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Photoreduction of Azoxybenzene to Azobenzene

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The photochemical reduction of azoxybenzene to azobenzene has been investigated. The direct irradiation of azoxybenzene leads to a rearrangement to 2-hydroxyazobenzene and to *cis-trans* isomerization, whereas the sensitized irradiation leads to a reduction to azobenzene in the presence of a sensitizer with a triplet excitation energy greater than *ca.* 62 kcal/mol. 2-Hydroxyazobenzene and *cis*-azoxybenzene seem to be formed from the excited singlet state of azoxybenzene, and azobenzene, from the excited triplet state. Even without a sensitizer, the irradiation of benzo[*c*]cinnoline *N*-oxide, which is incapable of undergoing rearrangement or isomerization, brings about a photochemical reduction, which is affected by a sensitizer or a quencher, and also by the hydrogen-donating ability of the solvent used (isopropanol>ethanol>cumene>toluene). Acetone is yielded when isopropanol is used as the solvent. On the basis of these results, a mechanism in which benzo[*c*]cinnoline is formed from the excited triplet state of benzo[*c*]cinnoline *N*-oxide, followed by hydrogen abstraction from a solvent, is proposed.

The photochemical rearrangement of azoxybenzene to 2-hydroxyazobenzene[1-4] is assumed to start from a $\pi \rightarrow \pi^*$ excitation, because the emission of the lines above 300 mμ in a mercury arc lamp causes the rearrangement, but it has not been established whether or not an excited triplet state

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1) H. M. Knipscheer, *Rec. trav. chim.*, **22**, 14 (1903).

2) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, **1954**, 2243.

3) M. M. Shemyakin, V. J. Maimind and B. K. Vaichunaite, *Chem. Ind.*, **1958**, 755.

4) S. Oae, T. Fukumoto and M. Yamagami, This Bulletin, **34**, 1873 (1961).

intermediate is involved. In order to clarify this situation, we irradiated a solution of azoxybenzene in the presence of benzophenone, we thus found the reaction to take a completely different course, *i. e.*, azobenzene was formed as the major product.⁵⁾ This photoreduction seems to be similar to the deoxygenation from an excited triplet state of pyridine *N*-oxide or of picoline *N*-oxide in the gas-phase photolysis.⁶⁾

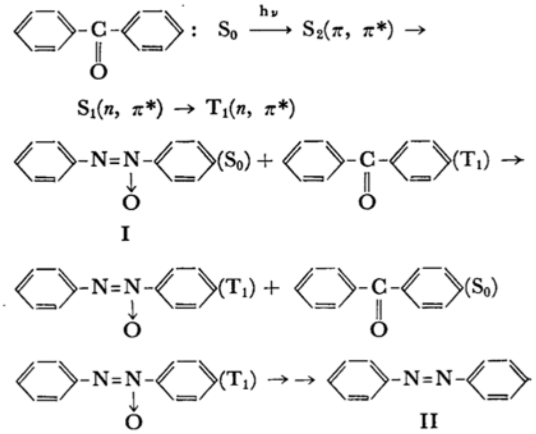
A principal objective of this work is to discuss the photochemical reduction of azoxybenzene to azobenzene, and to give some suggestions regarding the photochemical oxygen migration and the *cis-trans* isomerization.

It is also interesting to note that the photochemical deoxygenation process of a compound containing a N→O bond may be involved in the photoreduction of nitrosobenzene to azoxybenzene.⁷⁾

Results and Discussion

Photoreduction of Azoxybenzene (I) to Azobenzene (II). The irradiation of a degassed ethanolic solution of *trans*-azoxybenzene (I) in a quartz or Pyrex tube with a high-pressure mercury arc lamp afforded 2-hydroxyazobenzene (III) and *cis*-azoxybenzene (IV), but no azobenzene (II). On the other hand, II was obtained as the major product by the photolysis of a degassed solution of I, containing benzophenone as a sensitizer, in a quartz tube. The results of the irradiation of I in a quartz tube are given in Table 1.

