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Photochemical Rearrangement of Azoxybenzene to 2-Hydroxyazobenzene and *cis-trans* Isomerization

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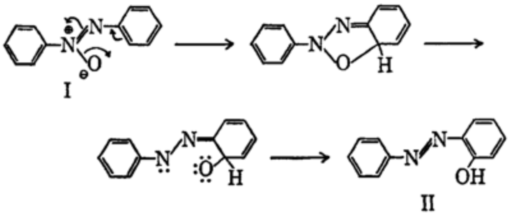
The photochemical oxygen migration and *cis-trans* isomerization of azoxybenzene have been investigated. The direct irradiation of *trans*-azoxybenzene leads to both rearrangement to 2-hydroxyazobenzene and *cis-trans* isomerization, whose rate is faster in a polar protic solvent and is never affected by a quencher. Direct irradiation does not afford any azobenzene formed from an excited triplet state of azoxybenzene. On the basis of these observations, the author proposes a mechanism in which 2-hydroxyazobenzene and *cis*-azoxybenzene are formed directly from an excited singlet state of *trans*-azoxybenzene. This mechanism is analogous to that for the photochemical rearrangement of nitrone to oxaziridine. Nitro- or dimethylamino-substituted azoxybenzene undergoes neither photochemical rearrangement nor *cis-trans* isomerization. Oxygen migration is not sterically hindered by a substituent in the 3-position of azoxybenzene.

The photochemical rearrangement of *trans*-azoxybenzene (I) to 2-hydroxyazobenzene (II) was first reported by Knipscheer,[1] and an intramolecular pathway was postulated by Badger *et al.*[2] because an oxygen atom was found to migrate from the azo-nitrogen atom, to which it was originally attached, to an ortho position of the aromatic nucleus adjoining the other azo-nitrogen atom.

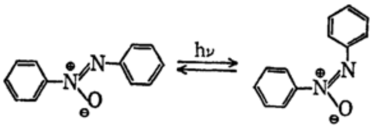


I

II

This intramolecular mechanism was confirmed by means of tracer methods.[3,4] Although it has not definitely been established whether or not an excited triplet state intermediate is involved, it may be suggested that II is formed directly from an excited singlet state of I, because an excited triplet state of I has been found to take a completely different course, *i.e.*, to undergo photochemical reduction to azobenzene.[5] Thus it is necessary to clarify this situation.

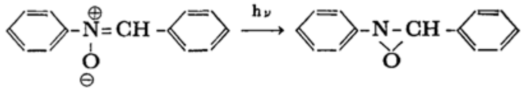
The photolysis of I affords *cis*-azoxybenzene (III) besides II,[6] but no effort has been made to discuss the rearrangement and the isomerization at the same time.



I III

A principal objective of this work is to propose a mechanism for these two photochemical reactions and to discuss the effect of solvents and substituents.

It is interesting to note that neither the photochemical rearrangement of N,α-diphenylnitrone (IV) to 2,3-diphenyl-oxaziridine (V)[7] nor the *cis-trans* isomerization of azobenzene[8] proceeds *via* its excited triplet state.



IV V

Results and Discussion

Reactive Intermediate. The photochemical rearrangement of *trans*-azoxybenzene (I) to 2-hydroxyazobenzene (II) was initiated with wavelengths longer than 300 mμ. The sole absorption

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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; M. M. Shemyakin, T. E. Agadzhanyan, V. J. Maimind, R. V. Kudryavtsev and D. N. Kursanov, *Doklady Akad. Nauk S. S. S. R.*, **135**, 346 (1960).

[4] S. Oae, T. Fukumoto and M. Yamagami, This Bulletin, **34**, 1873 (1961); **36**, 601 (1963).

[5] R. Tanikaga, K. Maruyama, R. Goto and A. Kaji, *Tetrahedron Letters*, **1966**, 5925; R. Tanikaga, This Bulletin, **41**, 1664 (1968).

[6] D. Webb and H. H. Jaffé, *Tetrahedron Letters*, **1964**, 1875; *J. Am. Chem. Soc.*, **86**, 2419 (1964), and other references cited therein.

[7] K. Shinzawa and I. Tanaka, *J. Phys. Chem.*, **68**, 1205 (1964); **69**, 2545 (1965).

[8] L. B. Jones and G. S. Hammond, *J. Am. Chem. Soc.*, **87**, 4219 (1965).

