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Evidence Against a Hydrogen Abstraction Mechanism in the Photorearrangement of Azoxybenzene to 2-Hydroxyazobenzene¹

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In an attempt to distinguish between ionic and free radical mechanisms for the photorearrangement of azoxybenzene to 2-hydroxyazobenzene, aromatic azoxycompounds carrying C-H functions ortho to the azoxy linkage have been prepared and irradiated. The failure of these weaker C-H bonds to divert the reaction from its normal course argues against a hydrogen abstraction - hydroxyl transfer mechanism. This conclusion is supported by the observation of a 30-fold increase in quantum yield for 2-hydroxyazobenzene formation on changing from a non-polar to a polar solvent and by the kinetic deuterium isotope effect, which is too small for the primary isotope effect required by the abstraction mechanism. It is concluded that the experimental observations to date may most easily be accommodated in the route originally proposed by Badger and Buttery, where the rearrangement is seen as a substitution by oxygen at the ortho ring carbon.

Afin de distinguer entre un mécanisme à caractère ionique et un mécanisme impliquant des radicaux libres lors du photoréarrangement de l'azoxybenzène en hydroxy-2 azobenzène, on a préparé et irradié des composés "azoxy" aromatiques comportant des fonctions C-H en position ortho du lien azoxy. Ces liens C—H plus faibles s'étant révélés incapables de dévier la réaction de son cours normal, on en conclut alors qu'un mécanisme impliquant l'enlèvement d'un hydrogène puis transfert du groupe OH ne saurait être considéré. Cette conclusion est d'ailleurs en accord avec l'observation selon laquelle une augmentation (par un facteur de 30) du rendement quantique est enregistrée lors de la formation de l'hydroxy-2 azobenzène lorsque l'on passe d'un solvant non-polaire à un solvant polaire, de même qu'elle est en accord avec l'effet isotopique causé par le deutérium trop faible pour être un effet isotopique primaire qui serait normal pour le mécanisme impliquant l'enlèvement d'un hydrogène. On en conclut alors que les données expérimentales, jusqu'à présent, conduisent au mécanisme proposé à l'origine par Badger et Buttery selon lequel le réarrangement est le résultat d'une substitution par l'oxygène au carbone du cycle en position ortho. [Traduit par le journal]

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The instability of aromatic azoxy compounds to light has long been recognized as being due to their transformation into o-hydroxyazo to compounds (1). The rearrangement apparently proceeds from the ${}^{1}\pi,\pi^{*}$ excited state of the azoxy compound, since Tanikaga et al. have shown (2) that no n,π^* band appears in the

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absorption spectrum of azoxybenzene and that deliberate excitation of the triplet state by photosensitization causes photoreduction as well as oxygen migration. Previously, Badger and Buttery (3) had found that unsymmetrical azoxybenzenes such as 1 rearrange exclusively



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SCHEME I

to 2, where the azoxy oxygen migrates to the aromatic ring farther from its point of departure. They proposed the intramolecular mechanism of Scheme 1, in which the rearrangement is initiated by nucleophilic attack of the azoxy oxygen on the appropriate ring carbon, giving the cyclic intermediate **A**. The intramolecular character of the reaction and the direction of oxygen migration have both been confirmed by ${}^{18}O(4)$ and ${}^{15}N(5)$ isotopic labelling experiments. All of this work has been reviewed recently (6).

Although the Badger and Buttery mechanism has been widely accepted, to date no other experiments have been carried out to support it and in one study (7), Oae *et al.* have argued that a radical mechanism for the photorearrangement better explains the experimental facts. One possibility for such a mechanism is a radical analog of Scheme 1, although it is questionable whether any distinction can be drawn between an ionic and a radical Scheme 1, since an excited state of azoxybenzene inevitably carries unpaired electrons. Another is the hydrogen abstraction pathway of Scheme 2, in which



homolytic hydrogen abstraction from the conveniently situated *ortho* position of the distant aromatic ring is followed by hydroxyl transfer. This route is similar to the mechanism widely accepted (8) for oxygen migration in the photorearrangement of *o*-nitrobenzaldehyde to *o*nitrosobenzoic acid and is attractive in view of the electronic similarities between the azoxy-



In addition, the crystal structure of an azoxybenzene derivative, 4,4'-azoxyanisole, shows that at least in the solid state, the azoxy group and the distant benzene ring are essentially coplanar, with the oxygen and *o*-hydrogen separated by only 2.3 Å (9). Assuming a comparable excited state geometry, this should facilitate a hydrogen abstraction mechanism.

The purpose of the present study has been to choose between these alternative modes of rearrangement on experimental grounds. We believe that the results presented here allow us to exclude the abstraction mechanism, but we are unable on the present evidence to confirm all the details of the Badger and Buttery mechanism (Scheme 1).

Results and Discussion

In the mechanism of Scheme 2, oxygen migration is preceded by homolytic hydrogen abstraction by oxygen. The ease of reaction should thus parallel the weakness of the C-H bond to be broken, as in typical hydrogen abstractions by free radicals (10), in the photochemical Norrish type II elimination of alkyl ketones (11), and in the intermolecular photoreduction of benzophenone by hydrogen-donating solvents (12). We therefore postulated that if there were available with comparable geometry a C-H bond weaker than the bonds to the distant ortho hydrogens, then the more weakly bound hydrogen should be abstracted preferentially. This would divert the arrangement from its usual course. We sought to study systems with the features of 3, where both the distant ortho hydrogen and the benzylic hydrogen are separated from the azoxy oxygen by four intervening atoms. Abstraction of the *ortho* hydrogen gives 4, the normal product, whereas abstraction of the

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benzylic hydrogen should lead to oxygen insertion at the benzylic site, *viz.* 5.

Azoxybenzenes with Benzylic Hydrogens: Synthesis

The compounds selected for study were 6-11, all of which were potentially able to undergo both normal and abnormal modes of rearrangement, and 12 and 13 in which the normal rearrangement pathway was blocked.



With the exception of the unsymmetrical 13, which was obtained by oxidation³ of the condensation product of nitrosobenzene and 2,6dimethylaniline, all the azoxy compounds were obtained by reduction of appropriate nitro compounds. Most of the nitro compounds were reduced using CH₃OH–NaOH (14), CH₃OH–Na (15), or by metallic thallium (16) giving the azoxy compound directly. For the tetramethyl compound 12, hitherto difficult to prepare (17), lithium aluminum hydride reduction to the azo compound was followed by peracid oxidation.⁴ An attempt to use this route to prepare 9 from o-nitrobenzaldehyde dimethylacetal failed because the metal hydride cleaved the acetal function, giving a variety of products including 2,2'-azotoluene but very little of the desired azo compound 16.



A major synthetic problem was the liberation of the azoxybenzaldehyde 11 from its acetals. Carefully controlled hydrolysis of 10 gave the best yield of 11, but even this was modest (25%); too-vigorous hydrolysis led to destruction of 11 and formation of colorless condensation products as noted previously (19). Very mild conditions gave incompletely hydrolyzed products identified as 2,2'-azoxybenzaldehyde 2dialkyl acetals; there is still some doubt as to whether these should be represented as 17 or 18, although we favor 17 slightly. No conclusions



could be drawn about the position of the azoxy oxygen by comparing the chemical shifts (recorded in the experimental section) of -CHO and $-CH(OCH_3)_2$ in 17 or 18 (R = CH₃) with those of model compounds 9, 11, 16, and 3hydroxy-2,2'-azobenzaldehyde bisdimethyl acetal (27). Mass spectrometry has been used to differentiate between the isomers of simple unsymmetrical azoxy compounds (20), since C-N cleavage occurs more abundantly on the side adjacent to the azoxy oxygen. Although our azoxybenzaldehyde derivatives undergo much more complex fragmentation than the compounds previously studied, the greater abundance of $[C_6H_4CHO]^+$ over $[C_6H_4CH(OR)_2]^+$ lends some support to structure 17 over 18. In addition, photolysis of small quantities of 17 $(R = CH_3 \text{ and } C_2H_5) \text{ did not give hydroxyazo}$

⁴Since completion of this work, the preparation of **12** by oxidation of 2,6-dimethylaniline with AgO has been reported (18).