Scarcely any II was formed in the presence of oxygen, presumably because the excited triplet state, T_1, of I was quenched by oxygen. Although it is desirable to use a $n \rightarrow \pi^*$ transition ($\lambda_{max}^{EtOH} = 333$ mμ, ε = 160) of benzophenone in any discussion of its photosensitization, the $n \rightarrow \pi^*$ excitation is not expected to occur in the presence of I because of the strong absorption of I ($\lambda_{max}^{EtOH} = 323$ mμ, ε = 14700). In fact, the photosensitization did not occur when a Pyrex filter was used. Thus, the photosensitization of benzophenone shown in Table 1 may result from its $\pi \rightarrow \pi^*$ transition ($\lambda_{max}^{EtOH} = 253$ mμ, ε = 18000).⁸⁾ A possible mechanism for the formation of II with a wavelength of about 250 mμ is as follows:



(1)

The irradiation of I without benzophenone never afforded II. This result indicates that III and IV may be formed directly from the excited singlet state, S_1, of I, but not through the excited triplet state, T_1.⁹⁾ The formation of III and IV even in the presence of benzophenone may be due to the direct photoreaction of I with a wavelength longer than 300 mμ, as is shown in Eq. (2):

$$I(S_0) \xrightarrow{h\nu} I(S_1(\pi, \pi^*)) \rightarrow \rightarrow III \qquad (2)$$

Table 1 shows that a side reaction took place from the sensitized photolysis. The by-products have not yet been identified, but hydrazobenzene and aniline derivatives may be formed by the reduction of II and III, because the azo bridge is able to abstract hydrogen atoms or free radicals upon

TABLE 1. IRRADIATION OF AZOXYBENZENE (10^{-2} M) AT 25.0±0.1°C

Irradiation time (min)	30	30	30	30	120
Solvent	EtOH	EtOH	EtOH	EtOH	*n*-Hexane
Concentration of benzophenone (M)	0	10^{-3}	10^{-2}	10^{-2}	10^{-2}
Quencher	None*	None	None	O_2	None
Yields of products (%)					
Azoxybenzene (I, IV)	65	50	40	64	79
Azobenzene (II)	0	4	21	Trace	5
2-Hydroxyazobenzene (III)	24	19	9	23	15

* None means a degassed state.

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5) R. Tanikaga, K. Maruyama, R. Goto and A. Kaji, *Tetrahedron Letters,* **1966**, 5925 .

6) N. Hata, This Bulletin, **34**, 1440, 1444 (1961); N. Hata and I. Tanaka, *J. Chem. Phys.*, **36**, 2070 (1962).

7) E. Bamberger, *Ber.*, **35**, 1606 (1902).

8) A process $S_2(\pi, \pi^*) \rightarrow S_1(n, \pi^*)$ of benzophenone is known to be efficient. N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York (1965), p. 78.

9) A detailed account of this problem will be the subject of a forthcoming publication.

TABLE 2. IRRADIATION OF BENZO[*c*]CINNOLINE *N*-OXIDE (10^{-2} M) AT 25.0±0.1°C

Irradiation time (hr)	1	1	1	3	3
Filter	Q	Q	Q	P	P
Concentration of benzophenone (M)	0	0	10^{-2}	0	0
Quencher	None*	O_2	None	None	O_2
Yields of products (%)					
Benzo[*c*]cinnoline *N*-oxide (V)	63	97	27	25	93
Benzo[*c*]cinnoline (VI)	31	3	49	53	5

* None means a degassed state. P: Pyrex, Q: Quartz.

TABLE 3. IRRADIATION OF BENZO[*c*]CINNOLINE *N*-OXIDE (10^{-2} M) AT 25.0±0.1°C

Solvent	*iso*-PrOH	EtOH	Cumene	Toluene	Anisole	CCl_4
Yields of products (%)						
V	26	25	68	70	75	90
VI	63	53	30	14	18	0

irradiation.[10-12] At any rate, irradiation for many hours is not desirable for the investigation of the photoreduction of I to II.

I could be photochemically reduced to II with the ketones other than benzophenone. The following ketones were efficient photosensitizers: acetophenone (triplet excitation energy $E_{T_1}=74$ kcal/mol[13]), benzaldehyde (72), benzophenone (69), thioxanthone (65), phenylglyoxal (63), and anthraquinone (62). On the other hand, the following ketones were not efficient: flavone (62), Michler's ketone (61), 2-acetonaphthone (59), biacetyl (55), benzil (54), and fluorenone (53). From these results, the T_1 state of I is assumed to be about 62 kcal/mol.

In order to discuss the solvent effect on the photoreduction of I, ethanol and *n*-hexane were used as solvents transparent above 210 mμ. Since the sensitized photoreduction is derived from a $\pi\rightarrow\pi^*$ transition of benzophenone, it is essential to use such a solvent as ethanol or *n*-hexane without any absorption about 250 mμ. Reduction was easier in ethanol than in *n*-hexane, as is shown in Table 1, but it cannot be determined which stage of Eq. (1) is affected by a solvent. Therefore, for a more detailed discussion it was desirable to irradiate an azoxybenzene derivative with a high efficiency for intersystem crossing without a sensitizer. One possibility was to use an azoxybenzene derivative containing a keto group. Therefore, a degassed solution of 4,4′-diacetylazoxybenzene or 4,4′-dibenzoylazoxybenzene in ethanol was irradiated. However, no azobenzene derivative was obtained. A heavy-atom effect was also expected to promote intersystem crossing. The irradiation of a degassed solution of 4,4′-dichloroazoxybenzene or 4,4′-dibromoazoxybenzene never led to reduction. Azobenzene was not formed from the photolysis of I in such a solvent as methylene chloride or methylene bromide containing heavy atoms. Interestingly, I thus contrasts with pyridine *N*-oxide, which is reduced to pyridine through an excited triplet state in methylene chloride or *n*-propyl bromide as a result of a heavy-atom effect.[14]

