The Photochemistry of Azo-dyes. The Wavelength-dependent Photoreduction of 4-Diethylamino-4'-nitroazobenzene

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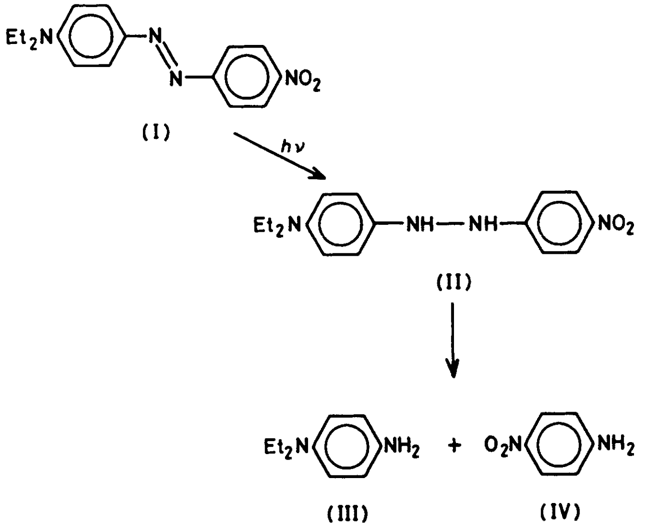
4-Diethylamino-4'-nitroazobenzene (I) is photoreduced upon irradiation at 254 nm, and in alcohols, also at 313 nm, while visible light is inactive. The products are the corresponding hydrazo-derivative (II) or the amines (III) and (IV). Triplet sensitizers of sufficiently high energy are effective, while the lowest triplet is not reduced. The reaction is inhibited by nitroxyl radicals. A mechanism implying hydrogen-abstraction on the part of some high lying triplet states of *trans*-(I) is proposed. Other than by energy transfer, these states can be reached by intersystem crossing from high lying singlet states.

THE irradiation of azobenzene in several solvents has been shown to cause three reactions, namely *trans–cis*-isomerisation, which occurs with quantum yield 0.1—0.3 depending on the choice of the solvent and of the wavelength of irradiation,[1] reduction, which occurs with a much lower quantum yield, *e.g.* 0.018 in Pr^{i}OH,[2] and electrocyclic reaction followed by oxidation to benzo[*c*]cinnoline, which has been observed only in strongly acidic medium and also with a low quantum yield.[3]

Much less is known about the photochemistry of the derivatives of azobenzene, particularly azo-dyes.[4,5] The occurrence of the *trans–cis* isomerisation has been ascertained also for these compounds by means of spectroscopic [6] or flash-spectroscopic investigation.[7] The *cis*-isomers photochemically generated revert to the *trans*-form at a rate which is generally higher in solvents of higher polarity. In any case they are too unstable to be isolated. The geometrical isomerisation has been observed for azo-dyes adsorbed on polymers as well as in solution; [8] in both cases the thermal reversion to the *trans*-form takes place with first-order kinetics. Despite the potential significance of the reductive pathway in the photofading of azo-dyes,[9] † the photoreduction of these compounds has been the subject of only one systematic investigation. In their study, Irick and Pacifici [11] measured the fading of the visible absorption of degassed 2.4×10^{-4} M solutions of 4-diethylamino-4'-nitroazobenzene (I) by irradiating at 254 nm in several solvents and, for the case of Pr^{i}OH, also at 310 and 366 nm. The disappearance quantum yields thus calculated for (I) are 4.8, 2.8, and 1.4×10^{-4}, respectively, for the irradiation at 254, 310, and 366 nm in Pr^{i}OH.[11] These authors observed that (I) was rapidly and completely regenerated on readmitting air into the irradiated samples and therefore they identified the photoproduct as the hydrazo-derivative (II).

Our preliminary experiments showed that the anaerobic irradiation, in a preparative reactor, of diluted (5×10^{-5} M) methanolic solutions of several azo-dyes, among them (I), caused fading at a rate larger by some orders of magnitude when a quartz-filtered rather than a Pyrex-filtered lamp was used. Moreover, (I) was not completely regenerated on readmitting air even for limited (<10%) conversions. This prompted us to a more extensive investigation and we report here our results from the irradiation of deaerated solutions of (I), both in a preparative reactor and in spectrophotometric cells.



SCHEME

EXPERIMENTAL

Materials.—Compound (I) (ACNA) was purified by column chromatography on alumina with toluene as eluant followed by recrystallisation of the key fraction from toluene. The sensitizers were also of commercial origin and were purified by repeated cyrstallisation, checking their purity by t.l.c. 3,3,4,4-Tetramethyldiazetine 1,2-dioxide [12] and 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxide [13] were prepared and purified according to literature methods. Spectroscopic grade solvents were used, without further purification.

Photolysis Procedure.—5×10^{-5} M solutions of (I) were irradiated as follows.

