The Photochemistry of Some Methoxy and Dimethylamino Derivatives of Azoxybenzene

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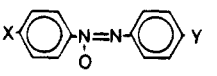
The photochemistry of the six azoxybenzene derivatives carrying a methoxy and/or a dimethylamino group in positions 4/4′ has been examined in alcohols and in benzene and found to lead to different processes. The photo-Wallach rearrangement takes place for all except the disubstituted derivatives. This process involves an intermediate, which either gives back the starting azoxy or is converted to the final *o*-hydroxy derivative through acid catalysis as well as by the previously reported basic catalysis or via cleavage to diazonium ions, which can be trapped before recombination. Oxygen shift to yield the isomeric azoxy derivative (only one precedent known) is a general, one-way process, leading in every case to the azoxy benzene with the N→O group far from the ring carrying the stronger electron-donating substituent. Differently from the photo-Wallach rearrangement, this process shows little solvent dependence. The dimethylamino derivatives undergo also or exclusively different fragmentations, such as intramolecular hydrogen abstraction and cleavage of either the N=N or the C–N bond. The solvent and substituent effect upon electronic spectra, reaction quantum yield, and product distribution are discussed. The photochemistry is attributed to a π,π^* state with strong internal charge transfer.

The photolability of azoxybenzene and its derivatives has long been known[1] and has been actively investigated in the last 20 years.[2] Irradiation of these compounds leads to *o*-hydroxy azo derivatives with migration of the oxygen to the aromatic ring "far" from the original N→O function, a process which has come to be termed photo-Wallach rearrangement, despite the fact that there are more differences than similarities with the thermal Wallach rearrangement.

Bunce has offered a detailed mechanistic scheme for this reaction[5] which considers the oxygen atom to behave as an electrophile in the attack to the benzene ring and thus accounts for the effect that substituents, or at least those exerting an inductive effect, have on the reaction efficiency. However, substituents having a strong donating mesomeric effect appear to cause a deeper change in the photochemistry of these compounds, either introducing a new mode of reaction (shift of the oxygen atom to the neighboring nitrogen, as has been reported for a methoxyazoxybenzene[6]) or completely inhibiting the photoreaction (as it is the case for 4,4′-bis(dimethylamino)azoxybenzene[7]). In the latter case the effect has been attributed to a change in the character of the excited state.

Precisely the desire to understand the nature of such a change in the excited state triggered the present investigation, with the double aim of obtaining more information about the mechanism(s) of the photochemistry of azoxybenzenes in general and of comparing the photochemical behavior of azoxybenzene bearing electron-donating substituents with that of the corresponding azobenzenes, the prototype of azo dyes, which is being investigated in this laboratory.[8]

The investigation has been extended to the six azoxybenzenes of structure **1**–**6**, with a methoxy and/or a dimethylamino group in position 4/4′.



1-6

	1	2	3	4	5	6
X	OMe	H	NMe_2	H	NMe_2	OMe
Y	H	OMe	H	NMe_2	OMe	NMe_2

Results and Discussion

Methoxyazoxybenzenes. It has been reported by Bunce[6] that on irradiation in ethanol through a Pyrex filter, (4-methoxyphenyl)phenyldiazene 2-oxide (**2**)[9] undergoes the "normal" photo-Wallach rearrangement to 2-hydroxy-4-methoxyazobenzene (**7**), and the corresponding 1-oxide (**1**) affords the same azo derivative **7**, formally the "abnormal" photo-Wallach product, as the oxygen atom attacks the ring *near* to the original N–O group), via previous isomerization to **2**. Shorter wavelength (quartz filter) irradiation, however, is effective in promoting the normal rearrangement of compound **1** to the azo derivative **9**[6] (Scheme I).

