colorless liquid: IR (film) 2.9, 3.4, 8.02, 11.7, 11.9 μm; NMR (CCl_4) δ 3.64 (m, 1 H), 1.7–0.7 (20 H), 0.00 (s, 9 H); mass spectrum, *m/e* (relative intensity) 212 (2, $M^+ - H_2O$), 201 (3), 145 (2), 140 (6), 138 (9), 97 (10), 84 (10), 83 (9), 75 (38), 73 (100). VPC analysis[24f] (165 °C, retention time for $C_{15}H_{32}$ = 7.7 min) showed the major peak (98% of peak area) at 7.7 min.

A β-elimination reaction under acidic conditions was carried out with a solution of 198 mg (0.86 mmol) of **12** in 10 mL of methylene chloride to which was added 0.50 mL (560 mg, 3.9 mmol) of BF_3·Et_2O. The resulting solution was stirred at room temperature for 1 h. Saturated $NaHCO_3$ (10 mL) was added, and the organic layer was separated. The aqueous layer was extracted with three portions of ether. The combined organic layers were dried ($MgSO_4$), concentrated, and evaporatively distilled (room temperature), yielding 108 mg (89.6%) of clear liquid having IR and NMR spectra and a VPC retention time identical with those of a commercial sample of *trans*-3-decene.

A β-elimination reaction under basic conditions was carried out with a suspension of pentane-washed potassium hydride (from 558 mg of a 24% slurry in oil, 3.3 mmol) in 10 mL of THF to which was added 246 mg (1.07 mmol) of **12**. The resulting mixture was stirred for 1 h at room temperature. Saturated NH_4Cl (5 mL) was added, and the resulting mixture was poured into water overlaid with pentane. The organic layer was separated, washed with two portions of water, dried ($MgSO_4$), concentrated, and evaporatively distilled (50 °C), yielding 135 mg (90%) of clear liquid having IR and NMR spectra and a VPC retention time identical with those of a commercial sample of *cis*-3-decene.

As *cis*- and *trans*-3-decene were not separable with our VPC conditions, the isomeric purity of the elimination products was determined by using the derived epoxides, which were prepared by treatment of the β-elimination products with *m*-chloroperbenzoic acid in methylene chloride in the presence of Na_2HPO_4. (The products had IR and NMR spectra identical with those of samples of *trans*- and *cis*-3-decene oxide[30] prepared by analogous epoxidations of commercial samples of *trans*- and *cis*-3-decene.) VPC analysis[24g] (110 °C) of the product derived from β elimination under acidic conditions showed two major peaks (99% of peak area) at 11.9 and 14.3 min in a ratio of 97:3, corresponding to *trans*-3-decene oxide and *cis*-3-decene oxide, respectively. VPC analysis[24g] (110 °C) of the product derived from β elimination under basic conditions showed two major peaks (>99% peak area) at 11.9 and 14.3 min in a ratio of 2:98, corresponding to *trans*-3-decene oxide and *cis*-3-decene oxide, respectively.

Acknowledgment. We thank the National Science Foundation and the Research Council of Rutgers University for their support of portions of this work.

Registry No. **1**, 16722-09-1; **2**, 56183-59-6; **3**, 60484-84-6; **4**, 74844-81-8; **4** acetate, 74844-82-9; **5**, 60484-89-1; **6**, 74844-83-0; **7**, 52917-13-2; **8**, 60484-84-6; **9**, 55095-11-9; **10**, 74844-84-1; **11**, 62427-10-5; **12**, 74844-85-2; *trans*-4-octene, 14850-23-8; *cis*-4-octene, 7642-15-1; *trans*-3-decene, 19150-21-1; *cis*-3-decene, 19398-86-8; *trans*-3-decene oxide, 54724-75-3; *cis*-3-decene oxide, 54724-74-2; *n*-butyl bromide, 109-65-9; *n*-propyl bromide, 106-94-5; ethyl bromide, 74-96-4.

(30) W. Dumont and A. Krief, *Angew. Chem., Int. Ed. Engl.*, **14**, 350–351 (1975).

Photobenzidine Rearrangements. 6. Mechanism of the Photodecomposition of 1,4-Diaryl-1,4-dialkyl-2-tetrazenes[1,2]

Dong-Hak Bae and Henry J. Shine*

Department of Chemistry, Texas Tech University, Lubbock, Texas 79409

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The photodecompositon of the tetrazene *p*-$XC_6H_4N(Me)N{=}N(Me)NC_6H_4Y$-*p* (**1e**, X = Y = Me) in dimethoxyethane (DME) gave 47.4% of *p*-$XC_6H_4(Me)NN(Me)C_6H_4Y$-*p* (**2e**, X = Y = Me) and 39.6% of *N*-methyl-*p*-toluidine. When irradiation was carried out in the presence of increasing initial concentrations of *n*-BuSH, the yield of **2e** fell and leveled off at 6%. Similar experiments in cyclohexane showed that the yield of **2e** fell from 45.1% and leveled off at 10%. The data indicate that **1e** decomposes by a radical pathway and that the **2e** is formed partly within and partly outside of a solvent cage. Similar studies with **1d** (X = Me, Y = CO_2Et) in DME gave three hydrazines: **2d** (X = Me, Y = CO_2Et) in 13% and 14.7% yield, **2e** in 7.3% and 8.0% yield, and **2f** (X = Y = CO_2Et) in 14.9% and 21.2% yield. The formation of three hydrazines again indicates the formation and intermolecular recombination of methylarylamino radicals. Irradiation of **1d** in DME solutions containing *n*-BuSH caused a fall in the yield of **2e** to zero and a leveling off in the yield of **2d** to 6%. The yield of **2f** also fell but could not be monitored at high concentrations of *n*-BuSH because of overlapping high-pressure LC peaks. The results with **1d** are also consistent with a cage-recombination process (for **2d**) and an intermolecular recombination of radicals (for **2d–f**). The methylarylamines *p*-XC_6H_4NHMe and *p*-YC_6H_4NHMe (X = Me; Y = CO_2Et) were also formed from **1d**. A sixth product was the bis(arylamino)methane *p*-$YC_6H_4NHCH_2NHC_6H_4Y$-*p* (**4f**, Y = CO_2Et) in 14–32% yield (three runs). The origin of **4f** is believed to be the disproportionation of radicals *p*-YC_6H_4NMe, giving *p*-YC_6H_4NHMe and *p*-$YC_6H_4N{=}CH_2$ (**7f**). Hydrolysis of **7f** (by small amounts of water in the solvent) to *p*-$YC_6H_4NH_2$ (**6f**) and HCHO followed by addition of **6f** to **7f** would give **4f**. HCHO was found as a volatile product after irradiation. The formation of **4f** is further evidence for the formation and intermolecular reaction of arylamino radicals in the photodecomposition of 1,4-dialkyl-1,4-diaryl-2-tetrazenes.

1,4-Diaryl-1,4-dialkyl-2-tetrazenes have a prominent absorption band in the region of 350 nm. When irradiated in this region in solution such a tetrazene decomposes readily, losing nitrogen and forming a 1,2-diaryl-1,2-dialkylhydrazine. Decomposition appears to involve a singlet excited state,[3] but the mechanism of this conversion of a tetrazene into a hydrazine is not known with certainty. Analogous thermal conversions have received quite a lot of attention and are thought with little doubt to involve the formation and recombination of alkylarylamino radicals.[4–6] There is also firm evidence that radicals are

(1) Supported by Grant No. D-028 from the Robert A. Welch Foundation.