³Oxidation of the 2,6-disubstituted azobenzene gives almost exclusively 2,6-dimethyl-*NNO*-azoxybenzene (13) because of steric hindrance (13).

compounds, nor indeed any tractable products; as shown below, this behavior is similar to that of 11, rather than of 9 and 10 which photorearrange normally. This also favors structure 17 rather than 18, since 17, like 11, has the CHO and N—O functions on adjacent carbon atoms.

Azoxybenzenes with Benzylic Hydrogens: Photolysis

In the first series of experiments, compounds 6-11 were irradiated in benzene solution using Pyrex equipment ($\lambda > 300$ nm). From compounds 6-10 no abnormal products of structure 5 were obtained; instead the expected 2-hydroxyazobenzene was the sole or major product. 2,2'-Azoxybenzaldehyde(11) behaved differently; it photolyzed more rapidly and gave a derivative of the abnormal rearrangement product but no hydroxyazo compound. The behavior of compounds 6-10 seems to be inconsistent with a rearrangement pathway initiated by hydrogen abstraction since the alternate C-H bonds available were in all cases weaker than an aromatic C-H bond. In contrast, typical free radical hydrogen abstractors are very unreactive towards aromatic hydrogens (21) but abstract readily from the appropriate positions of toluenes (21), cumenes (21), diphenylmethanes (21), acetals (22), and aldehydes (23). In the following paragraphs the results of the photolyses are examined in more detail.

Photolysis of the dimethyl compound 6 gave a different product mixture according to the conditions. Direct photolysis in dilute benzene solution gave the normal product 19; using a more concentrated solution, 19 was accompanied by a new photoproduct, a deep red



compound whose mass spectrum (M^+ 344) and n.m.r. spectrum indicated a structure with three tolyl rings, one of them hydroxyl substituted. An identical substance was obtained by the action of *o*-toluenediazonium chloride on **19**; since diazonium couplings invariably take place at a

free *para* position (24), this suggests **20** as the structure of the new compound.



An irradiation of 6 was carried out in the presence of benzophenone to determine whether oxygen migration into the side chain could be induced under conditions known (2) to favor hydrogen abstraction. Under these conditions the reaction was much slower but no insertion into the side chain was observed. Instead, the normal product 19 was accompanied by the isomer 21, previously obtained by Lewis and Reiss (25) as a by-product of the rearrangement of 6 in ethanol. Lewis and Reiss also obtained another isomeric photoproduct, 22, but we did not observe this in our reactions in benzene.



These abnormal products 20-22 look as though they might arise through the coupling of an o-toluenediazonium cation with an appropriate phenol. Lewis and Reiss (25) considered the possibility of fragmentation of 19 on photolysis giving the by-products by the mechanism of Scheme 3 but had to reject this proposal on the grounds that 19 is photostable, an observation which we confirm. In addition, photolysis of azobenzene in a mixture of benzene and phenol gives neither p-hydroxyazobenzene (from attack of a benzenediazonium radical or ion on phenol) nor biphenyl (from the action of a phenyl radical on benzene), indicating that C-N bond fission did not occur; indeed, the available evidence (26) suggests that aromatic azo compounds cleave at the N-N rather than the C-N bonds upon irradiation. We currently believe that diazonium ion intermediates are involved as intermediates in the formation of these side products 20-22 but that they are the result of fragmentation of a precursor of 19

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rather than of **19** itself. This work is still in progress and will be published elsewhere.

Azoxytoluene 6 has also been photolyzed in quartz equipment in the presence of benzophenone using 2-propanol as the solvent. Under these conditions photoreduction to 2,2'-azotoluene accompanied the photorearrangement, thereby demonstrating that hydrogen abstraction was occurring. Even so, no migration of oxygen into the side chain was observed, implying that hydrogen abstraction was wholly intermolecular (from the solvent).

It was thus concluded that oxygen migration to a side chain methyl group is less facile than insertion into the benzylic bond, despite the higher bond dissociation energy of the latter (27). This conclusion is confirmed by the results of photolysis of 12 and 13, where the normal rearrangement cannot occur. These compounds do not undergo benzylic insertion; instead they are very photostable, being slowly converted to tar but not to tractable products. A parallel observation has been made previously (25) regarding 14 which suffers no change in electronic spectrum on irradiation. We observed reaction only in 13, which underwent *cis-trans* photoisomerization.

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Photolysis of 7 proceeded normally, giving only the expected rearrangement product 23 and a compound believed to be the *cis* isomer of 7 because it reverted to 7 on work-up. A variety of low yield photoproducts was obtained on illumination of azoxydiphenylmethane 8; of these, three were isolated in quantities sufficient to permit a partial characterization. They are believed to be 24–26, the analogs of 19, 21, and 22 formed on irradiation of 6.

Irradiation of the acetals 9 and 10 gave the *o*-hydroxyazo compounds, 27 and 28 respectively, together with numerous other low yield products which were incompletely characterized. The products from 9, which we were unable to purify, had n.m.r. spectra with resonances typical of —CHO and $-CO_2CH_3$ groups as

well as OCH₃, OH, and aromatic C—H linkages, suggesting the possibility of photofragmentation of the acetal group (CHO) and oxygen insertion into the benzylic side chain (CO₂CH₃). In the presence of benzophenone, none of the usual product 27 could be obtained from 9, but compounds with CHO and CO₂CH₃ groups in their n.m.r. spectra were still observed.

2,2'-Azoxybenzaldehyde photolyzed faster than the other compounds but gave no *o*-hydroxyazo compound. Instead, there was obtained the lactone **29**, a known (19, 28) transformation product of 2'-formylphenylazo-2-benzoic acid (**30**), the expected result of oxygen migration into the benzaldehyde group. While **11** thus



undergoes the abnormal rather than the normal mode of oxygen migration on photolysis, the greater rapidity of reaction of 11 than of 6-10 and the structural similarity between 11 and *o*-nitrobenzaldehyde, which also photorearranges efficiently (8), suggests the possibility of a change of mechanism in this case.

From this series of experiments we may conclude that while oxygen migration to a benzylic site is possible, as in 11, or cannot be excluded, as in 9 and 10, it does not take place as readily as would be predicted on the basis of the hydrogen abstraction mechanism of Scheme 2. Direct competition between abstraction of an aromatic hydrogen and a more weakly bound benzylic hydrogen should have resulted in preferential abstraction at the benzylic site. Scheme 1 is thus more consistent with these observations than Scheme 2, although we must add this reservation: steric factors might make attainment of the transition state for benzylic abstraction less facile than that for aromatic C-H removal, causing the weak benzylic bonds

	Φ			
Solvent	Relative	Absolute	k2 ^e	$\Phi^{ extsf{H}}/\Phi^{ extsf{D}}$
95% ethanol	1.00 ^a	0.22	1.00ª	$1.26 \pm 0.07(6)$
100% ethanol	$0.875 \pm 0.03(8)^{b}$	0.19	0.84	$1.27 \pm 0.10(8)^{d}$
Methanol	$0.761 \pm 0.04(9)$	0.16	0.71	$0.98 \pm 0.05(4)$
Acetic acid	$0.998 \pm 0.08(7)$	0.22	0.99	
Acetonitrile	$0.509 \pm 0.03(7)$	0.11	0.45	_
10% aqueous acetonitrile	$0.764 \pm 0.02(7)$	0.17	0.72	
Benzene	$0.170 \pm 0.01(8)$	0.037	0.14	$1.25 \pm 0.15(6)$
Cyclohexane	$0.038 \pm 0.004(4)$	0.008	0.03	

TABLE 1.	Variation with solvent in the quantum yield and deuterium isotope effect for 2-hydroxyazobenzene
	formation on photolysis of azoxybenzene and its d_{10} analog

*Assumed; data are for appearance of 2-hydroxyazobenzene. *Number of determinations in parentheses; \pm values are statistical deviations (58). *Measured directly; other values calculated from relative Φ . *Data for disappearance of azoxybenzene were 1.37 \pm 0.15 (2). *Refers only to mechanism of Scheme 2; see text.

of 6–10 and of 12 to be immune towards attack. This kind of argument has been made by Gore and Wheeler (29), who have interpreted anomalies in the electronic spectra of 2,2'-disubstituted azoxybenzenes in terms of steric hindrance to coplanarity. On the other hand, Tanikaga (30) in his study of the normal azoxybenzene photorearrangement has presented evidence that steric factors are unimportant in his systems. To try to gain information about the possible influence of steric factors in the azoxybenzene photorearrangement, we carried out a number of experiments using azoxybenzene itself, where steric factors should be unimportant.