We repeated the irradiation of compounds **1** and **2** in ethanol and confirmed the above results, with the exception that in our apparatus (fitted with a Helios 125-W mercury arc) compound **1** reacts to both Wallach products **7** and **8** (the former via the isomeric azoxy **2**) even with Pyrex-filtered light. This is apparently due to a difference in the wavelength distribution of the absorbed light

The irradiation was then carried out in benzene, as solvent polarity is known to affect the photochemistry of similar compounds. It turns out that compound **2**, the more reactive of the two isomers in alcohol is only slowly photodegraded in benzene, while the reaction of **1** is unaffected and yields **8** and the other azoxy **2**, the latter accumulating in solution as it does not react further in this case (Table I).

Experiments were also performed in the presence of 2-naphthol, as the formation of the corresponding phenylazonaphthols during the irradiation of azoxybenzene and of some 2,2-disubstituted azoxybenzene afforded positive evidence that the photorearrangement of azoxy derivatives proceeds, at least under certain circumstances, via cleavage–recombination involving "free" diazonium and phenolate ions.[11] The product distribution from the

(1) Wacker, L. *Justus Liebigs Ann. Chem.* **1901**, *317*, 375.
(2) This subject has been repeatedly reviewed, along with the photochemistry of other compounds containing the *N*-oxide function.[3,4]
(3) Albini, A.; Alpegiani, M. *Chem. Rev.* **1984**, *84*, 43.
(4) Spence, G. G.; Taylor, E. C.; Buchardt, O. *Chem. Rev.* **1970**, *70*, 231.
(5) Bunce, N. J.; Schoch, J. P.; Zerner, M. C. *J. Am. Chem. Soc.* **1977**, *99*, 7986.
(6) Bunce, N. J. *Can. J. Chem.* **1975**, *53*, 3477.
(7) Tanigaka, R. *Bull. Chem. Soc. Jpn* **1968**, *41*, 2151.
(8) Albini, A.; Fasani, E.; Pietra, S.; Sulpizio, A. *J. Chem. Soc., Perkin Trans 2* **1984**, 1689 and references cited therein.
(9) The commonly used nomenclature distinguishes substituted azoxybenzenes as α and β derivatives. As this leads to some confusion in the case of unsymmetrically disubstituted derivatives, the use of the Chemical Abstracts accepted nomenclature is preferred in this paper.
(10) For preparation, purification and criteria of purity for the azoxy derivatives, see Experimental Section.
(11) (a) Bunce, N. J. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 725. (b) Bunce, N. J. *Can. J. Chem.* **1977**, *55*, 383.

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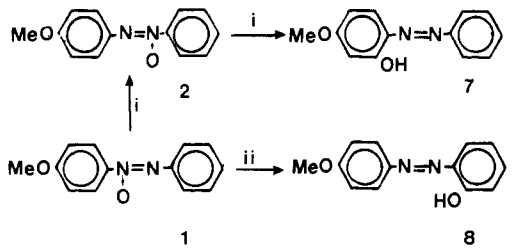
Table I. Results from the Irradiation of the Methoxyazoxybenzenes 1 and 2

starting azoxy	solvent	additive	irradiation time, h	converted azoxy, %	products (% yield)
1	ethanol	none[a]	6	55	7 (39), 8 (34)
1	benzene	none	6	75	2 (34), 8 (35)
1	benzene	0.01 M 2-naphthol	4	76	7 (38), 9 (17), 10 (8), 11 (8)
2	ethanol	none[a]	3	48	7 (79)
2	benzene	none	6	10	7 (40)
2	benzene	0.01 M 2-naphthol	3	95	7 (45), 10 (12)
2	benzene	0.01 M AcOH	6	50	7 (80)

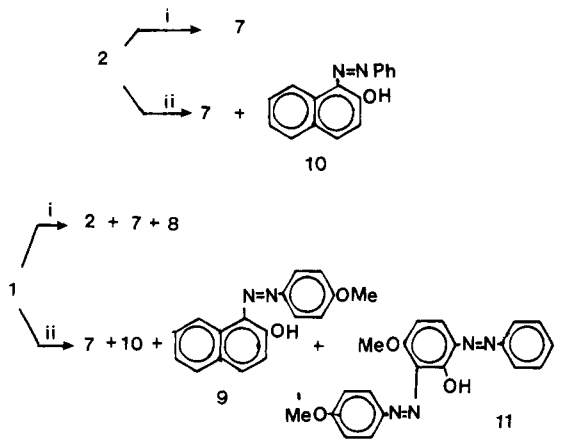
[a] No appreciable change in reaction rate or product distribution in the presence of 0.01 M 2-naphthol.