(2) Part 5: Cheng, J.-D.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 2835.

(3) Hull, V. J.; Shine, H. J. *J. Am. Chem. Soc.* **1973**, *95*, 8102.

(4) Nelsen, S. F.; Heath, D. H. *J. Am. Chem. Soc.* **1969**, *91*, 6452.

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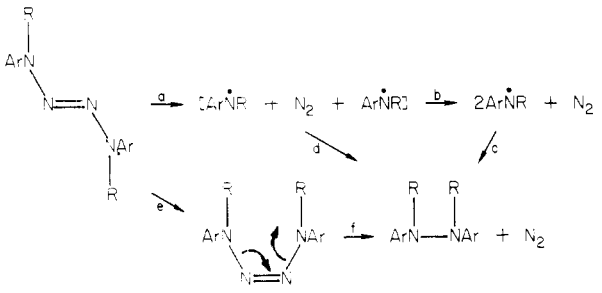
Scheme I

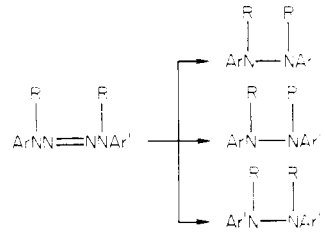


formed in the photodecomposition of tetrazenes. In particular, Nelsen and co-workers have measured spin densities in radicals obtained from 1,4-diaryl-1,4-di-*tert*-butyl-2-tetrazenes and have shown the radicals to be members of Walter's "class S" radicals.[7] Triplet radical pairs were detected from photolyses at low temperatures.[8] Also, Cheng and Shine have trapped *N*-ethyl- and *N*-methylanilino radicals, obtained from the corresponding tetrazenes, with nitrosoarene spin traps.[9] Circumstantial evidence for the formation of an alkylarylamino radical has always been present, too, in the formation of an alkylarylamine which accompanies formation of the hydrazine.[3,9] 1,2-Diaryl-1,2-dialkylhydrazines are also photolabile, but at wavelengths in the region of 250 nm. Irradiation in this region causes benzidine-type rearrangements.[2,10,11] The hydrazines are stable to irradiation in the region of 350 nm over the period of time in which a tetrazene decomposes completely.[9] Therefore, the formation of *N,N'*-diethyl-*N*-phenyl-*p*-phenylenediamine (formally a product of rearrangement of *N,N'*-diethylhydrazobenzene) from irradiation of 1,4-diethyl-1,4-diphenyl-2-tetrazene at 350 nm is also circumstantial evidence for the formation and recombination of *N*-ethylanilino radicals.[9]

In spite of the direct and indirect evidence for the formation of alkylarylamino radicals, there is no direct evidence that shows that a hydrazine is formed by recombination of these radicals in the photoconversion of a tetrazene. Assuming that a tetrazene has the trans geometry in its usual state, one can set out the possible pathways for photoconversion as in Scheme I. The paths ad and abc are caged-radical and free-radical recombinations as are frequently found in radical reactions. The path ef is nonradical and would require the photoisomerization of the tetrazene to an excited cis configuration followed by a [2 + 2] pericyclic reaction to give the product.

Distinction between paths abc and ad can be made, in principle, by conventional trapping methods. In principle, also, distinction between path ef and the others can be made with nitrogen CIDNP. To do this one would need to make a tetrazene containing, say, ^{15}N in the 1,4-positions and also two different substituents in, say, the aryl groups so as to supply alkylarylamino radicals with different *g* values. In those circumstances, paths abc and ad, if they occurred, would produce CIDNP effects in the product's ^{15}N NMR spectrum. The complexity of products which

Scheme II



one obtains from working with an unsymmetrical tetrazene (shown later) and the anticipated complexity of NMR data that would result make the CIDNP approach somewhat unattractive. In order to provide insight into the photoconversion, therefore, we have chosen to work with trapping methods and also with an unsymmetrical tetrazene. The objective was to prepare an unsymmetrical tetrazene and to find (a) whether one or three hydrazines were formed (Scheme II) and (b) if hydrazine formation could be prevented by introducing a radical trap. Formation of three hydrazines would be evidence for the formation and recombination of ArNR and Ar'NR, (path abc) while radical trapping would also give a measure of cage recombination (path ad) or intramolecular cyclization (path ef).

Results

Products from the Irradiation of 1d. An unsymmetrical tetrazene (1) can be made by the oxidation of a mixture of two *N*-methylhydrazines (eq 1). Three tet-

$$XC_6H_4N(Me)NH_2 + YC_6H_4N(Me)NH_2 \rightarrow XC_6H_4N(Me)N{=}NN(Me)C_6H_4Y \quad (1)$$
$$1$$

razenes are produced, from among which it is necessary to separate the unsymmetrical one. Our first attempt to do this with X = 4-H and Y = 4-Br failed. Oxidation proceeded well, but we were unable to separate the unsymmetrical tetrazene **1c** (X = 4-H, Y = 4-Br) from the other two, **1a** (X = Y = 4-H) and **1b** (X = Y = 4-Br). Therefore, we oxidized a mixture of *N*-methyl-*p*-tolylhydrazine and methyl-*p*-(ethoxycarbonyl)phenylhydrazine according to Nelsen's procedure.[4] The mixture of tetrazenes was separable by column chromatography and gave us **1d** (X = 4-Me, Y = 4-CO_2Et). The symmetrical tetrazenes **1e** (X = Y = 4-Me) and **1f** (X = Y = 4-CO_2Et) were obtained but were also made by separate oxidations of the appropriate hydrazines. The three tetrazenes **1d–f** were used for the present study.

Irradiation of 1d in Dimethoxyethane. Irradiation of **1d** was carried out on degassed, approximately 2×10^{-3} M solutions in dimethoxyethane (DME) at ambient temperature. Pyrex vessels were used, and the irradiation was performed with Rayonet U-tube lamps whose major output was in the region of 350 nm. During the short irradiation times (50–60 min) the temperature within the reactor stayed within the range of 20–26 °C. A control run in which the vessel was shielded from light by being wrapped in aluminum foil showed that a solution of **1d** was stable under these circumstances in the dark. The disappearance of **1d** was monitored by thin-layer chromatography (TLC) and by absorption spectroscopy. For this purpose, 1-mL aliquots were withdrawn at 5-min intervals and diluted quantitatively with 95% ethanol. The spectroscopic monitoring showed that all of the tetrazene decomposed within about 50 min. In another sense the spectroscopic work was deceptive, however, in that the changes in the spectrum, as time increased, went through a clean isosbestic point, suggesting that a very simple conversion of **1d** into product had occurred. This can be seen in Figure

(5) Nelsen, S. F.; Landis, R. T., II *J. Am. Chem. Soc.* **1973**, *95*, 8707.
(6) Oda, T.; Maeshima, T.; Sugiyama, K. *Makromol. Chem.* **1978**, *179*, 2331.
(7) Nelsen, S. F.; Landis, R. T.; Kiehle, L. H.; Leung, T. H. *J. Am. Chem. Soc.* **1972**, *94*, 1610.
(8) Nelsen, S. F.; Landis, R. T., II; Calabrese, J. C. *J. Org. Chem.* **1977**, *42*, 4192.
(9) Cheng, J.-D.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 336.
(10) Shine, H. J.; Cheng, J.-D. *J. Org. Chem.* **1971**, *36*, 2787.
(11) Sullivan, J. F.; Hailey, J.; Shine, H. J. *Tetrahedron Lett.* **1970**, 2007.

