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Photolysis of Nitrosobenzene

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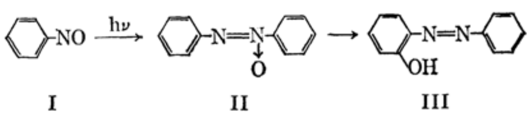
The mechanism of the photochemical reaction of nitrosobenzene (I) has been investigated. The irradiation of I leads to the formation of a phenyl radical and nitric oxide. The reaction of the phenyl radical with I yields diphenylnitroxide, which is then easily reduced to diphenylamine. The reaction of diphenylamine with the nitric oxide gives *C*-nitrosodiphenylamines, which are then photochemically oxidized to *C*-nitrodiphenylamines. On the other hand, I is oxidized to nitrobenzene and is, at the same time, reduced to azoxybenzene and azobenzene. Azoxybenzene is photochemically rearranged to 2-hydroxyazobenzene.

Nitrosobenzene (I) is known to be photochemically unstable.

Bamberger reported that azoxybenzene (II), 2-hydroxyazobenzene (III), 4-hydroxyazobenzene, 2-hydroxyazoxybenzene, nitrobenzene, aniline, and other minor products were obtained by the photolysis of I in benzene with sunlight,[1] but it is not clear whether or not his products other than II and III were really formed by the photolysis, because his assignment was doubtful and his analytical methods involved such improper procedures as treatment with heat, an acid and a base.



I II III

We found, by means of the ESR technique that the irradiation of I in tetrahydrofuran with a high-pressure mercury lamp led to the fission of the phenyl-nitroso bond and yielded diphenylnitroxide (IV).[2]

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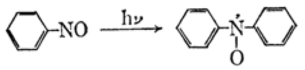
[1] E. Bamberger, *Ber.*, **35**, 1606 (1902).

[2] K. Maruyama, R. Tanikaga and R. Goto, This Bulletin, **37**, 1893 (1964).



I IV

Recently Shamma *et al.* irradiated I in ethanol at 253.7 mμ and obtained diphenylamine and *C*-nitrodiphenylamines by means of column chromatography; they then, without proof, assumed that the formation of diphenylamines could be followed by that of *N*-nitrosodiphenylamine.[3]

A principal objective of this work is to clarify the mechanism of the photochemical reaction of I by assigning the products.

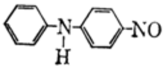
Results and Discussion

An ethanolic solution of nitrosobenzene (I) (10^{-1} M) in a Pyrex tube was irradiated with a high-pressure mercury lamp. The results are given in Table 1.

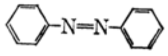
TABLE 1. IRRADIATION OF NITROSOBENZENE (10^{-1}M) AT 25.0±0.1°C

	Yields of products (%)	
Irradn. time (hr)	2	10
Nitrosobenzene (I)	85.4	63.9
Diphenylnitroxide (IV)	2.0	1.2
Diphenylamine (V)	2.9	6.4
4-Nitrosodiphenylamine (VI)	0.1	0.2
4-Nitrodiphenylamine (VII)	0.4	1.0
2-Nitrodiphenylamine (VIII)	0.6	1.5
Azoxybenzene (II)	3.9	5.4
2-Hydroxyazobenzene (III)	1.8	5.0
Azobenzene (IX)	0.9	3.1
Nitrobenzene (X)	—	*ca.* 1.0
Aniline (XI)	—	<0.5

No remarkable differences from the above results were found upon the irradiation of I in benzene under a nitrogen atmosphere. VI and IX had not previously been obtained.



VI



IX

Thin layer chromatography (TLC) of the irradiated solution showed that the expected β-phenylhydroxylamine, *N*-nitrosodiphenylamine, and 3-nitrodiphenylamine were not formed; on the other hand, tarry materials and smaller amounts of by-products were present, especially after a long irradiation. Hence, irradiation for many hours is not desirable in the investigation of the photolysis of I.

