dimethylaniline (or refluxed with 3.7 g of KOH in 500 mL of dioxane) was refluxed for 24 h. The yield was 85–90%.

1,2-Dibromo-1,2-bis(*p*-ethylphenyl)ethane (21). Compound **21** was prepared in the standard manner by using *p,p'*-diethylstilbene (**22**)[19] and Br_2 in CCl_4 under cold, dark conditions. The yield was quantitative. The needles thus obtained melted at 175.5–177 °C dec (EtOH): NMR δ 1.26 (t, CH_3, 6 H, $J = 7$ Hz), 2.72 (q, CH_2, 4 H, $J = 7$ Hz), 7.40 (Ar protons, 8 H). Anal. Calcd for $C_{18}H_{20}Br_2$: Br, 40.40. Found: Br, 40.22.

Dehydrobromination of 21. A mixture of 1.68 g (4.24 mmol) of **21** and 50 mL of 43% KOH in 95% ethanol was stirred and refluxed for 24 h. After the mixture was worked up, the crude product was recrystallized from methanol to give colorless crystals of 1,2-bis(*p*-ethylphenyl)acetylene (**20**): mp 69–70 °C;[7] 90% yield; NMR δ 1.23 (t, CH_3, 6 H, $J = 7$ Hz), 2.69 (q, CH_2, 4 H, $J = 7$ Hz), 7.22 (dd, Ar protons, 8 H). This dehydrobromination temperature seemed critical. When **21** was refluxed with *N,N*-dimethylaniline, one obtained only the debrominated product, *p,p'*-diethylstilbene (**22**): NMR δ 1.23 (t, CH_3, 6 H, $J = 7$ Hz), 2.63 (q, CH_2, 4 H, $J = 7$ Hz), 7.04 (s, $CH{=}CH$, 2 H), 7.12–7.60 (dd, Ar protons, 8 H).

Hydration[31] of Bis(*p*-isopropylphenyl)acetylene (1a) and Bis(*p*-*tert*-butylphenyl)acetylene (1b). A mixture of 0.5 g of bis(*p*-alkylphenyl)acetylene (**1a** or **1b**), 10 mL of glacial acetic acid, 0.05 g of mercuric sulfate, and 2 g of concentrated sulfuric acid was stirred and refluxed for 20 min. Then, 40 mL of water was added slowly and the mixture refluxed for 2 h. After the mixture was worked up, 4,4'-dialkyldeoxybenzoin (**15**) was obtained in 85–92% yield (see Table II for physical constants).

4,4'-Dialkyldeoxybenzoins (15).[32,33] To a stirred mixture of 0.5 g of 4,4'-dialkylbenzoin (**10**), tin amalgam (from 0.33 g of tin, 0.0524 g of mercuric chloride, and 10 mL of water), and 10 mL of 95% ethanol was added 1 mL of concentrated HCl slowly. The resulting mixture was then refluxed for 3 days. The corresponding **15** was obtained in 70–90% yield after the mixture was worked up. The melting point of the mixture of compound **15** thus obtained and the hydration product of bis(*p*-alkylphenyl)acetylene (**1**) showed no depression (see Table II for physical constants).

Reduction of Bis(*p*-isopropylphenyl)acetylene (1a) and Bis(*p*-*tert*-butylphenyl)acetylene (1b). Method A. Catalytic Hydrogenation. In a low-pressure Parr apparatus operating at 45 psi was hydrogenated a solution of 0.2 g of compound **1a** or **1b** in 150 mL of isopropyl alcohol for 3 h at 60 °C by using 0.05 g of platinum black (0.5 g of 10% palladium on charcoal, 1 g of 5% platinum asbestos, and 0.5 g of W-2 Raney Ni were used in different experiments as the catalysts). The recovery of compound **1** was quantitative after the workup. Upon reclamation, these catalysts were still pyrophoric. In selected cases, samples from the same batch of catalysts were used successfully to reduce stilbene and *m*-bromocinnamic acid.

Method B. Chemical Reduction. A stirred mixture of 0.2 g of compound **1**, 25 mL of benzene, and 0.30 g of sodium was added dropwise 25 mL of absolute ethanol and the mixture allowed to stand overnight at room temperature (or refluxed with 0.9 g of zinc dust in a mixture of 25 mL of acetic acid and 5 mL of concentrated HCl for 24 h). Bis(*p*-alkylphenyl)ethane (**4**), the reduced product, was obtained.