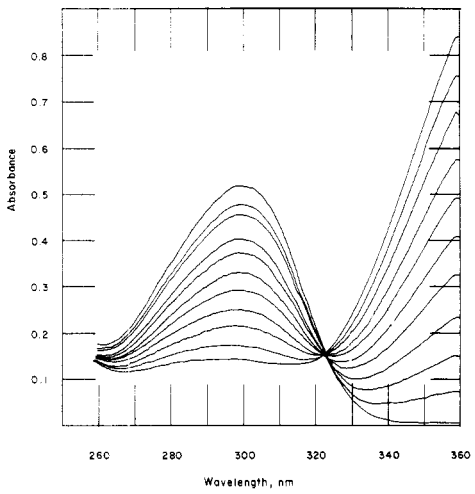
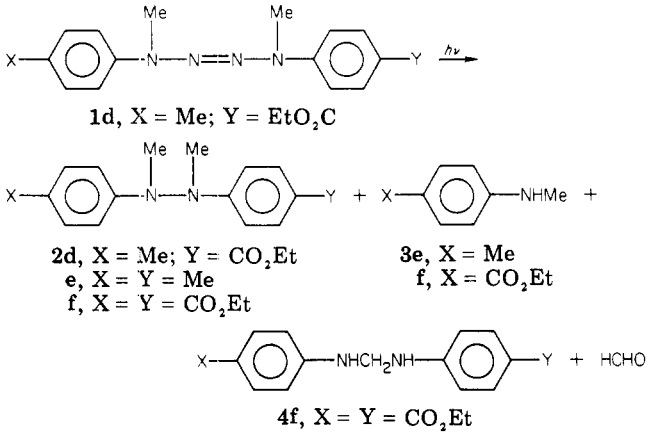


Figure 1. Change in the absorption spectrum of **1d** caused by irradiation at 350 nm. Compound **1d** was irradiated as a 2×10^{-3} M solution in dimethoxyethane. Spectra were recorded in ethanol solutions as described in the Experimental Section and show the disappearance of **1d** (360-nm band) and the formation of products (band near 300 nm). Aliquots for the 11 scans were taken at 5-min intervals, totaling 50 cumulative min of irradiation.

Scheme III

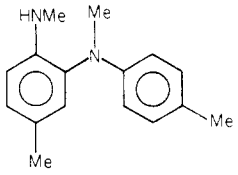


1, in which the disappearance of **1d** is monitored at 360 nm and the isobestic point occurs at 322 nm. A similar observation had been made earlier with **1e**[3] and has also been made in the present work with **1b**. However, these spectral changes are not necessarily diagnostic of a simple conversion, since in the case of **1d** at least six products are formed, all of which have a chromophore which gives rise to a band in the region of 300 nm.

The products formed from irradiation of **1d** are shown in Scheme III. The products were separated by thick-layer chromatography and were identified by either comparison with authentic samples or by one or both of the techniques of ^{1}H NMR and mass spectrometry. For the thick-layer chromatography most of the DME was pumped off from the irradiation solution and the residue was applied to plates of Woelm silica gel.

Scheme III shows immediately that three hydrazines, **2d–f**, were formed from **1d**. The two corresponding methylarylamines **3e,f** were also formed. To our surprise there was a sixth product, the bis(arylamino)methane **4f**. The analogous bis(*p*-tolylamino)methane did not appear to be present in the mixture of products, but we are not certain if it was formed or not. Also listed as a product is formaldehyde. This has to do with the formation of **4f**, as is discussed later.

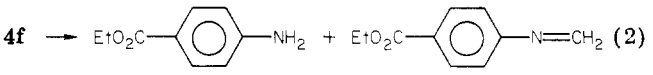
The hydrazine **2e** was not stable on silica plates. Instead it changed in time into what we believe to be the *o*-semidine **5e**, and both **2e** and **5e** migrated together. The



5e

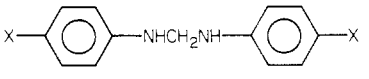
conversion of **2e** into **5e** was demonstrated separately. In fact, after partial conversion had occurred with authentic **2e**, the mixture of **2e** and **5e** was removed from the plate and applied to a fresh plate. This was repeated until conversion of all of the **2e** into **5e** had occurred. Identification of **5e** was made by monitoring the plates with authentic **5e** and by ^{1}H NMR after the product was removed from the plates.

Product **4f** was identified from its ^{1}H NMR spectrum and by comparison with authentic **4f** made from the condensation of ethyl *p*-aminobenzoate with formaldehyde. Interestingly, **4f** could not be identified mass spectrometrically by its parent ion. Instead, two high-intensity peaks were obtained of *m/e* 165 and 177. These masses correspond with the fragmentation of **4f** according to eq 2. We



6f, *m/e* 165 **7f**, *m/e* 177

have observed this fragmentation and failure to obtain the parent ion in a number of other bis(arylamino)methanes (**4a,g,h**), so that it may be a general phenomenon of this



4a, X = H
g, X = NO_2
h, X = OMe

class of compounds. These compounds are also very sensitive to decomposition by acid and acidic solvents, resulting in considerable difficulties in recrystallization. Decomposition leads to the formation of a cyclic trimer and/or a polymer of the methylenimine fragment (e.g., of **7f**). We hope to report on the details of this behavior separately.

Determination of the amounts of products formed from **1d** has not been entirely satisfactory. Because of limitations in solubility at room temperature and also in order to ensure reasonably short times of irradiation so as to minimize side reactions, we kept the concentrations of the solutions of **1d** being irradiated low ($\sim 2 \times 10^{-3}$ M). This, in turn, led in the initial stages of the work to separation of products by thick-layer chromatography. The yields of unpurified products so obtained appear to have substantial errors. Yields of hydrazines **2d–f** were also determined by high-pressure LC and are probably more representative of the conversion of **1d** into the hydrazines. Satisfactory separation of the other products (**3e**, **3f**, and **4f**) by high-pressure LC was unsuccessful and was complicated also by overlap of the residual solvent (DME) front into the high-pressure LC peaks of these products. The yields are expressed here as the percentage of the available fragment, ArNMe, incorporated into a product. That is, for example, by thick-layer chromatography 32% of the MeC_6H_4NMe groups available in **1d** ended up as **2d**. The compounds and their yields by the two methods were, from thick-layer chromatography, as follows: **2d** (32%), **2e** (39%), **2f** (12%),

3e (10%), **3f** (28%), **4f** (14%). From high-pressure LC (two runs) the results were as follows: **2d** (13%, 15%), **2e** (7%, 8%), **2f** (15%, 21%).

Two other runs were made in order to isolate usable quantities of **4f**. In these runs the other products were not assayed. Much of the **4f** crystallized from the concentrated DME solution, and yields obtained in this way from the three runs were scattered, e.g., 14%, 26%, and 32%.

