BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 725—728 (1974)

Implication of Diazonium Cations as Intermediates in the Photorearrangement of Azoxybenzenes

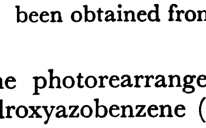
Nigel James Bunce
Department of Chemistry, University of Guelph, Guelph, Ontario, Canada

(Received March 28, 1973)

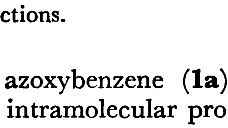
Photolysis of azoxybenzene and 2,2′-azoxytoluene in the presence of 2-naphthol gives, in addition to *o*-hydroxyazocompounds, 1-arylazo-2-naphthols, sometimes as the major products. This implies that cleavage into diazonium ions may sometimes be a major pathway in the irradiation of aromatic azoxycompounds. A mechanism is proposed to account for the formation of azonaphthols as well as the various side products that have previously been obtained from these reactions.

The photorearrangement of azoxybenzene (**1a**) to *o*-hydroxyazobenzene (**2a**) is an intramolecular process in which the azoxy oxygen migrates to a free *ortho* position in the more distant aromatic ring.[1] Tanikaga showed[2] that the reaction involves the singlet π,π^* state of **1a** because, when the triplet excited state is populated by photosensitisation, oxygen migration is suppressed and photoreduction occurs instead. Iwata and Emoto[3] observed minor products additional to **2a** on photolysis of **1a** in chloroform solution; photoreduction concurrent with rearrangement occurred even in the absence of a photosensitiser, and *p*-hydroxyazobenzene (**3a**) was also formed. The authors speculated that photodissociation of **1a** into azobenzene and an oxygen atom might account for these minor products.

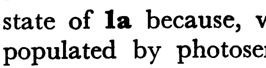
Side products have also been observed in irradiations of 2,2′-azoxytoluene (**1b**). Lewis and Reiss[4] observed the azocompounds (**3b**) and **4** in addition to expected product (**2b**), when ethanol was used as the solvent. Recently we have obtained **2b**, **4**, and the bis-azocompound **5** in our laboratory on photolysis of **1b** in benzene.[5] Similar behaviour was also observed with 2,2′-dibenzylazoxybenzene.