Catalytic Hydrogenation of Bis(*p*-ethylphenyl)acetylene (20). Compound **20** (0.20 g) dissolved in 150 mL of 95% ethanol was hydrogenated for 6 h at 60 °C with 0.05 g of 10% palladium on charcoal as the catalyst in a Parr hydrogenator under a 45-psi pressure. After the mixture was worked up, it was found through NMR spectral analysis that the white crystals obtained were a mixture of compound **20** and the reduced product, *p,p'*-diethylstilbene (**22**).

Registry No. 1a, 79135-52-7; **1b**, 61440-86-6; **2**, 98-51-1; **3**, 110-05-4; **4a**, 5789-33-3; **4b**, 22927-07-7; **5**, 79135-53-8; **6a**, 23429-40-5; **6b**, 79135-54-9; **7a**, 79135-55-0; **7b**, 79135-56-1; **8b**, 79135-57-2; **9b**, 939-97-9; **10a**, 5623-24-5; **10b**, 77387-64-5; **11a**, 79135-58-3; **11b**, 76471-78-8; **12a**, 79152-62-8; **12b**, 79135-59-4; **13b**, 79135-60-7; **14b**, 75966-32-4; **15a**, 79135-61-8; **15b**, 79135-62-9; **16a**, 79135-63-0; **16b**, 79135-64-1; **17a**, 79135-65-2; **17b**, 79135-66-3; **18a**, 79135-67-4; **18b**, 79135-68-5; **20**, 79135-69-6; **21**, 79135-70-9; **22**, 25347-49-3.

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Photobenzidine Rearrangements. 7. Disproportionation and Recombination of *N*-Methylarylamino Radicals in the Photodecomposition of 1,4-Bis(*p*-cyanophenyl)-1,4-dimethyl-2-tetrazene and Other 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 photochemical decomposition of 1,4-bis(*p*-cyanophenyl)-1,4-dimethyl-2-tetrazene (**1c**) in 1,2-dimethoxyethane (DME) was studied in detail. It was deduced that *N*-methyl-*p*-cyanoanilino radicals are formed and undergo three reactions: recombination into 1,2-bis(*p*-cyanophenyl)-1,2-dimethylhydrazine (**2c**, 21%), disproportionation (70%) into *N*-methyl-*p*-cyanoaniline (**3c**) and *N*-methylene-*p*-cyanoaniline (**4c**), and hydrogen atom abstraction (7%). A small amount of a *p*-semidine is thought to be formed also. These deductions were made from quantitative high-pressure LC measurements of yields of **2c**, **3c**, *p*-cyanoaniline (**5c**), and formaldehyde, the last two products arising from hydrolysis of **4c**. Quantitative measurement of the conversion of **4c** into **3c** by hydrogenation and by trapping of radicals with butyl mercaptan was also used. Approximately 10% of **2c** is formed in a solvent cage. Disproportionation also appears to occur within the cage. Less detailed studies were carried out with 1,4-diphenyl-1,4-dimethyl-2-tetrazene (**1d**) and 1,4-bis(*p*-bromophenyl)-1,4-dimethyl-2-tetrazene (**1e**). Decomposition of **1d** led to 40% of *N,N'*-dimethyldiphenylhydrazine (**2d**, 10% in cage) and 40% of disproportionation products. The remaining 20% of the **1d** is thought to form a *p*-semidine (*N,N'*-dimethyl-*N*-phenyl-1,4-benzenediamine) and the dibenzocarbazole related to it. Radicals from the decomposition of **1e** led to 37% of 1,2-bis(*p*-bromophenyl)-1,2-dimethylhydrazine (**2e**, 10% in cage), 47% of disproportionation, and 16% of hydrogen atom abstraction.

1,4-Dialkyl-1,4-diaryl-2-tetrazenes undergo singlet-state photochemical conversion into *N,N'*-dialkylhydrazoarenes.[3,4] A second major product is the *N*-alkylarylamine. Recently we were able to show with **1a** (X = Me) and **1b**

[†] Contributed with best 60th birthday wishes for Professor George S. Hammond.

