Yields by isotopic dilution were determined by adding labeled product to the initial reaction mixture and recrystallizing the recovered product to constant activity.

Other Peptide Derivatives. Table III reports properties for other peptides prepared in this study. Detailed experimental procedures may be found in Z. Bernstein, Ph.D. Dissertation, Massachusetts Institute of Technology, 1971.

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Registry No.—Z-Gly-L-Leu-GlyOH, 16295-38-8; L-leucine, 61-90-5; 3-carbobenzoxyglycyloxy-2-hydroxy-*N*-ethylbenzamide, 16859-24-8; Z-Gly-L-LeuOH, 1421-69-8; 3-carbobenzoxyglycylleucyloxy-2-hydroxy-*N*-ethylbenzamide, 51876-76-7; glycine, 56-40-6; HGly-L-Leu-GlyOH, 2576-67-2; 2-(Z-Gly-L-Leu-Gly)-*N*-ethylsalicylamide, 51876-77-8; Z(Gly-L-Leu-Gly)$_2$OH, 51876-78-9; H(Gly-L-Leu-Gly)$_2$OH, 2576-71-8; 2-[Z(Gly-L-Leu-Gly)$_2$O]-*N*-ethylbenzamide, 51876-79-0; Z(Gly-L-Leu-Gly)$_4$OH, 51876-80-3; H(Gly-L-Leu-Gly)$_4$OH·HBr, 51876-81-4; 2-[Z(Gly-L-Leu-Gly)$_4$O]-*N*-ethylbenzamide, 51876-82-5; Z(Gly-L-Leu-Gly)$_8$OH, 51876-83-6; H(Gly-L-Leu-Gly)$_8$OH·HBr, 51876-84-7; 2-[Z(Gly-L-Leu-Gly)$_8$O]-*N*-ethylbenzamide, 51876-85-8; Z(Gly-L-Leu-Gly)$_{16}$OH, 51876-86-9; TFA, 76-05-1.

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Photobenzidine Rearrangements. V. Mechanistic Aspects. Rearrangement of Mixtures of Different *N,N'*-Dimethylhydrazo Aromatics, and the Nature of the Excited State[1-3]

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Quantum yields of rearrangement of *N,N'*-dimethyl-*p*-hydrazotoluene (**1a**) to the *o*-semidine (**2a**) under irradiation in cyclohexane solution at 298 nm were unaffected by the triplet quencher, 1,3-cyclohexadiene. None of **2a** could be detected in the products of irradiation at 335 ± 2.5 nm in the presence of the triplet sensitizer, xanthone. The rearrangement appears to occur in the singlet excited state. Irradiation of a mixture of **1a** and *N,N'*-dimethyl-*p*-hydrazobiphenyl (**1d**) at 350 nm led to the formation of a new hydrazo compound, 4-phenyl-*N,N'*,4'-trimethylhydrazobenzene (**1e**). Irradiation of a mixture of *N,N'*-dimethyl-*p*-hydrazoanisole (**1b**) and *N,N'*-dimethylhydrazomesitylene (**1c**) at 300 nm also gave a new hydrazo compound, *N,N'*-2,4,6-pentamethyl-4'-methoxyhydrazobenzene (**1f**). Irradiation of **1f** at 300 nm led to the formation of **1b** and **1c**. Crossed rearrangement products (*i.e.*, crossed semidines) were not found. It is proposed that although radicals are probably involved in the formation of scission products (*N*-methylarylamines), the formation of *o*-semidines may be intramolecular, and the formation of new hydrazo compounds may involve biomolecular, four-center reactions.

In contrast with acid-catalyzed and thermal reactions of hydrazo aromatics,[4,5] little is known about photochemical ones. The few studies that have been made show that hydrazobenzene and ring-substituted hydrazobenzenes are dehydrogenated by irradiation in solution,[6-8] whereas *N,N'*-dimethylhydrazobenzenes rearrange.[6,9] No mechanistic details are known about these rearrangements, however, and the present paper describes our attempts to obtain some understanding of them. We have tried to find if the photochemical rearrangements are intra- or intermolecular and, also, whether they occur in the singlet or triplet excited state. For the former purpose we have carried out rearrangements of mixtures of hydrazo compounds and of one unsymmetrical hydrazo compound and have searched for "crossover" rearrangement products. For the latter purpose we have measured the fluorescence and phosphorescence characteristics of several of the hydrazo compounds, to establish singlet and triplet state characteristics, and have made quantum yield measurements for rearrangement of a representative compound, *N,N'*-dimethyl-*p*-hydrazotoluene (**1a**) in the absence and presence of triplet quenchers.