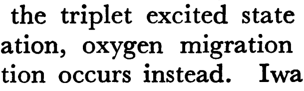
1a R=H
1b R=CH$_3$



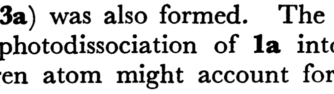
2a R=H
2b R=CH$_3$



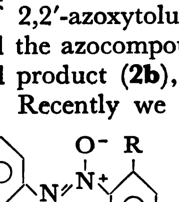
3a R=H
3b R=CH$_3$



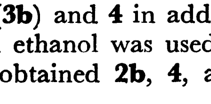
4



5



6a R=H
6b R=CH$_3$

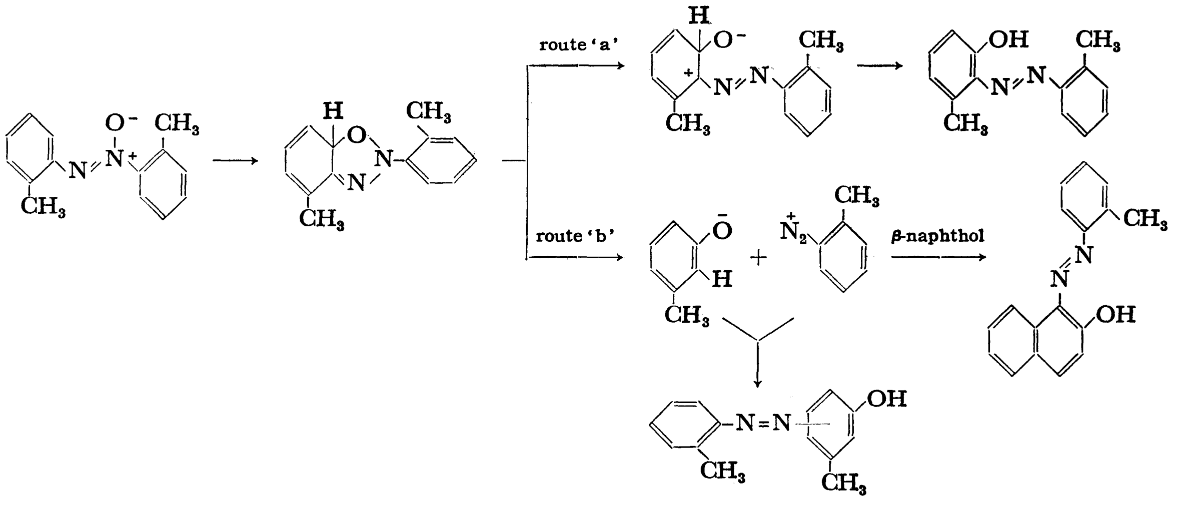


7

The abnormal products **3b** and **5** especially are reminiscent of the coupling products of a diazonium ion cation with an appropriate phenol; however, both we and Lewis and Reiss noted that **2b** is stable to the photolysis conditions and hence that the abnormal products do not arise as secondary products through the photochemical cleavage of **2b** into diazonium cations. By contrast, in this paper are reported observations which strongly implicate the participation of diazonium ion intermediates at some stage in the reaction. A modification of the widely accepted Badger and Buttery[6] rearrangement mechanism is proposed to account for the various side products that have been observed in the photolyses alluded to above.

Irradiation in ethanol of **1b** in the presence of 2-naphthol gave the usual rearrangement product **2b**, but the anomalous products **3**—**5** were suppressed. Instead there were obtained *m*-cresol and 1-*o*-tolylazo-2-naphthol (**6b**), the coupling product of an *o*-toluenediazonium cation with 2-naphthol. Photolysis of **2b** in the presence of 2-naphthol gave none of this compound. Observation of *m*-cresol and **6b** thus suggests that fragmentation of some intermediate is occurring, with one of the fragments being the *o*-toluenediazonium cation. The photostability of **2b** implies that such diazonium ions are formed not from **2b** but from one of its precursors. Tentatively, the accompanying reaction scheme is proposed to account for those observations. The Badger and Buttery cyclic intermediate **7** may either cleave the N–O bond to yield eventually **2b** as Badger and Buttery proposed; alternatively, the *o*-toluenediazonium ion may be expelled with the formation of a phenoxide anion. The diazonium ion reacts with the *m*-cresol or its anion, giving **3b** and **4**, or couples with preformed **2b**, when the bis-azocompound **5** results. In the presence of 2-naphthol the side products are suppressed because the diazonium ion is trapped by 2-naphthol.

An attractive feature of this proposal is that the ejection of the diazonium ion from **7** will be facilitated by the bulky alkyl group already in the 6-position of the intermediate. This is consistent with the fact that abnormal rearrangement products have only been observed during photolyses of 2,2′-disubstituted azoxybenzenes. It was thus anticipated that azoxybenzene **1a** itself, being sterically unencumbered, would afford



only small quantities of products arising from diazonium ion precursors. From an irradiation in ethanol, this was indeed the case, but unexpectedly, irradiation of **1a** and 2-naphthol in benzene gave 1-phenylazo-2-naphthol (**6a**) as the major product (60% based on reacted **1a**) together with 22% of **2a**. If formation of (**6a**) may be considered diagnostic of a diazonium ion precursor, it follows that, in this system at least, most azoxybenzene molecules photolyse by cleavage to a trappable diazonium cation. This implies that in the absence of 2-naphthol, even the normal product **2a** may arise, at least in part, by recombination of a geminate pair of diazonium cation and phenoxide ion (or phenol). Clearly the diazonium cation and the phenoxide anion never become free of each other, else *p*-hydroxyazobenzene would be a major product, since diazonium couplings invariably take place at an available *para* position.[7] The above implication opens up the question of whether aromatic azoxycompounnds in general photorearrange by the Badger and Buttery pathway (route 'a') or whether cleavage into diazonium ions (route 'b') can be a major, or even the exclusive, route to *o*-hydroxyazocompounds. Further work is in progress to test this possibility and to try to determine the cause of the marked change in product distribution observed when the solvent is changed from ethanol to benzene. Thus, photolysis of **1b** with 2-naphthol in benzene led to an increase in the proportion of the azonaphthol **6b** in the product mixture, analogous with the observations with **1a**.