Although the photolysis involves very complex reactions, it seems to be possible to divide these reactions into the following three classes:

i) Reaction Process A: The bimolecular reaction of nitrosobenzene (I), followed by a phenyl-nitroso bond-rupture, affords diphenylnitroxide (IV), diphenylamine (V), 4-nitrosodiphenylamine (VI), 4-nitrodiphenylamine (VII), and 2-nitrodiphenylamine (VIII).

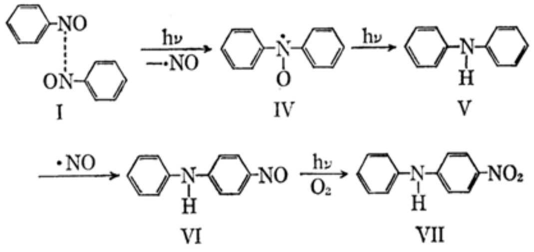
ii) Reaction Process B: The bimolecular reaction of I, followed by a N–O bond-rupture, affords azoxybenzene (II), 2-hydroxyazobenzene (III), and azobenzene (IX).

iii) Reaction Process C: The oxidation or the reduction of monomeric I affords nitrobenzene (X) or aniline (XI).

The mechanisms of these processes will be described below.

Reaction Process A:

Scheme A:



The photochemical reaction of I to IV was described in a previous paper.[2] Later, a similar reaction of nitrosoalkane was reported.[4,5] The finding that no benzene was obtained suggests that the dimeric or a similar form gave rise to the formation of IV.[6] This result is also consistent with the fact that no IV is formed from the photolysis of I with red light,[5] with which only the monomeric form could be excited.

IV is known to be unstable and has been supposed to give V in connection with aryl-*t*-butylnitroxides.[7] Indeed, the irradiation of IV in ethanol produces V easily.

In order to discuss the V-to-VI process, *N*-nitrosodiphenylamine (XII), which had been

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[3] M. Shamma, J. K. Whitesell and P. L. Warner, Jr., *Tetrahedron Letters,* **1965**, 3869.

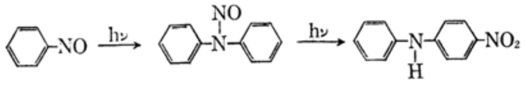
[4] E. T. Strom and A. L. Bluhm, *Chem. Commun.,* **1966**, 115.

[5] A. Mackor, T. A. J. W. Wajer, T. J. de Boer and J. D. W. van Voorst, *Tetrahedron Letters,* **1966**, 2115; T. A. J. W. Wajer, A. Mackor, T. J. de Boer and J. D. W. van Voorst, *Tetrahedron,* **23**, 4021 (1967).

[6] It has been discussed which form, monomeric[5] or dimeric[4] form, of nitrosoalkane gives rise to the formation of nitroxide upon the irradiation.

[7] A. R. Forrester and R. H. Thomson, *Nature,* **203**, 74 (1964); A. Calder and A. R. Forrester, *Chem. Commun.,* **1967**, 682.

assumed to be an intermediate by Shamma *et al.*,[3] was chosen as a model compound for two reasons. One reason was that XII was expected to give both V and nitric oxide, as in the photolysis of *N*-nitrosamides.[8] The other was that no XII was obtained from the photolysis of I; therefore, it had to be decided whether XII was not an intermediate, or whether the photochemical reaction of XII was so fast that no XII could be detected.



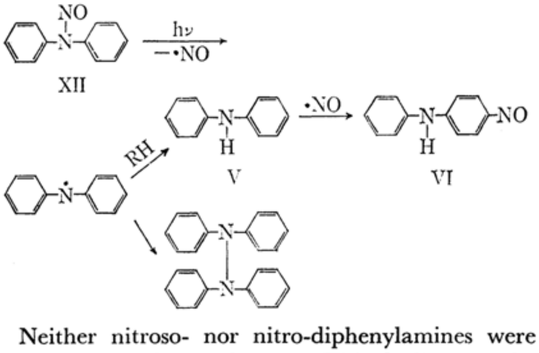
I XII VII

An ethanolic solution of XII (10^{-2} M) was irradiated with a Pyrex filter. The results are given in Table 2.

