Photochemical Decomposition of 4-Arylazo- and 4-Arylazoxy-*N,N*-dialkylaniline *N*-Oxides

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The 4-aryl-*N,N*-dialkylaniline *N*-oxides (**1a**—**c**) decompose on u.v. irradiation in aprotic solvents, undergoing deoxygenation as well as intramolecular hydrogen abstraction, to give amides and dealkylated products. The latter process is more important for the diethyl derivative (**1b**) (photo-Cope elimination). Visible irradiation is ineffective. The 4-arylazoxy-*N,N*-dialkylaniline *N*-oxides (**2a**—**d**) undergo photochemical deoxygenation from the amino group (major process) as well as from the azo group. The mechanism of these photoprocesses is discussed in general and in relation to the possible involvement of these *N*-oxide derivatives in photofading of the related azo dyes.

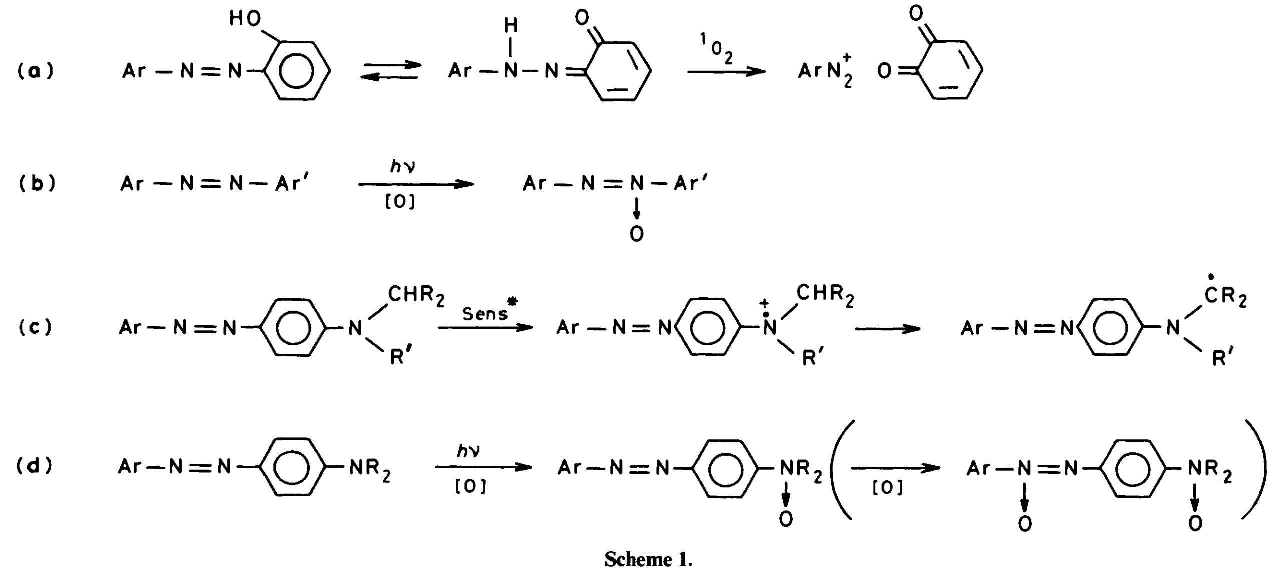
An oxidative mechanism is often considered to be important in the photofading of azo dyes.[1,2] However, the evidence cited in favour of this view is mainly indirect, including the accelerating effect of electron-donating substituents on fading,[3–7] the Becquerel effect observed on irradiation of a dye-coated electrode,[8] and the similarity between the rates of photofading and of chemical oxidation for some series of dyes.[5,6]