Results

Irradiation of Mixtures of Hydrazo Aromatics. A. *N,N'*-Dimethyl-*p*-hydrazotoluene (1a) and *N,N'*-Dimethyl-*p*-hydrazobiphenyl (1d). Although **1a** rearranges slowly when irradiated at 300 nm (19% yield after 10 hr),[9] it did not rearrange after 14 hr of irradiation at 350 nm in cyclohexane solution. On the other hand, **1d** rearranged quite readily under the latter conditions. When a mixture of **1a** and **1d** was irradiated in cyclohexane solution at 350 nm for 14 hr at room temperature, almost 90% of the **1a** and 65% of the **1d** were recovered. Rearrangement of **1d** to the *o*-semidine (**2d**) and scission to *N*-methyl-4-aminobiphenyl (**3d**) and 4-aminobiphenyl (**4d**) occurred also. At the same time a new hydrazo aromatic (**1e**) was formed, too (Scheme I).

Scheme I

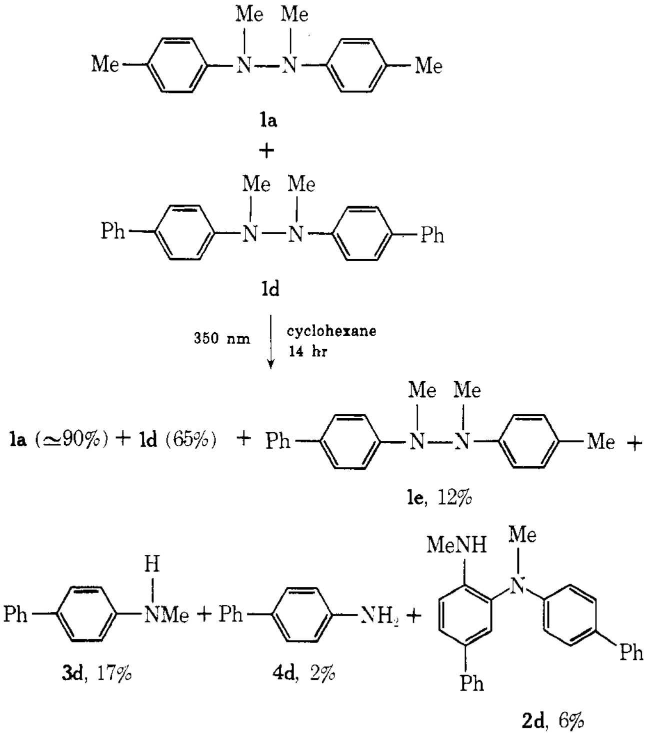


Table I
Quantum Yields of Formation of 2a from 1a in the Presence and Absence of 1,3-Cyclohexadiene (Q)

[Q] × 10^2 *M*	[**1a**]$_0$ × 10^2 *M*	$\Phi \times 10^3$	Φ_0/Φ
0	1.5	5.98[a]	
4.66	1.5	5.33[a]	1.12
8.24	1.5	6.18[a]	0.97
9.15	1.5	4.56[a]	1.31
0	2.0	39.6[b]	
2.65	2.0	38.0[b]	1.04