An additional, minor product of the reaction of **1a** with 2-naphthol in benzene was an isomer of **6a** according to mass spectrometry, although insufficient material was obtained for complete identification. The isomer appears to be much too stable thermally to be the *cis* isomer of **6a**, aside from which, previous attempts to prepare *cis*-*o*-hydroxyazocompounds have been without success.[8] The new compound was not produced by photolysis of **6a** either alone or in the presence of either **1a** or 2-naphthol. It was felt that this could be a constitutional isomer of **6a** formed by a photochemical coupling reaction between a benzenediazonium cation and 2-naphthol. However, photolysis of sodium phenylazosulphonate (which gives diazonium ions on irradiation[9]) in the presence of 2-naphthol gave **6a**, but none of the other isomer, whose origin is therefore still a mystery.

The *p*-hydroxyazobenzene obtained by Iwata and Emoto may now be accounted for as the product of reaction of a separated diazonium ion with phenol. Their isolation of azobenzene however most likely involves a quite different mechanism, since Tanikaga[2] showed that, while **2a** derives from singlet excited **1a**, azobenzene is a triplet state product. Heavy atom solvents are well known to promote intersystem crossing, so it is likely that in chloroform solution intersystem crossing would occur more readily than in ethanol, and the resultant population of the triplet state of **1a** would allow a small amount of photoreduction to occur. On the scale of his experiments, Tanikaga did not observe any photoreduction in heavy atom solvents; perhaps the quantum yield for photoreduction is low.

TABLE 1. PHOTOREARRANGEMENT OF **1a** TO **2a** IN ETHANOLIC MIXTURES

Added solvent	**2a**, mg	Recovered **1a**, mg	**2a**/**1a**
None	186	223	0.83
$CH_3CH_2CH_2Cl$	117	248	0.47
$CHCl_3$	112	252	0.44
$CH_3CH_2CH_2Br$	88	287	0.31
CCl_3Br	58[a]	252	0.23
CH_3CH_2I	78	296	0.26

a) Brominated *o*-hydroxyazobenzenes (61 mg) were formed in addition.

In support of a heavy atom effect, the photorearrangement of **1a** in ethanol has been found to be retarded considerably when halogenated compounds are added to the solvent (see Table 1) and the heavier the halogen concerned, the slower the reaction. On the scale of these experiments, azobenzene was again not formed in isolable quantities; nevertheless, the results are consistent with the idea of a heavy atom effect promoting intersystem crossing, with the consequent removal of some of the singlet excited **1a** molecules, making them unavailable for photorearrangement. In one solvent, ethanol/bromotrichloromethane, brominated *o*-hydroxy-

Table 2. Physical properties of brominated *o*-hydroxyazobenzenes

Compound	Mp	UV data		
		Conc. mg/100 ml	λ_{max}nm(A) in ethanol	λ_{max} nm(A) in ethanol/0.1 M KOH
Monobromide (photoreaction)	117—120°	0.9	376(0.43), 320(0.97)	462(0.44)
Dibromide (photoreaction)	132—134°	1.9	380(0.40), 325(1.10)	470(0.38)
Monobromide (**2a**+equimolar Br_2)	110—115°	2.0	377(0.94), 317(2.08)	467(1.04)
Dibromide (**2a**+equimolar Br_2)	125—129°	2.1	382(0.43), 327(1.13)	474(0.35)
Dibromide (**2a**+excess Br_2)	173—175°	2.7	380(0.55), 334(1.33)	480(0.45)
5-Bromo-**2a**($C_6H_5N^+_2$+*p*-BrC_6H_4OH)	120—122°	1.9	378(0.57), 317(1.24)	465(0.42)

azobenzenes were formed additionally; these probably arise through photolysis of bromotrichloromethane to molecular bromine,[10] which brominates the **2a** already produced. Indeed, independent bromination of **2a** gave the same mixture of mono- and di-bromohydroxyazobenzenes, but isolation of pure compounds from these mixtures was difficult because of problems of separation (see Experimental section).