In a limited number of cases the photoproducts have been isolated and the mechanism has been discussed. These correspond substantially to three reaction types. (i) Oxidative cleavage of the aryl–nitrogen bond [Scheme 1(a)]. This is now a well documented reaction involving singlet oxygen and the hydrazine tautomer,[9–12] and is therefore important for *o*- and *p*-hydroxy azo derivatives. (ii) *N*-Oxidation of the azo linkage [Scheme 1(b)]. This is an attractive possibility, as azoxy derivatives are known to undergo a further photoreaction to *o*-hydroxy azo derivatives;[13] this mode of reaction has been considered as early as 1924.[14] However, formation of an azoxy derivative has been actually demonstrated for only one dye, in 1974.[15] The mechanism of the reaction has been elucidated recently.[16] (iii) Oxidation of the amino group, for the large class of amino azo dyes. Aromatic amines physically quench singlet oxygen rather than chemically reacting with it;[17] we have confirmed that irreversible fading of simple amino azo dyes caused by singlet oxygen is very slow.[18] However, the possibility of a 'Type I' photo-oxygenation, *i.e.* involving preliminary interaction of the excited sensitizer with the substrate, followed by reaction with oxygen, has been considered;[2] we recently showed that ketonic sensitizers react with dialkylamino azo dyes by electron abstraction followed by hydrogen transfer [Scheme 1(c)], with ensuing reaction of the radicals with oxygen.[16]

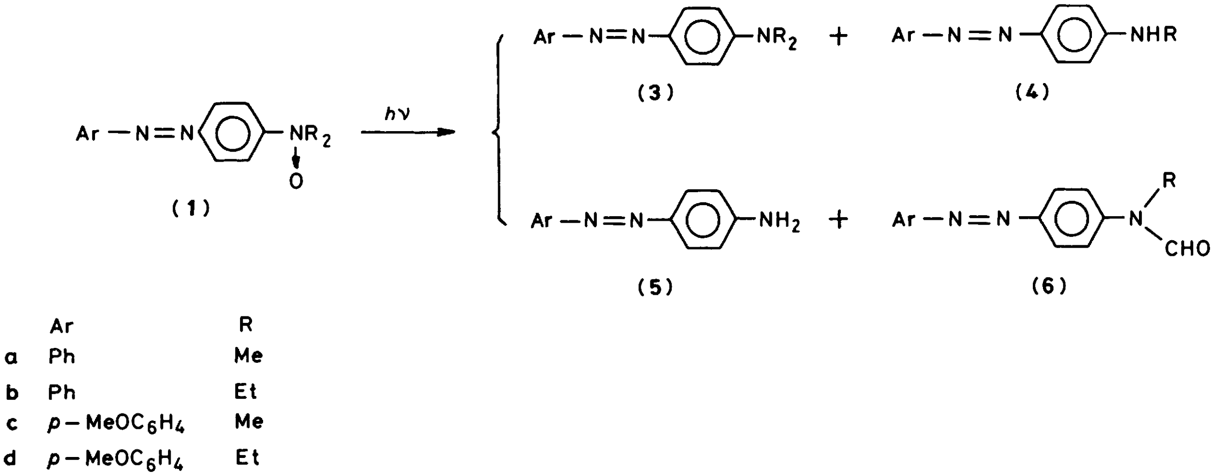
Another possibility that appears not to have been considered in this connection is *N*-oxidation of the amino group [Scheme 1(d)]. The amine nitrogen is far more electron-rich than the azo linkage, and therefore it is to be expected that azo *N*-oxide derivatives will be formed during photo-oxidation. No such derivative has as as yet been isolated from the products of photo-fading of azo dyes, but this could be due to fast secondary decomposition. Therefore, it appeared desirable to investigate the photochemistry of such compounds.

Results and Discussion

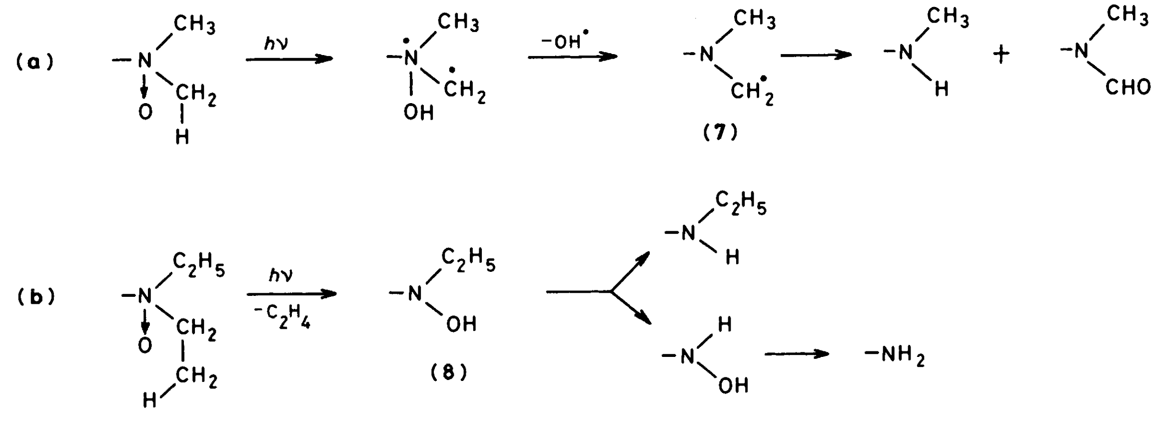
To our knowledge the reported photochemistry of *N*-oxides of azo dyes is limited to the photocyclization in 22N-sulphuric acid of 4-phenylazo-*N,N*-dimethylaniline *N*-oxide (**1a**) to the corresponding benzo[*c*]cinnoline.[19,20] Nothing has been