Solvent Effects

In the first series of these experiments, the rate of photorearrangement of azoxybenzene was compared in eight solvents of differing polarity. Relative and absolute quantum yields for 2-hydroxyazobenzene formation are given in Table 1. To try to interpret the results obtained, the following analysis was used. Schemes 1 and 2 may both be abbreviated as in eq. 1 in terms of an excited state of azoxybenzene A* and an intermediate I which yields product. Assuming

[1]
$$A_0 \xrightarrow{h_{\nu}} A^* \xrightarrow{k_2} I \xrightarrow{k_3} Product$$

steady states of A^* and I, the quantum yield Φ for product formation is given in eq. 2.

[2]
$$\Phi = k_2 k_3 / (k_3 + k_4) (k_1 + k_2)$$

This expression only simplifies significantly if $k_3 \gg k_4$ when

[2a]
$$\Phi \simeq k_2/(k_1 + k_2)$$
 or $k_2 = k_1 \Phi/(1 - \Phi)$

If the abstraction mechanism, Scheme 2, were to represent the reaction pathway, it could be shown that k_3 would indeed be greater than k_4 by the following argument. Since proton transfer reactions are very rapid, it is likely that intermediate B of Scheme 2 would have a long enough lifetime to exchange its proton with the medium; if it now returns to azoxybenzene, the hydrogen atoms of the medium should be incorporated into the starting material. Photolyses of azoxybenzene in CH₃CN-D₂O and of azoxybenzene- d_{10} in ethanol gave no incorporation of the alternate hydrogen isotope into the starting azoxy compound when the irradiations were carried out to partial conversion and the starting material recovered. Thus if Scheme 2 is the mechanism, $k_3 \gg k_4$, and the rates of the abstraction steps (k_2) are proportional to $\Phi/(1 - \Phi)$, assuming that the fluorescence lifetime of azoxybenzene $(1/k_1)$ is independent of solvent; this is probably true within the approximations of the above argument (31).

The relative quantum yields of Table 1 thus approximate to relative rate constants (k_2) as applied to Scheme 2. They cannot be applied to Scheme 1, since we have no knowledge of the relative magnitude of k_3 and k_4 if this mechanism is operating. However, the data of Table 1 make it unlikely that Scheme 2 is the proper mechanism, in that a factor of about 30 separates the quantum yields for cyclohexane and 95%ethanol. This is suggestive of a polar mechanism. Polar media may either increase the rate of formation of the intermediate, or they must promote the breakdown of the intermediate to product rather than to A_0 .

Deuterium Isotope Effect

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The hydrogen abstraction pathway of Scheme 2 ought to show a moderately large primary deuterium isotope effect for the rate-limiting removal of the strongly bound aromatic hydrogen. Relative quantum yields Φ^{H}/Φ^{D} for the rearrangement of azoxybenzene- d_0 and $-d_{10}$ were determined in four different solvents and are reported in Table 1; in each case the isotope effect was very small.

The problem in interpreting this isotope effect is that we may not in this case simply assume that the fluorescent lifetimes of the d_0 and d_{10} compounds will be equal, since the triplet excited state lifetimes of aromatic molecules are now well known to be increased by up to a power of 10 by perdeuteration (32). Several theories have been advanced to account for this effect (32), which is known to be due to changes in the rates of radiationless return to the ground state in the protio and deuterio molecules. One possibility (33) is a decrease in the Franck-Condon factor for the deuterio molecule, since T_1 has to overlap with a higher vibrational level of S_0 in the deuterio than in the protio molecule, due to C-D vibrational quanta being smaller than those of C-H. This reduces the probability of radiationless transition and increases the triplet lifetime. Similar considerations should apply to radiationless decay from singlet excited states but less is known about the magnitude of the effect for lack of experimental data. Ideally one would like to measure the fluorescence lifetimes of azoxybenzene- d_0 and $-d_{10}$ experimentally. An attempt to do this was made in collaboration with Dr. W. R. Ware and Mr. T. Nemzek of the University of Western Ontario, using the single photon counting technique, but unfortunately, azoxybenzene was found to be non-fluorescent, an upper limit on Φ_F being about 10^{-4} .

Studies on the aromatic hydrocarbons pyrene and coronene and their perdeuterated analogs have indicated that deuteration has very little effect on the fluorescence lifetimes of these molecules either at 77 °K or at room temperature (34). In private correspondence, Dr. J. L. Kropp of TRW Inc. has suggested that the change in lifetime would not normally exceed $\pm 20\%$ on deuteration. This may not be true of our system however, where almost 80\% of all excited singlet molecules are disappearing by non-radiative and non-photochemical processes.

To the extent that we can assume that there is no large deuterium isotope effect on the rate constants for radiationless processes, we believe that the observed small isotope effect is not the result of superimposing a large kinetic isotope effect upon a longer singlet lifetime in the d_{10} system. Taking the mean value from Table 1 of $\Phi^{\rm H}/\Phi^{\rm D} = 1.22$, a 20% spread in either direction gives us a likely range of $k^{\rm H}/k^{\rm D} = 0.98-1.46$, which is smaller than would have been expected for a primary effect for abstraction from the strong aryl C-H bond. For example, abstraction by oxygen from saturated sites in the type II reaction of analyli ketones displays $k^{\rm H}/k^{\rm D}$ = 4.8 (35), comparable with the isotope effects observed in wholly aliphatic ketones (36) and comparable also with hydrogen abstraction by oxygen in the t-butoxy radical (37). For the isotope effect exhibited in the azoxybenzene photorearrangement to be primary, the azoxy oxygen would have to be at least as reactive a hydrogen abstractor as the chlorine atom and far more so than typical oxyradicals (37). Taken together with the evidence already presented, this small isotope effect excludes Scheme 2 as a likely mechanism.⁵

Scheme 1 could accommodate the observed isotope effect in one of two ways: first, if the removal of hydrogen from the Badger and Buttery intermediate A rather than the formation of the intermediate is the slow step in the reaction; second, if the formation of the intermediate is the slow step but the isotope effect being observed is secondary rather than primary. This latter explanation seems less likely in that conversion of sp² centers to sp³ is usually accompanied by an inverse isotope effect $k^{\rm H} < k^{\rm D}$ (38), although both normal and inverse secondary deuterium isotope effects have been

⁵The small isotope effect cannot be the result of hydrogen abstraction being either non-rate-determining or reversible $(k_4 > k_3)$ from the lack of isotopic exchange in the experiments of the previous section.

observed in electrophilic aromatic substitution (39). At present, we cannot distinguish these possibilities.

Conclusions

Taken together, we believe that the experiments described constitute strong evidence against a hydrogen abstraction mechanism for the azoxybenzene photorearrangement. First, the benzylic C—H bonds of the 2,2'-disubstituted azoxybenzenes are unreactive despite the lower bond dissociation energies of benzylic vs. aryl C—H bonds. Second, the rate of reaction increases in polar solvents, suggestive of a polar rather than a radical pathway. Third, the deuterium isotope effect is far too small to be associated with a primary isotope effect for abstraction of the strongly bound aryl hydrogen.

In addition, a ${}^{1}\pi,\pi^{*}$ state is responsible for the azoxybenzene photorearrangement (2), whereas most photochemical hydrogen abstractions *e.g.* of ketones (40) or nitrocompounds (41) proceed from n,π^{*} states. Although exceptions are known (42, 43), this behavior is suggestive of a mechanism not involving hydrogen abstraction. Lastly, we have found that the photorearrangement of azoxybenzene in styrene solution does not cause polymerization of the styrene, indicating that free radical intermediates are not present.

On all these grounds, we believe that a mechanism involving aromatic substitution, as proposed by Badger and Buttery (3) better accommodates our experimental data than a hydrogen abstraction pathway. A remaining problem is whether the azoxy oxygen attacking the aromatic ring is electron rich, as originally proposed by Badger and Buttery, or electron poor, since the azo linkage is known (44) to be able to stabilize the charge of the intermediates for either nucleophilic or electrophilic substitution at the ortho and *para* positions. The literature is unhelpful on the effect of polar substituents on the rate of photorearrangement; Tanikaga (30) found that electron donating or withdrawing substituents at the 4,4'-positions of azoxybenzene alike reduced the efficiency of oxygen migration. We are currently investigating this aspect of the problem and hope to report our findings in a later paper.