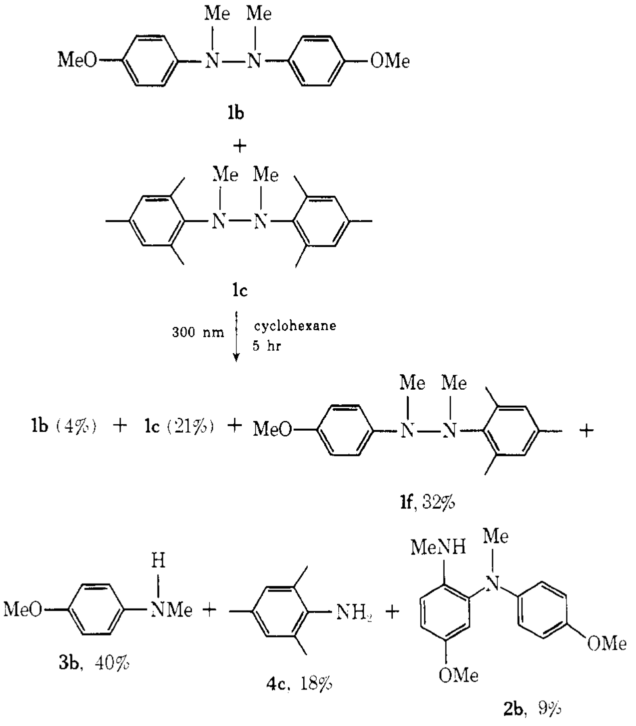
[a] Photolysates were separated by Eastman Chromagram sheet 6060, silica gel with fluorescent indicator, and the *o*-semidine was removed with cyclohexane (spectrograde). Work-up conditions were standardized. [b] Photolysates were separated by tlc on Brinkmann GF-254 silica gel and the *o*-semidine was removed with chloroform.

Authentic **1e** was synthesized, compound **2d** is known from our earlier work,[9] and **3d** and **4d** were suitably identified.

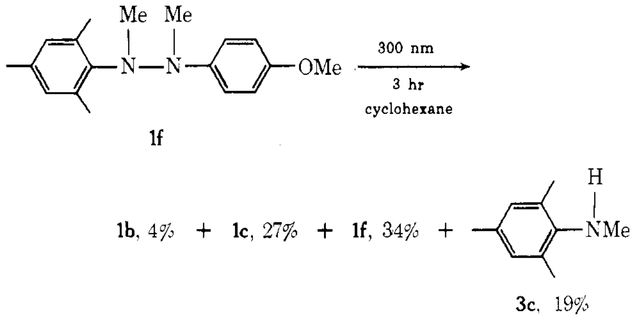
B. *N*-*N'*-Dimethyl-*p*-hydrazoanisole (1b) and *N*,*N'*-Dimethylhydrazomesitylene (1c). When **1b** is irradiated it rearranges to the *o*-semidine (**2b**), while irradiation of **1c** causes scission to *N*-methylmesitylamine (**3c**) and mesitylamine (**4c**).[9] When a mixture of **1b** and **1c** in cyclohexane solution was irradiated at 300 nm for 5 hr at room temperature 4% of the **1b** and 21% of the **1c** were recovered. The *o*-semidine (**2b**), a new hydrazo compound (**1f**), and a number of scission amines were also obtained (Scheme II). Compound **1f** was synthesized for comparison with the compound isolated from this experiment, and for irradiation in solution by itself. All of the other products were known and suitably identified.

Irradiation of *N*,*N'*,2,4,6-Pentamethyl-4'-methoxyhydrazobenzene (1f). Irradiation in cyclohexane solution at 300 nm for 3 hr at 19° gave **1b** (4%), **1c** (27%), **1f** (recovered, 34%), and scission amine **3c** (19%) (Scheme III). *N*-Methyl-*p*-anisidine (**3b**) was not observed in this experiment.

Scheme II



Scheme III



Luminescence and Quenching Experiments. From fluorescence and phosphorescence data the singlet (E_{S_1}) and triplet (E_T) energies of several of the *N*,*N'*-dimethylhydrazo aromatics were calculated. They were found to be in the range 81–88 and 57–66 kcal/mol, respectively (see Experimental Section). One compound, *N*,*N'*-dimethyl-*p*-hydrazotoluene (**1a**), was chosen for detailed quantum yield work. It was found that the quantum yield of formation of the *o*-semidine (**2a**) was not affected by the presence of the triplet-state quencher 1,3-cyclohexadiene. Ratios of Φ_0/Φ were close to 1 for four different concentrations of quencher (Table I). No **2a** was formed when a solution of **1a** and xanthone (E_T = 74 kcal/mol) was irradiated at 335 ± 2.5 nm.