Scheme 1.



Scheme 2.



Scheme 3.

Table 1. Thermal and photochemical decomposition of azo *N*-oxides

Compound	Solvent	Conditions (time)	Recovered starting material (%)	Products (% yield)[a]
(**1a**)	Methanol	*h*ν (6 h)	100	
	Benzene	*h*ν (6 h)	58	(**3a**) (76), (**4a**) (12), (**6a**) (5)
	Benzene	Reflux (1 h)	100	
(**1b**)	Methanol	*h*ν (6 h)	100	
	Benzene	*h*ν (5 h)	23	(**3b**) (28), (**4b**) (10), (**5b**) (23)
	Benzene	Reflux (1 h)	80	*b*
(**1c**)	Methanol	*h*ν (6 h)	100	
	Benzene	*h*ν (6 h)	63	(**3c**) (43), (**4c**) (32), (**6c**) (19)
	Benzene	Reflux (1 h)	100	

[a] Isolated yields, based on reacted (**1**). [b] Complex mixture of products (t.l.c.).

reported about the photochemistry of the *N*-oxides of aromatic amino azoxy derivatives.

The present report concerns the thermal and photochemical reactivity of 4-phenylazo-*N*,*N*-dimethyl- and *N*,*N*-diethylaniline *N*-oxides (**1a** and **b**) and of the 4-(4-methoxyphenylazo) derivative (**1c**), as well as of 4-(phenyl-*ONN*-azoxy)-*N*,*N*-dimethyl- and -*N*,*N*-diethyl-aniline *N*-oxides (**2a** and **b**) and the 4-methoxyphenylazoxy derivatives (**2c** and **d**). The experiments were carried out in methanol and in benzene. Test experiments in other protic and aprotic solvents gave results qualitatively similar to those reported for these two solvents.

Photochemical Decomposition of Azo N-*Oxides*.—Compound (**1a**) is known[21] and compounds (**1b** and **c**) were similarly prepared by room temperature oxidation of the corresponding azo dyes with perbenzoic acid.*

The *N*-oxides (**1a** and **c**) are indefinitely stable in the crystalline state (with one or two molecules of water of crystallization) and are recovered unaltered after some hours refluxing in methanol or ethanol. However, although the dimethylamino *N*-oxides (**1a** and **c**) are stable when refluxed in benzene, the diethylamino derivative (**1b**) is more reactive; it undergoes 20% decomposition on 1 h refluxing in benzene, yielding a complex mixture.

On irradiation with Pyrex-filtered light, the *N*-oxides are stable in alcohols but reactive in aprotic solvents. In benzene, a clean reaction takes place for compounds (**1a**—**c**); the products are the corresponding azo derivatives (**3**), as well as the monoalkylamino- (**4**), the amino- (**5**), and, from the dimethylamino *N*-oxides, the *N*-formyl-*N*-methylamino (**6**) azo derivatives in various proportions (Scheme 2; Table 1).