Experimental

Irradiations were carried out in an immersion well apparatus, using a Hanovia Model 679A 450 W mercury

arc and a cooling well constructed of Pyrex glass to filter out short wave ($\lambda < 300$ nm) radiation. The outer jacket, which was equipped with a reflux condenser, had a volume of 300 ml with the cooling well in place and was constructed with a flat base to permit agitation of the solution by means of a magnetic stirrer. For irradiations carried out in the absence of oxygen, a similar outer vessel was used except that agitation was provided by means of a nitrogen flush through a porosity C sintered glass disc which was positioned near the base of the apparatus, an inlet tube for the nitrogen being sealed into the outer wall of the jacket. Relative rate and quantum yield experiments used the same source and cooling jacket, and were run in corked Pyrex ampoules in batches of eight using a Rayonet "Merry-go-round" apparatus.

Chromatographic separations on columns were run using standard alumina and silica gel adsorbents; preparative t.l.c. was run on 20×40 cm plates using a Brinkmann "sandwich" style apparatus or on 20 cm × 1 m plates using a Shandon preparative layer apparatus. The adsorbent was E. Merck Type 7747 silica gel PF254 incorporating a fluorescing agent to locate the bands; the developing solvent is indicated in parentheses in the individual procedures. Analytical t.l.c. plates were prepared using the same silica gel adsorbent and occasionally also using J. T. Baker Type 9F alumina. After separation of the reaction mixtures by preparative t.l.c., the bands were scraped off and extracted using a Soxhlet extractor for further purification. For identification of the 2hydroxyazo compounds, use was made of the characteristic (45) mass spectral fragmentation pattern of azo compounds (ArN=NAr' \rightarrow Ar⁺, ArN₂⁺, Ar'⁺, Ar'N₂⁺) and the well-known (46) low field n.m.r. resonance exhibited by a hydroxyl group situated ortho to an azo linkage. Microanalyses on purified samples were carried out either by Mr. H. S. McKinnon of this department or by Dr. C. Daesslé, Montreal.

Solvents were reagent grade materials and were dried and distilled before use. Petroleum ether, b.p. 30-60°, was fractionally distilled to remove high boiling residues. Melting points were run on a Mel-Temp apparatus and are uncorrected. Spectroscopic instruments used included a Pye Unicam SP800 u.v.-visible, Beckman IR5A i.r., Varian Associates A60-A n.m.r., and Varian MAT model CH7 mass spectrometer, which was operated at 70 eV ionizing voltage.

2,2'-Azoxytoluene (6)

2-Nitrotoluene (British Drug Houses, 0.5 mol) was added over a period of 40 min to a mixture of sodium hydroxide (1 mol) and methanol (100 ml) at reflux. The mixture was heated to reflux for 1 h, cooled, and poured into water (250 ml). The solids were collected by suction, dissolved in benzene, and passed through a 2.5×16 cm column of alumina, using benzene as the eluent. Recrystallization from methanol of the material obtained gave 2,2'-azoxytoluene (18 g, 32%): m.p. $57.5-58^{\circ}$ (lit. (47) 59°); n.m.r. (CCl₄) δ 2.28, 2.42 (2 singlets, 2 CH₃ groups), 7.0–8.1 (multiplet, 8 ArH).

Irradiation of 6

(a) A solution of 6 (0.149 g) in benzene (300 ml) was irradiated for 35 min. Evaporation of the solvent and resolution of the residue by preparative t.l.c. (40%) benzene in petroleum ether) gave 0.031 g of red solid:

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m.p. 70-80°; m.p. after recrystallization from ethanol a 92-93.5° (lit. (25) for 2-hydroxy-6,2'-dimethylazobenzene F 97°); n.m.r. (CDCl₃) δ 2.7 and 2.8 (2 singlets, 2 CH₃ n groups), 6.8-8.2 (multiplet, 7 ArH), 14.0 (singlet, OH).

(b) A solution of 6 (0.20 g) in benzene (200 ml) was irradiated for 30 min. Evaporation of the solvent and resolution by preparative t.l.c. gave two bands. The more mobile band (97 mg) was 19, red needles from methanol: m.p. 95–96°; u.v. (EtOH) λ_{max} 395 (sh) (ε 10 000), 335 (21 000), and 240 nm (8500).

Anal. Calcd. for C14H14N2O: N, 12.4. Found: N, 12.4.

The less mobile band (12 mg), a dark brown solid, m.p. 167–169°, was identified as 3-methyl-2,4-bis(otolylazo)phenol (20), having i.r., n.m.r., and mass spectra identical to authentic 20, prepared in 48% yield by the action of excess o-toluenedizaonium chloride on 19 (0.04 g). Data obtained for authentic sample of 20: m.p. 168–171°; n.m.r. (CDCl₃) & 2.61, 2.70, 3.12 (3 singlets, 3 CH₃ groups), 6.6–8.0 (multiplet, 10 ArH), 14.65 (singlet, OH); u.v. (EtOH) λ_{max} 420 (sh) (ϵ 5900), 350 (32 000), and 235 nm (11 000); mass spectrum M⁺ 344, other prominent peaks at *m/e* 243, 215, 119, 91.

Anal. Calcd. for $C_{21}H_{20}N_4O$: N, 16.3. Found: N, 16.7.

(c) Sensitized irradiation: a solution 6 (0.998 g) and benzophenone (4.3 g) in benzene (260 ml) was degassed under reflux using oxygen-free nitrogen,⁶ then irradiated for 35 min under nitrogen. The solvent was removed, the residue taken up in ethanol, and a solution of 2,4dinitrophenylhydrazine (4.7 g) in $H_2SO_4-H_2O$ -EtOH was added. Filtration of the cooled solution afforded benzophenone 2,4-dinitrophenylhydrazone (9.0 g), m.p. 229-230° (lit. (48) 231°). Neutralization of the excess acid, drying, and evaporation afforded a residue which was resolved by preparative t.l.c. (20% benzene in petroleum ether) to give four bands.

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Band 1 (13 mg) would not crystallize and was discarded. Band 2 (87 mg), a mixture, was red crystals, m.p. 100-102°, and was further resolved by preparative t.l.c. (petroleum ether) to give two major bands, 2A and 2B. Band 2A (21 mg) had m.p. 86-88°, and on recrystallization from ethanol was identified as 19: m.p. 94.5-95°; n.m.r. (CCl₄) δ 2.66 and 2.70 (2 singlets, 2 CH₃ groups), 6.7-8.0 (multiplet, 7 ArH), 13.5 (singlet, OH); mass spectrum *m/e* (relative intensity) 226 (M⁺) (37), 135 (24), 107 (69), 91 (100). Band 2B (30 mg) was obtained as fine orange needles from ethanol: m.p. 123-124° (lit. (25) for 2-hydroxy-4,2'-dimethylazobenzene (21), 126°); n.m.r. (CCl₄) & 2.36 and 2.60 (2 singlets, 2 CH₃ groups), 6.7-8.0 (multiplet, 7 ArH), 11.1 (singlet, OH); mass spectrum m/e (relative intensity) 226 (M⁺) (47), 135 (31), 107 (100), 91 (91).

Band 3 (10 mg) was a brown semi-solid. Recrystallization from ethanol gave 1 mg, m.p. $184-185^{\circ}$. This compound is possibly 20; the mass spectrum showed a probable molecular ion near m/e 340.

Band 4 (538 mg) was an orange solid, m.p. 39-43°,

and had the n.m.r. spectrum of the starting material. Recrystallization from ethanol gave recovered 6, 480 mg, m.p. $56-57.5^{\circ}$.

(d) Sensitized irradiation using an unfiltered mercury arc: a solution of 6 (0.50 g), and benzophenone (1.0 g) in 2-propanol (300 ml) was degassed and irradiated for 20 min. Resolution of the evaporated reaction mixture by t.l.c. gave 2,2'-azotoluene (107 mg), m.p. $52-54^{\circ}$ (lit. (49) 55°); M⁺ 210, azoxytoluene (30 mg, estimated by u.v., λ_{max} 312 nm, ε 11 000); and the hydroxyazo compound 19 (34 mg, estimated by u.v.).