Experimental

Separation and analytical procedures have been described in detail previously.[5]

Irradiation of 1b with 2-Naphthol. i) A solution of **1b** (0.650 g) and 2-naphthol (2.0 g) in ethanol (30 ml) was irradiated with an external source for 17 hr. After evaporation of the solvent, the residue was taken up in chloroform and extracted with 3 M sodium hydroxide solution. The organic phase was dried, evaporated, and separated by preparative tlc on silica gel (E. Merck No. 7747) (benzene: ligroin, 1: 4) to give three bands, each of which was shown after extraction to be pure (tlc). Band 1 (129 mg) was **2b**, red needles from ethanol, mp 92—94 °C (lit,[5] 96 °C). Band 2 (81 mg) was an oil, which crystallised from ethanol, mp 50—52 °C, and was starting material. Band 3 (226 mg), red leaflets from ethanol, had mp 126—128 °C. Its mass spectrum, m^+/e 262 (M^+ 74%), 245 (11), 234 (17), 171 (17), 144 (14), 143 (100), 128 (10), 115 (61), 107 (12), 106 (22), 91 (68), and mp were identical with those of an authentic sample of 1-(*o*-tolylazo-)-2-naphthol, **6b**, (lit, mp[11] 131 °C), obtained by coupling *o*-toluenediazonium chloride with 2-naphthol.

The sodium hydroxide extract of the crude photolysis mixture was acidified and extracted into chloroform, dried and evaporated. Vapour phase chromatography of the extract (10% SE30 on 30/80 Celite, 100°) showed a peak of retention time identical to that of *m*-cresol. The residue was distilled from a bulb using an oilbath at 260 °C to give *m*-cresol (99 mg) having IR spectrum identical to that of an authentic sample.

ii) A solution of **1b** (0.650 g) and 2-naphthol (2.0 g) in benzene (20 ml) was irradiated with an external source for 21 hr. After removal of most of the 2-naphthol by base extraction, the organic material was separated by preparative tlc as described above. The bands obtained were, in increasing order of polarity, **2b** (16 mg), recovered **1b** (0.26 g) and **6b** (133 mg), mp 128—129 °C. UV spectra of each of these compounds were identical with those of authentic samples.

Photolysis of **2b**. A solution of **2b** (26 mg) in benzene (2.0 ml) was irradiated for 6 hr in a 5 ml Pyrex flask equipped with reflux condenser, using an external source. Analytical tlc showed only one spot in the reaction mixture, and passage of the reaction mixture through a short column of silica gel, eluting with benzene, allowed recovery of **2b** (22 mg), mp 94—96 °C. Similar results were obtained in a 6 hr irradiation of **2b** (45 mg) in the presence of 2-naphthol (199 mg).

Irradiation of 1a with 2-Naphthol. (i) A solution of **1a** (0.45 g) and 2-naphthol (2.0 g) in 95% ethanol (40 ml) was irradiated in a corked Pyrex test tube for 90 hr using an external source. After extraction with 0.5 M NaOH solution to remove most of the 2-naphthol, the residue was resolved by preparative tlc (benzene: ligroin, 1: 9) affording **2a** (110 mg), mp 80—81 °C, recovered **1a** (322 mg), and **6a** (0.6 mg), estimated from its UV spectrum which was identical with that of an authentic sample (see below).

(ii) A solution of **1a** (0.40 g) and 2-naphthol (1.00 g) in dry benzene (20 ml) was irradiated for 12 hr in a stoppered Pyrex ampoule using a Hanovia 450 W medium pressure mercury arc. Analytical tlc on silica gel (benzene: ligroin, 1:4) showed three compounds besides starting materials. After removal of most of the 2-naphthol by extraction with 0.5 M NaOH, the organic residue was resolved by preparative tlc on silica gel.

The most mobile band was **2a** (43 mg), red needles from ethanol, mp 78—80 °C. Band 2 (213 mg) was recovered **1a**. Band 3 (19 mg) separated incompletely from band 2; fractional crystallisation from ethanol gave dark red needles (3 mg), mp 130—132 °C, softened at 117 °C. Mass spectrum (70 eV): m^+/e 248 (M^+, 100%), 171 (18), 143 (90), 115 (52), 77 (42); UV (EtOH): λ_{max} 487 nm (log ε 4.6), 352 (4.5), 288 (4.6). The least mobile material on the tlc plate was **6a** (153 mg), mp 130—131 °C (lit,[6] 133 °C). Mass spectrum: m^+/e 248 (M^+, 100%), 171 (25), 143 (98), 115 (72), 77 (49); UV (EtOH): λ_{max} 475 nm (log ε 4.17), 413 sh (4.00), 309 (3.85), 258 sh (3.99), 251 (4.02) very similar to that reported.[6]

