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PHOTOCHEMISTRY OF AZO COMPOUNDS. I.

PHOTOREDUCTION OF 4-DIETHYLAMINO-4'-NITROAZOBENZENE

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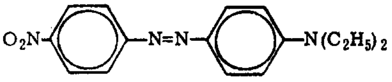
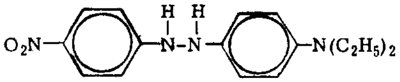
We wish to report some preliminary results concerning the sensitized and nonsensitized photoreduction of 4-diethylamino-4'-nitroazobenzene(I) (1).



I

Although the photoreduction of ketones in hydrogen donor systems has been studied extensively (2), little is known about either the qualitative or mechanistic aspects of the photoreduction of azo compounds. Some earlier work showed that azobenzene and 4-amino-4'-nitroazobenzene are photoreduced in isopropanol (3). However, it was uncertain whether the nitro-substituted compound underwent reduction at the nitro group or at the azo linkage. No quantum yields were reported for the reductions.

We have found that photoreduction of I in alcoholic media, under degassed conditions (4), with 254-, 310-, or 366-nm light occurs with low quantum efficiency (Table I) to yield 4-diethylamino-4'-nitrohydrazobenzene (II) as the major product.



II

The identification of II was based on its ultraviolet absorption properties and on the observation that it was oxidized rapidly and completely by air to azo compound I. Attempts to isolate the hydrazo compound in pure form were unsuccessful. The absence of a thermal dark reaction subsequent to photolysis demonstrated that I did not isomerize detectably to the cis isomer. Ultraviolet and visible spectral analyses of the photolysis mixtures at various times showed that 4-amino-4'-diethylaminoazobenzene (λ_{max}^{ipa}[1] 444, 415 nm; $\epsilon = 2.5 \times 10^4$, 2.6×10^4) was not formed.

TABLE I

Photolysis of Azo Compound I in Solution (a)

Solvent(b)	Additive(c)	Wavelength, Nm	Φ_D(d)
Methanol	None	254	1.2×10^{-4}
Ethanol	None	254	0.96×10^{-4}
Isopropanol	None	254	4.8×10^{-4}
Benzene	None	254	$< 1 \times 10^{-6}$
Isopropanol	None	310	2.8×10^{-4}
Isopropanol	None	366	1.4×10^{-4}
Ethanol	Naphthalene	254	2.2×10^{-4}
Isopropanol	Benzene	254	11.5×10^{-4}
Isopropanol	Naphthalene	310	4.5×10^{-4}

(a) Concentration of I was 2.4×10^{-4} moles/liter.

(b) All alcohols used were anhydrous.

(c) Additive concentration was 0.5 mole/liter.

(d) Quantum yields for the disappearance of I were determined from the first 10% of reaction and were based on ferrioxalate actinometry (5).

The absorption spectrum of I shows strong bands in the ultraviolet and visible regions [280 nm ($\epsilon = 1.2 \times 10^4$) and 485 nm ($\epsilon = 3.4 \times 10^4$)]. The intensity of the lower energy band and its sensitivity to solvent polarity (λ_{max}^{hexane} 455 nm and λ_{max}^{dmso}[2] 510 nm) suggest that this band corresponds to an intramolecular charge transfer transition. Low quantum yields for the reductions of I can be rationalized in view of the charge transfer character of the lowest excited state. The lack of reactivity in hydrogen abstraction observed for some aromatic ketones having strong electron-donating substituents has been ascribed to the charge transfer nature of the lowest triplets (6-10). A low quantum yield for photoreduction would also be predicted if intersystem crossing to a

[1] Isopropanol

[2] Dimethyl sulfoxide

triplet state was inefficient. To determine if there were reactive triplet levels which were not populated by direct absorption, photolyses were performed with benzene and naphthalene as sensitizers. The quantum yields increased only slightly in the presence of these sensitizers, indicating that the low quantum yields obtained in the experiments done without sensitizers were not a result of inefficient intersystem crossing to a photoreducible triplet. One alternative explanation for the inefficiency of these compounds as sensitizers would require the efficient quenching of the sensitizer singlets by I. However, preliminary data on the quenching of naphthalene fluorescence by I showed that only partial quenching occurred when the concentration of I was 2×10^{-4} molar. The fluorescence quenching studies were complicated by the broad absorption bands characteristic of azo compounds.

There was no isomerization of I in either the presence or absence of the sensitizers. The failure to observe cis isomer showed that either the photostationary state was virtually all trans or the thermal half-life of the cis isomer was so short that re-equilibration occurred before it could be detected. Short thermal half-lives have been reported for azobenzenes substituted by strong electron-donor and strong electron-acceptor groups (11).

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4. Solutions of I (3.00 ml.) were photolyzed in quartz cells having a path length of 1.0 cm.; a 0.1-cm. optical cell for absorbance measurements was attached. The initial concentration of I was such that >99% of the incident light was absorbed. The photolyses were run in a Rayonet Photochemical Reactor (Southern New England Ultraviolet Co., Middletown, Conn.) equipped with a rotating cell holder and 0.91 cm^2 light entrance slits.

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