Photolysis of 19

A solution of **19** (26 mg) in benzene (2.0 ml) was irradiated for 6 h in a 5 ml Pyrex flask equipped with reflux condenser, using an external source. Analytical t.l.c. 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 **19** (22 mg), m.p. $94-96^{\circ}$.

Irradiation of Azobenzene

(a) A solution of azobenzene (0.75 g) in benzene (200 ml) was irradiated for 13 h. Evaporation of the solvent and chromatography on alumina (60 g), eluting with benzene, gave *trans*-azobenzene (0.53 g), m.p. $67-68^{\circ}$ and *cis*-azobenzene (0.14 g), which changed to *trans* by heating in benzene. No biphenyl could be detected (t.l.c., v.p.c.).

(b) A mixture of azobenzene (0.1 g), phenol (2.0 g), and benzene (200 ml) was irradiated for 3 h. After evaporation of the solvent, neutral and acidic extracts were made. The neutral extract contained *cis*- and *trans*azobenzene (0.09 g) but not biphenyl (t.l.c. analysis, alumina plates), and the colorless acidic material contained only phenol (1.95 g).

2,2',6,6'-Tetramethylazoxybenzene (12)

To a solution of lithium aluminum hydride (5.0 g) in dry ether (500 ml) was added in small portions a solution of 2,6-dimethylnitrobenzene (Eastman Kodak, 20 g) in ether (30 ml) and the mixture was heated to reflux for 17 h. After quenching the excess lithium aluminum hydride with ethyl acetate, the organic phase was washed with 2 *M* sulfuric acid, dried, and evaporated. The residue was chromatographed on silica gel (120 g) when 5% benzene in petroleum ether (b.p. 60-80°) eluted 2,2',6,6'tetramethylazobenzene (2.0 g), m.p. 46-47° (lit. (50) 47°). Later fractions gave recovered starting material (3.1 g).

The azocompound (1.65 g) was oxidized with 30% H₂O₂ (10 ml) in acetic acid (100 ml) at 60° affording 2,2',6,6'-tetramethylazoxybenzene in quantitative yield. After recrystallization from methanol, the product was yellow rods, m.p. 89.5-90° (lit. (17) 91°).

Anal. Calcd. for $C_{16}H_{18}N_2O$: C, 75.5; H, 7.1; N, 11.0. Found: C, 75.8; H, 6.8; N, 11.2.

Irradiation of 12

A solution of 12 (0.495 g) in benzene was irradiated for 5 h. Evaporation of the solvent and preparative t.l.c. (20% benzene in petroleum) gave the starting material (0.386 g), m.p. $90-91^{\circ}$, as the only isolable material. An irradiation in the presence of benzophenone gave similar results.

⁶Prepared by passing commercial high purity nitrogen through a chromous chloride solution (made from $HgCl_2$ (15 g), zinc dust (5 g), and $CrCl_3$ (5 g) in 200 ml water), then dried by passage through concentrated H_2SO_4 and a tower of granular CaCl₂, and finally saturated with benzene to minimize loss of the solvent.

2,6-Dimethyl-NNO-azoxybenzene (13)

To a solution of nitrosobenzene (1.6 g), prepared by the method of Vogel (51), in ethanol (15 ml), was added a solution of 2,6-dimethylaniline (3.0 ml) in acetic acid (5 ml). The mixture was heated to 80° for 15 min, cooled, washed with base, taken up into ether, dried, and evaporated. The residue was chromatographed on silica gel (60 g) when 30% benzene in petroleum ether, b.p. $60-80^{\circ}$, eluted 2,6-dimethylazobenzene (1.07 g) as a red oil (52), pure by t.l.c.

Anal. Calcd. for C₁₄H₁₄N₂: N, 13.3. Found: N, 13.5.

Oxidation of the azo compound (1.03 g) using 30% H₂O₂ (2.0 ml) in acetic acid (15 ml) at 60° for 6 h gave 2,6-dimethyl-*NNO*-azoxybenzene (1.09 g) as a pale yellow oil.

Anal. Calcd. for $C_{14}H_{14}N_2O$: N, 12.6. Found: N, 12.5.

N.m.r. (CCl₄) δ 2.07, 2.27 (2 singlets, ratio 78:22, CH₃ groups), 6.8-8.5 (multiplet, 8 ArH).

Irradiation of 13

A solution of 13 (107 mg) in benzene (75 ml) was irradiated with an external source for 1 h. Evaporation of the solvent and chromatography of the residue on alumina (50 g), eluting with benzene, gave the starting material (98 mg); the n.m.r. spectrum was unchanged from that of the starting material except that the ratio of the two CH₃ resonances was now 91:9.

2,2'-Azoxycumene (7)

2-Nitrocumene (K and K) was found by n.m.r. to be a mixture of approximately 70% ortho, 25% para, and 5% meta isomers. Resolution was effected on 1.5 g samples using alumina columns (350 g), eluting with benzenepetroleum (15:80), when the first fractions to elute were pure by t.l.c. From two such resolutions a total of 1.65 g of material was obtained⁷, n_D^{20} 1.5200 (lit. (53) for onitrocumene 1.5248; for m- 1.5303; for p- 1.5369). This material was reduced at reflux for 2 h using thallium⁸ (6.1 g) and ethanol (55 ml) (16). After the addition of potassium iodide (6 g) the mixture was stirred for 1 h, filtered and evaporated. The residue, dissolved in benzene, was chromatographed over alumina (30 g) when benzenepetroleum (4:6) eluted the azoxy compound (0.63 g, 44%), an oil which was purified by crystallization from ethanol at -80° and dried in vacuo for several hours. N.m.r. (CCl₄) δ 1.22, 1.29 (two doublets, J = 7 Hz, 12H, CH₃), 3.35, 3.45 (two superimposed septets, J = 7 Hz, 2 CH), 7.10-8.30 (multiplet, 8 ArH); mass spectrum (relative intensity) m/e 282 (M⁺) (<1), and prominent ions at m/e 266, 250, 240, 149, 133, 131, 121, 119, 118, 116, 107, 106, 105, 104, 103, 91 (100).

Anal. Calcd. for $C_{18}H_{22}N_2O$: C, 76.55; H, 7.86; N, 9.93. Found: C, 76.43; H, 7.59; N, 10.11.

Irradiation of 7

A solution of 7 (0.630 g) in benzene (300 ml) was irradiated under nitrogen for 1 h, during which time the starting material completely reacted (t.l.c.) and was

replaced by two major components. Evaporation of solvent and resolution by preparative t.l.c. (20% benzene in petroleum) gave four bands. The most mobile, band 1 (123 mg), a red oil, was a mixture containing one major component, which was isolated pure by running a second preparative plate. Subsequent precipitation from methanol at -80° followed by drying *in vacuo* gave 2-hydroxy-6,2'-diisopropylazobenzene, **23** (60 mg): n.m.r. (CCl₄) δ 1.25, 1.35 (two doublets, J = 7 Hz, 2 CH), 6.75–7.90 (multiplet, 7 ArH), 12.70 (singlet 1H, OH); u.v. (ethanol) λ_{max} 337 (ϵ 18 500), 248 (8200), and 243 nm (8000); mass spectrum *m/e* (relative intensity) 282 (M⁺) (61), 267 (94), 135 (39), 133 (100), 132 (55), 91 (84).

Anal. Calcd. for C₁₈H₂₂N₂O: C, 76.55; H, 7.86; N, 9.93. Found: C, 77.21; H, 7.53; N, 10.10.

Band 2 from the t.l.c. resolution (16 mg) was a mixture and could not be resolved further. Band 3 (290 mg) on isolation had the n.m.r. and R_r of the starting material and was presumed to be the *cis* isomer of 7 which on work-up reverted to starting material; band 4 (32 mg) was shown by t.l.c. to be a mixture of at least four compounds and was discarded.