Despite the similarity of physical properties of bands 3 and 4, they were shown to be different as follows. Band 3 was a red spot (R_f 0.25) on analytical tlc whereas band 4 gave an orange spot (R_f 0.15). Band 3 was not converted to band 4 either by fusion at 150 °C or by heating in chlorobenzene to 160 °C for 21 hr. Likewise band 4 could not be converted to band 3 by photolysis either alone in benzene solutions of varying concentration, or by photolyses in benzene solution in the presence of either **1a** or 2-naphthol. In each case **6a** was recovered unchanged.

Irradiation of Sodium Phenylazosulphonate with 2-Naphthol. A solution of sodium phenylazosulphonate[9] (2.0 g) and 2-naphthol (1.0 g) in 100 ml ethanol and 225 ml water was irradiated in an immersion well apparatus with an unfiltered mercury arc for 1 hr by which time a suspension of a red substance was present. Extraction into chloroform gave a solution containing **6a**, unreacted 2-naphthol, and a tarry residue, but no other products, according to tlc on silica gel (benzene: ligroin, 1:9). Passage through a short column of alumina eluting with benzene: chloroform, 4:1 gave **6a** (0.43 g), which crystallised as red needles from ethanol, mp 131—132 °C.

Irradiation of 1a in Mixtures of Ethanol and Halogenated Solvents. Solutions of **1a** (0.40 g) in equal volumes of ethanol and the halogenated solvent (total volume 40 ml) were irradiated simultaneously for 100 hr using a Rayonet "Merry-go-round". The solvent was evaporated and each residue was separated by preparative tlc (benzene: ligroin, 1:9), giving the quantities of **1a** and **2a** recorded in Table 1. When ethanol/bromotrichloromethane was the solvent the *o*-hydroxyazobenzene was obtained contaminated with other products. These could not be resolved on silica gel or by fractional crystallisation; partial separation was achieved by preparative tlc on alumina (J. T. Baker, Type 9F; developing solvent benzene, or benzene: ether, 9:1), followed by repeated crystallisation from ethanol.

Physical characteristics of the purest samples obtained from both the photoreaction and from the bromination of **2a** in CCl_4 are given in Table 2. The identities of the products were established by mass spectrometry, but since the mass spectra of the monobromide always showed small amounts of the dibromide and *vice versa*, the raw UV absorbance data are recorded rather than the molar extinction coefficients. It seems most likely that the monobromide is 5-bromo-2-hydroxyazobenzene since its mp, mass spectrum, and UV correspond closely to those of authentic material, prepared in low yield by coupling benzenediazonium chloride with *p*-bromophenol. Also given for comparison are the physical properties of a second dibromohydroxyazobenzene, which crystallises from solution when **2a** is treated with a large excess of bromine.

The author thanks the National Research Council of Canada for generous financial support.

References

1) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970); E. Buncel, in "Mechanisms of Molecular Migrations," Vol. 1, Ed. B. S. Thyagarajan, Interscience, (1969), pp. 104—110.

2) R. Tanikaga, This Bulletin, **41**, 1664, 2151 (1968).

3) M. Iwata and S. Emoto, *ibid.*, **43**, 946 (1970).

4) G. E. Lewis and J. A. Reiss, *Aust. J. Chem.*, **19**, 1887 (1966).

5) D. J. W. Goon, N. G. Murray, J-P. Schoch, and N. J. Bunce, *Can. J. Chem.*, **51**, 3827 (1973).

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

7) H. Zollinger, "Azo and Diazo Chemistry," Interscience (1961), p. 253.

8) Ref. 7, pp. 59—61.

9) R. Dijkstra and J. de Jonge, *Rec. Trav. Chim.*, **77**, 538 (1958).

10) E. S. Huyser, *J. Amer. Chem. Soc.*, **82**, 391 (1960).

11) T. Zincke and F. Rathgen, *Ber.*, **19**, 2482 (1886).