Scheme I[a]



[a] (i) hν (Pyrex), EtOH; (ii) hν (Quartz), EtOH.

Scheme II[a]



[a] (i) hν, (ii) hν, benzene, 2-naphthol.

photolysis of compounds 1 and 2 in ethanol was not affected by 0.01 M 2-naphthol, whereas an important change results in the reactions in benzene. Thus, the formation of the *o*-hydroxy derivative 8 from 1 is suppressed, giving place to 1-[(4-methoxyphenyl)azo]-2-hydroxynaphthalene (9), whereas product 7 formed from 2 remains predominant, the corresponding trapping product 10 being formed only in minor amounts. Even more interestingly, the azoxy 2 is now more reactive than its isomer 1 also in benzene, so that the amount of 2 formed in the photolysis of 1 undergoes further photorearrangement to 7. The latter compound in turn functions as a trap for the (4-methoxybenzene)diazonium cation formed from 1, yielding the bisazo derivative 11 (Scheme II).

Apparently, 2-naphthol is not only acting as trap of diazonium cations, but also in some way favors the reaction, conceivably as it is a weak acid. Consistently with this idea 0.01 M acetic acid is effective in promoting the rearrangement of 2 to 7. It is unlikely that additives at this low concentration have any effect on the short-lived excited state of azoxybenzenes or that solvents change the nature of the reacting excited state, as only slight modifications of the absorption spectra are registered (vide infra).

Thus, solvent and acid effects have to be referred to the modification of the reactivity of an intermediate, e.g., the

Scheme III

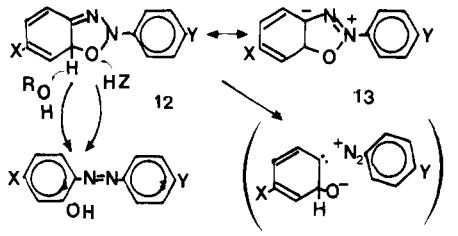


Table II. Results from the Irradiation of the (Dimethylamino)azoxybenzenes 3–6[a,b]

starting azoxy	solvent	converted azoxy, %	products (% yield)
3	methanol	35	4 (52)
3	benzene	48	4 (17), 14 (2)
4	methanol	25	15 (32)
4	benzene	6	15 (75), 16 (10), 17 (10)
5	methanol	40	6 (63)
5	benzene	60	18 (15)
6	methanol	16	
6	benzene	10	19 (80)

[a] Irradiation time: 7 h. [b] No appreciable change in reaction rate or product distribution in the presence of 0.02 M 2-naphthol.

benzoxadiazolidine 12, already considered as the first step in the rearrangement.[3-5] Proton shift mediated not only by nucleophilic solvents, as previously suggested[11b] but also by acids leads to the *o*-hydroxyazo derivative. On the other hand, bulky substituents hindering coplanarity of intermediate 12, as in the case of 2,2′-disubstituted azoxybenzenes, or electron-donating substituents (e.g., Y = OMe in Scheme III) favor heterolytic cleavage of 12 to diazonium and (after hydrogen shift) phenolate ions. These either recombine or are trapped[12] by suitable acceptors (Scheme III). If neither mechanism is efficient, intermediate 12 collapses back to the starting material.