When a solution of benzo[*c*]cinnoline *N*-oxide (V), incapable of undergoing *cis-trans* isomerization nor oxygen migration, was directly irradiated, V was found to lead to a photoreduction to benzo[*c*]cinnoline (VI). Therefore, V can be chosen as a model compound in consideration of the solvent effect on the photoreduction of I to II.

Photoreduction of Benzo[*c*]cinnoline *N*-Oxide (V) to Benzo[*c*]cinnoline (VI). The results of the photolysis of a solution of benzo[*c*]cinnoline *N*-oxide (V) in ethanol ($\lambda_{max}=332$ mμ, $\varepsilon=8700$) are given in Table 2.

The effect of oxygen and benzophenone can be explained if benzo[*c*]cinnoline (VI) is assumed to proceed *via* an excited triplet state of V. Moreover, the identification of the triplet state as a reactive intermediate is consistent with the quenching effect of 1-chloronaphthalene in the irradiation of an ethanolic solution of V with a wavelength longer than 350 mμ. A light longer than 300 mμ was efficient for photoreduction, but it cannot been determined what excitation is the first stage of the reaction, because no electronic spectrum of V has yet been assigned.

The results of the photolysis of degassed solutions of V in various solvents for 3 hr with a

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[10] J. K. S. Wan, L. D. Hess and J. N. Pitts, Jr., *J. Am. Chem. Soc.*, **86**, 2069 (1964).

[11] S. Hashimoto, H. Fujii and J. Sunamoto, Preprints for the 18 th Annual Meeting of the Chemical Society of Japan (1965), p. 422; S. Hashimoto, J. Sunamoto and H. Fujii, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 699 (1967).

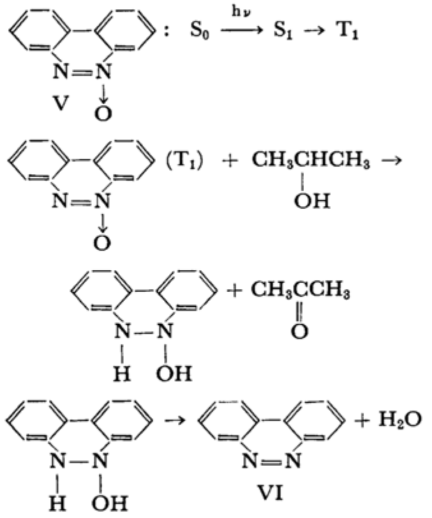
[12] D. C. Neckers, private communication.

[13] The E_{T_1} values used here are according to a table in Ref. 8, p. 132.

[14] N. Hata, Preprints for the 20 th Annual Meeting of the Chemical Society of Japan (1967), Vol. 1, p. 483.

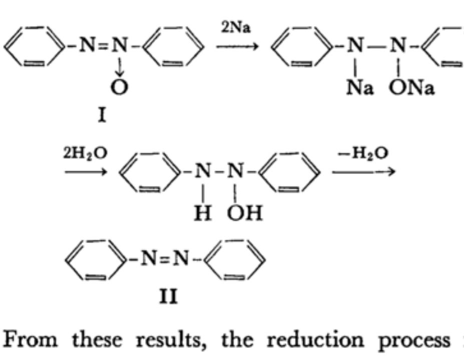
Pyrex filter are given in Table 3.

Table 3 shows that the reduction of V was promoted and that a side reaction was suppressed in a solvent with a great hydrogen-donating ability. Besides, V was similar to benzophenone in its competitive hydrogen abstraction reaction, *i. e.*, isopropanol : cumene : toluene = 9.3 : 3.4 : 1.0.15) The importance of hydrogen abstraction was implied by the fact that no VI was yielded upon the irradiation of V in carbon tetrachloride or in a solid phase; moreover, it was confirmed by the formation of acetone and water from the photolysis of V in isopropanol. Since the yields of acetone and water corresponded roughly with the amount of V reacted, VI may be produced by the following reaction sequence:



(3)

The hydrogen abstraction is a rate-determining process in the photoreduction of V to VI, although an intersystem-crossing process controls the reactivity of the photoreduction of pyridine *N*-oxide.14) The mechanism shown in Eq. (3) is, interestingly, similar to that for I in reduction with an alkali metal:16)



(4)

From these results, the reduction process from the excited triplet state of I to II may also be supposed to be followed by hydrogen abstraction.