The formation of **4f** requires that a methyl group be lost by one of the two $EtO_2CC_6H_4NMe$ units from which **4f** is constructed. This methyl group, we believe, is converted into formaldehyde (see Discussion). Therefore, attempts were made to detect and assay formaldehyde, by Hantzsch's method, in the DME which was pumped off the solution of **1d** after the photoreaction was complete. Our attempts were thwarted to some extent by the fact that formaldehyde was detected in the DME itself even after lengthy attempts were made to purify the DME. Therefore, a control was run in which purified, degassed DME was irradiated alongside a degassed, 2.1×10^{-3} M solution of **1d**. The DME was recovered in each case by being pumped off at room temperature. The concentration of formaldehyde in the DME from the control was 5.88×10^{-6} M while from the **1d** solution it was 3.94×10^{-5} M. The difference shows that formaldehyde was produced in the photolysis of **1d**, but the amount recovered (corrected for the control experiment) was far less (i.e., 1.9% of the $EtO_2CC_6H_4NMe$ units in the **1d**) than that expected on the basis of the amounts of **4f** which had been isolated from three runs.

Monochromatic Irradiation of 1d and 1e in Cyclohexane. A 2.02×10^{-5} M solution of **1d** in cyclohexane was irradiated in a cuvette placed in a monochromator. Periodically the cuvette was transferred to a spectrophotometer, and the spectrum of its contents was recorded over a period of 105 min. Again, a clean isosbestic point was present in the changing spectra. A plot of the decreasing concentration of **1d** vs. time was linear for a short time, indicating that the disappearance of **1d** was zero order in **1d** and that all of the incident light was being absorbed during that time. Larger scale runs (2.02×10^{-3} M) were made with a Rayonet reactor. The products, identified by TLC, were again **2d–f**, **3f**, and **4f**. We could not be certain that **3e** was present. Attempts to detect formaldehyde in the pumped-off solvent failed, and control experiments for detecting formaldehyde in cyclohexane also failed, possibly because of the immiscibility of cyclohexane with the reagent solution.

The tetrazene **1e** was treated similarly in the monochromator according to the procedure used earlier by Hull and Shine.[3] Disappearance of **1e** was again accompanied spectroscopically by a clean isosbestic point. The products of photolysis were assayed by high-pressure LC (two runs) and were **2e** (43%, 42.5%), and **3e** (30.6%, 29.2%). These yields differ from the earlier work (83% of **2e**) in which assays were made by thick-layer chromatography.

Radical Trapping with 1e. Two tetrazenes (**1d** and **1e**) were used in the radical-trapping part of our work. The procedure was developed with the simpler, symmetrical **1e** and then applied to **1d**. *n*-Butyl mercaptan was chosen as the trapping agent in analogy with earlier work by Hammond with azobis(isobutyronitrile).[12] Control experiments were made with **1e** and **2e** in DME. That is, *n*-BuSH and **1e** did not react to give **2e** over a period of 60 min in the absence of 350-nm irradiation. Also, irradiation of a solution of **2e** and *n*-BuSH at 350 nm for 60 min left the **2e** unchanged. In order to search for radical trapping, we made ten solutions of **1e**, each 2×10^{-3} M in **1e** and nine of them containing *n*-BuSH in appropriate concentrations. The solutions were irradiated for 60 min in a Rayonet reactor after being purged with nitrogen and while being stirred magnetically. After irradiation the solutions were worked up, and the yield of **2e** was determined by high-pressure LC, with tetraphenylethylene as an internal standard. Similar runs were made in cyclohexane. The results are given in Table I and Figure 2.

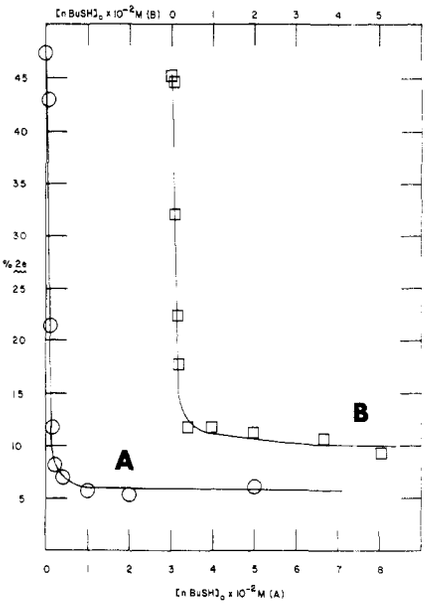


Figure 2. Effect of $[n\text{-BuSH}]_0$ on the yield of **2e** obtained from irradiation of **1e**: A, lower scale in DME solution; B, upper scale in cyclohexane solution. $[\mathbf{1e}]_0$ was 2.0×10^{-3} M.

Table I. Yields[a] of 2e Obtained from Irradiation of Solutions of 1e[b] Containing *n*-Butyl Mercaptan

$[n\text{-BuSH}]/[\mathbf{1e}]_0$	% 2e[c]	% 2e[d]	$[n\text{-BuSH}]/[\mathbf{1e}]_0$	% 2e[c]	% 2e[d]
0.0	47.4	45.1	2.0	6.9	11.7
0.25	43.0	44.7	5.0	5.7	11.7
0.5	21.3	32.0	10.0	5.3	11.1
0.75	11.7	22.2	17.7		10.6
1.0	8.1	17.6	25.2	6.1	9.2

[a] By high-pressure LC. [b] $[\mathbf{1e}]_0 = 2 \times 10^{-3}$ M. [c] In DME. [d] In cyclohexane.

It was not possible to measure, by peak integration, the amount of **3e** being formed in these experiments because of overlap interference by the solvent DME. (This was true even for irradiations in cyclohexane, where, for high-pressure LC assay in 70% aqueous methanol, it was necessary to replace the cyclohexane with DME after irradiation.) However, for the initial experiment with $[n\text{-BuSH}]_0 = 0$ it was possible to measure manually the area under the reconstructed **3e** peak of the high-pressure liquid chromatogram. This gave a yield of **3e** of 39.6%.

The data show, therefore, that in the absence of *n*-BuSH **1e** is converted into **2e** (47.4%) and **3e** (39.6%), for a total of 87% conversion. The high-pressure liquid chromatogram also had in it a third peak, but we have not looked for its origin. The data also show that *n*-BuSH reduces the yield of **2e** to the level of about 6% in DME and 10% in cyclohexane.

Radical Trapping with 1d. Experiments analogous to those with **1e** were carried out with **1d**. In the initial runs, $[n\text{-BuSH}]_0 = 0$, the high-pressure liquid chromato-

(12) Hammond, G. S.; Sen, J. N.; Boozer, C. E. *J. Am. Chem. Soc.* **1955**, *77*, 3244.