(Dimethylamino)azoxybenzenes. The introduction of a dimethylamino group considerably diminishes the photoreactivity of the azoxybenzenes 3–6, as well as affecting the product distribution. Thus, the main process from [4-(dimethylamino)phenyl]phenyldiazene 1-oxide (3) leads to the isomeric azoxy derivative 4, a reaction corresponding to the previously mentioned rearrangement of 1 to 2. A minor product in benzene, probably again through a cleavage–recombination mechanism, is 4-(dimethylamino)-2′-hydroxyazobenzene (14), the photo-Wallach product. For the corresponding 2-oxide 4 the

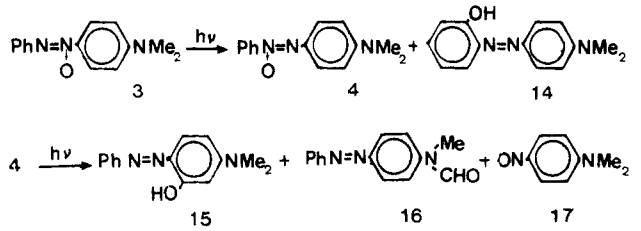
(12) Obviously, should the diazonium cation couple too fast with the phenol, no trapping by 2-naphthol would be observed. Thus, a possible rationalization of the fact that trapping is more important in the case of the azoxy 1 than in the case of the isomer 2 is that in the latter case the diazonium cation formed by cleavage reacts with resorcinol rather than with phenol. However, this rationalization fails to account for the unreactivity of 2 in benzene. Notice also that 7 undergoes coupling by the methoxybenzenediazonium ion ortho to the hydroxy group rather than, as it would be expected, para to it. The reaction scheme involving "free" diazonium ions might be oversimplified.

Table III. Absorption Spectra and Reaction Quantum Yield for Some Azoxybenzenes

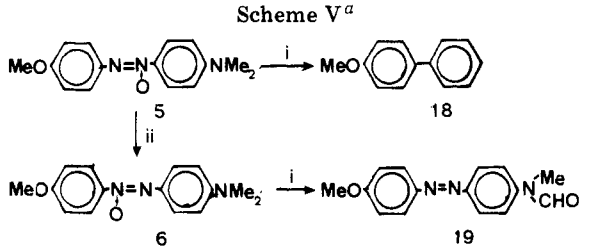
compound	substituents X	substituents Y	λ_{max} (log ϵ) benzene	λ_{max} (log ϵ) methanol	$\Delta\lambda$	Φ_{reacn}[a]	$\Phi_{p\text{-}W}$[b]
azoxybenzene	H	H	326 (4.217)	322 (4.151)	4	0.022[c]	0.017[f]
1	OMe	H	339 (4.306)	334 (4.265)	5	0.022[c]	0.005
2	H	OMe	350 (4.297)	349 (4.293)	1	0.021[c]	0.017
3	NMe_2	H	391 (4.397)	393 (4.354)	−2	0.002[d]	[g]
4	H	NMe_2	410 (4.452)	416 (4.452)	−6	0.0025[d,e]	[g]
5	NMe_2	OMe	393 (4.509)	395 (4.510)	−2	0.002[d]	
6	OMe	NMe_2	410 (4.475)	415 (4.472)	−5	0.008[d,e]	

[a] Quantum yield for the decomposition of the azoxybenzene in methanol. [b] Quantum yield for the formation of the corresponding hydroxyazo derivative in methanol (see text). [c] Irradiation at 313 nm. [d] Irradiation at 366 nm. [e] The azoxybenzenes 4 and 6 absorb strongly in the visible spectrum and undergo an efficient, thermally reversible photoreaction (trans–cis isomerization?). The data reported here refer to solution equilibrated several hours in the dark and to irreversible photochemical transformation. [f] Literature value, 0.016 (Goon, D. J. W.; Murray, N. G.; Schoch, J. P.; Bunce, N. J. *Can. J. Chem.* **1973**, *51*, 3827). [g] Low.

Scheme IV



Scheme V[a]



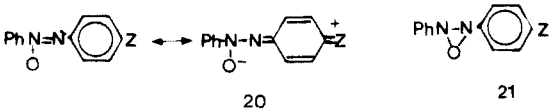
[a] (i) hν, benzene; (ii) hν, MeOH.

photo-Wallach rearrangement is the main pathway both in methanol and in benzene. Minor products from **4** in benzene are (*N*-methyl-*N*-formyl-4-amino)azobenzene (**16**) and a product arising from cleavage of the N=N bond, the nitroso derivative **17** (Scheme IV, Table II).