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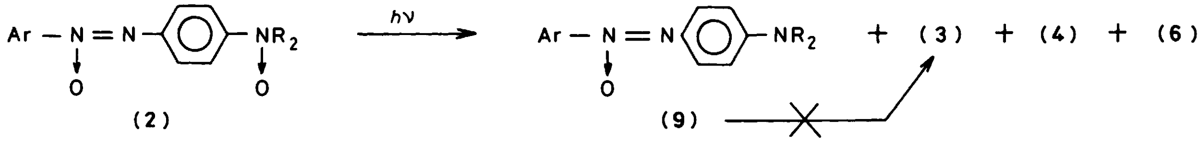
* Under these conditions, however, 4-(4-methoxyphenylazo)-*N*,*N*-diethylaniline reacts only slowly, and product decomposition is significant; thus we did not succeed in isolating the *N*-oxide (**1d**) in sufficiently pure form.

Table 2. Absorption spectra and reaction quantum yields

Compound	$\lambda_{max.}$/nm (log ε) Benzene	$\lambda_{max.}$/nm (log ε) Methanol	$\varphi_{dec.}$(benzene)
(1a)	321 (3.86), 440 (2.77)	228 (4.05), 318 (4.26), 436 (2.64)	0.14,[a] 2 × 10^{-4} [b]
(1b)	334 (4.14), 440sh	228 (3.99), 317 (4.19), 441 (2.82)	
(1c)	324 (3.93), 436 (2.95)	241 (4.00), 350 (4.25), 434 (3.15)	
(2c)	324 (4.08)	223 (4.04), 318 (4.13)	0.013[a]
(2b)	330 (4.09)	231 (3.95), 319 (4.22)	
(2c)	349 (4.19)	241 (3.98), 349 (4.23)	
(2d)	349 (4.10)	239 (4.02), 347 (4.18)	

[a] At 313 nm. [b] At 433 nm.



Scheme 4.

Apparently the photochemistry involves oxygen transfer to the solvent as well as intramolecular hydrogen abstraction, the latter process being accounted for in Scheme 3, where it is assumed that the oxygen atom has radical character in the excited state. Thus, in the case of the dimethylamino derivatives, abstraction from the α-position and homolytic cleavage lead to the α-amino radical (**7**) [Scheme 3(a)]. The end products [monomethyl derivative (major); formyl derivative (minor)] correspond to those observed when the radical (**7**) is formed by photosensitized reaction of an azo dye [Scheme 1(c)].[16]

The product distribution from the diethylamino derivative (**1b**) is different because of the easy intramolecular abstraction from the β-position, leading to ethylene elimination in a way similar to the Cope elimination observed on pyrolysis of *N*-oxides[22] [Scheme 3(b)]. This explains the increased importance of fragmentation *vs.* intermolecular oxygen transfer with respect to the dimethylamino derivatives [the ratio of the two process is *ca.* 1.2:1 in the case of (**1b**), and 0.2:1 in the case of (**1a**)]. The primarily formed hydroxylamine (**8**) undergoes further (probably photochemical) fragmentation to the observed products. The analogous photodecomposition of phenylhydroxylamine to aniline has been documented.[23] The Cope fragmentation probably explains also the decomposition of (**1b**) in refluxing benzene in contrast to the stability of (**1a**). Under thermal conditions, however, secondary reactions lead to a complex mixture, whereas irradiation at room temperature gives a clean reaction.

The electronic spectrum of the *N*-oxides (**1a** and **c**) shows a band with low extinction coefficient in the visible and two strongly absorbing bands in the u.v. (Table 2; Figure). This spectrum is almost identical with that of azobenzene; *N*-oxidation virtually cancels the electron-donating contribution of the amino group, which is the origin of the allowed, low-energy charge-transfer band of the parent dialkylamino azo derivatives (compare the discussion by Pentimalli in ref. 21). The effect of solvent polarity on the spectrum is limited to a shift of a few nanometres again in analogy with azobenzene.[24] These *N*-oxides show no luminescence, either in fluid solution or in ether–pentane–ethanol glass at 77 K.