Table II. Yields[a] of 2d-f Obtained from Solutions of 1d[b] Containing *n*-Butyl Mercaptan in DME

[*n*-BuSH]/[1d]$_0$	run 1			run 2		
	2d	2e	2f	2d	2e	2f
0.0	13.0	7.3	14.9	14.7	8.0	21.2
0.25	12.8	15.4	17.8	12.8	15.8	18.6
0.5	8.9	4.0	8.6	8.2	2.9	13.8
0.75	7.3	2.0	10.0	8.0	2.1	13.0
1.0	8.0	1.7	*c*		1.4	*c*
2.0	8.4	1.0		7.2	0.0	
5.0	6.3	0.0		6.4		
10.0	6.6			6.3		
18.0	5.8			5.5		
25.7	5.8			4.2		

[a] By high-pressure LC; yields express the percent of fragment ArNMe in 1d found in each product. [b] [1d]$_0$ = 2×10^{-3} M. [c] Beyond this point two overlapping peaks appeared in the high-pressure liquid chromatogram, so that measurements were stopped.

gram was uncomplicated, and the three hydrazine peaks were cleanly separate from each other. As the concentration of *n*-BuSH increased, however, new peaks began to appear and made the quantitative analysis of the hydrazines by peak integration more difficult. The data for **2d** (Table II) are reliable, however, since the peak for **2d** suffered no interference from other peaks. The data for **2e** are thought to be reliable in that the formation of **2e** was completely stopped as the concentration of *n*-BuSH approached that of **1d**. We are unable to explain the apparent rise in yield of **2e** at the concentration ratio of 0.25. Since the two runs were independent ones, the increase appears to be real, but, if so, we cannot explain why. As for assays of product **2f**, these were made impossible by the eventual development of an overlapping peak in the chromatogram.

However, before this occurred it appeared that the yield of **2f** began to fall with increasing concentration of *n*-BuSH, but not as sharply as the fall in the yield of **2e**.

Discussion

The formation of the three hydrazines (**2d-f**) from irradiation of **1d** shows that hydrazine formation occurs from the combination of methylarylamino radicals. The effect of *n*-butyl mercaptan on the yield of **2e** from **1e** shows that hydrazine formation occurs from the combination of methylarylamino radicals. The effect of *n*-butyl mercaptan on the yield of **2e** from **1e** shows that a large part of the **2e** is formed outside of a solvent cage. This amounts to 87% of the **2e** in DME and 80% in cyclohexane. Whether or not the remaining intramolecularly formed **2e** is a caged-radical product or is an electrocyclic product cannot be said, but it is most probably the former. Thus, **1e** decomposes by pathways ad and abc (Scheme I). The same deduction can be made from irradiations of **1d**. It is seen here that product **2e**, as expected, arises from the recombination of *N*-methyl-*p*-toluidinyl radicals and that the recombination is stopped by *n*-butyl mercaptan. In contrast, formation of **2d** has both free-radical recombination and caged-radical recombination pathways. The former accounts for 54-66% of the **2d**. One expects that the formation of **2f** must also be an out-of-cage process, preventable by the presence of *n*-butyl mercaptan. Unfortunately, the high-pressure LC analyses for **2f** were made impossible by products arising from the *n*-butyl mercaptan, and this part of the complete reaction pattern cannot be supplied.

It is a matter of curiosity that although the photolysis of tetrazenes has now received a fair amount of attention and although the formation of nitrogen-centered radicals thereby is well demonstrated, the recombination of these radicals is not a well-documented event. Among tetraalkyltetrazenes the fate of the resulting dialkylamino radicals is usually one of disproportionation. In fact, in the photolysis of tetraisopropyltetrazene, Roberts and Ingold provide kinetic evidence ruling out the formation of tetraisopropylhydrazine.[13] Disproportionation, rather than recombination, also occurs when dibenzylamino radicals are formed from the photolysis of tetrabenzyltetrazene.[14] On the other hand, photodecomposition of tetramethyltetrazene has been reported to give tetramethylhydrazine in 32% yield,[15] in small but definite amounts (from vapor-phase photolyses),[16] in identifiable amounts,[17] as a major product,[18] and as a probable product.[19] Frequently, the fate of the radicals obtained from tetrazenes is not mentioned.[7,8,20-25] Hydrazine formation is best documented in the photolyses of 1,4-dialkyl-1,4-diaryltetrazenes.[3,5,9,26] Radicals from these are less suited to disproportionation (because of the aryl group) so that the recombination is not unreasonable.

Our findings with **1d** and **1e** are that about 35-45% of the radicals end up as hydrazine. These data are from high-pressure LC results and are felt to be more reliable than earlier[3] and present thick-layer chromatographic results. Recombination of methylarylamino radicals to give benzidine-type rearrangement products is also possible and, in fact, was observed by Cheng and Shine with 1,4-diphenyl-2-tetrazene.[9] In the present work such recombinations would give *o*-semidines because of the blocked para positions. We have not observed these products from **1d** and **1e**, but it is possible that they may account for unidentified smaller peaks in the high-pressure liquid chromatograms.

Most of the remaining radicals in these cases end up as methylarylamines, but the *p*-carbethoxy radicals also appear to undergo disproportionation. We interpret the formation of **4f** as originating from the disproportionation of the radicals as shown in eq 3-5 (Ar = $EtO_2CC_6H_4$). The

$$2ArNCH_3 \rightarrow ArNHCH_3 + ArN{=}CH_2 \quad (3)$$

$$ArN{=}CH_2 + H_2O \rightarrow ArNH_2 + HCHO \quad (4)$$

$$ArNH_2 + ArN{=}CH_2 \rightarrow ArNHCH_2NHAr \quad (5)$$

water needed for hydrolysis of the methylene imine (eq 5) is assumed to be present in the solvent. Formaldehyde was found in small amounts, but we have concluded, neverthless, that the amount was larger than should be attributed to solvent-based formaldehyde.

It is interesting that we could find only **4f** and not **4e** (Scheme III, X = Y = Me) from the photolysis of **1d**. **4f**

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was also formed from the photolysis of **1f**. We did not find **4f** from the thermolysis of **1d**, nor did we find **4e** from the photolysis of **1e**, but we cannot say with certainty that in these cases none of the bis(arylamino)methanes were formed. It appears though that the photolytically formed *p*-carbethoxy radicals differ from the *p*-methyl ones in their tendency to disproportionate. The effect of substituents on these reactions is being investigated.

Although disproportionation of dialkylamino radicals has been documented,[13,14] there is only one other reference, that we have been able to find, to the formation of a diaminomethane, namely, in trace amounts from the vapor-phase photolysis of tetramethyltetrazene and in very small amounts from the thermolysis of the same tetrazene; the origin of the product was not known.[15]

To our knowledge no other investigation into cage effects in the photodecompositions of tetrazenes has been reported. Cage recombination has been investigated in the thermal decomposition of **1a**, but the emphasis was on the recombination of triazenyl and arylamino radicals and the effect of solvent viscosity on this recombination,[27] as measured by the rate of decomposition of **1a**. Oda and co-workers found that the fraction of cage return to **1a** ranged between 0.27 and 0.50 at 95 °C, depending on the solvent.[27] This work and our own give some definition to the decompositions of 1,4-diaryl-1,4-dialkyltetrazenes. Whether or not there is a photolytic counterpart to the first thermal cage process and a thermolytic counterpart to the hydrazine cage process remains to be investigated.

One further aspect of our trapping/cage work needs comment. We recognize that induced decomposition of the tetrazenes by *n*-BuS· radicals may occur. However, it is evident that even if this does occur, it has not interfered with the formation of hydrazines within the solvent cage.