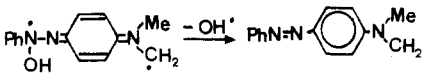
As for the azoxybenzenes carrying both a dimethylamino and a methoxy group, isomerization of [4-(dimethylamino)phenyl](4-methoxyphenyl)diazene 1-oxide (**5**) to the corresponding 2-oxide (**6**) is observed also in this case, at least in methanol. In benzene the main process from **5** is C–N bond cleavage leading through solvent trapping to 4-methoxybiphenyl (**18**). The 2-oxide (**6**) shows lower photoreactivity. In methanol we did not isolate any product, and in benzene we obtained (*N*-methyl-*N*-formyl-4-amino)-4′-methoxyazobenzene (**19**) as the main product (Scheme V).

Different from the previous case, the photo-Wallach rearrangement is not observed with either **5** or **6**. 2-Naphthol (0.02 M) does not affect the reactivity and the product distribution of compounds **3–6** either in methanol or in benzene. This point must not be unduly stressed as with these compounds, which are much less photoreactive than the methoxyazoxybenzenes **1** and **2**, intermediates might be (reversibly?) formed at too low a concentration for an appreciable trapping to take place.

A comment is in order for the photoprocesses differing from the photo-Wallach rearrangement observed with azoxybenzenes **1–6**. A generally observed reaction is 1,2-oxygen shift from the diazene 1-oxides **1**, **3**, and **5** to the corresponding 2-oxides **2**, **4**, and **6**. This is a one-way isomerization, in every case bringing the oxygen atom far from the ring carrying the electron-donating (or the more powerful electron-donating) group, i.e., toward the isomer receiving more resonance stabilization through limiting structures such as **20**.



The rearrangement differs from the photo-Wallach rearrangement in that it shows little solvent dependence (except in the case of compound **5**) and apparently occurs through a completely different pathway, possibly involving the intermediacy of an oxadiaziridine (**21**). Some minor cleavage reactions are related to this process, e.g., the formation of the nitrosoaniline **17**, which can be rationalized as arising from an oxadiaziridine, as related cleavage reactions of oxaziridines to carbonyl derivatives and nitrenes are known.[13a–b] As for the *N*-formyl derivatives **16** and **19**, it must be pointed out that these do not arise from deoxygenation of the azoxy to the corresponding azo derivatives and subsequent oxidation of a *N*-methyl group. In fact, no trace of azoderivatives was detected from the irradiation of the azoxy, and from separate experiments it was ascertained that these azo dyes are inert by direct irradiation, but hydrogen abstraction by photoexcited ketones in aerated solution does lead to the α-amino radical and hence to the *N*-formyl derivatives **16** and **19**.[14] Apparently the same radical is formed from the azoxy by *intramolecular* attack and OH· elimination.



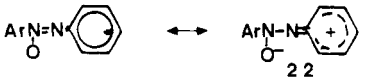
Quantitative Measurements and Mechanistic Discussion. In order to get more insight into the mechanism of these photoreactions, absorption data and reaction quantum yield for compounds **1–6** as well as for the parent molecule azoxybenzene are collected in Table III. The shape of the first absorption band is fairly symmetric and similar in every case, with gradual shift toward the red with the substituents. None of these compounds show any emission at room temperature or at 77 K in glass. The quantum yield of reaction for the methoxy azoxybenzenes is the same as for the parent molecule, and it drops by a factor of 3 to 10 in the case of the dimethylamino derivatives. All azoxybenzenes for which measurements have

(13) (a) Meyer, E.; Griffin, G. W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 634. (b) Splitter, J. S.; Calvin, M. *Tetrahedron Lett.* **1968**, 1445. (c) Fabian, J.; Hartmann, H. "Light Absorption of Organic Colorants"; Springer-Verlag: Berlin, 1980. (d) Rau, H. *J. Photochem.* **1984**, *26*, 221. (e) Gorner, H.; Gruen, H.; Schulte-Frohlinde, D. *J. Phys. Chem.* **1980**, *84*, 3031.

(14) Unpublished results from this laboratory.

been made show quantum yields of this order of magnitude, and it appears unlikely that a substantial change in the characteristics of the excited state occurs along the series.