The quantum yield of reaction for compound (**1a**) on irradiation in the visible region is very low, whereas a value of 0.14 has been measured for irradiation at 313 nm. Thus the lowest excited singlet is not involved in the photoreactions in Table 1; in accord with the foregoing spectroscopic evidence, it is an *n*–π* state closely corresponding to that of azobenzene, and likewise undergoing only *trans–cis* isomerization (compare ref. 25). The presence of the strongly polar amino *N*-oxide group accelerates the thermal reversion of this reaction, so that no net decomposition results. In azobenzene the strongly allowed π–π* transition involves a certain amount of charge transfer from the aromatic ring to the azo group.[26] In the case of the amino *N*-oxides (**1**) this transition involves electron withdrawal from the substituent, and this is responsible for the radical and electrophilic character of the oxygen atom in the π–π* state, explaining the observed intramolecular hydrogen abstraction and oxygen transfer to the solvent. The decomposition quantum yield of 0.14 shows that reversible geometric isomerization remains nevertheless the main pathway from the π–π* state also (as is the case for azobenzene). As far as can be judged from the absorption spectra, aprotic solvents do not appreciably affect the excited-state energy. However, they quench the photodecomposition of (**1**) and (**2**) probably through reversible proton transfer to the excited state.

Photochemical Decomposition of Azoxy N-*Oxides*.—Compounds (**2a**—**d**) were prepared, according to the reported procedure for (**2a**), by oxidation with peracetic acid of the corresponding azo derivatives. Recent evidence[27] confirms a previous report[21] that the second oxygen atom is predominantly linked to the nitrogen far from the amino substituted ring, and recrystallization affords products (**2a**—**d**) reasonably free from the isomeric phenyl-*NNO*-azoxy derivatives.

Solutions of these derivatives in benzene, methanol, or ethanol suffer no noticeable decomposition on refluxing in the dark but, analogously to (**1b**) again the diethylamino *N*-oxide (**2b**) is thermally reactive in benzene. The compounds are stable to irradiation in alcoholic solvents, but are decomposed on irradiation in benzene solution, yielding a mixture of the corresponding azoxy (**9**) and azo (**3**) derivatives, as well as, in the case of (**2a**), minor amounts of the monomethyl (**4a**) and the *N*-methyl-*N*-formyl (**6a**) azo derivatives (Scheme 4; Table 3). Control experiments on the azoxy derivatives (**9**) show that these are photochemically reactive, but undergo no significant deoxygenation under these conditions.

Therefore, the two N→O groups present in compounds (**2a**—**d**) are concurrently deoxygenated on irradiation, reaction at the amine *N*-oxide group being the major process, particularly in the case of the methoxy derivatives (**2c** and **d**). This process yields the comparatively unreactive azoxy derivatives (**9**), whereas concurrent reaction at the azoxy group leads to the highly photoreactive amino azo *N*-oxides (**1**) and thus to secondary fragmentation according to the pathways already discussed [compare in particular the formation of products (**3a**), (**4a**), and (**6a**) in the same proportions from both (**2a**) and (**1a**)].

The electronic spectra of compounds (**2a**—**d**) are, as expected,

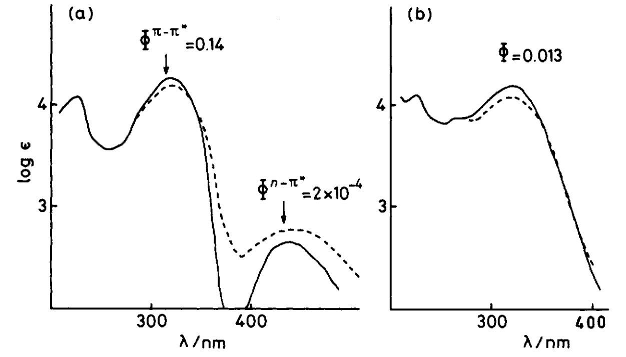


Figure. Absorption spectrum of (a) the amino azo *N*-oxide (**1a**) and (b) the amino azoxy *N*-oxide (**2a**) in methanol (——) and in benzene (– – – –); quantum yields for photodecomposition in benzene are marked

Table 3. Thermal and photochemical decomposition of azoxy *N*-oxides

Compound	Solvent	Conditions (time)	Recovered starting material (%)	Products (% yield)[a]
(**2a**)	Methanol	*h*ν (6 h)	100	
	Benzene	*h*ν (6 h)	64	(**3a**) (13), (**4a**) (11), (**6a**) (2), (**9a**) (33)
	Benzene	Reflux (1 h)	100	
(**2b**)	Methanol	*h*ν (6 h)	100	
	Benzene	*h*ν (5 h)	46	(**3b**) (10), (**9b**) (22)
	Benzene	Reflux (1 h)	35	*b*
(**2c**)	Methanol	*h*ν (6 h)	100	
	Benzene	*h*ν (6 h)	58	(**3c**) (5), (**9c**) (49)
	Benzene	Reflux (1 h)	100	
(**2d**)	Methanol	*h*ν (6 h)	100	
	Benzene	*h*ν (6 h)	58	(**3d**) (3), (**9d**) (39)
	Benzene	Reflux (1 h)	100	