Experimental Section

Tetrazenes. These were prepared by oxidizing the appropriate 1-aryl-1-methylhydrazine with lead(IV) oxide according to the procedure of Nelsen and Heath.[4] Oxidation of 1-(*p*-bromophenyl)-1-methylhydrazine gave **1b** (mp 180–181 °C dec) in 62% yield after crystallization from carbon tetrachloride. Oxidation of an equimolar mixture of 1-(*p*-tolyl)-1-methylhydrazine and 1-[*p*-(ethoxycarbonyl)phenyl]-1-methylhydrazine gave a mixture of **1d–f**. These were separated on a column of silica gel (Woelm, 70–230 mesh) by elution with benzene, giving 33% of **1d**, 32% of **1e**, and 19% of **1f**. Compound **1d** was crystallized from ethanol: mp 122–123 °C dec (lit.[4] mp 118–119 °C); ^{1}H NMR [$(D_3C)_2C{=}O$] δ 8.10–7.20 (m, 8 H), 4.26 (q, 2 H), 3.53 (s, 3 H), 3.46 (s, 3 H), 2.27 (s, 3 H), 1.35 (t, 3 H). Compound **1e** was crystallized from carbon tetrachloride: mp 152–153 °C dec (lit.[4] mp 148–149 °C); ^{1}H NMR (C_6D_6) δ 7.18 (s, 8 H), 3.18 (s, 3 H), 2.17 (s, 3 H). Compound **1f** was crystallized from benzene: mp 183.5–184 °C dec (lit.[4] mp 180–181 °C); the NMR spectrum was not taken because of the poor solubility of **1f**. Each tetrazene also gave a satisfactory elemental analysis.

Attempted Preparation of 1c. Oxidation of a mixture of 1-methyl-1-phenylhydrazine (2.13 g, 15.5 mmol) and 1-(*p*-bromophenyl)-1-methylhydrazine (3.52 g, 15.5 mmol) in 80 mL of benzene with 22 g of lead oxide gave 5.22 g of a mixture of tetrazenes **1a–c**. Repeated attempts to separate these by column chromatography were unsuccessful.

1-Aryl-1-methylhydrazines were made by reducing the corresponding *N*-nitroso-*N*-methylarylamines with zinc powder. *N*-methyl-*p*-toluidine (**3e**) was made by the formylation of *p*-toluidine and reduction of the formamide with lithium aluminum hydride. Ethyl *N*-methyl-*p*-aminobenzoate (**3f**) was made by esterifying commercial *N*-methyl-*p*-aminobenzoic acid.

1,2-Diaryl-1,2-dimethylhydrazines (2b,d–f). The general method was to reduce the azoarene to the hydrazoarene with zinc powder in acetic acid–pyridine. The hydrazoarene was then methylated by successive treatment with butyllithium and methyl iodide.

p-Azotoluene **5e** (mixed with some *p*-azoxytoluene which also reduces to the *p*-hydrazotoluene) was made by reducing *p*-nitrotoluene with sodium stannite.[28] 4,4′-Dibromoazobenzene (**5b**; mp 206.5–207.5 °C, from benzene–hexane) and 4,4′-bis(ethoxycarbonyl)azobenzene (**5f**; mp 145.5–146.5 °C from ethanol) were made by oxidizing the arylamine[29] in benzene solution with manganese dioxide.[30] 4-(Ethoxycarbonyl)-4′-methylazobenzene (**5d**) was made by a similar oxidation of a mixture of 20.3 g (0.123 mol) of ethyl *p*-aminobenzoate and 10.9 g (0.103 mol) of *p*-toluidine with 110 g of manganese dioxide in 500 mL of benzene. Chromatography of the product on alumina (Woelm, neutral, activity IV) gave 6.0 g (55.5%) of *p*-azotoluene after elution with 95:5 petroleum ether–benzene and 5.6 g (20.4%) of **5d** after elution with 90:10 petroleum ether–benzene. Compound **5d** was crystallized from methanol: mp 104–105 °C; ^{1}H NMR ($CDCl_3$) δ 8.00 (m, 6 H), 7.30 (d, 2 H), 4.38 (q, 2 H), 2.45 (s, 3 H), 1.45 (t, 3 H). Anal. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.6; H, 6.01; N, 10.4. Found: C, 71.5; H, 6.13; N, 10.4. The third azoarene was abandoned on the column. Reduction of the azoarenes was achieved by heating at 60–80 °C (**5b,e,f**) or by stirring at room temperature (**5d**) with a suspension of zinc powder in a solution of acetic acid (about 20 mL) in pyridine (about 100 mL). Each product was obtained by filtering the mixture into water, which gave *p*-hydrazotoluene (**6e**; mp 131.5–132.5 °C, ethanol), 4,4′-dibromohydrazobenzene (**6b**; mp 132–133 °C, from ethanol), 4,4′-bis(ethoxycarbonyl)-hydrazobenzene (**6f**; mp 119.5–120.5 °C, from benzene), and 4-(ethoxycarbonyl)-4′-methylhydrazobenzene (**6d**; mp 112–113 °C, from heptane). The ^{1}H NMR spectrum of each compound was in agreement with the structure. Methylation of **6b,d–f** was achieved by treating a solution of **6** in dry ether with an appropriate amount of commercial butyllithium in hexane at 0–5 °C followed by addition of methyl iodide and stirring at room temperature overnight. In the case of **6d**, diisopropylamine (10.6 mmol) was added to the *n*-BuLi (6.2 mmol) solution followed by **6d** (3.0 mmol) in ether. In this way **2e** was obtained in 43% yield after repeated crystallization from methanol; mp 64–65 °C. It was necessary to use column chromatography on alumina (activity III) to purify the products: **2b**, mp 84–85 °C (from ethanol), 46% yield; **2d**, yellow oil, 76% yield; **2f**, yellow oil, 76% yield. The ^{1}H NMR spectrum of each hydrazine (**2b,d–f**) agreed with its structure.

Preparation of 4f. The method used was that which is given for the corresponding parent compound bis(phenylamino)methane (**4a**).[31] To a nearly boiling solution of 3.6 g (0.022 mol) of ethyl *p*-aminobenzoate in 30 mL of ethanol was added 2.7 mL of 37% formalin solution. In a short time a precipitate formed. After being stirred about 20 min, the suspension was filtered to give 1.40 g (38%) of white needles, mp 193–194 °C. Attempts at recrystallization caused, instead, variable extents of decomposition: ^{1}H NMR [$(D_3C)_2S{=}O$] δ 7.71 (d, 4 H), 7.22 (t, 2 H), 6.73 (d, 4 H), 4.56 (br t, d, 2 H), 4.21 (q, 4 H), 1.26 (t, 6 H).

Photochemistry. Most of the irradiations were carried out in a Rayonet photochemical reactor, Type RS, which was equipped with seven 350-nm lamps. Irradiations were carried out at ambient temperatures, and these ranged between 20 and 26 °C. Two techniques were used, one (A) for monitoring the course of the reaction and the other (B) for analysis of the products.

Method A. A Pyrex tube wrapped in aluminum foil was charged with 200 mL of a 2×10^{-3} M solution of a tetrazene. The solution was then deoxygenated either by bubbling nitrogen through it for 15 min or by three cycles of a freeze–thaw vacuum-line technique. After removal of the foil, the tube was placed in the reactor and the solution was stirred magnetically. At 5-min intervals the irradiation was stopped, the tube was opened, and

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two 1-mL aliquots of solution were withdrawn for ultraviolet and TLC monitoring. When spectroscopic monitoring showed that all of the tetrazene had disappeared, irradiation was stopped. The solvents used for the irradiation were dimethoxyethane and cyclohexane.

Method B. A solution, prepared as in method A, was irradiated in a sealed tube for a period of time as determined in A. After the irradiation was stopped, the solution was removed for quantitative analysis of the products by either thick-layer chromatography or high-pressure LC.