Bunce observes that the photorearrangement of azoxybenzenes has the character of an electrophilic attack by the oxygen atom (vide supra) and attributes this reaction to a low lying n,π^* state on the basis of the interpretation of the electronic spectrum (a small bump in the gas-phase spectrum of azoxybenzene) and of INDO calculations. Although the latter result might be an artifact of the method, as calculation of this type are liable to give unrealistic low n,π^* states for these molecules (compare the situation with the structurally related aromatic *N*-oxides[3]), this is certainly an appealing and consistent proposal. However, the present results suggest that a different rationalization can be considered. Indeed, the high extinction coefficient and the strong substitution effect on the absorption spectrum point to a π,π^* state with internal change-transfer character, i.e., involving a different mixture of mesomeric formulae such as **22**.



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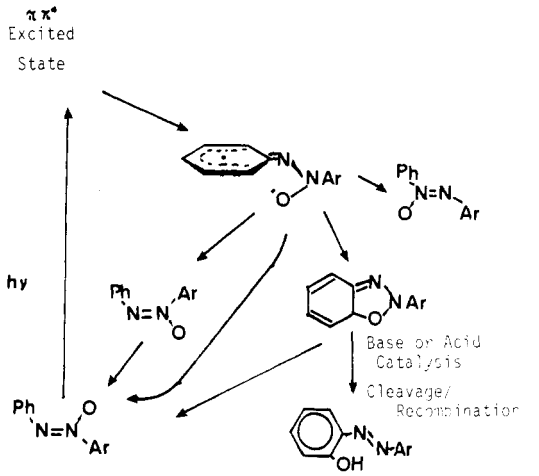
The excited state of these azoxy derivatives is thus similar to that of the corresponding azo dyes, which in fact show a similar substituent and solvent effect on the absorption spectra, or better to protonated azo derivatives (azoxybenzene, just as protonated azobenzene, does not show a n,π^* band). The radiative lifetime of these CT states is short, and again analogously to azo dyes,[13d,e] the actual lifetime will be much shorter due to the availability of a facile deformation for the excited state, viz rotation around the N=N bond, as the bond order is lower in the excited state.

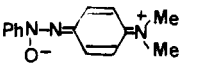
This postulate accounts both for the lack of emission and for the low quantum yield of reaction. Indeed, if rotation around the N–N bond occurs to a limited degree, it simply affords a "chemical" pathway for internal conversion to the starting material. On the other hand, if deformation of the excited state proceeds further isomerization to the cis azoxy derivative results. Thermal back-isomerization, however, is fast, particularly when electron-donating substituents are present, so that no net chemical change is again registered.

Only a small fraction of the excited state takes some different pathways. Thus, after initial deformation, cyclization to the benzoxadiazolidine **12** may occur, as already suggested by Bunce. This again may result in a dead end, as our data clearly show at least for the methoxy derivatives that unless nucleophilic solvents or added acids favor hydrogen shift to the final product, oxygen attack is reversible (thus, e.g., **2** does not react in benzene but the presence of 0.01 M AcOH, while not influencing the excited state reaction, is sufficient to avoid collapse of the intermediate to the starting material and make irreversible reaction efficient). The comparison between the photo-Wallach rearrangement and electrophilic substitution is validated, as, considering pairs of isomeric para-substituted azoxybenzenes, oxygen attack to an electron-rich ring is more efficient (at least in alcohols not so in inert solvents) as it is the case with **2** vs. **1** or **4** vs. **3**. However, the whole story is clearly more complicated than that, as collapse of **12** to the starting material or cleavage to diazonium and phenolate ions, the latter process being favored by electron-donating substituents in the ring *near* to the N→O function, not the reacting ring, contributes to determine the final efficiency of the process (Scheme VI).