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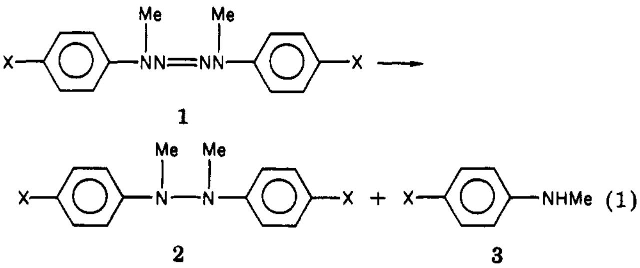
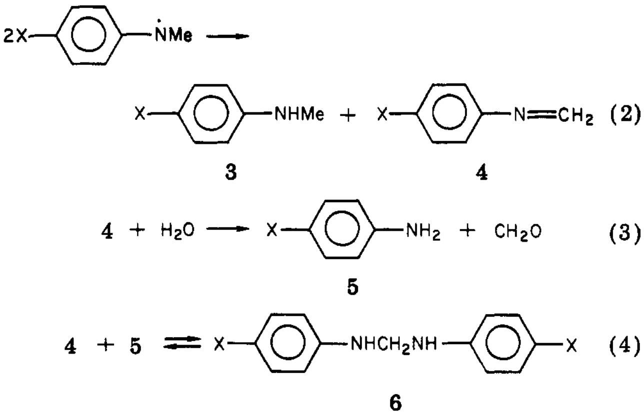
($X = CO_2Et$) (eq 1) and radical-trapping with butyl



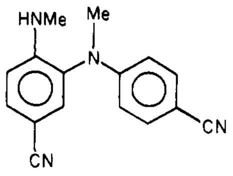
mercaptan that compounds **2a** and **2b** were formed by the recombination of *N*-methylarylamino radicals, primarily outside of a solvent cage. Trapping of these radicals resulted in a decrease and eventual leveling-off in the yields of **2a** and **2b** and a corresponding increase and leveling-off in the yields of **3a** and **3b**. Evidence was also presented for the disproportionation of the *N*-methylarylamino radicals, in that the compound **6b** ($X = CO_2Et$) was isolated from reactions of **1b**. The formation of **6b** was attributed to the initial disproportionation of radicals which gave **3b** and the *N*-methylene amine **4b** ($X = CO_2Et$) (eq 2). Subsequent reactions of **4b** then led to **6b** (eq 3 and 4).



We have continued this work with **1c** (X = CN) and are able to provide more direct and quantitative evidence for reactions 2 and 3. We have also followed the photodecomposition of **1d** (X = H) and **1e** (X = Br). We are able to show that the formation of products from these tetrazenes also can be accounted for almost entirely in terms of reactions of *N*-methylarylamino radicals.

Results and Discussion

Photochemistry of 1c (X = CN). The tetrazene **1c** is not very soluble in DME. We were obliged to work with sevenfold more dilute solutions (2.9×10^{-4} M) than earlier[2] but nevertheless have been able to make a virtually complete analysis of the products by using high-pressure LC. For the purpose of simplifying discussion a representation is given in Figure 1 of a high-pressure liquid chromatogram made at the completion of photolysis. The peaks A, C, and E were identified with the use of authentic compounds as belonging respectively to *p*-cyanoaniline (**5c**), *N*-methyl-*p*-cyanoaniline (**3c**), and the hydrazoarene **2c**. Quantitative measurements of the yields of these compounds were made and are discussed later. The peak D is attributed from earlier analogy[4] to a small amount of the *o*-semidine **7**, but firm characterization was not pursued.



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The peak B has considerable significance and was deduced in three ways to belong to the *N*-methylene amine **4c** (eq 2, X = CN).

The first way of identifying **4c** was by following its conversion into *p*-cyanoaniline (**5c**) by hydrolysis (eq 3). As soon as photolysis was complete, an aliquot of the DME solution was placed in 43.5% aqueous methanol. The composition of this solution, measured by high-pressure LC and shown in Figure 1 at so-called zero time, changed slowly with time. This was seen as the gradual disappearance of peak B (monitored daily by high-pressure LC) and a corresponding increase in peak A. The other peaks remained constant. The change from B to A was complete after 25 days of keeping the solution of photolysate in 43.5% methanol. We attribute the change to the slow hydrolysis of the *N*-methylene amine **4c** into *p*-cyanoaniline (**5c**). The yields of products at zero time and 25 days of storage are given in Table I. They show that at zero time the solution contained 16.6% of *p*-cyanoaniline (**5c**). The origin of **5c** at this stage is the hydrolysis of **4c** by water adventitiously in the DME during photolysis, in the 43.5% aqueous methanol stock solution, and in the 20% aqueous methanol flow solution used for separating peaks A and B. After 25 days of storage the amount of

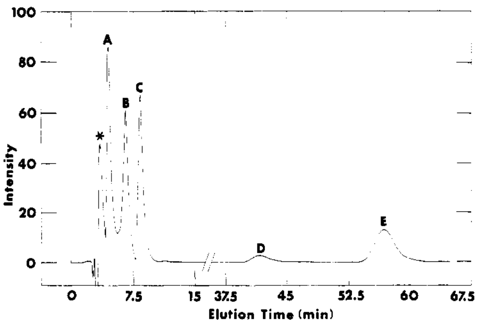

Figure 1. High-pressure liquid chromatogram after irradiation of a 2.9×10^{-4} M solution of **1c** in DME to complete disappearance of **1c**. The chromatogram is of a solution of the photolysate in 43.5% aqueous methanol obtained with a flow solvent of 43.5% aqueous methanol. The abscissa has been compressed in scale. The asterisked peak is from the photolysis solvent DME.