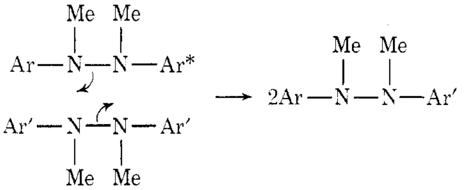
Discussion

The luminescence and quenching results (Table I) indicate that the rearrangement of **1a** to **2a** occurs in the singlet excited state or from singlet-state precursors rather than the triplet state. This would place then the rearrangement of **1a** among some other photoreactions of hydrazo and azo compounds. That is, the photodehydrogenation of hydrazobenzenes to azobenzenes[6-8] appears to be a singlet-state reaction.[8] The photodecomposition of 1,4-diaryl-1,4-dimethyl-2-tetrazenes to *N,N'*-dimethylhydrazoarenes also appears to be a singlet-state reaction,[10] and the role of singlet states in the photodecomposition of azo compounds has recently been summarized and discussed by Engel and Bartlett.[11]

Mechanistic details of the photorearrangement are not yet clear. It is probable that *N*-methylarylamino radicals are formed because *N*-methylarylamines are among the photoproducts. It is not known, though, that it is recombination of these radicals which leads to rearrangement products. Irradiation of a mixture of **1b** and **1c** did not lead to a "crossed" rearrangement product. The *o*-semidine **2b** was obtained, but although **1c** itself cannot rearrange (*i.e.*, there is no analog, **2c**), no rearrangement product corresponding to half of each of **1b** and **1c** was found, although if one had been formed in small amount it could have gone unnoticed. Instead, a new hydrazo compound (**1f**) was formed (Scheme II).

Most interestingly, when a mixture of **1a** and **1d** was irradiated under conditions in which **1d** absorbed over 97% of the incident light, another new hydrazo compound (**1e**) was obtained. Again, a crossed rearrangement product was not found, but, again, may have escaped our finding.

These results suggest that the new hydrazo compounds may be formed by a nonradical route. Collision of an excited hydrazo molecule with another hydrazo molecule could, through a four-center process, lead in principle to a molecule of a new hydrazo compound (eq 1). Such a process, if it



$$\begin{array}{c}\mathrm{Ar{-}N(Me){-}N(Me){-}Ar^{*}} \\ \mathrm{Ar'{-}N(Me){-}N(Me){-}Ar'}\end{array} \longrightarrow 2\mathrm{Ar{-}N(Me){-}N(Me){-}Ar'} \quad (1)$$

occurs, would not appear to involve energy transfer also. None of the rearrangement or scission products, for example, of **1a** was found, whereas those of **1d** (**2d** and **3d**) were. That is, excited **1a** does not seem to have been formed. Under appropriate irradiation conditions **1a** will, of course, rearrange readily.[9]

In line with the formation of a new hydrazo compound from each of the two mixture experiments is the formation of two symmetrical hydrazo compounds (**1b** and **1c**) from an unsymmetrical one (**1f**). *o*-Semidines were again not found, suggesting once more that the hydrazo-forming reaction may be a four-center one, *i.e.*, the reverse of eq 1. The yields of **1b** and **1c** were unequal (4 and 27%), but this may have been caused by the difficult separation and isolation problems encountered.

The overall picture emerging from these photoreactions is that *N,N'*-dialkylhydrazobenzenes rearrange (in contrast with the unalkylated parents) and probably intramolecularly, but this is as yet by no means certain.

Experimental Section

Hydrazo compounds **1a–d** were described earlier.[9]

4-Methyl-4'-phenylazobenzene (5e). A mixture of 5.7 g (47.1 mmol) of *p*-nitrosotoluene[12] and 8 g (47.3 mmol) of 4-aminobiphenyl in 40 ml of ethanol and 10 ml of acetic acid was boiled for 30 min. On cooling, 7.0 g (54%) of **5e**, mp 138–141°, crystallized. Recrystallization from ethanol gave mp 144.5–145°.

Anal. Calcd for $C_{19}H_{16}N_2$: C, 83.8; H, 5.92; N, 10.3. Found: C, 83.7; H, 6.21; N, 10.4.