2,2'-Dibenzylazoxybenzene (8)

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2-Nitrodiphenylmethane was prepared from o-nitrobenzyl chloride (Aldrich) and benzene-AlCl₃ by the method of Geigy and Königs (54). The procedure was modified in that the crude product was partly purified by passage through a 30 g column of alumina before steam distillation. From 6.5 g of benzyl chloride was obtained 6.5 g of partly purified material, 3 g of which was steam distilled to give 1.7 g of 2-nitrodiphenylmethane (pure by t.l.c.). Thallium reduction (16) of this material overnight and the usual work-up gave an oil; this crystallized on standing and was further purified by preparative t.l.c. (benzene-petroleum, 1:1) affording the product (0.60 g), which crystallized from ethanol, 0.48 g: m.p. 53-56°; mass spectrum m/e 378 (M⁺), see Table 2; n.m.r. (CCl₄) & 3.99, 4.17 (singlets, two CH₂ groups), 7.0-8.2 (multiplet 18 ArH).

Anal. Calcd. for $C_{26}H_{22}N_2O$: C, 82.50; H, 5.86; N, 7.41. Found: C, 82.56; H, 6.16; N, 7.65.

Irradiation of 8

A solution of 8 (0.45 g) in benzene (300 ml) was irradiated for 2 h, after which the solvent was evaporated and the residue resolved by preparative t.l.c. (benzenepetroleum, 1:1). Three major bands were obtained. The most mobile band comprised 50 mg red solid, m.p. 95-105°, not improved by repeated recrystallization from ethanol, and was found to be a mixture by t.l.c. on alumina. Chromatography of band 1 on alumina (20 g), eluting with petroleum containing increasing amounts of benzene (up to 25% v/v), gave three fractions. The most mobile, band 1A (2 mg), red crystals, had m.p. 168-170°; band 1B, red crystals (2 mg), had m.p. 102-105°; band 1C, red crystals (8 mg), had m.p. 130-131°, softened at 121°. The mass spectra of these three compounds, recorded in Table 2, showed that they were all isomers of 8, consistent with structures 24-26. Too little material was obtained to run n.m.r. spectra, but using the reported (25) method, it was shown that 1C was compound 26 by u.v., since it alone had a pronounced red shift when the spectrum was run in the presence of 10^{-2} M potassium

⁷The purified *o*-nitrocumene discolored rapidly upon exposure to air, so it and the subsequent cumyl derivatives were handled and stored under nitrogen.

⁸Molten commercial thallium (British Drug Houses) was poured into water and washed with ethanol.

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TABLE 2.Mass spectral fragmentation patterns of
compounds 8, 24, 25, and 26

		Relative	abundance of i	on
m/e	8	Band 1A	Band 1B	Band 1C (26)
379	31	30	19	29
378(M+)	100	93	61	100
377	25	47	23	17
363	4	_	_	
362	5	4		-
302	24	18	24	20
301	100	100	100	84
287	10	13	14	4
223	3	9	_	_
211	13	_	_	8
199	4	_	9	5
196	8	11	14	
195	7	_		
183	28	10	34	27
182	19	19	24	13
181	19	10	10	15
180	46	25	7	35
168	11	4	11	9
167	41	12	21	28
166	20	11	16	16
165	59	37	49	43
155	6	_	_	_
154	5	-	—	
153	16		13	13
152	31	6	22	24
151	5	14	7	4
150	9	3	8	7

hydroxide (see Table 3). Hence 1A and 1B were 24 and 25, though not necessarily respectively. Attempts to find free (compound 26) and chelated (24 and 25) hydroxyl stretching frequencies in the i.r. were unsuccessful due to lack of material, though there was some indication of a free hydroxyl group in 1C (v_{max} (CS₂) 3550 cm⁻¹).

Band 2 from the preparative t.l.c. plate was starting material (200 mg), while band 3 (red oil 80 mg) was a mixture by t.l.c. Attempts to obtain pure materials from this fraction were unsuccessful.

2-Nitrobenzaldehyde Dimethyl Acetal (34)

2-Nitrobenzaldehyde (Aldrich, 0.1 mol) was dissolved in a mixture of methanol (100 ml) and concentrated hydrochloric acid (1.5 ml). After 17 h at room temperature, the solution was basified with sodium methoxide, evaporated down, and water added. Extraction with ether, followed by evaporation of the organic phase gave the acetal (94%) as a colorless or yellow oil: n.m.r. (neat liquid) δ 3.33 (singlet, 6H, OCH₃), 5.95 (singlet, 1 CH), 7.31-7.95 (multiplet, 4 ArH).

2,2'-Azoxybenzaldehyde Bisdimethyl Acetal (9)

The acetal 34 was reduced by the method of Bamberger (15) using sodium and methanol. The crude azoxy compound was recrystallized from ethanol giving 9 (65%), m.p. $52-56^{\circ}$ (lit. (15) 59°). When the reaction time was prolonged in order to improve the conversion, further reduction occurred. Fractional crystallization

gave 9 (20%), together with 2,2'-azobenzaldehyde bisdimethylacetal (16) (13%): m.p. 142–143° (lit. (55) 144°); n.m.r. (CCl₄) δ 3.25 (singlet, 12H, OCH₃), 6.27 (singlet, 2CH), 7.25–7.85 (multiplet, 8 ArH).

Anal. Calcd. for C₁₈H₂₂N₂O₄: C, 65.43; H, 6.71; N, 8.48. Found: C, 65.48; H, 6.90; N, 8.44.

An attempt to prepare 9 by lithium aluminum hydride reduction of 34 to 16 followed by oxidation was unsuccessful. A reaction using 34 (0.06 mol) gave a crude reduction product (6.9 g) which was partly resolved by chromatography on silica gel. The least polar material, a red solid (0.25 g), eluted with 20% benzene in petroleum, n.m.r. (CCl₄) § 2.16 (singlet), 7.2 (multiplet), area ratio 3:4. Oxidation with hydrogen peroxide in acetic acid gave a pale solid (0.24 g), m.p. 56-57.5°, undepressed by admixture with authentic 2,2'azoxytoluene (6), and with an identical n.m.r. Intermediate fractions from the column were red and had n.m.r. resonances characteristic of CHO, aromatic, OCH₃, and CH₃ protons, but were all mixtures. These were followed by unreacted 34 (2.5 g). The last fraction, removed from the column with methanol crystallized from methanol as orange plates (0.10 g), m.p. 139-141° with n.m.r. identical to 16 described above. Anal. for C18H22N2O4: Found: C, 65.42; H, 6.64;

Anal. for $C_{18}H_{22}N_2O_4$: Found: C, 65.42; H, 6.64; N, 8.50.

Mass spectrum m/e 330 (M⁺ absent), prominent peaks at m/e 282, 268, 267, 251, 237, 236, 235, 221, 194, 159, 130.

The best route to 9 was thallium reduction of 34.

	Neutral solution		10 ⁻² <i>M</i> KOH	
Compound	λ_{max} (nm)	log ε	λ _{max} (nm)	log ε
Band 1A	340	4.22	338	4.12
	243	3.80	243	3.84
	237	3.76	236	3.80
Band 1B	342	4.33	338	4.21
	245	3.84	246	3.89
	240	3.84	240	3.89
Band 1C (26)	376 sh	4.19	441	4.01
	334	4.31	325	4.11
	245	3.99	242	4.05
	240	3.93		

TABLE 3. Ultraviolet absorptions in ethanol of the products of irradiation of 8

After the usual work-up, **9** was obtained as orange crystals from ethanol (64%): m.p. 54-56° (lit. (15) 59°); n.m.r. (CCl₄) δ 3.22, 3.24 (two singlets, 12H, OCH₃), 5.60, 5.90 (two singlets, 2 CH), 7.08-7.84 (multiplet, 8 ArH); u.v. (ethanol) λ_{max} 232 (log ϵ 4.0) and 307 nm (3.9).

Anal. Calcd. for $C_{18}H_{22}N_2O_5$: C, 62.41; H, 6.40; N, 8.09. Found: C, 62.79; H, 6.52; N, 8.07.

Irradiation of 9

A solution of 9 (1.00 g) in benzene (300 ml) was irradiated for 8 h. After removal of solvent, the residue was resolved by preparative t.l.c. (chloroform) to give three bands.

The most mobile band, band 1, was orange (439 mg), m.p. $82-84^{\circ}$ after several recrystallizations from ethanol, and was identified as 3-hydroxy-2,2'-azobenzaldehyde bisdimethylacetal (27): n.m.r. (CCl₄) δ 3.50, 3.52 (two singlets, 12H, OCH₃), 6.07, 6.48 (two singlets, 2 CH), 7.00-8.14 (multiplet, 7 ArH), 12.76 (singlet, OH).