TABLE 2. IRRADIATION OF *N*-NITROSODIPHENYLAMINE (XII)(10^{-2}M) AT 25.0±0.1°C FOR 3 hr

Compd.	Yields of products (%)		
	Air	N_2	Degassed
XII	33.4	60.0	60.5
V	25.7	9.8	12.5
VI	0.5	1.7	0.0
VII	3.6	0.3	0.0
VIII	4.5	0.1	0.0
Carbazole	2.3	1.0	0.1

Table 2 shows that the N–N bond of XII was broken, and that then the nitric oxide intermolecularly attacked V to give VI. The homolytic fission of the N–N bond was also confirmed by the formation of tetraphenylhydrazine by the photolysis of a saturated ethanolic solution of XII.



Neither nitroso- nor nitro-diphenylamines were obtained in a degassed state. This finding can be explained by the removal of nitric oxide from the solution.

The well-known photochemical cyclization of V to carbazole[9] will not be discussed.

Under a nitrogen atmosphere, no nitro-compounds were obtained. This suggests that the nitrosodiphenylamine was photochemically oxidized to nitrodiphenylamine. In order to discuss this novel photochemical oxidation of a nitroso-compound to a nitro-compound, an ethanolic solution of VI (10^{-3} M) was irradiated with a Pyrex filter. The results are given in Table 3.

TABLE 3. IRRADIATION OF 4-NITROSODIPHENYLAMINE (10^{-3}M) AT 25.0±0.1°C

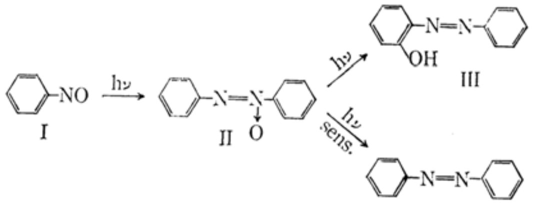
	Yields of products (%)		
Irradn. time	3 hr	3 hr	5 min
Sensitizer	—	V (10^{-2}M)	Ph_2CO (10^{-2}M)
VI	46.0	20.3	23.1
VII	13.8	17.3	24.4

Table 3 shows that VI underwent a photosensitized oxidation to VII, and that V could be a sensitizer, though not as efficient a one.

The results described above support Scheme A. XII cannot be an intermediate of I to nitrodiphenylamines, because the irradiation of I never afforded XII, whereas the photochemical reaction of XII was not fast enough.

Reaction Process B:

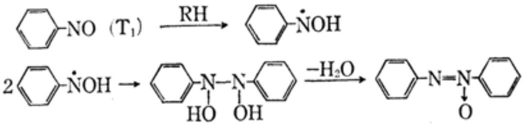
Scheme B:



I II III IX

III is formed from the excited singlet state of II,[10] and IX is formed from the excited triplet state of II,[11] as has been reported in previous papers. Although IX was never obtained upon the direct irradiation of II without a sensitizer, IX was obtained upon the irradiation of I. This finding can probably be explained in terms of sensitization of I through its excited triplet state.

Mauser *et al.*[12] postulated, without proof, the following mechanism for the photochemical reduction of I:



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[8] L. P. Kuhn, G. G. Kleinspehn and A. C. Duckworth, *J. Am. Chem. Soc.*, **89**, 3858 (1967).

[9] D. C. Neckers, "Mechanistic Organic Photochemistry," Reinhold Publishing Corp., New York, N. Y. (1967), p. 239.

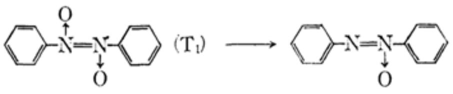
[10] R. Tanikaga, This Bulletin, **41**, 2151 (1968).