Table I. Yields of Products Obtained from Storing the Photolysate of 1c in 43.5% Aqueous Methanol^a

	yield,^{b} %			
	before H_2/Pt		after H_2/Pt	
product	0 day	25 days	0 day	25 days
2c	20.8	20.9	21.7	*c*
3c	41.4	42.9	63.9	*c*
4c	16.6	35.3	*c*	
5c	18.7^d	0.0		10.6

^{a} A 10-mL aliquot of the photolysate (DME) after photolysis was complete was added to a mixture of 3 mL of DME containing the internal standard and 12 mL of 43.5% aqueous methanol. ^{b} Percent of $[\mathbf{1c}]_0$. ^{c} Not measured. ^{d} The difference between yields of **4c** at zero and 25 days.

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(2) Part 6: Bae, D. H.; Shine, H. J. *J. Org. Chem.* **1980**, *45*, 4448.

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

(4) Cheng, J.-D.; Shine, H. J. *J. Org. Chem.* **1974**, *39*, 2385.

p-cyanoaniline (**5c**) in the stock solution had increased by 18.7%, and the *N*-methylene amine **4c** (peak B) had disappeared. We deduce, therefore, that at zero time a minimum of 18.7% of **4c** was present in the stock solution. The summation of yields in the stock solution, then, accounts for 97% of the initial **1c** at zero time and 99% after 25 days of storage.

The identity of **4c** was established also by hydrogenation and with assays of formaldehyde. An aliquot of the DME photolysate was hydrogenated over platinum black before dilution with aqueous methanol. Analysis showed that the yield of **2c** remained sensibly the same while that of **3c** had increased from 42.1% (average) to 63.9% (table I). These data show that the *N*-methylene amine **4c** had been present in the DME photolysate to the extent of nearly 22% and had been converted into **3c** by hydrogenation. The results suggest also that about 14% (i.e., the balance of $[\mathbf{1c}]_0$) of *p*-cyanoaniline (**5c**) was present in the DME solution. We failed to measure the amount of **5c** in the solution of hydrogenated photolysate at zero time but only after 25 days of storage, when it was found to be 10.6%. We feel that this is a reasonable agreement, accounting for 96% of $[\mathbf{1c}]_0$.

Hydrolysis of the *N*-methylene amine gives formaldehyde. The amounts of formaldehyde were assayed by using Hantzsch's reagent and Nash's method.[5] This technique not only assays formaldehyde already present but also causes hydrolysis of remaining *N*-methylene amine into formaldehyde. It is therefore a measure of the total *N*-methylene amine that may have been formed. Our results were 35% of formaldehyde before and 15.9% after hydrogenating the DME photolysate and show that 19.1% of *N*-methylene amine **4c** was present in the photolysate and was removed by hydrogenation. The result is in good agreement with that (22%) obtained by measuring the amounts of **3c** before and after hydrogenation, and with that (18.7%) by measuring the amounts of **5c** before and after hydrolysis by storage of the stock solution in 43.5% methanol.

The summary of our results is that photolysis of **1c** gives *N*-methyl-*p*-cyanoanilino radicals of which about 21% combine to give hydrazine (**2c**) and 70% disproportionate (that is, giving about 35% each of **3c** and **4c**). Of the remainder, about 7% (the difference in assayed yields of **3c** and total **4c**) undergo hydrogen atom abstraction (to give **3c**), and a small amount recombine to give what we assume to be the *o*-semidine (peak D, Figure 1).

These data show that by far the largest fate of *N*-methyl-*p*-cyanoanilino radicals is disproportionation. It appeared also in our earlier work with **1b** (X = CO_2Et) that radicals having an electron-withdrawing group prefer to disproportionate rather than recombine. In the earlier work, disproportionation led eventually to the bis(arylamino)methane **6b** (X = CO_2Et, eq 4).[2] The corresponding product (**6c**, X = CN) was not found in the present work. The reason for this may be that, because of the lower solubility of **1c**, we worked with lower concentrations of **1c** than of **1b** and that reaction 4 lay to the left.