($\lambda_{max}^{EtOH}=323$ mμ, $\varepsilon_{max}=14700$) above 300 mμ in the electronic spectrum of I is assigned to a $\pi\rightarrow\pi^*$ transition,[9,10] and $n\rightarrow\pi^*$ transition is assumed to be submerged under the high-intensity band of the $\pi\rightarrow\pi^*$ transition.[9] Therefore, the photochemical rearrangment of I probably starts from its $\pi\rightarrow\pi^*$ transition.

The irradiation of I in a solution or in a solid phase yielded II and *cis*-azoxybenzene (III). An example of the time dependencies of their yields is given in Fig. 1.

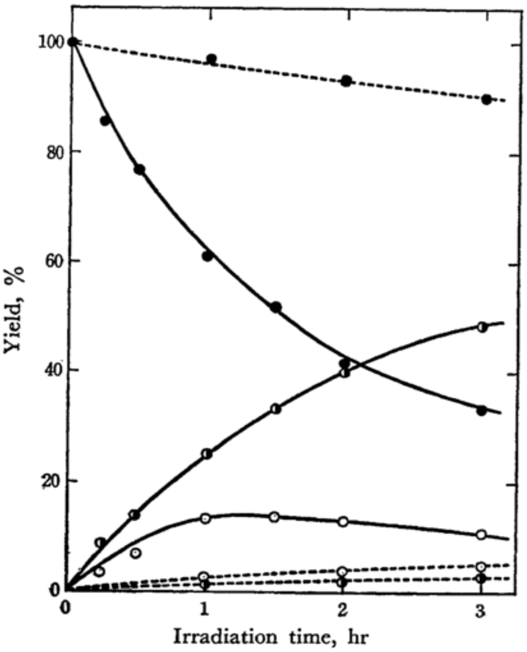
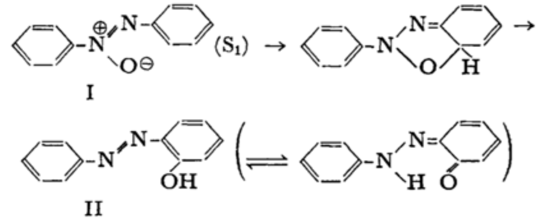


Fig. 1. Irradiation of azoxybenzene (10^{-2} M) at 25.0±0.1°C.
● *trans*-Azoxybenzene (I)
◑ 2-Hydroxyazobenzene (II)
○ *cis*-Azoxybenzene (III)
—— In ethanol ---- In *n*-hexane

Figure 1 shows the photostationary state of a *trans*-isomer I; a *cis*-isomer III was not established so easily. The thermal isomerization of III to I was slow under these experimental conditions.

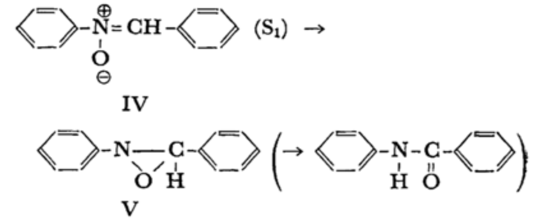
Even if an oxygen-saturated or degassed solution of I containing naphthalene or iodine was irradiated, no difference from the results shown in Fig. 1 was found; that is to say, neither the rearrangement to II nor the isomerization to III was affected by a quencher. On the other hand, when a degassed solution of I with a sensitizer was irradiated, azobenzene was obtained as a major product. This photochemical reduction was thought to proceed *via* the excited triplet state of I.[5] However, the direct irradiation of I without a sensitizer never afforded azobenzene. These results show that the rearrangement to II probably occur directly from the excited singlet state, S_1, of I, not from its excited triplet state.



The driving force of cyclization may be attributed to the attack of an oxyanion, as has been implied by Badger *et al.*[2] Interestingly the excited singlet state S_1 of I is more basic than its ground state.[11]

II and III were obtained upon the irradiation of I in carbon tetrachloride or in a solid phase, while acetone was not formed upon the irradiation of I in isopropanol. These results are consistent with the above-mentioned mechanism, in which hydrogen abstraction is not expected to take place. On the other hand, the photochemical reduction of the excited triplet state of I is followed by hydrogen abstraction.[5]

The mechanism for the rearrangement of I to II is assumed to be similar to that for the photochemical rearrangement of *N*,α-diphenylnitrone (IV) to 2,3-diphenyl-oxaziridine (V).[7]



The rearrangement of I to II is always accompanied by *cis-trans* isomerization. A *cis-trans* isomerization is often considered to involve an excited triplet state; indeed, the isomerization of IV is thought to proceed *via* the excited triplet state.[7] However, the *cis-trans* isomerization of I probably occur directly from the excited singlet state, not the triplet state for the reaction was not affected by a quencher, and azobenzene, which could be expected to be formed from the excited triplet state of I, was not obtained.