[a] Isolated yield, based on reacted (**2**). [b] Complex mixture of products (t.l.c.).

similar to that of azoxybenzene, and not to that of the amino-azoxybenzenes (**9**) [π–π* band, 322 nm for azoxybenzene, 319 for (**2a**), and 416 for (**9a**); in no case there is a distinguishable *n*–π* band]; again *N*-oxidation precludes electron donation. These compounds show none of the typical photochemistry of azoxy derivatives, *viz.* isomerization to the corresponding *o*-hydroxy azo derivatives, and are rather similar to the *N*-oxides (**1**), the main consequence of excitation being again oxygen transfer to the solvent although with less efficiency than in the latter case. The quantum yield of irreversible decomposition decreases by a factor of 10 in going from (**1a**) to (**2a**); apparently the main photochemical process is *trans–cis* isomerization, which, however, is again thermally reversible.

Conclusions

N-Oxidation makes the lone pair of the amino group unavailable for conjugation and completely cancels its otherwise dramatic effect on the spectra of amino azo and amino azoxy derivatives (*viz.* a bathochromic shift of 70—100 nm and a strong hyperchromic effect). There are no irreversible photoreactions of the azo of azoxy moiety; the photochemistry of these compounds is dominated by reaction at the *N*-oxide function (oxygen transfer and intramolecular hydrogen abstraction) as excitation to the π–π* state, involving some charge transfer from the ring (and the substituent) to the azo group, makes the oxygen atom more electrophilic and radical in character.

The present results are limited in scope, but it is likely that the observed photochemistry is general for *N*,*N*-dialkylarylamine *N*-oxides.

In relation to the fading of azo dyes, it appears that photodecomposition of these *N*-oxides with u.v. light in aprotic solvents is much more efficient than direct photodecomposition of azo dyes of similar structure (φ_{dec} *ca.* 10^{-4} at 313 nm;[18] however, photosensitized decomposition is faster[16]). Contrary to the case of *N*-oxides, photodecomposition of azo dyes shows little dependence on the nature of the solvent. Thus, it appears that *N*-oxides, should they be formed, would not be further decomposed at such a rate as to make their detection impossible, at least at an early stage of the photoreaction and in alcoholic solvents.

Experimental

U.v. and visible spectra were recorded with a Cary 19 spectrophotometer, i.r. spectra with a Perkin-Elmer 197 spectrophotometer, n.m.r. spectra with a Brucker 80 instrument, and luminescence spectra with a Aminco-Bowman MPF spectrophotofluorometer.

N,N-*Dimethyl-4-phenylazoaniline* N-*Oxide* (**1a**).—A solution of freshly prepared perbenzoic acid (1.2 g) in chloroform (15 ml) was added dropwise to a solution of *N*,*N*-dimethyl-4-phenylazoaniline (1 g) in chloroform (10 ml). After 30 h at room temperature in the dark the solution was evaporated and the residue stirred with a saturated aqueous solution of sodium carbonate, filtered off, dried, and crystallized from benzene, yielding yellow needles (0.9 g, 73%) of product (**1a**), containing two molecules of water of crystallization; m.p. 124—125 °C [lit.,[21] 126 °C (anhydrous)] (Found: C, 60.7; H, 7.0; N, 15.1. Calc. for $C_{14}H_{15}N_3O{\cdot}2H_2O$: C, 60.6; H, 6.9; N, 15.15%).