Monitoring by Ultraviolet Spectroscopy. At each 5-min time interval a 1-mL aliquot of solution was placed in a 100-mL volumetric flask which was filled to the mark with 95% ethanol, stoppered, and wrapped in aluminum foil to prevent further irradiation. The spectrum of each solution was recorded with a Beckman DK-2A spectrophotometer using one piece of chart paper on a flat-bed recorder. In this way it was possible to follow the disappearance of the tetrazene and the appearance of products. In the case of **1b** the band at 354 nm was replaced by one at 254 nm, and two isosbestic points were observed at 224 and 228 nm. The complete change took about 35 min. In the case of **1d** the band at 360 nm was replaced by one at 300 nm with an isosbestic point at 322 nm. The complete change took about 50 min (Figure 1).

Monitoring by TLC. At each 5-min time interval a 1-mL aliquot was placed in a foil-wrapped vial which was stoppered and kept for use. At the end of the irradiation, as determined spectroscopically, all of the TLC samples were spotted on the same plate of neutral alumina (Woelm). Authentic samples of anticipated products and of the tetrazene were also spotted on the plate. The plate was developed with benzene–petroleum ether (30:70). In this way the gradual disappearance of the tetrazene could be observed, and the formation of specific products could be established.

Irradiation with a Monochromator. A Bausch and Lomb monochromator was used as described earlier.[3] Both **1d** and **1e** were used, and their disappearance was followed by placing the cuvette in the Beckman DK-2A spectrophotometer at 5-min intervals. The disappearance of **1d** (2.02×10^{-5} M) was complete in 105 min. A plot of absorbance against time was linear over a period of 20 min, showing that during this time all of the incident light was absorbed by **1d**. The change in the spectrum was again accompanied by an isosbestic point.

Irradiation of **1e** (1.75×10^{-3} M) to complete disappearance took 5 h. After the irradiation was complete, the cyclohexane solution was used for analysis of the products by high-pressure LC. The products from two analyses were **2e** (43.0%, 42.5%) and **3e** (30.6%, 29.2%).

Product Analyses. The products of irradiation of **1d** were determined by thick-layer chromatography and, separately, by high-pressure LC. Products from **1e** were determined by high-pressure LC only.

(A) Products from 1d by Thick-Layer Chromatography. A solution of 133 mg of **1d** in 200 mL of DME was degassed with three freeze–thaw cycles. The sealed solution was irradiated for 60 min. Evaporation of the solvent in a rotary evaporator gave 135 mg of brown oil. This was streaked on two 20 × 40 cm preparative thick-layer chromatography plates, each plate bearing 40 g of silica gel (Brinkman GF-254). The plates were developed with 95:5 benzene–ether. Band separation was quite good. The bands were removed from the plates, and the products were extracted from plate material with acetone. The product in each band was identified first by TLC comparison with authentic compounds and, next, where possible, by ^{1}H NMR spectroscopy. The products are listed in order of decreasing R_f, with the weights of crude material and the yields. No attempt was made to purify the products: **2e** (0.93, 19 mg, 39%), **2d** (0.78, 36 mg, 32%), **3e** (0.64, 5 mg, 10%), **3f** (0.53, 21.4 mg, 28%), **2f** (0.53, 8.7 mg, 12%), **4f** (0.29, 10 mg, 14%). The product **2e** was a mixture of **2e** and its *o*-semidine rearrangement product. Rearrangement of **2e** to the *o*-semidine occurred on the plate, as was demonstrated with authentic **2e**. Both **2e** and *o*-semidine migrated together. The total product is listed, therefore, as **2e**. Products **2f** and **3f** migrated together. The composition of the mixture in the thick-layer chromatography band was determined by ^{1}H NMR spectroscopy. The bis(arylamino)methane **4f** also had a tendency to crystallize from the reaction solution after it was concentrated, so that it was possible to separate it in other runs by filtration.

(B) Products by High-Pressure LC. In order to assay products by high-pressure LC it was necessary first to prepare calibration plots for authentic products whose concentrations were measured against an internal standard. This was first carried out with **2e** and **3e**, the anticipated products from photolysis of **1e**. The solvent for separation of **2e**, **3e**, and the internal standard (tetraphenylethylene) was first established as 70% aqueous methanol on a Waters Associates MicroBondapak-Phenyl column. Nine solutions in DME were then prepared, each containing known, different concentrations of **2e** and **3e** and a fixed concentration of tetraphenylethylene. An aliquot of 50 μL was used for analysis. The customary plots of the ratio of integrations against the ratio of known concentrations were made and were used for assaying the mixture of products of photolysis.

The plots for both **2e** and **3e** were linear and had the form $y = 2.1764x - 0.0158$ for **2e** and $y = 0.4199x - 0.0117$ for **3e**, where y is the integration ratio and x the concentration ratio of substrate and internal standard.

The high-pressure liquid chromatograms of the products of photolysis of **1e** showed that a small amount of a third product was present. This was not identified and was therefore not assayed.

In the case of the products of photolysis of **1d**, a MicroBondapak-C-18 column was used, the internal standard was perylene, and the solvent for separation was again 70% aqueous methanol. In this case, though, it was possible to separate only the three anticipated hydrazines, **2d–f**. The methylarylamines **3e** and **3f** appeared close together and partially merged with the solvent DME. Therefore these products were not assayed. This was a compromise accepted for the main purpose of the high-pressure LC work which was to assay the yields of the hydrazines in the presence of *n*-butyl mercaptan.

The calibration plots for **2d–f** were linear and had the form $y = 0.7728x - 0.02148$ for **2e**, $y = 0.2799x - 0.0035$ for **2d**, and $y = 0.1084x - 0.0015$ for **2f**.

Trapping Experiments. The general procedure was to irradiate a series of nine or ten 25-mL solutions of tetrazene, each solution containing a fixed concentration of tetrazene and a particular concentration of *n*-butyl mercaptan. Each solution was placed in a 50-mL, Pyrex, round-bottomed flask flushed with nitrogen for 10 min, capped, and irradiated for the prescribed time, as determined earlier, while being stirred magnetically. After irradiation, an aliquot was taken for analysis by high-pressure LC using the appropriate internal standard. When cyclohexane was used as the photolysis solvent, it was necessary to remove the cyclohexane after irradiation and replace it with DME because cyclohexane is not miscible with 70% aqueous methanol, the solvent used for the high-pressure LC.

The trapping experiments were successful for hydrazine assay over the entire range of *n*-BuSH concentrations when **1e** was used. However, the peak for **3e** was partially overlapped by the peak of an unknown product of trapping, and therefore assay of **3e** was not possible. In the case of $[n\text{-BuSH}]_0 = 0$ the peak for **3e** was overlapped only to a small extent and was reconstructed by drawing; it was then cut from the chromatogram and assayed by weighing. The amount of **3e** was 39.6%. Results are given in Table I and Figure 2.

The trapping experiments with **1d** were partially successful. At low concentrations of *n*-BuSH the chromatogram peaks were separate from each other and clearly assignable to products **2d–f**. As the concentration of *n*-BuSH was increased, however, new peaks appeared in the chromatograms. Identification of the peaks for **2d** and **2e** continued to be reliable, but the peak for **2f** became merged with another of unknown origin, and assay of **2f** became impossible. The peak of **2e** eventually disappeared at $[n\text{-BuSH}]_0/[\mathbf{1d}]_0 = 2$–5. The peak for **2d** did not disappear but remained constant in integration in the range of $[n\text{-BuSH}]_0/[\mathbf{1d}]_0 = 5$–25. Results are given in Table II and Figure 3.