4-Methyl-4'-phenylhydrazobenzene (6e). A suspension of 5 g (18.3 mmol) of **5e** in a mixture of 50 ml of pyridine, 15 ml of acetic acid, and a small amount of acetone was kept on an ice bath. Small amounts of zinc powder were added until the solution was colorless. The filtrate was poured into 400 ml of ice water and the precipitate obtained was dried under vacuum, giving 4.7 g (17.2 mmol, 94%) of 4-methyl-4'-phenylhydrazobenzene (**6e**): mp 105–106° dec; nmr (CCl_4) δ 2.18 (s, 3), 5.17 (s, 1), 5.25 (s, 1), 6.35, 6.58, and 6.75 (3 d, 6), 7.15 (m, 7).

4-Phenyl-*N,N'*,4'-trimethylhydrazobenzene (1e). To a cold solution of 4.5 g of **6e** in 80 ml of dry THF was added 8 ml of *n*-butyllithium solution (commercial, 90% in hydrocarbon). The red solution was stirred until hydrogen evolution ceased, and 10 ml of methyl iodide was added dropwise. After stirring for a further 45 min, 100 ml of ether was added, and the solution was washed with 3 × 100 ml of water, dried over K_2CO_3, and evaporated to give 6.7 g of yellow oil. This was crystallized from *n*-hexane containing a very small amount of ether to give 4.2 g (85%) of **1e:** mp 52–54°; nmr (CCl_4) δ 2.17 (s, 3), 2.83 (s, 6), 6.46 and 6.75 (2 d, 6), 7.11 (m, 7).

Anal. Calcd for $C_{21}H_{22}N_2$: C, 83.4; H, 7.33; N, 9.26. Found: C, 83.6; H, 7.37; N, 9.45.

***N,N'*,2,4,6-Pentamethyl-4'-methoxyhydrazobenzene (1f).** This was prepared by methylation of the azo compound (**5f**). 4-Methoxyphenylhydroxylamine (**7**), mp 86–94°, was prepared by the reduction of *p*-nitroanisole with zinc and NH_4Cl.[13] Oxidation of **7** with aqueous ferric chloride gave *p*-nitrosoanisole (**8**) as a green oil (lit. mp 23°). A solution of 4.8 g (35 mmol) of **8** and 5.0 g (37 mmol) of mesidine (**4c**) in a mixture of 50 ml of ethanol and 35 ml of acetic acid was boiled for 1 hr and stirred at room temperature for 2 hr. The ethanol was removed under reduced pressure, ether was added, and the solution was washed with 2 × 100 ml of saturated $NaHCO_3$ and 3 × 100 ml of 10% HCl, dried over $MgSO_4$, and evaporated to give 6.9 g of brown oil. Chromatography on a silica gel column using 95:5 petroleum ether–ether gave 3.4 g (38%) of 4-methoxy-2',4',6'-trimethylazobenzene (**5f**): mp 65–66° (methanol); nmr (CCl_4) δ 2.30, 2.40 (2 s, 9), 3.82 (s, 3), 6.92, 6.97 (m, 4), 7.93 (d, 2).

Anal. Calcd for $C_{16}H_{18}N_2O$: C, 75.6; H, 7.13; N, 11.0. Found: C, 75.3; H, 7.18; N, 11.3.

A solution of 5.06 g (19.8 mmol) of **5f** in dry THF was stirred under nitrogen with 1.2 g (43.5 mmol) of sodium for 23 hr, and 13 ml of methyl iodide was added dropwise at 0°. After stirring at room temperature for 4 hr the solution was filtered and evaporated to give a residue which was extracted by trituration with ether. The ether solution was evaporated and the orange-yellow solid was crystallized from ether–methanol, giving 3 g (10.5 mmol, 53%) of **1f:** mp 110–111°; nmr (CCl) δ 2.18, 2.20 (2 s, 9), 2.83, 2.88 (2 s, 6), 3.70 (s, 3), 6.75 (m, 6).

Anal. Calcd for $C_{18}H_{24}N_2O$: C, 76.1; H, 8.51; N, 9.85. Found: C, 76.2; H, 8.27; N, 10.0.