Solvent Effect. The results of the photolysis of I in various solvents using a Pyrex filter are given in Table 1.

The finding that the yield of II was higher in a polar protic solvent can be explained by an ionic

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[9] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley & Sons, Inc., New York (1962), p. 282.

[10] C. Tosi, *Spectrochim. Acta*, **22**, 1701 (1966), and other references cited therein.

[11] H. H. Jaffé, D. L. Beveridge and H. L. Jones, *J. Am. Chem. Soc.*, **86**, 2932 (1964); H. H. Jaffé and H. L. Jones, *J. Org. Chem.*, **30**, 964 (1965).

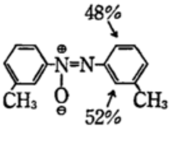
TABLE 1. IRRADIATION OF AZOXYBENZENE (10^{-2} M) FOR 2 HR AT 25.0 ± 0.1°C

Solvent	Dielectric constant	Yield of Product (%)		
		I	II	III
EtOH	24.3	42.3	40.3	12.8
iso-PrOH	18.3	47.2	38.8	12.0
MeCN	37.5	58.3	11.7	12.8
Benzene	2.28	80.0	4.1	14.9
n-Hexane	1.89	93.0	2.0	4.3

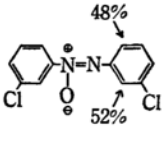
mechanism containing the attack of an oxyanion. The solvent effect on the rearrangement and the isomerization of I is in contrast to the effect on the reduction, whose reactivity is controlled by the hydrogen-donating ability of the solvent used (for example, isopropanol>ethanol).⁵⁾ Photolysis for different times showed that the faster II was formed, the faster was the photostationary state of I and III established.

Substituent Effect. Although the irradiation of an ethanolic solution of 4,4′-dimethyl-, 4,4′-dichloro-, 4,4′-dibromo-, and 4,4′-dimethoxy-azoxybenzene gave the corresponding 2-hydroxyazobenzene and *cis*-azoxybenzene, 4,4′-dinitro- and 4,4′-bis-(dimethylamino)-azoxybenezene were photochemically unreactive. This is presumably the result of an excitation of a nitro- or dimethylamino-group, not an azoxy-group. It is interesting to note that both the rearrangement and the isomerization always take place at the same time.

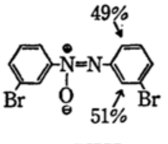
Steric Effect. Cumming's report that the irradiation of an ethanolic solution of 3,3′-dimethylazoxybenzene (VI) yielded only 2-hydroxy-3,3′-dimethylazobenzene¹²⁾ is difficult to understand in view of the steric effect of a methyl group. In order to discuss whether or not a substituent at a 3-position of the aromatic nucleus hinders an oxygen atom from migrating to a 2-position, an ethanolic solution of VI, 3,3′-dichloroazoxybenzene (VII) or 3,3′-dibromoazoxybenzene (VIII), was irradiated. The ratios of the migration of an oxygen atom to the 2- and 6-positions were as follows:



VI



VII



VIII

A bulky substituent like a bromo-group had no steric effect on the rearrangement. This can be explained by the fact that a migrating group is a small oxyanion. The 2-hydroxy-3,3′-dimethylazobenzene obtained by Cumming *et al.* may have been a mixture of 2-hydroxy-3,3′-dimethyl-azobenzene and 6-hydroxy-3,3′-dimethylazobenzene.

Experimental

Materials. The azoxybenzenes were prepared by the reduction of the corresponding nitro compound (Method A) or nitroso compound (Method B), or by the oxidation of the corresponding azobenzene (Method C). They were purified by recrystallization or column chromatography until their thin-layer chromatography (TLC) showed only one spot (see Table 2).