Anal. Calcd. for C₁₈H₂₂N₂O₅: C, 62.48; H, 6.39; N, 8.07. Found: C, 62.65; H, 6.48; N, 8.08.

Bands 2 and 3 were incompletely resolved and were further separated by t.l.c. Band 2 (54 mg) was starting material. Band 3 (34 mg) was an oil: n.m.r. (CCl₄) δ 3.30, 3.40, 3.50 (singlets OCH₃?), 3.80, 3.87 (singlets, COOCH₃?), 5.57, 5.62, 5.74, 6.23 (singlets CH), 6.7–7.7 (multiplet ArH). This substance was a mixture and could not be resolved further.

A second irradiation gave, in addition to 27, various other poorly resolved and incompletely characterized materials whose n.m.r. spectra showed resonances

typical of aromatic, --CHO,
$$-CHO$$
, -COOCH₃,

 $-OCH_3$ and hydrogen bonded -OH groups. When the irradiation was carried out under nitrogen and in the presence of benzophenone, three products were obtained, but none could be obtained pure. Their n.m.r. spectra all showed the presence of -CHO protons, but low field resonances characteristic of hydrogen-bonded OH groups were absent.

2,2'-Azoxybenzaldehyde Bisdiethyl Acetal (10)

2-Nitrobenzaldehyde was converted to its diethylacetal in 91% yield: n.m.r. (neat) δ 1.10 (triplet, J = 7 Hz, 6H,

CH₃), 3.50 (quartet, J = 7 Hz, 4H, CH₂), 5.84 (singlet, 1 CH), 7.16-7.74 (multiplet, 4 ArH). Thallium reduction (16) of the acetal gave the azoxycompound 10 (42%), m.p. 70-72°. A better yield was obtained by reduction of the acetal with sodium and methanol (15); after recrystallization of the crude product from ethanol the yield of 10 was 65%: m.p. 73-75° (lit. (15) 76°); n.m.r. (CCl₄) δ 1.13 (triplet, J = 7 Hz, 12 H, CH₃), 3.4 (two close quartets, J = 7 Hz, 8H, CH₂), 5.90, 6.17 (two singlets, CH), 7.2-8.0 (multiplet, 8 ArH). The mass spectrum showed a very small M⁺ (m/e 402), first major peak m/e 384.

Anal. Calcd. for $C_{22}H_{30}N_2O_5$: C, 65.65, H, 7.51; N, 6.96. Found: C, 65.81; H, 7.57; N, 6.92.

Irradiation of 10

A solution of 10 (1.00 g) in benzene (300 ml) was irradiated for 1 h. Evaporation of solvent and resolution of the residue by t.l.c. (chloroform) gave four bands. Band 1 (131 mg) was a mixture: n.m.r. (CCl₄) δ 1.20 (two triplets, area 103, CH₃), 3.6 (two quartets, area 63, CH₂), 5.86, 6.00, 6.15, 6.43 (singlets areas 5:3:5:2, CH), 7.15–8.06 (multiplet, area 59, ArH), 12.36, 12.74 (two singlets, areas 1:4, OH). Recrystallization from petroleum ether, b.p. 30–60°, then from ethanol gave the major component; m.p. 85–86°; mass spectrum *m/e* (relative intensity) 402 (M⁺ absent), 356 (2), 328 (20), 327 (100), 312 (20), 311 (31), 284, (47), 253 (80), 237 (71), 151 (31), 120 (7).

Anal. Calcd. for **28**, $C_{22}H_{30}N_2O_5$: C, 65.65; H, 7.51; N, 6.96. Found: C, 65.38; H, 7.83; N, 6.98.

Band 2 from the t.l.c. plate (646 mg) was starting material, m.p. 72.5–74°, after crystallization from petroleum. Band 3 (156 mg), an oil, appeared to be the *cis* isomer of the starting material, since on recrystallization it was converted to 10, m.p. 71–73°. Band 4, a red oil (32 mg), was unidentified; its n.m.r. spectrum was similar to that of 10 and had no low field resonances typical of hydrogen-bonded OH protons.

2,2'-Azoxybenzaldehyde Bisethylene Acetal (15)

2-Nitrobenzaldehyde was converted to its ethyleneacetal (90%), n.m.r. (neat): δ 3.90 (singlet, 4H, CH₂), 6.47 (singlet, 1 CH), 7.3-8.0 (multiplet, 4 ArH). The acetal was reduced by the thallium and ethanol method

(16) to give the azoxy compound **15** as yellow needles from ethanol (66%): m.p. 103.5–104.5°; n.m.r. (CDCl₃) δ 3.95 (close multiplet, 8H, CH₂), 6.30, 6.48 (two singlets 2H, CH), 7.24–8.30 (multiplet, 8 ArH). The mass spectrum showed M⁺ (*m*/*e* 342) and other prominent ions at *m*/*e* 296, 253, 234, 192, 177, 163.

Anal. Calcd. for $C_{18}H_{18}N_2O_5$: C, 63.13; H, 5.30; N, 8.19. Found: C, 62.61; H, 5.37; N, 8.00.

2'-Formylphenyl-ONN-2-azoxybenzaldehyde Dimethyl Acetal (17), $R = CH_3$

The bisdimethylacetal 9 (1.95 g) was dissolved in warm methanol (50 ml), then water (20 ml) and concentrated hydrochloric acid (1 ml) were added with stirring. After 2 min, the solution was diluted with water (50 ml) and extracted with chloroform. The organic phase was washed (NaHCO₃), dried (MgSO₄), and evaporated, and the residue recrystallized from ethanol to give the compound (0.52 g) as tan crystals: m.p. 59–60°; n.m.r. (CDCl₃) δ 3.30 (singlet, 6H, OCH₃), 5.95 (singlet, 1 CH), 7.26–8.10 (multiplet, 8 ArH), 10.44 (singlet, 1 CHO); u.v. (EtOH); λ_{max} 308, 248, and 214 nm (ε undetermined but smaller for the 308 nm band); mass spectrum *m/e* (relative intensity) 300 (M⁺ absent), 246 (26), 233 (52), 220 (38), 193 (28), 180 (100), 151 (6), 150 (12), 149 (44), 119 (32), 105 (48), 91 (72), 77 (86).

Anal. Calcd. for $C_{16}H_{16}N_2O_4$: C, 63.99; H, 5.37; N, 9.33. Found: C, 64.00; H, 5.45; N, 9.23.

From a 1 h irradiation of this substance (0.255 g) in benzene, only starting material (94 mg) could be recovered.

2'-Formylphenyl-ONN-2-azoxybenzaldehyde Diethyl Acetal (17), $R = C_2 H_5$

To a solution of **10** (1.0 g) in glacial acetic acid (3 ml) and acetonitrile (2 ml) cooled in an ice-bath was added water (0.75 ml) and 0.2 *M* hydrochloric acid (0.7 ml). After 2 min, water (10 ml) was added dropwise. Extraction into chloroform and treatment of the organic phase as above gave an oil (0.61 g) which was purified by preparative t.l.c. (benzene) to give the azoxy compound as a yellow oil (0.54 g) which crystallized at -80° from petroleum: m.p. 37-38.5°; n.m.r. (CCl₄) δ 1.12 (triplet, J = 7 Hz, 6H, CH₃), 3.53 (quartet, J = 7 Hz, 4H, CH₂), 6.13 (singlet, 1 CH), 7.17-8.23 (multiplet, 8 ArH), 10.48 (singlet, 1 CHO); mass spectrum *m/e* 328 (M⁺ absent), major peaks at *m/e* 311, 237, 211, 208, 134, 105. Only very minor peaks were present at *m/e* 179, 180.

Anal. Calcd. for $C_{18}H_{20}N_2O_4$: C, 65.84; H, 6.14; N, 8.53. Found: C, 65.66; H, 6.13; N, 8.65.

2,2'-Azoxybenzaldehyde (11)

After several unsuccessful attempts to hydrolyze the acetals 9, 10, and 15, the most successful procedure was the following modification of Bamberger's method (19).