Detection and Assay of Formaldehyde. The objective here was to detect and assay by Nash's method[32] the formaldehyde which could be pumped off a photolysis solution. Hantzsch's

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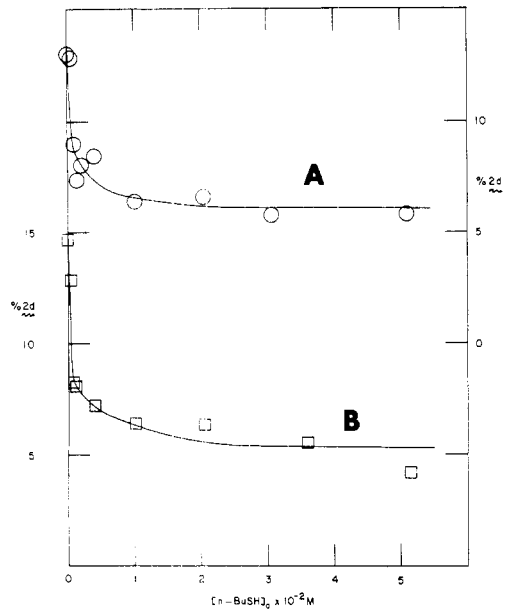

Figure 3. Effect of $[n\text{-BuSH}]_0$ on the yield of **2d** obtained from irradiation of **1d** in DME: A, scale at right, run 1; B, scale at left, run 2. $[\mathbf{1d}]_0$ was 2.0×10^{-3} M.

reagent solution was prepared as directed. Ten milliliters of this solution and 10 mL of the test solution were mixed and warmed for 10 min at 50 °C. The yellow color which developed was assayed at 412 nm. Formaldehyde was detected in this way in DME which had been distilled over lithium aluminum hydride (LAH). Therefore, DME was distilled over a mixture of sodium bisulfite and sodium sulfite. The distillate was free of formaldehyde but had a bad odor (H_2S?). Therefore, it was redistilled over LAH. The first fraction again gave a strong positive response to Hantzsch's reagent. The second fraction gave a weak response while the third gave a negative response. The third distillate was used in photolysis experiments and as a blank.

For assaying formaldehyde which was formed in a photolysis, 10 mL of a 2.07×10^{-3} M solution of **1d** was degassed by three freeze–thaw cycles and irradiated for 60 min in the Rayonet reactor while being stirred magnetically. The solvent from the irradiated solution was pumped off at room temperature and collected in a trap cooled in liquid N_2. The trapped distillate was warmed to room temperature and assayed with Hantzsch's reagent. The concentration of formaldehyde was assayed as 3.94×10^{-5} M. A 10-mL aliquot of the solvent, DME, tested out as being free from formaldehyde, but when 50 mL of DME was irradiated and worked up as with the solution of **1d**, formaldehyde was detected and assayed as being 5.88×10^{-6} M. The amount of formaldehyde obtained from **1d**, corrected for the blank, was 1.9% of the **1d** used.

Registry No. **1b**, 74763-65-8; **1d**, 26190-53-4; **1e**, 26190-49-8; **1f**, 26190-51-2; **2b**, 74763-66-9; **2d**, 74763-67-0; **2e**, 30724-66-4; **2f**, 51596-02-2; **3e**, 623-08-5; **3f**, 10541-82-9; **4f**, 74763-68-1; **5b**, 1601-98-5; **5d**, 74763-69-2; **5e**, 501-60-0; **5f**, 7250-68-2; **6b**, 19717-43-2; **6d**, 74763-70-5; **6e**, 637-47-8; **6f**, 19672-25-4; 1-(*p*-bromophenyl)-1-methylhydrazine, 74763-71-6; 1-(*p*-tolyl)-1-methylhydrazine, 24006-21-1; 1-[*p*-(ethoxycarbonyl)phenyl]-1-methylhydrazine, 74763-72-7; *p*-nitrotoluene, 99-99-0; *p*-bromoaniline, 106-40-1; ethyl *p*-aminobenzoate, 94-09-7; *p*-toluidine, 106-49-0.

Frontier-Controlled Pericyclic Reactions of Powerful Electron-Attracting Cyclic Dienones and Diazadienones with 1*H*-Azepine: Molecular Structures of Cycloadducts and Some Comments

Kazunobu Harano, Masami Yasuda, Takashi Ban, and Ken Kanematsu*

Institute of Synthetic Organic Chemistry, Faculty of Pharmaceutical Sciences, Kyushu University 62, Maidashi, Higashi-ku, Fukuoka 812, Japan

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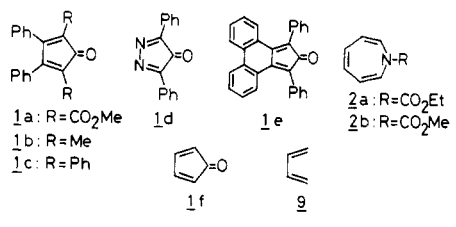
Pericyclic reactions of 2,5-bis(methoxycarbonyl)-3,4-diphenylcyclopentadienone (**1a**) and 2,5-diphenyl-3,4-diazacyclopentadienone (**1d**) with *N*-(ethoxycarbonyl)azepine (**2a**) were investigated. For **1a**, novel exo $[4 + 6]\pi$ and anti endo $[2 + 4]\pi$ cycloadducts were obtained, whereas for **1d**, only the anti endo $[2 + 4]\pi$ cycloadduct was obtained. These structures were verified by X-ray crystallography. The anti endo $[2 + 4]\pi$ cycloadduct was found to be formed via Cope rearrangement of the endo $[4 + 2]\pi$ cycloadduct by UV spectrometry. Compounds **1** are found to have high reactivities toward **2a**, and the selectivities were discussed in terms of frontier molecular orbital theory, indicating that **1** is a useful 4π component with inverse electron demand.

Pericyclic syntheses are very valuable for the high stereo-, regio-, and periselective controls they could provide for a logical assembling of molecules, especially highly strained cage compounds which either are available or are not available from natural sources.

In the past decade, the pericyclic reactions of conjugated medium-ring polyenes have aroused considerable interest and much effort has been made to establish their capability for cycloaddition. In general, cycloaddition reactions of medium-ring unsaturated compounds with electron-deficient dienophiles are extensively studied.

On the other hand, it is well-known that cyclopentadienone and its analogues are reactive and versatile diene components in Diels–Alder reactions.[1] We have also

Chart I



elucidated that phencyclone (2-oxo-1,3-diphenyl-2*H*-cyclopenta[*l*]phenanthrene, **1e**; see Chart I) shows high reactivity and selectivity toward various olefins and conjugated medium-ring polyenes on the basis of MO calculations and kinetic evidence, indicating that the reaction can be rationalized as a "neutral" Diels–Alder reaction where both electron-releasing and -attracking substituents

(1) Hoffmann, R.; Woodward, R. B. *J. Am. Chem. Soc.* **1965**, *87* 4388–4389; *Angew. Chem.* **1969**, *81*, 797–869.

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