The photochemical deoxygenation of a compound containing a N→O bond *via* an excited triplet state seems important in the photoreduction of dimeric nitrosobenzene to azoxybenzene.7) This problem is currently being investigated.

Experimental

Materials. Azoxybenzene (I) was prepared by the reduction of nitrobenzene with sodium hydroxide in methanol, and was then recrystallized from methanol (mp 35.5°C).17) Benzo[*c*]cinnoline *N*-oxide (V) was prepared by the reduction of 2,2′-dinitrodiphenyl with sodium sulfide in ethanol, and was then recrystallized from ethanol-water (mp 139.5°C).18)

Photolysis of Azoxybenzene (I). The irradiation source was a 100 W, high-pressure mercury arc lamp fitted with a water-cooled immersion well (Eikosha Halos PIH 100). The degassed or oxygen-saturated solution (3 m*l*) of I was irradiated in a quartz tube (inner diameter 13 mm) directly attached to the lamp, and was thermostated at 25.0±0.1°C. The other reaction conditions, such as the solvent used, the irradiation time, and the concentration of benzophenone, were as shown in Table 1. After the irradiation, each component was separated by thin-layer chromatography (TLC) on silica gel (Merck silica gel G according to Stahl; an *n*-hexane - benzene mixture (2 : 1 in volume)) and was identified by the comparison of the infrared and ultraviolet spectral data, the melting point, and the R_f value with those of an authentic sample. The yield of the product was determined as follows. After the irradiation, the solution was left at *ca.* 40°C for one day to transform the *cis*-isomer into the more thermally-stable *trans*-isomer. 4,4′-Dichloro-2-hydroxyazobenzene (VII) was then added as an internal standard. Each component was then separated by TLC on silica gel and extracted with chloroform. The yield was determined from the intensity of the maximum absorption of the extract in an electronic spectrum, whose extinction coefficient had been previously determined by means of an authentic sample. The extinction coefficients used in this work were: $\mathrm{I}\varepsilon_{326\,\mathrm{m}\mu}=14800$, $\mathrm{II}\varepsilon_{319\,\mathrm{m}\mu}=18500$, $\mathrm{III}\varepsilon_{325\,\mathrm{m}\mu}=18000$ and $\mathrm{VII}\varepsilon_{339\,\mathrm{m}\mu}=19500$ (in chloroform).

Photolysis of Benzo[*c*]cinnoline *N*-Oxide (V). A solution (2 m*l*) of V was irradiated in a quartz or Pyrex tube (inner diameter : 13 mm) with a 100-W, high-pressure mercury lamp at 25.0±0.1°C. The other reaction conditions were as shown in Table 2 or 3. The products were separated by TLC (silica gel, chloroform), and their yields were determined as has been described above. 1-Benzeneazo-2-naphthol (VIII) was used as an internal standard. The extinction coefficients used in this work were: $\mathrm{V}\varepsilon_{333\,\mathrm{m}\mu}=8700$, $\mathrm{VI}\varepsilon_{309\,\mathrm{m}\mu}=8600$ and $\mathrm{VIII}\varepsilon_{317\,\mathrm{m}\mu}=7470$ (in chloroform).

Photolysis of V in Isopropanol. A degassed solution (5 m*l*) of V (5×10^{-2} M) in isopropanol (purified by drying over magnsium ribbon and by fractional

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15) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **86**, 3902 (1964).

16) T. Kauffmann, S. M. Hage and G. Ruckelshauss, *Chem. Ber.*, **100**, 1235 (1967).

17) A. Lachman, *J. Am. Chem. Soc.*, **24**, 1180 (1902).

18) F. Ullmann and P. Dieterle, *Ber.*, **37**, 24 (1904).

distillation) was irradiated in a Pyrex tube for 30 hr as has been described above. The yields of V and VI were then determined by TLC on silica gel, while that of acetone was determined by gas chromatography (Yanagimoto GCG-5DH, polyethylene glycol 20 M 4.5 m, 80°C, He). The presence of water was established by titration with a Karl-Fischer reagent (Mitsubishi Chemical Industries, Ltd.; Karl-Fischer Reagent SS). The yields of the products were as follows: V, 37%; VI, 56%; acetone, 70%, and water, 75—85%.

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