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

[12] H. Mauser and H. Heitzer, *Z. Naturforsch.*, **20b**, 200 (1965).

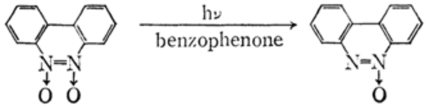
This mechanism may be probable in view of the mechanisms for the photochemical reduction of nitrobenzene[13,14] and the base-catalyzed reduction of I.[15,16]

Since nitrosobenzene in a solution exists in an equilibrium of a monomeric form (I) and a dimeric form (XIII),[17] the other possible mechanism is that II is formed from the excited triplet state of dimeric nitrosobenzene.



XIII   II

This mechanism, similar to that for the photochemical reduction of II to IX *via* the excited triplet state,[11] may be supported by the findings that the irradiation of solid nitrosobenzene with a XIII structure also yielded II, and that an ethanolic solution of benzo[*c*]cinnoline 5,6-dioxide (XIV) with a structure similar to XIII underwent photochemical reduction of benzo[*c*]cinnoline 5-oxide (XV) in the presence of benzophenone.

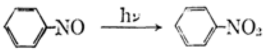


XIV   XV

However, it is impossible to decide which mechanism is more reasonable, because the reaction is very complex.

Reaction Process C:

Scheme C:



I   X

I as well as VI was slightly oxidized, but the unimolecular reaction of I rarely occurred. This result is in contrast with that of the photolysis of I with hydrochloric acid, in which primary amines were obtained as the major products.[18]

At any rate, the dimeric or a similar form may be assumed to be important in the photolysis of nitrosobenzene.

Conclusion

The mechanism of the photolysis of nitrosobenzene (I) is as follows:

i) I undergoes the homolytic fission of a nitroso-phenyl bond. The phenyl radical formed reacts with I to yield diphenylnitroxide, which is then reduced to diphenylamine. The nitric oxide reacts with diphenylamine to afford *C*-nitrosodiphenylamines, which are photochemically oxidized to *C*-nitrodiphenylamines.

ii) I is reduced to azoxybenzene, which is rearranged to 2-hydroxyazobenzene. Azoxybenzene undergoes a photosensitized reduction to azobenzene.

iii) I is slightly oxidized to nitrobenzene.

Experimental

Materials. Nitrosobenzene (I) was prepared by the reduction of nitrobenzene and was then recrystallized from ethanol (mp 68.0°C).[19] The authentic materials shown in Table 4 were also synthesized in order to determine the products.

TABLE 4. MELTING POINTS AND ABSORPTION SPECTRA OF AUTHENTIC MATERIALS

Compd.	Mp (°C)	$\lambda_{max}^{CHCl_3}$ (mμ)	$\varepsilon_{max}^{CHCl_3}$	Ref.
II	35.5	326	14800	20
III	84.0	325	18000	21
IV	61.5	314	17500	22
V	54.0	290	17000	—
VI	145.0	414	26000	23
VII	134.5	380	19000	24
VIII	75.5	263	14500	—
IX	68.0	319	18500	—
XII	66.5	292	7650	25
Carbazole	245.5	292	17100	—

Photolysis of Nitrosobenzene (I). The irradiation source was a 100-W high-pressure mercury arc lamp fitted with a water-cooled immersion well (Eikosha Halos PIH-100). An ethanolic solution (2 m*l*) of I (10^{-1} M) was irradiated in a Pyrex tube (inner diameter; 13 mm) attached directly to the lamp, and was then thermostated at 25.0±0.1°C. The R_f values and the

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[13] R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

[14] R. Hurley and A. C. Testa, *J. Am. Chem. Soc.*, **88**, 4330 (1966).

[15] C. J. W. Gutch and W. A. Waters, *Proc. Chem. Soc.*, **1964**, 230.