Attempts to assay the distribution of products and the fate of the *N*-methyl-*p*-cyanoanilino radicals by trapping with butyl mercaptan (BuSH) were only partly successful. Inclusion of BuSH caused a decrease in the yield of hydrazine **2c** and an increase in the yield of *N*-methylarylamine **3c**. But, the sum of these yields at high $[\mathrm{BuSH}]_0$ was only 65% of the $[\mathbf{1c}]_0$. Trapping of radicals appeared to be inefficient. The concentrations of BuSH needed to cause decreases in the yield of **2c** were unusually large, as compared with experiments with **1d** and **1e**. The peak for **5c** continued to be seen at high $[\mathrm{BuSH}]_0$. Furthermore, a new, unidentifiable, product peak appeared in the high-pressure LC, overlapping that of **5c**. We think that this may have been the free-radical adduct of BuSH to **4c**, but we were unable to resolve this possibility (see Experimental Section). The data for yields of **2c** and **3c** in the presence of various $[\mathrm{BuSH}]_0$ are given in Table II.

Table II. Yields[a] of 2c and 3c Obtained from Irradiation of Solutions of 1c[b] Containing *n*-Butyl Mercaptan

$[\mathrm{BuSH}]/[\mathbf{1c}]_0$	% 2c	% 3c	$[\mathrm{BuSH}]/[\mathbf{1c}]_0$	% 2c	% 3c
0.0	21.5	41.0	2.0	13.0	
0.25	22.3	41.2	5.0	11.3	42.4
0.50	22.1	40.5	10.0	10.9	52.0
0.75	20.1	44.2	15.0	10.3	56.8
1.0	19.0	45.8	25.0	9.4	55.3

[a] Determined by high-pressure LC using *p*-dibromobenzene as an internal standard. [b] $[\mathbf{1c}]_0$ was 2.9×10^{-4} M in DME.

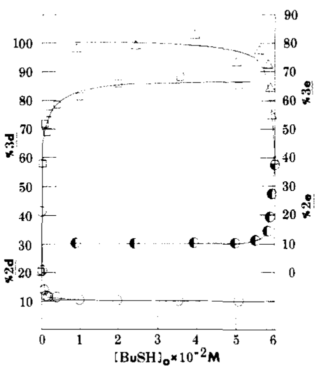

Figure 2. Effect of $[\mathrm{BuSH}]_0$ on the yields of **2d** (○) and **3d** (□) obtained from the irradiation of **1d** and of **2e** (◐) and **3e** (△) obtained from the irradiation of **1e**. Both $[\mathbf{1d}]_0$ and $[\mathbf{1e}]_0$ were 2.0×10^{-3} M in DME. The upper BuSH abscissa is for the **1e** case, while the lower one is for the **1d** case.

Our inability to trap the *N*-methyl-*p*-cyanoanilino radicals well and the persistence of product **5c** suggest that disproportionation was occurring to some extent in the solvent cage, leading to **4c** which would subsequently be hydrolyzed in part to **5c**. Disproportionation within the solvent cage would be consistent with the apparent overall preference for disproportionation shown by the *N*-methyl-*p*-cyanoanilino radicals.

Photochemistry of 1d (X = H) and 1e (X = Br). The photochemistry of **1d** and **1e** was not followed in as much detail as that of **1c**. However, the reactions were clean and, in fact, in the presence of BuSH were much more easy to follow than the reaction of **1c**.

Irradiation of a 2.0×10^{-3} M solution of **1d** in DME was complete within 20 min and gave 40.8% of **2d** (X = H) and 19.8% of **3d** (X = H). In the presence of increasing initial concentrations of BuSH the yield of **2d** decreased steadily, leveling off at close to 10%, while the yield of **3d** increased steadily, leveling off at approximately 85% (Figure 2). Thus, 95% of the tetrazene was accounted for in the presence of an excess of BuSH.

