quantity of I through a break seal. The initial esr spectrum of the benzophenone ketyl was replaced by that of the radical anion of I. No evidence was seen in the resulting spectrum for the presence of benzophenone ketyl, thus indicating that electron transfer to I is an energetically favored process.

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Received May 31, 1969

Electron Spin Resonance Studies on Oxidation with Nickel Peroxide. Spin Trapping of Free-Radical Intermediates

Sir:

During the course of an investigation on the mechanism of oxidation with nickel peroxide¹ it became de-