Scheme VI



The stronger the effect of electron-donating substituents, the shorter the excited-state lifetime due to easier rotation around the N–N bond is and thus the lower the efficiency of the photo-Wallach rearrangement. Conversely, reactions essentially determined by the charge-transfer characteristic such as the 1,2-oxygen shift (see Scheme VI) or intrinsically slow such as hydrogen abstraction from the dimethylamino group become more important at least in relative terms. As for the latter process, its occurrence can be taken either as an indication that the excited state exhibits also a degree of radical reactivity or, more likely, as another manifestation of the charge-transfer character of the excited state if it proceeds by proton rather than by hydrogen atom transfer. Support for this hypothesis comes from the fact that this reaction is observed for azoxy derivatives for which the mesomeric formula **23** is possible, viz., for compound **4** and **6** rather than for their isomers **3** and **5**.



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Conclusion

We think that the data obtained on the photochemistry of methoxy and dimethylaminoazoxybenzenes allow an advancement toward the understanding of the scope of the photo-Wallach rearrangement, as well as of the 1,2-oxygen shift, a process little documented up to now in the photochemistry of azoxybenzenes. Furthermore, the reversibility of the former process is revealed, and the proposal that the reactive excited state is a π,π^* CT state allows to reach a unitary mechanistic picture of both reactions as well as of other minor processes observed with these azoxy derivatives.

Experimental Section

Synthesis and Purification of the Azoxybenzenes. The methoxy derivatives **1** and **2** were prepared by peracetic acid oxidation of methoxyazobenzene according to Bunce.[6] The isomers were separated by repeated chromatography on silica gel eluting with benzene–cyclohexane mixtures (**2** elutes first) and repeated crystallization from methanol. We find that mp is not a satisfactory test of purity, a better check being NMR in C_6D_6 (MeO absorption, δ 3.15 for **1**, δ 3.25 for **2**). Samples used for preparative photolysis contained up to 5% of the other isomer.

The dimethylamino derivatives **3** and **4** were prepared by condensation of phenylhydroxylamine and *N,N*-dimethyl-4-nitrosoaniline according to Anderson.[15] The isomers were separated by chromatography on silica gel eluting with cyclo-

(15) Anderson, W. *J. Chem. Soc.* **1952**, 1722.

hexane–ethyl acetate mixtures and recrystallized from petroleum spirit, bp 80–100 °C.

The methoxy dimethylamino derivatives **5** and **6** were prepared according to the procedure suggested by Suschitzky[16] for **5**. Thus, refluxing 0.3 g of *N,N*-dimethyl-4-nitrosoaniline and 0.3 g of 4-methoxyphenyl azide in 3 mL of bromobenzene for 1 h under nitrogen, evaporation of the solvent, chromatography of the residue on alumina, and double recrystallization from cyclohexane yielded 0.325 g (60%) of compound **5**, yellow needles, mp 133–134 °C. Compound **6** (0.2 g, 35%) was similarly obtained from 10 min of refluxing of 0.3 g of methoxynitrosobenzene and 0.36 g of 4-(dimethylamino)phenyl azide, chromatography, and several recrystallyzations from methanol, mp 135–136 °C.

Photochemical Reactions. A solution of 100 mg of (4-methoxyphenyl)phenyldiazene 1-oxide (**1**) in 100 mL of ethanol was irradiated for 6 h at 17 °C by means of a Helios Italquartz 125-W medium-pressure arc through a Pyrex filter. Evaporation of the solvent and chromatography on silica gel eluting with a cyclohexane–benzene mixture yielded 45 mg of unreacted **1**, 25 mg (39% of reacted **1**) of 2-hydroxy-4-methoxyazobenzene (**7**), and 22 mg (34%) of 4-hydroxy-4′-methoxyazobenzene (**8**). Similar irradiation of compounds **1–6** in the conditions stated in Tables I and II yielded the reported products.

Physical Data. UV spectra were recorded with a Cary 19 spectrophotometer and luminescence spectra with a Aminco Bowman MPF spectrophotofluorometer. IR spectra were recorded in KBr pellets by means of a Perkin-Elmer 197 spectrophotometer, ^{1}H NMR spectra (in C_6D_6 or $CDCl_3$) by means of a Bruker 80 instrument with tetramethylsilane as internal standard.