Irradiation Equipment and Method. Irradiations were carried out with a Rayonet reactor "Merry-Go-Round" Model Type RS. The top opening of the reactor was connected to the output of an air conditioner by flexible conduit so that the whole of the inside of the reactor could be flushed continuously with cold air. In this way an ambient temperature of 15–25° was maintained. Irradiation at 300 and 350 nm means that banks of 300- and 350-nm lamps were used. Solutions for irradiation were degassed by three cycles of freeze–thaw technique and were sealed before being placed in the reactor. Silica vessels were used for 300-nm and Pyrex vessels were used for 350-nm irradiations. Cyclohexane solvent was from Eastman Kodak, spectrograde, and was used without further treatment.

Irradiation of *N,N'*-Dimethyl-*p*-hydrazotoluene (1a), *N,N'*-Dimethyl-*p*-hydrazobiphenyl (1d), and a Mixture of 1a and 1d. Control Experiments. Three tubes were used. One contained 240 mg (1.0 mmol) of **1a** in 150 ml of cyclohexane. The second contained 364 mg (1.0 mmol) of **1d** in 150 ml of cyclohexane. The third contained a mixture of 48 mg (0.20 mmol) of **1a** and 73 mg (0.20 mmol) of **1d** in 30 ml of cyclohexane, and was wrapped in aluminum foil to prevent access of light. The purpose of wrapping was to test the stability of the mixture to the reactor environment. The three tubes were irradiated with 350-nm lamps for 14 hr, opened, and examined by tlc on Eastman Kodak Chromagram sheets 6060 silica gel, using as solvent a mixture of 55 ml of *n*-hexane, 10 ml of benzene, 5 drops of ethanol, and 10 drops of acetone. The solution from **1a** showed only one spot corresponding to **1a.** However, column chromatography on alumina (Fisher, 80–200 mesh) gave 207 mg (86%) of **1a** and 23 mg (9.6%) of *N*-methyl-*p*-toluidine (**3a**). The solution from **1d** showed four spots corresponding to **1d**, the *o*-semidine (**2d**), *N*-methyl-4-aminobiphenyl (**3d**), and 4-aminobiphenyl (**4d**). The solution containing **1a** and **1d**

showed spots of **1a** and **1d** only. Column chromatography gave quantitative separation and recovery of the two components. No scission or rearrangement products were observed.

Irradiation of a Mixture of 1a and 1d. A solution of 311 mg (1.29 mmol) of **1a** and 365 mg (1.0 mmol) of **1d** in 150 ml of cyclohexane was irradiated at 350 nm for 14 hr. Evaporation of the solvent and trituration of the solid residue with *n*-hexane left 176 mg (48%) of **1d.** The hexane solution was chromatographed on an alumina column, using petroleum ether, mixtures of petroleum ether–ether, and finally ether as the eluent. A total of 66 75-ml fractions was collected. Fractions 1–26 (petroleum ether) gave 313 mg (100%) of crude **1a,** from which by trituration with cold ethanol was obtained 227 mg (73%) of **1a,** mp 64.5–65.5°, mmp with **1a** 64.5–66.5°. Fractions 27–37 (95:5 petroleum ether–ether) gave 38 mg (12.5%) of a yellow oil whose nmr and mass spectrum (parent peak *m/e* 302) corresponded with those of **1e.** Crystallization gave mp 48.5–50.5° (ethanol). Fractions 38–41 (90:10) gave 5.2 mg of a three-component mixture which was discarded. Fractions 42–49 (90:10) gave 77.6 mg of yellow solid from which trituration with ethanol gave 62 mg of **1d,** mp 177–178°. The total recovery of **1d,** therefore, was 65%. Fractions 50–54 (90:10) and 55–66 (85:15) gave 23 mg (6.4%) of the *o*-semidine **2d,** as shown by tlc, nmr, crystallization to give mp 168–169.5° (ethanol–chloroform), and undepressed mixture melting point with authentic **2d.**[9] Elution of the column with 1 l. of solvent (60:40) gave 61 mg (17%) of **3d** as shown by tlc, nmr, benzenesulfonyl derivative, mp 150–152°, and undepressed mixture melting point.[9] Final wash of the column with 400 ml of ether gave 8.4 mg (2%) of **4d,** as shown by tlc.