The bisdiethylacetal **10** (2.0 g) was dissolved in glacial acetic acid (7 ml) with the minimum amount of heating. The yellow solution was cooled in ice, and water (1.5 ml) and 2 *M* hydrochloric acid (1.4 ml) were added. A white emulsion formed; this clarified on shaking, and after < 30 s, the solution began to turn brown. After a further 2.5 min, water (9 ml) was added dropwise with shaking (a white precipitate formed after 6 ml had been added), and the mixture was kept at 0° for 15 min more before suction filtration. The crude solid was taken into chloroform, washed (NaHCO₃), dried (MgSO₄), and the solution by

t.l.c. (chloroform). The one major band afforded 1.8 g of crude solid, yellow needles (0.31 g) from ethanol⁹: m.p. 113–114° (lit. (19) 118°); n.m.r. (CDCl₃) δ 6.97–8.33 (multiplet, 8 ArH), 10.45 (singlet, 2 CHO); mass spectrum M⁺ (*m/e* 254).

Anal. Calcd. for C₁₄H₁₀N₂O₃: C, 66.13; H, 3.96; N, 11.02. Found: C, 65.30; H, 3.92; N, 10.88.

The poor analysis is probably because 11 decomposes to a considerable extent in a few days at the ambient temperature.

Irradiation of 11

(a) In benzene: a solution of **11** (0.769 g) in benzene (300 ml) was irradiated for 20 min by which time a yellow solid was present. The solvent was removed and the residue (including the yellow substance) was resolved by preparative t.l.c. (chloroform) to give two major bands, neither of them red. Band 1 (225 mg) crystallized from ethanol as tan needles, m.p. 109–110°, and had the same n.m.r. spectrum as **11**. Band 2 (26 mg) was **29**, colorless crystals from chloroform-ether: m.p. 288–290° (lit (19) 294°); i.r. (CHCl₃) v_{max} 1690 cm⁻¹; mass spectrum *m*/*e* (relative intensity) 236 (M⁺) (100), 208 (38), 179 (33), 76 (37).

(b) In isopropanol: a solution of 11 (0.296 g) in isopropanol (300 ml) was irradiated for 1 h. Evaporation and t.l.c. resolution as above gave two colorless bands. Band 1 (6 mg) was unidentified; band 2 (36 mg) was starting material, tan needles from ethanol, m.p. $105-110^\circ$.

Quantum Yield Determinations

Azoxybenzene, m.p. 35-36°, was prepared by the method of Lachman (14): u.v. (ethanol) λ_{max} 231 (ϵ 9560), 267 (7990), and 323 nm (15 800), ε < 140. Irradiation in benzene and resolution by preparative t.l.c. (benzene-petroleum, 1:1) gave 2-hydroxyazobenzene, red needles from ethanol: m.p. 79-80° (lit. (56) 81°); u.v. (ethanol) λ_{max} 244 (ϵ 8110), 325 (16 800), 375 nm (8250), $\varepsilon_{410} = 4480$. For the quantum yield measurements, solutions of azoxybenzene in 95% ethanol and of the modified ferrioxalate actinometer described by Kurien (57) were irradiated simultaneously using a Rayonet 'Merry-go-round". A filter solution (5 cm) of NiSO4. $6H_2O$ (90 g/l) and $CoSO_4 \cdot 7H_2O$ (48 g/l) was used to restrict the absorption of light to the region 300-330 nm where both azoxybenzene and the actinometer absorb strongly. Samples were withdrawn during the irradiation and analyzed by u.v. (Bausch and Lomb, Spectronic 70); ferrous phenanthroline formation was monitored at 510 nm (ɛ 11 000) and 2-hydroxyazobenzene formation at 410 nm. Knowing the quantum yield (1.10) for ferrous ion formation in the actionometer, the ratio of the initial slopes of the plots of ferrous phenanthroline and 2-hydroxyazobenzene formation with time gave the quantum yield for 2-hydroxyazobenzene formation as 0.217 ± 0.015 (11 runs).¹⁰ Deviations were calculated by the usual method (58).

⁹It is important not to heat solutions of **11** any more than necessary, or decomposition results.

¹⁰NOTE ADDED IN PROOF: The quantum yield for this reaction has been determined (61) as ~ 0.008 in 95% ethanol. At present, we see no cause for discrepancy between our results and theirs. We wish to thank Dr. Jaffé for sending us a copy of his paper before publication.

Solvent Effect on Photoreactivity of Azoxybenzene

Solutions (about 7×10^{-5} M) of azoxybenzene in various solvents were irradiated simultaneously using the "Merry-go-round". Aliquots of the reaction mixture were withdrawn at intervals, and the formation of 2-hydroxy-azobenzene was followed by monitoring the absorbance at 410 nm. First-order rate constants were evaluated by plotting log $(A_{\infty} - A_0)/(A_0 - A_1)$ against time, first-order kinetics being followed for better than one half-life. From the results obtained were calculated the data of Table 1.

Azoxybenzene-d10

Thallium reduction (16) of nitrobenzene- d_5 (Stohler Isotope Chemicals) gave the azoxycompound as yellow needles from ethanol (36% after two recrystallizations): m.p. 34.5–36°; mass spectrum *m/e* (relative intensity) 208 (M⁺) (37), 192 (5), 157 (6), 110 (11), 98 (8), 96 (24), 83 (100), 70 (18), 68 (16), 54 (30).

Anal. Calcd. for $C_{12}D_{10}N_2O$: N, 13.45. Found: N, 13.41.

Deuterium Isotope Effect for Azoxybenzene Photorearrangement

Solutions of azoxybenzene and azoxybenzene- d_{10} were irradiated simultaneously and first-order rate constants for 2-hydroxyazobenzene formation at 410 nm (in one experiment for azoxybenzene disappearance, monitored at 265 nm) were obtained as described above. The data are summarized in Table 1.

Irradiation of Azoxybenzene-d10 in Ethanol

A solution of azoxybenzene- d_{10} (302 mg) in 95% ethanol (300 ml) was irradiated for 1.5 h. The solvent was evaporated and the residue resolved by preparative t.l.c. (20% benzene in petroleum). Azoxybenzene- d_{10} (187 mg), m.p. 34.5-35°, and 2-hydroxyazobenzene-d₉ (89 mg), m.p. 79-80°, were obtained. After reservation of a sample of azoxybenzene- d_{10} for mass spectrometry, 185 mg was dissolved in fresh 95% ethanol (300 ml), and irradiated for a further 1.5 h. Azoxybenzene-d10 (57 mg) and 2hydroxyazobenzene-d₉ (85 mg) were recovered. Several mass spectra were run on the starting sample of azoxybenzene- d_{10} and on each of the recovered samples, and the ratios of the peaks at m/e 206, 207, 208 were compared: starting material, (4.9 ± 0.2) : (6.9 ± 0.2) :100; first recovered sample, (4.9 ± 0.4) : (6.1 ± 0.3) : 100; second recovered sample, (4.5 ± 0.1) : (6.9 ± 0.2) :100.

Irradiation of Azoxybenzene in CH₃CN-D₂O

A solution of azoxybenzene (305 mg) in dry (59) acetonitrile (300 ml) and deuterium oxide (20 ml) was irradiated for 1 h. Work-up as above gave azoxybenzene (60 mg) and 2-hydroxyazobenzene (77 mg). Several mass spectra were run to compare the ratio of the peaks at m/e 198 and 199 in the starting and recovered azoxybenzene samples: starting material, 100:(14.5 \pm 0.3); recovered sample, 100:(14.3 \pm 0.3).

Fluorescence Measurements

Using a Farrand Mark I fluorometer no fluorescence could be observed from azoxybenzene $(10^{-3}-10^{-5} M)$ or azoxybenzene- d_{10} in purified ethanol, methanol, or hexane solutions. Ethanol and hexane solutions were also examined by Dr. W. R. Ware and Mr. T. Nemzek of the University of Western Ontario using the single photon

counting technique (60), but again, no emission was observed.

Irradiation of Azoxybenzene in Styrene

Solutions of azoxybenzene (0.10 g) in styrene (30 ml) from which the stabilizer had been removed were irradiated in corked ampoules for 6 h using the Merry-goround. The solutions were poured into methanol and the weight of polystyrene determined. From two experiments the weight of polymer was 0.01 and 0.01 g; in control experiments where the azoxybenzene was omitted the weight was 0.50 and 0.55 g.

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