Structure Assignment. In most cases, photochemical products were recognized by direct comparison with authentic samples. The hydroxy azo dyes **7**,[17] **9**,[18] **10**,[19] **14**,[20] and **15**[21] were prepared according to published methods, as was the biphenyl **18**.[22] The formyl derivatives **16** and **19** were prepared by formylation of the corresponding *N*-methyl derivatives.[14] The hydroxyazo derivative **8** corresponds to the product described by Bunce[6] in its physical and spectroscopic properties.

The structure of 2,4′-dimethoxy-4-hydroxy-5-phenylazoazobenzene was assigned to product **11**, orange crystals, mp 63–66 °C, on the basis of the elemental analysis (C, 65.9; H, 5.2; H, 15.3. Calcd for $C_{20}H_{18}N_4O_3$: C, 66.3; H, 5; N 15.5) and spectroscopic properties: NMR (C_6D_6) δ 3.15 (3 H); 3.2 (3 H), Aromatic signals between δ 6.5 and 8.18 include an AA′BB′ and an AB systems but no proton with only para or meta coupling. Mass spectrum is in accord with the structure.

Reaction Quantum Yield. The photochemical reaction was effected with 313- or 366-nm radiation (intensity ca. 10^{-7} einstein min^{-1} cm^{-2}) obtained from a focalized high-pressure mercury arc by means of an interference filter ($\Delta\lambda_{1/2}$ 5 nm).

Solutions of 10^{-4} M **1–6** were irradiated to a ca. 15% conversion. Light intensity was measured by ferrioxalate actinometry. Formation of the hydroxy azo derivative was measured by either of two methods, viz., either making the irradiated solution 0.5 M in KOH and measuring the absorbance of the corresponding anion or by HPLC chromatography (Waters apparatus, Corasyl 18 column). Disappearance of the starting material was determined by chromatography and UV absorbance measurements.

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Notes

Proton Inventory Investigation of the Specific Acid Catalyzed Hydrolysis of γ-Ethoxy-γ-butyrolactone

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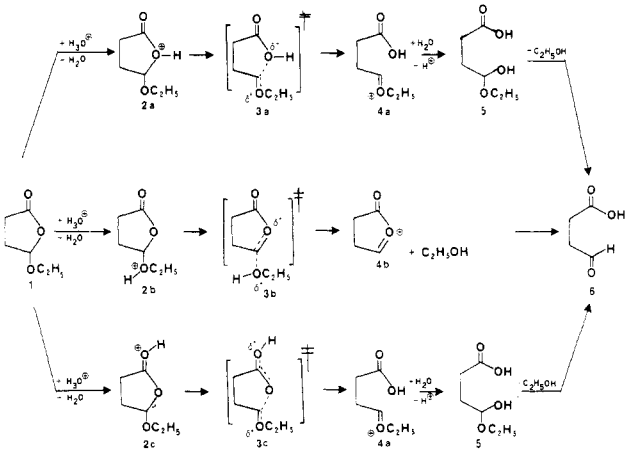
It has been proposed that some enzyme-catalyzed hydrolyses of glycosidic bonds or enzyme-catalyzed transglycosylations may involve a mixed acetal–acylal intermediate that would then rapidly hydrolyze.[1] We report a study of the hydrolysis of such a compound, γ-ethoxy-γ-butyrolactone (**1**), as a model for such a process.[1] Fife has previously explored the hydrolysis of the compound and has proposed an A-1 mechanism for the acid-catalyzed hydrolysis of **1** as shown in path **a** of Scheme I.[2] Protonation of the lactone gives intermediate **2a** that breaks down in the rate-determining step to yield **4a**. The intermediate **4a** then suffers attack by water to give the hemiacetal **5** that rapidly hydrolyzes to the aldehyde **6**. The aldehyde chromophore allows the reaction to be monitored spectrophotometrically.

Scheme I



Fife's mechanism was based on the following pieces of information, among other things. A specific acid-catalyzed reaction that exhibits a solvent deuterium isotope effect of $k(D_2O)/k(H_2O) = 2.37$ is observed at low pH. The

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