[16] G. A. Russell and E. J. Geels, *J. Am. Chem. Soc.*, **87**, 122 (1965).

[17] W. Lüttke, *Z. Elektrochem.*, **61**, 976 (1957) and other references cited therein.

[18] S. Hashimoto, J. Sunamoto and K. Kano, Preprints for the 20th Annual Meeting of the Chemical Society of Japan (Tokyo, 1967), Vol. III, p. 179.

[19] G. H. Coleman, C. M. McCloskey and F. A. Stuart, "Organic Syntheses," Coll. Vol. III, p. 668 (1955).

[20] A. Lachman, *J. Am. Chem. Soc.*, **24**, 1180 (1902).

[21] W. M. Cumming and G. S. Ferrier, *J. Chem. Soc.*, **127**, 2375 (1925).

[22] H. Wieland and M. Offenbächer, *Ber.*, **47**, 2114 (1914).

[23] O. Fischer and E. Hepp, *ibid.*, **19**, 2994 (1886).

[24] I. Goldberg, *Chem. Zentr.*, **1907-II**, 957.

[25] L. Vanino, "Handbuch der Präparativen Chemie," Vol. II, Verlag von Ferdinand Enke, Stuttgart (1937), p. 672.

color reactions with concentrated sulfuric acid upon the TLC (silica gel) of the solution showed the compounds, II—IX, in Table 1, but no *β*-phenylhydroxylamine, *m*-nitrodiphenylamine, *N*-nitrosodiphenylamine, and carbazole. The minor products other than II—IX could not be assigned. A small amount of nitrobenzene was detected by gas chromatography (Yanagimoto GCG-5DH, polyethylene glycol, He), but no aniline was. On the other hand, when the solution was diazotized and treated with 2-naphthol or NW-acid (1-naphthol-4-sulfonic acid), no coupling compound with aniline was detected on TLC. Since it was difficult to detect benzene in ethanol, I in cumene was irradiated in the same manner as has been described above for the detection of benzene, but the gas chromatography of the solution showed the absence of any benzene, while its TLC showed the presence of II—IX.

The yield of the product was determined as follows. After the irradiation, 2-hydroxy-4,4′-dichloroazobenzene ($\lambda_{max}^{CHCl_3}=339$ mμ, $\varepsilon_{max}^{CHCl_3}=19500$) was added to the solution as an internal standard. Each component was separated by TLC (Merck silica gel G, *n*-hexane - chloroform (3 : 1)) and then 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, as is shown in Table 4.

The amount of I unreacted was determined as follows. After the irradiation, ethanol (*ca.* 50 m*l*) was added to the solution; both ethanol and I were then distilled *in vacuo* at the room temperature and trapped in a receiver cooled by dry ice-acetone. The same procedure was repeated until no further I was distilled. The amount of I was determined from the intensity of the maximum absorption of the distillate (*ca.* 250 m*l*).

Photolysis of N-Nitrosodiphenylamine (XII). An ethanolic solution (2 m*l*) of XII (10^{-2} M) was irradiated in a Pyrex tube at 25.0±0.1°C for 3 hr. TLC (silica gel G, *n*-hexane - benzene (2 : 1)) showed the presence of V—VIII, carbazole, and some minor products not identified. Their yields were determined by the method described above. III was used as the internal standard.

When benzene was used as a solvent, the amounts of nitroso- and nitro-derivatives were larger.

Photolysis of 4-Nitrosodiphenylamine (VI). An ethanolic solution (2 m*l*) of VI (10^{-3} M) was irradiated in a Pyrex tube at 25.0±0.1°C. III or 1-benzeneazo-2-naphthol ($\lambda_{max}^{CHCl_3}=317$ mμ, $\varepsilon_{max}^{CHCl_3}=7470$) was added as an internal standard, and then VI and VII were separated by TLC (silica gel G, benzene - *n* - hexane (4 : 1)). Their yields were determined as above. The assignment of the other products was not attempted.

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