Irradiation of *N,N'*,2,4,6-Pentamethyl-4'-methoxyhydrazobenzene (1f). A solution of 500 mg (1.76 mmol) of **1f** in 200 ml of cyclohexane was irradiated at 300 nm for 3 hr at 15–20°. Removal of solvent gave 650 mg of brown solid which was chromatographed on alumina as described above. Fractions 1–3 (petroleum ether) gave 70 mg (27%) of an oil which was crystallized from ethanol to give **1c,** mp 117–118°, mmp with authentic **1c** 117–118°. Fractions 10–12 (95:5) gave a solid from which by trituration with cold methanol was obtained 170 mg (34%) of **1f,** mp and mmp 115–116°. Evaporation of the methanol gave 50 mg (19%) of an oil, shown by nmr and benzenesulfonyl derivative (mp and mmp 117–119°) to be *N*-methylmesitylamine (**3c**). Fractions 18 and 19 (90:10) gave 28 mg of an oily solid, from which trituration with cold methanol gave 10 mg (4.0%) of **1b,** mp 105–106°, mmp with authentic **1b**[9] 104–105.5°. Other fractions gave a total of 160 mg of unidentified oils.

Irradiation of a Mixture of *N,N'*-Dimethyl-*p*-hydrazoanisole (1b) and *N,N'*-Dimethylhydrazomesitylene (1c). A solution of 300 mg (1.09 mmol) of **1b** and 500 mg (1.69 mmol) of **1c** in 450 ml of cyclohexane was irradiated at 300 nm for 5 hr at 15–25°. Chromatography was carried out on a basic alumina (Alcoa F-20) column. Elution with 500 ml of petroleum ether gave 104 mg (21%) of **1c,** mp and mmp 115–116°. Elution with 500 ml of 90:10 petroleum ether–ether mixture gave 200 mg (32%) of **1f,** mp 111–112°, identified by nmr, elemental analysis, and comparison with authentic **1f.** Elution with 500 ml of 85:15 mixture gave 84 mg (18%) of mesitylamine (**4c**), identified by its dibenzenesulfonyl derivative, mp and mmp 178.5–179.5°.[9] Elution with 500 ml of 80:20 mixture gave 44 mg of residue from which trituration with petroleum ether gave 14 mg (4%) of **1b,** identified by nmr, melting point, and mixture melting point (103–104°). Elution with 500 ml of 70:30 mixture gave 24 mg of unidentified oil. Further elution with 500 ml of 70:30 mixture gave 27 mg (9%) of the *o*-semidine **2b,** identified by nmr.[9] Finally, elution with 500 ml of ether gave 120 mg (40%) of *N*-methyl-*p*-anisidine (**3b**), identified by nmr.

Extinction Coefficients of 1a and 1d. These compounds have similar spectra but quite different absorbancies. For **1a,** at λ_{max} 296 nm, ϵ is 4.7×10^4. Values of ϵ at 5-nm intervals were calculated, and are given as λ ($\epsilon_{(1a)}$, $\epsilon_{(1d)}$): 320 (435, 14,250), 325 (79, 7170), 330 (13, 2590), 335 (3, 732), 340 (2, 198), 345 (~1–2, 54), 350 (~1–2, 17). It was calculated from the lamp output characteristics supplied by Rayonet and the transmission of Pyrex glass that in the irradiation of the mixture of **1a** and **1d** (see above) with a 350-nm lamp 97% of the light between 320 and 350 nm was absorbed by **1d.**