Photolysis of Azoxybenzene (I). An irradiation source was a 100 W high-pressure mercury arc lamp fitted with a water-cooled immersion well (Eikosha Halos PIH 100). A degassed solution (10 m*l*) of I (10^{-2}M) was irradiated in a Pyrex tube (inner diameter, 15 mm) directly attached to the lamp, and was thermostated at 25.0 ± 0.1°C. TLC (Merck silica gel G, *n*-hexane-benzene (2: 1)) showed two products, namely, 2-hydroxyazobenzene (II) and *cis*-azoxybenzene (III). The yield of the product was determined as follows. After irradiation, 2-hydroxy-4,4′-dichloroazobenzene (IX) was added to the solution as an internal standard. Each

TABLE 2

Substituent	Preparation method	Mp (°C)	λ_{max}^{EtOH} (mμ)	ε_{max}^{EtOH}	Ref.
—	A	35.5	323	14700	13
4,4′-Me	A	70.5	331	18100	14
4,4′-Cl	A	155.5	332	18700	15
4′4′-Br	A	172.0	333	22100	15
4,4′-MeO	A	113.0	356	13900	16
4,4′-NO_2	C	192.5	342	25700	17
4,4′-Me_2N	B	247.0	427	41000	18
3,3-Me	A	34.0	325	14700	14
3,3′-Cl	A	98.0	324	12500	15
3,3′-Br	A	110.0	323	15700	15

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12) W. M. Cumming and G. S. Ferrier, *J. Chem. Soc.*, **127**, 2377 (1925).
13) A. Lachman, *J. Am. Chem. Soc.*, **24**, 1180 (1902).
14) L. Zechmeister and P. Rom, *Ber.*, **59**, 870 (1926).
15) C. M. Suter and F. B. Dains, *J. Am. Chem. Soc.*, **50**, 2734 (1928).
16) D. Vorländer, *Ber.*, **40**, 1422 (1907).
17) A. Werner and E. Stiasny, *ibid.*, **32**, 3272 (1899).
18) J. Pinnow and G. Pistor, *ibid.*, **26**, 1313 (1893).

TABLE 3. IRRADIATION OF 4,4′-DISUBSTITUTED AZOXYBENZENE

Substituent	2-Hydroxyazobenzene				*cis*-Azoxybenzene
	Mp (°C)	$\lambda_{max}^{\mathrm{CHCl_3}}$ (mμ)	ε_{max}	Yield (%)	Yield (%)
H	84.5	325	18000	60	9
Me	153.5	339	19100	51	8
Cl	176.5	339	19500	35	8
Br	181.5	342	21100	29	9
MeO	133.0	384	23700	17	2
NO_2	—	—	—	0	0
Me_2N	—	—	—	0	0

component was 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 previously been determined by means of an authentic sample. Before the absorption of the extract containing a *cis*-isomer III was measured, the extract had been left at *ca.* 35°C in the dark for 10 hr to transform it to a more thermally-stable *trans*-isomer. The extinction coefficients used in this work were: I $\varepsilon_{326\,\mathrm{m}\mu}=14800$, II $\varepsilon_{325\,\mathrm{m}\mu}=18000$, and IX $\varepsilon_{339\,\mathrm{m}\mu}=19500$ (in chloroform).

The time dependencies of the product composition are given in Fig. 1.

The results of the irradiation of I in various solvents for 2 hours are given in Table 1.

No change in the product ratio was detected from the irradiation of I with a quencher like oxygen (saturated), naphthalene (10^{-1}—1 M), or iodine (10^{-1} M).

A degassed isopropanolic solution of I (5×10^{-2}M) was irradiated for 20 hr as described above, and then analyzed by gas chromatography (Yanagimoto GCG-5DH, polyethylene glycol 20M 4.5 m, He), but no acetone was detected.

Photolysis of 4,4′-Disubstituted Azoxybenzene. A degassed ethanolic solution (10 m*l*) of 4,4′-disubstituted azoxybenzene (10^{-2}M) was irradiated in a Pyrex tube at 48.0±0.1°C for 3 hr. TLC on silica gel showed two products, namely, the corresponding 2-hydroxyazobenzene and *cis*-azoxybenzene. Their yields were determined as above. The results obtained are shown in Table 3.

Photolysis of 3,3′-Dimethylazoxybenzene (VI). *Qualitative Analysis of Products.* An ethanolic solution (200 m*l*) of VI (10^{-2}M) in a flask was irradiated with an unfiltered internal lamp for 100 hr. TLC on silica gel showed two products, which were supposed to be azobenzene derivatives from their color reactions with concentrated sulfuric acid on silica gel thin-layer chromatography. After the removal of the ethanol, the chromatography of the residue on a column of silica gel and elution with petroleum ether (bp 40—60°C) - benzene (2:1) gave two compounds, A and B.

The first compound, A, was red crystals, mp 69°C (from ethanol).