These data indicate that **1d** decomposed into radicals which, in the absence of BuSH, recombined to give **2d** (about 10% in cage and 30% out of cage) and disproportionated to give **3d** and the methylene amine **4d** (X = H)

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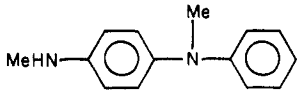
[5] Nash, T. *Biochem. J.* **1953**, *55*, 416.

each in about 20% yield. Evidence of the formation of **4d** was not obtained but is deduced from the trapping data and analogous work with **1c**. Thus, we can account for about 80% of the **1d** in the absence of BuSH. The remaining 20%, we feel, formed the *p*-semidine **8** and its



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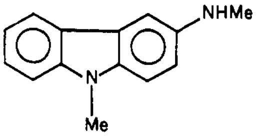

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derivative, the carbazole **9**. The ethyl analogues of **8** and **9** were isolated by Cheng and Shine from the photodecomposition of the *N,N'*-diethyl analogue of **1d**.[4] In the present work high-pressure LC showed, in fact, the presence of two other products whose small peaks near that of **2d** also diminished in the presence of BuSH. However, we did not characterize these small peaks with authentic compounds.

If we may assume that **8** is formed and in about the same cage and noncage proportions as **2d**, we can summarize the fate of the *N*-methylanilino radicals in the absence of BuSH as follows: approximately 60% undergo recombination to give **2d** (mostly) and **8**, and of these radicals 15% recombine in the solvent cage; approximately 40% of the radicals undergo out-of-cage disproportionation.

The behavior of **1e** in the absence and presence of BuSH was similar to that of **1d**. In the absence of BuSH, 37.3% of **2e** and 39.1% of **3e** were obtained. A small peak was seen in the high-pressure liquid chromatogram near that of **2e** and is assumed to be due to the *o*-semidine. The amount of **3e** obtained in the absence of BuSH is too large to be attributable to disproportionation of radicals only, since that would require 78% of these radicals to give **3e** (and **4e**). We assume, therefore, that some of the *N*-methyl-*p*-bromoanilino radicals form **3e** by hydrogen atom abstraction from the solvent and calculate that the division of pathways is then 16% hydrogen atom abstraction and 46.7% disproportionation.

The effect of BuSH (Figure 2) is to cause a leveling off of the yield of **2e** to about 10% and of **3e** to 80%. A small amount of the *o*-semidine (assumed) also remained at high $[\mathrm{BuSH}]_0$. Once again we base our evidence for disproportionation not only on the trapping data but also on the work with **1c**.

Experimental Section

Tetrazenes 1c–e. These were prepared by oxidation of the corresponding 1-aryl-1-methylhydrazines with lead(IV) oxide.[2,6] Compounds **1d** and **1e** have been reported before.[2,6] For preparing **1c**, 20 g of lead oxide was added to a mixture of 1.00 g (6.84 mmol) of 1-methyl-1-(*p*-cyanophenyl)hydrazine, 7 g of anhydrous magnesium sulfate, and 100 mL of benzene at 5 °C. The mixture was stirred at room temperature for 12 h and filtered. The residue was washed with benzene until the washings were colorless. Evaporation of the benzene left 564 mg (62.5%) of *N*-methyl-*p*-cyanoaniline. The washed residue was next extracted with benzene in a Soxhlet extractor, giving 344 mg of yellow solid which was pulverized under a small amount of benzene. Filtration left 285 mg (29%) of yellow solid, mp 226.5–227.5 °C dec.

Anal. Calcd for $C_{16}H_{14}N_6$: C, 66.2; H, 4.86; N, 28.9. Found: C, 66.1; H, 4.77; N, 28.9.

The 1-methyl-1-(*p*-cyanophenyl)hydrazine needed for making **1c** was prepared as described by Ashley and Berg[7] and had the following: mp 70.5–71 °C; ^{1}H NMR ($CDCl_3$) δ 3.24 (s, 3 H), 3.78 (br s, 2 H), 6.94 (d, 2 H), 7.45 (d, 2 H).

1,2-Diaryl-1,2-dimethylhydrazines 2c–e. Authentic **2c** (X = CN) was prepared as described earlier.[7] Authentic **2d** (X = H) was prepared by Cheng as described for the ethyl analogue[8] and had a melting point of 32–33 °C and a satisfactory ^{1}H NMR spectrum. Authentic **2e** (X = Br) was prepared by us earlier.[2] High-pressure LC has now shown the product (mp 84–85 °C) to contain a small amount of an impurity, and this was shown by mass spectrometry[9] to be 4-bromo-4'-iodo-*N,N'*-dimethylhydrazobenzene. We presume that the source of the iodine was the methyl iodide used in methylating 4,4'-dibromohydrazobenzene. The amount of the impurity was estimated to be 3% by mass spectrometry. The impurity did not interfere with the use of the **2e** for calibrating the high-pressure LC work with **1e**, and a correction of 3% was made for [**2e**] measurements.