Singlet and Triplet Energies of *N,N'*-Dimethylhydrazo Compounds. Fluorescence spectra of these compounds in cyclohexane and phosphorescence spectra in either ethanol or cyclohexane were taken at 77°K with an Aminco-Bowman spectrophotofluorometer. An estimate of the fluorescence 0–0 band was made from the point of intersection of fluorescence excitation and emission bands. An estimate of the lowest singlet energy (E_{S_1}) was made either from the 0–0 band or as the average of E_a and E_s, where E_a is the energy at the absorption maximum and E_s the energy at the fluorescence emission maximum.[14] An estimate of the triplet energy (E_T) was made from the phosphorescence band. Values of E_{S_1} were, for **1a, 1b, 1c, 1d,** and **1f,** 88, 81, 88, 84, and 85 kcal/mol. Values of E_T were, for **1a, 1b, 1d,** and **1f,** 66, 63, 57, and 64 kcal/mol. The difference between E_{S_1} and E_T for each compound indicates that in each case π–π^* excitation occurred. It is recognized that these methods of measuring excitation energies are not exact. Attempts were made to obtain a high-resolution phosphorescence spectrum of **1a** for the precise calculation of E_T from the 0–0 phosphorescence band, but sufficient resolution could not be obtained.[15] Knowledge of E_T was necessary for planning the triplet quenching experiments. Triplet lifetimes were measured from phosphorescence decays plotted on an *x–y* recorder, and were, for **1a, 1b,** and **1d,** 1.6, 1.2, and 3.7 sec. Phosphorescence of **1c** was too weak for making triplet data measurements.

Triplet Quenching of 1a. Quantum yields for the formation of the *o*-semidine (**2a**) were measured. Three milliliters of a degassed and sealed solution of **1a,** with or without quencher, in cyclohexane was irradiated at 298 nm for 8 hr at 18–20° in a Bausch and Lomb monochromator. The instrument slits were set for a 10-nm band pass. The solution was evaporated, and the residue was dissolved in 1 ml of cyclohexane and streaked on a silica gel tlc plate. The **2a** band was removed and assayed by uv spectroscopy. Light intensities were measured before and after irradiation by the method of Hatchard and Parker.[16] Results using 1,3-cyclohexadiene (E_T = 54 kcal/mol)[17] as quencher (Q) are given in Table I.

Triplet Sensitization of 1a (Attempted). Monochromatic Irradiation. Four milliliters of a solution which was 1.02×10^{-3} *M* in xanthone (E_T = 74 kcal/mol) and 1.5×10^{-2} *M* in **1a** was degassed, sealed, and irradiated at 335 ± 2.5 nm for 9 hr in a Bausch and Lomb monochromator, Model 33-86-07. The solution was cooled externally by circulating water at 20°. After irradiation the solution was evaporated at room temperature in a rotary evaporator and the residue was taken up in ethanol and spotted on a silica gel sheet (Eastman Chromagram 6060). Development with a mixture of 40 ml of cyclohexane, 15 ml of benzene, and 0.3 ml of acetone, and monitoring with authentic samples, showed the presence of **1a** (R_f 0.46), and *N*-methyl-*p*-toluidine (**3a,** R_f 0.26). No trace of the *o*-semidine)**2a,** R_f 0.43) was seen. An unknown compound, R_f 0.36, λ_{max} (ethanol) 253 and 301 nm, was formed. Compound **2a** has λ_{max} 247 and 303 nm, and **1a** has λ_{max} 253 and 298 nm. Authentic **2a** was added to the product mixture and was readily separated from these three compounds by tlc. Two-directional tlc also failed to show the presence of **2a** in the product mixture.

The absorbance of xanthone at 335 nm is approximately 550 times greater than that of **1a,** so that under the conditions used ample opportunity existed for excitation of xanthone and energy-transfer from excited xanthone to **1a** (E_T = 66 kcal/mol).

Registry No.—**1a,** 30724-66-4; **1b,** 30724-67-5; **1c,** 30788-04-6; **1d,** 30788-03-5; **1e,** 52032-51-6; **1f,** 52032-52-7; **2a,** 30724-68-6; **2b,** 30745-00-7; **2d,** 30724-70-0; **3a,** 623-08-5; **3b,** 5961-59-1; **3c,** 13021-14-2; **3d,** 3365-81-9; **4c,** 88-05-1; **4d,** 92-67-1; **5e,** 30821-46-6; **5f,** 52032-53-8; **6e,** 52032-54-9; **7,** 4546-20-7; **8,** 1516-21-8; *p*-nitrosotoluene, 623-11-0.

References and Notes

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