Found: C, 74.49; H, 6.44; N, 12.11%. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38%.

The second compound, B, was red needles, mp 101°C (from ethanol).

Found: C, 74.45; H, 6.40; N, 12.32%. Calcd for $C_{14}H_{14}N_2O$: C, 74.31; H, 6.24; N, 12.38%.

From the results of elemental analysis and the usual example of the photochemical rearrangement of azoxybenzene, the two compounds, A and B, may be supposed to be 2-hydroxy-3,3′-dimethylazobenzene (X) and 6-hydroxy-3,3′-dimethylazobenzene (XI). On the other hand, the reaction products from diazotized *m*-toluidine and *o*-cresol were separated by TLC on silica gel to give a compound identical with Compound A in its melting point, R_f value, ultraviolet spectrum, and infrared spectrum; it did not give any Compound B. Hence Compound A was assigned to X. Similarly, the reaction of diazotized *m*-toluidine and *p*-cresol[19] gave Compound B, which was assigned to XI.

Quantitative Analysis of Products. A degassed ethanolic solution (10 m*l*) of VI (10^{-2}M) was irradiated in a Pyrex tube for 30 hr as has been described in discussing the photolysis of I. The products were separated by TLC, and their yields were determined from the absorption intensities in their electronic spectra in a manner described earlier. The extinction coefficients used were: X $\varepsilon_{332\,\mathrm{m}\mu}=19300$ and XI $\varepsilon_{326\,\mathrm{m}\mu}=19000$ (in chloroform). The product ratio of X to XI was 52 to 48.

Photolysis of 3,3′-Dichloroazoxybenzene (VII) and 3,3′-Dibromoazoxybenzene (VIII). *Qualitative Analysis of Products.* An ethanolic solution (200 m*l*) of VII or VIII (10^{-2}M) was irradiated for 100 hr. The products were separated by TLC (silica gel, *n*-hexane). Two products, C and D, were obtained from the photolysis of VII, and two others, E and F, from the photolysis of VIII. On the other hand, the reaction of diazotized *m*-chloroaniline and *p*-chlorophenol gave Compound C, and the reaction of diazotized *m*-bromoaniline and *p*-bromophenol gave Compound E. Thus Compound C was assigned to 6-hydroxy-3,3′-dichloroazobenzene(XII); D, to 2-hydroxy-3,3′-dichloroazobenzene (XIII); E, to 6-hydroxy-3,3′-dibromoazobenzene (XIV), and F, to 2-hydroxy-3,3′-dibromoazobenzene (XV).

XII was orange crystals, mp 158°C (from ethanol).

Found: C, 54.12; H, 3.26; N, 10.41; Cl, 26.57%. Calcd for $C_{12}H_8N_2OCl_2$: C, 53.97; H, 3.02; N, 10.49; Cl, 26.55%.

XIII was orange needles, mp 144°C (from ethanol).

Found: C, 54.21; H, 3.26; N, 10.72; Cl, 26.74%. Calcd for $C_{12}H_8N_2OCl_2$: C, 53.97; H, 3.02; N, 10.49; Cl, 26.55%.

XIV was reddish orange crystals, mp 171°C (from ethanol).

Found: C, 40.59; H, 2.49; N, 7.86; Br, 44.99%. Calcd for $C_{12}H_8N_2OBr_2$: C, 40.48; H, 2.27; N, 7.87; Br, 44.89%.

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[19] P. Jacobson and P. Piepenbrink, *ibid.*, **27**, 2703 (1894).

XV was reddish-brown crystals, mp 144°C (from ethanol).

Found: C, 40.76; H, 2.39; N, 7.79; Br, 45.11%. Calcd for $C_{12}H_8N_2OBr_2$: C, 40.48; H, 2.27; N, 7.87; Br, 44.89%.

Quantitative Analysis of Products. A degassed ethanolic solution (10 m*l*) of VII or VIII (10^{-2}M) was irradiated in a Pyrex tube for 30 hr as has been described in connection with the photolysis of I. The yields of the products were determined as has been described above. The extinction coefficients used were: XII $\varepsilon_{316\,\mathrm{m}\mu}=16700$, XIII $\varepsilon_{330\,\mathrm{m}\mu}=18800$, XIV $\varepsilon_{318\,\mathrm{m}\mu}=16400$, and XV $\varepsilon_{332\,\mathrm{m}\mu}=19100$ (in chloroform). The product ratio of XI to XII was 48 to 52, and that of XIV to XV was 49 to 51.

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