Photochemistry. The procedure was essentially the same as described before, with 350-nm lamps.[2] The concentration of **1c** was 2.9×10^{-4} M, while the concentration of both **1d** and **1e** was 2.0×10^{-3} M. Solvent 1,2-dimethoxyethane (DME) was purified as described earlier.[2] The DME solutions were purged of air with nitrogen, and the vessels were stoppered during irradiation. Samples were taken periodically for ultraviolet monitoring and high-pressure LC. The ultraviolet spectra changed cleanly going through isosbestic points as in our earlier experiences,[2] and we were able to tell easily when all of the tetrazene had disappeared. In the case of **1c** (30 mL of a 2.9×10^{-4} M solution) this took 150 s. In the other cases the times were as follows: **1d** (25 mL of a 2.0×10^{-3} M solution), 20 min; **1e** (400 mL of a 2.0×10^{-3} M solution), 35 min. The tetrazene band which disappeared was for **1c–e**, respectively, at 360, 345, and 354 nm; the band which appeared was, respectively, at 281, 247, and 254 nm, while isosbestic points were seen at 315 and 222 nm for **1c**, 281 and 222 nm for **1d**, and 288 and 224 nm for **1e**.

High-Pressure Liquid Chromatography. A Waters instrument was used with a μ-Bondapak C-18 column in all analyses. Calibration curves for authentic compounds were made against internal standards. For the photolyses of **1d** and **1e**, in which only products **2d**, **3d** and **2e**, **3e** were assayed, the calibrations were straightforward, and the internal standards were as follows: for **2d** and **3d**, perylene, with a flow solvent of 78% aqueous methanol; for **2e** and **3e**, tetraphenylethylene with a flow solvent of 75% aqueous methanol.

In the work with **1c** where three products were assayed (**2c**, **3c**, and **5c**), it was not possible to use one flow solvent and one standard for separating all peaks. Therefore, 43.5% aqueous methanol (435 mL of methanol/L) was used for separating the peaks of **2c** and **3c**, and 20% aqueous methanol was used for separating **5c** from other peaks in the chromatogram.

The internal standard, *p*-dibromobenzene, used for assaying **2c** and **3c** with 43.5% aqueous methanol had too long a retention time for use in 20% aqueous methanol. Therefore, we used the product **3c** itself as an internal standard for **5c**, and a calibration curve of **5c** against **3c** was made.

In practice, then, an aliquot of the photolysate (DME) was diluted to volume with 43.5% aqueous methanol. The concentrations of **2c** and **3c** in this solution were determined first, with 43.5% aqueous methanol also used as the flow solvent. Next, the concentration of **5c** was determined by using 20% aqueous methanol and the now-known amount of **3c** as the standard.

Trapping experiments were carried out as described earlier.[2] The results for photolyses of **1d** and **1e** are given in Figure 2. The data for the photolysis of **1c** accounted for only 65% of the **1c** and are given in Table II.

Hydrogenation and Hydrolysis Experiments with 1c. A 100-mL portion of a 3.1×10^{-4} M solution of **1c** in DME was irradiated for 2 min. A 10-mL aliquot was withdrawn and placed in a foil-wrapped 25-mL volumetric flask for later analysis. The remaining solution was hydrogenated at atmospheric pressure over 3 mg of Adam's catalyst for 6 h. This solution was filtered, and 10 mL was withdrawn for analysis. Each 10-mL aliquot was diluted to 25 mL with 43.5% aqueous methanol and analyzed immediately (zero time) by high-pressure LC. A composite

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chromatogram of the unhydrogenated photolysate is shown in Figure 1. Assays of this photolysate were made periodically until the peak B (Figure 1) had disappeared (25 days). The results are given in Table I.

Assay of Formaldehyde. Hantzsch's reagent solution was prepared as described.[5] The molar absorbtivity of diacetyldihydrolutidine (the product of reaction of Hantzsch's solution with formaldehyde) was determined in aqueous DME as follows. A solution of 2.46 mg (8.2×10^{-2} mmol) of paraformaldehyde was made in 100 mL of Hantzsch's solution, and this was diluted to 200 mL with DME. The mixture was incubated at 45–50 °C for 12 h and diluted appropriately with a 50:50 mixture of Hantzsch's solution and DME for spectrophotometry at three dilutions. The molar absorptivity was $7.48 \pm 0.06 \times 10^3$. Nash reports a molar absorptivity of 8.0×10^3 in aqueous solutions.[5] Assays of formaldehyde in photolysis solutions were carried out before and after hydrogenation in the same way. This means necessarily that the assay before hydrogenation refers to free formaldehyde plus that obtained by hydrolysis of **4c** by Hantzsch's reagent. Assay after hydrogenation refers to free formaldehyde only.