Under these conditions were also obtained the *product* (**1b**), yellow needles (from benzene), m.p. 96—97 °C, yield 32% (Found: C, 62.5; H, 8.1; N, 13.7. $C_{16}H_{19}N_3O{\cdot}2H_2O$ requires C, 62.9; H, 7.6; N, 13.8%); and *product* (**1c**), yellow needles (from benzene), m.p. 151—153 °C, yield 81% (Found: C, 62.5; H, 6.6; N, 14.2. $C_{15}H_{17}N_3O_2{\cdot}H_2O$ requires C, 62.3; H, 6.6; N, 14.5%). Under these conditions oxidation of 4-(4-methoxyphenylazo)-*N*,*N*-diethylaniline is very slow. After 3 days, work-up as above yielded samples of (**1d**), m.p. 90—92 °C (Found: C, 64.2; H, 7.3; N, 13.1. Calc. for $C_{17}H_{21}N_3O_2{\cdot}H_2O$: C, 64.3: H, 7.3; N, 13.2%), which presented two spots on t.l.c.; this material was not used for decomposition studies.

N,N-*Dimethyl-4-(phenyl-*ONN-*azoxy)aniline* N-*Oxide* (**2a**).—*N*,*N*-Dimethyl-4-phenylazoaniline (6 g) was dissolved in acetic acid (70 ml) at 40 °C, and 35% hydrogen peroxide (45 ml) was added. The solution was maintained at 40 °C for 15 h. After cooling, 2N-sulphuric acid (240 ml) was added. The crystalline precipitate of the sulphate thus obtained was filtered off and redissolved in water (300 ml) containing concentrated sulphuric acid (5 ml). Overnight a crystalline precipitate was obtained. This was stirred with aqueous 5% sodium carbonate solution (30 ml), and the residue was washed with t-butyl methyl ether and recrystallized from nitroethane, to yield yellow needles (4 g, 55%), m.p. 107—108 °C, containing one molecule of water of crystallization [lit.,[21] m.p. 125—126 °C (anhydrous)] (Found: C, 60.8; H, 6.3; N, 15.3. Calc. for $C_{14}H_{15}N_3O_2{\cdot}H_2O$: C, 61.1; H, 6.2; N, 15.3%).

Under the same conditions were obtained *product* (**2b**), yellow needles (from nitroethane), m.p. 68—70 °C, yield 52% (Found: C, 63.8; H, 6.95; N, 14.05. $C_{16}H_{19}N_3O_2{\cdot}H_2O$ requires C, 63.35; H, 7.0; N, 13.85%); *product* (**2c**), yellow needles (from nitroethane), m.p. 113—115 °C, yield 72% (Found: C, 55.8; H, 6.4; N, 13.0. $C_{15}H_{17}N_3O_3{\cdot}2H_2O$ requires C, 55.7; H, 6.55; N, 13.0%); and *product* (**2d**), yellow needles (from nitroethane), m.p. 100 °C (decomp.), yield 79% (Found: C, 61.6; H, 7.0; N, 12.2. $C_{17}H_{21}N_3O_3{\cdot}H_2O$ requires C, 61.2; H, 6.95; N, 12.6%).

Photochemical Reactions.—Solutions of compounds (**1**) and (**2**) (5×10^{-3}M) were irradiated in an immersion well apparatus at 17 °C by means of a Pyrex-filtered medium-pressure mercury arc (Philips HPK, 125 W). Irradiation times and solvents are reported in Tables 1 and 3. The reactions were followed by absorption spectroscopy and t.l.c. The solutions were then evaporated and the residues chromatographed on silica gel, eluted first with various cyclohexane–benzene–ethyl acetate mixtures, then with chloroform–methanol mixtures. The procedure for the thermal reactions was analogous.

The isolated products were compared with reference compounds. The azo derivatives (**3**)—(**5**) were obtained by standard procedures, the formyl derivatives (**6**) by refluxing the monomethyl derivatives (**4**) with formic acid,[28] and the amino azoxy derivatives (**9**) by reported procedures.[29]

Quantitative Measurements.—The quantum yields for decomposition of products (**1a**) and (**2a**) were measured with 2×10^{-4}M-solutions in spectrophotometric couvettes. The light source was a high-pressure Osram HBO W/2 mercury arc monochromatized by means of interference filters. Light intensity was measured by ferrioxalate actinometry. Product decomposition was followed by u.v. absorption and h.p.l.c. measurements.

Acknowledgements

This work was supported in part by a grant from the Ministry of Education.

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Received 14*th October* 1985; *Paper* 5/1762