(a) In a preparative reactor (300 ml) by means of a low-pressure mercury arc (Hanau TNN 15) after deaeration by boiling and cooling under argon. The reaction was quen-

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† Another process of potential significance for the photofading, oxidation *via* singlet oxygen, has been documented for some azo-dyes exhibiting azo–hydrazone tautomerism.[10]

ched at *ca.* 10% conversion and the concentrated photolysate examined by t.l.c. (silica gel), g.l.c. (OV 17.3% on Gaschrom Q column, 2 m long), and g.l.c.–mass spectroscopy (Du Pont 492-B spectrometer) by comparison with authentic samples of compounds (III) and (IV).

(b) In spectrophotometric cuvettes (1 cm optical path) after four or five freeze–degas–thaw cycles to *ca.* 5×10^{-6} Torr. The 313, 366, and 434 nm wavelengths were isolated from the collimated beam of a high-pressure mercury arc (Osram 200 w/4) by means of interference filters ($\Delta\lambda_{\frac{1}{2}}$ 9—12 nm). The light intensity was measured by ferrioxalate actinometry with flow rates 3.3 (at 254 nm), 2 (313), and 4.4 (434) $\times 10^{-7}$ einstein min^{-1} over a 3 cm^2 area. The bleaching of the dye was followed by absorbance spectroscopy. In the sensitized experiments the concentrations were adjusted so that the light was completely adsorbed by the sensitizer. Reported values are the average of at least three separate determinations.

RESULTS AND DISCUSSION

In accord with Irick and Pacifici [11] we find that (I) is completely regenerated on readmitting air into a solution in $\mathrm{Pr^iOH}$ after irradiation both to low and high conversions. Thus (II), which appears to be stable for days in the absence of air, can be identified as the photoproduct in this case. On the other hand, solutions in MeOH or cyclohexane irradiated to different degrees of conversion always show a limited reoxidation (<3% of the initial concentration) on readmitting air. Analysis (t.l.c., g.l.c., mass spectrometry) of a methanolic solution of (I) irradiated in the preparative reactor to up to 10% conversion showed the presence of *NN*-diethyl-*p*-phenylenediamine (III) accounting for >50% of the stoicheiometry and, to a lesser extent, of 4-nitroaniline (IV).* The cleavage to aromatic amines is not the consequence of disproportionation of (II), since the spectrum shows no significant variation after a prolonged stay in the dark and, on readmitting air, shows the same partial return. Also, it seems unlikely that (II) undergoes further photoreaction to the amines (III) and (IV) in MeOH, as no such reaction is observed in $\mathrm{Pr^iOH}$. Therefore, the reduction of (II) appears to be caused by further reaction with radicals present in solution.

TABLE 1

Quantum yields for the disappearance of (I) (5×10^{-5} M). Direct irradiation

	$\lambda_{\mathrm{irr.}}$/nm			
Solvent	254	313	366	434
Cyclohexane	3×10^{-3}	$\leqslant 2 \times 10^{-5}$	$\leqslant 2 \times 10^{-5}$	$\leqslant 2 \times 10^{-5}$
Methanol	7×10^{-3}	1.5×10^{-3}	5×10^{-5}	5×10^{-5}
Propan-2-ol	15×10^{-3}			$\leqslant 2 \times 10^{-5}$
Methyl t-butyl ether	2×10^{-3}			$\leqslant 2 \times 10^{-5}$

Chemically sensitized photobleaching (*via* irradiation in acetone–methanol) leads partly to (II), which is reoxidized by air, and partly to (III) and (IV). Table 1 gathers the quantum yields measured for the direct photoreduction of (I) in various conditions and Table 2 the quantum yields for the reduction in the presence of various sensitizers. These data show that the photoreduction of (I) is strongly wavelength-dependent. Thus, irradiation in the first absorption band ($n\pi^*$-charge transfer) has practically no effect, while the photoreduction begins to occur, at least in MeOH, on irradiation at 313 nm, and thus to some higher lying state S_m (see Figure). The reactivity then sharply increases, although the absolute quantum yield is still low, on excitation at 254 nm, say to S_n. This is reminiscent of what was found in the case of azobenzene, where photoreduction requires excitation to higher lying $\pi\pi^*$ states, while the low-lying $n\pi^*$ state is inactive.[2,4]

The data in Table 2 show that, besides the known chemical sensitisation through radical initiation,† triplet energy transfer is also effective in promoting the reduction. Moreover, the energy of the photosensitizer plays an important role. Thus anthracene is wholly ineffective towards photoreduction, although its triplet is higher than the T_1 state of (I), measured at *ca.* 40 kcal mol^{-1} by Schulte-Frohlinde *et al.*[15] On the other hand high-energy sensitizers are effective. In particular, sensitizers with $E_{\mathrm{T}} \geqslant 67$ kcal mol^{-1} cause reduction more effectively than direct irradiation. The values reported for the sensitized reduction are somewhat underestimated, as no correction has been made for the non-unitary intersystem crossing of the sensitizer and transfer efficiently at these low acceptor concentrations.