***N*-Methylbutane-*p*-cyanosulfenanilide.** There are two possible adducts of BuSH to the *N*-methylene amine **4c**. One of these is *N*-methylbutane-*p*-cyanosulfenanilide, $NCC_6H_4N(SBu)CH_3$ (**10**), and the other is *N*-[(butylthio)methyl]-*p*-cyanoaniline, $NCC_6H_4NHCH_2SBu$ (**11**). The former (**10**) could arise from ionic addition and the latter (**11**) from free-radical addition of BuSH to **4c**. It was thought that either one could be responsible for the new unidentified peak which appeared in the HPLC chromatograms when **1c** was photolyzed in the presence of BuSH. The preparation of **10** was carried out by reaction of *N*-methyl-*p*-cyanoaniline with butanesulfenyl chloride according to the procedure of Ainpour and Heimer.[10] The product [bp 132–136 °C (0.03 mmHg] was found by ^{1}H NMR and high-pressure LC to contain some *N*-methylaniline. The retention time of **10** in the high-pressure LC was greater than that of the unidentified peak. Attempts to make **11** for high-pressure LC comparison with the unidentified peak were not successful.

Registry No. 1c, 79121-25-8; **1d**, 5579-27-1; **1e**, 74763-65-8; **2c**, 79121-26-9; **2d**, 14996-70-4; **2e**, 74763-66-9; **3c**, 4714-62-9; **3d**, 100-61-8; **3e**, 6911-87-1; **4c**, 79121-27-0; **5c**, 873-74-5; 1-methyl-1-(*p*-cyanophenyl)hydrazine, 79121-28-1.

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Cation–Anion Combination Reactions. 20.[1] Reactions of Nucleophiles with *trans*-3-Methoxy- and *trans*-3-(Methylthio)acrylophenones

Calvin D. Ritchie* and Atsushi Kawasaki

Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214, and College of General Education, Shinshu University, 3-1-1 Asahi, Matsumoto 390, Japan

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The reactions of a number of nucleophiles with *trans*-3-methoxyacrylophenone (MeOAcr) and with *trans*-3-(methylthio)acrylophenone (MeSAcr) in water and methanol have been studied. The reactions of amines produce enamines as the first observable products, and primary amines show simple kinetics: first-order with respect to amine and first-order with respect to the acrylophenone. Piperidine reactions show kinetics which are consistent with a change in the rate-determining step with a change in amine concentration. Methoxylamine reactions produce the monooximes, and semicarbazide reactions produce the monosemicarbazone with MeOAcr but the disemicarbazone with MeSAcr. The reactions of hydroxide ion produced the enolate of benzoylacetaldehyde, which, at the high base concentration used in the MeSAcr reaction, was further converted to acetophenone and formate ion. Methoxide and cyanide ion reactions given addition across the double bond. Rate constants for the reactions of MeOAcr are 20–1000 times greater than those for corresponding reactions of MeSAcr. There is a very good correlation of the rate constants for reactions of nucleophiles with MeOAcr and those with 2,4-dinitrophenyl acetate in both water and methanol solution.

Some years ago, Friedman and his co-workers[2,3] showed that the relative rates of reactions of a series of amines and thiolates with a variety of compounds of the type $CH_2=CHX$, with X = CN, $CONH_2$, CO_2R, $PO(OR)_2$, and SO_2R, are independent of the identity of X. The Brønsted slopes for the reactions of amines are all very close to 0.4, and the thiolate/amine rate ratios are ca. 150. These characteristics are very similar to those which we have reported for reactions of these nucleophiles with a range of electrophiles.[1]

Fedor and his co-workers[4] have carried out mechanistic studies of the reactions of amines with a series of para-substituted *trans*-3-methoxyacrylophenones which support the addition–elimination mechanism proposed by Rappoport[5] for these types of reactions and which indicate that attack of amine is the rate-determining step of the reactions.

We became interested in these latter reactions for two primary reasons: first, we wished to examine further cases of neutral electrophiles reacting with nucleophiles in different solvents in order to gain further information on the variations in relative reactivities of electrophiles with change in solvent[6]; second, the replacement of the methoxy group with a methylthio group offered the opportunity of investigating the effect of this change from a group with high to a group with low polarizability directly bonded to the electrophilic reaction site. The first reason above was strengthed by Hoz's recent report[7] that the reactions of nucleophiles with α,α-dinitromethylenefluorene in several different solvents followed the N_+ relationship based on

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