As for the relationship between photoreduction and photoisomerisation, it must be recalled that *cis*-(I) reverts very quickly to the *trans*-isomer (k_{is} 7×10^{-3} s^{-1} in hexane, 17 s^{-1} in $\mathrm{Pr^iOH}$).[7] In accord with these data we find that in the conditions of our experiments (I_{a} *ca.* 10^{-7} E min^{-1}) in cyclohexane only a low percentage of the

TABLE 2

Quantum yields for the disappearance of (I) (5×10^{-5} M). Sensitized reactions at $\lambda_{\mathrm{irr.}}$ 254 nm

Solvent	Sensitizer	Concentration (M)	Φ_{-1}
Methanol	Benzene	2×10^{-2}	2.4×10^{-2}
	Fluorene	1.2×10^{-3}	2×10^{-3}
	Naphthalene	1.2×10^{-3}	5×10^{-3}
	Anthracene	1.2×10^{-3}	$\leqslant 2 \times 10^{-5}$
	Acetone	1.17	0.18
Cyclohexane	Benzene	2×10^{-2}	4×10^{-3}
	Anthracene	1.2×10^{-3}	$\leqslant 2 \times 10^{-5}$
Methyl t-butyl ether	Benzene	2×10^{-2}	6×10^{-3}

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* This compound is photoreactive in these conditions.

† For the mechanism of the photoreduction in the presence of ketonic sensitizers see ref. 14.

cis-form builds up in steady-state conditions ($\leqslant 2\%$), while in alcohols this percentage is immeasurably low.

Thus it is apparent that the reduction proceeds from some excited state of *trans*-(I), the participation of excited *cis*-(I) being negligible in alcohols and low in cyclohexane, different from the case of azobenzene, where isomerisation followed by excitation to a high-lying triplet of the *cis*-form is the mechanism of the reduction.

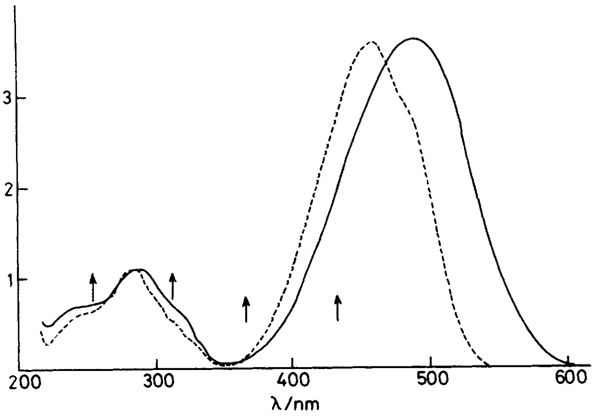

FIGURE Absorption spectra of compound (I) in methanol (——) and cyclohexane (- - - -). Arrows show the irradiation wavelengths

In view of the reactivity of the high-lying triplet state of (I) and of the excessively short lifetime of its singlet excited states (for S_1, τ is in the picosecond range) it appears likely that triplet states are also involved in direct photoreduction. Thus, while for S_1 and T_1, both of charge transfer character, no reaction other than geometric isomerisation is observed, for higher singlet states of $\pi\pi^*$ character there is a non-zero probability of crossing over to high-lying triplets, also of $\pi\pi^*$ character. In the latter states the azo-group abstracts hydrogen from the solvent, while no reaction from the nitro-group is observed, as already noticed by Irick and Pacifici.[11]

The reaction obviously follows a radical pathway. Indeed, apart from the extreme sensitivity to oxygen (reproducible results are obtained only after four–five degassing cycles to $<10^{-5}$ Torr), the photoreaction is quenched by low concentrations of 3,3,4,4-tetramethyldiazetine 1,2-dioxide and 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxide (almost complete suppression with quencher as low as 5×10^{-4} M). The first additive is a known triplet quencher,[12] but here it is acting in the same way as the latter, a well known radical trap, as the short lifetime of the triplet states of (I)* excludes the possibility of triplet quenching by means of the diazetine oxide or oxygen. The trapping activity is specific, since, with other additives, such as 2,6-di-t-butylphenol, the same effect is apparent only at much higher concentration. The oxygen effect may be partly due to the formation of a nitroxyl derivative from the hydrazyl radical formed in the first act of the photoreduction of (I). In propan-2-ol, a more viscous medium with easily abstractable hydrogen, the reaction is simple, leading only to the hydrazo-derivative (II), while in methanol a stepwise pathway is followed, leading in the end to substantial reduction to the amines.

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* For T_1 τ 0.5 ns was measured in methyltetrahydrofuran at − 148 °C.[15]

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