Photoinduced Ring Enlargement Reactions of 2*H*-1,2,4-Benzothiadiazine 1,1-Dioxides. Steady-State and Laser Flash Photolysis Studies[1]

C. V. Kumar,[2a,b] K. R. Gopidas,[2a] K. Bhattacharyya,[2b] P. K. Das,*[2b] and M. V. George*[2a,b]

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India, and Radiation Laboratory and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received November 8, 1985

Ring-enlargement reactions of several 2*H*-1,2,4-benzothiadiazine 1,1-dioxides under photoexcitation have been studied by steady-state irradiation, product analysis, and laser flash photolysis. Irradiations in benzene or methanol gave moderate yields (14–70%) of 6-methyl-5*H*-dibenzo[*b*,*g*][1,4,6]thiadiazocine 12,12-dioxides in most cases. The product formation may take place either by a direct ring enlargement process to a precursor (**7**), which rapidly isomerizes to the photoproduct (**6**) or through a pathway involving a diradical intermediate (**5**). Laser flash photolysis under direct excitation (308 and 266 nm) gave long-lived transients characterized by weak absorptions at 315–420 nm and attributed to either **7** or **5**. Both benzophenone and *p*-methoxyacetophenone triplets were quenched by the benzothiadiazine dioxides with rate constants (0.58–7.8) × 10^9 M^{-1} s^{-1}. The triplets were shown to be photoreactive in the ring-enlargement reaction.

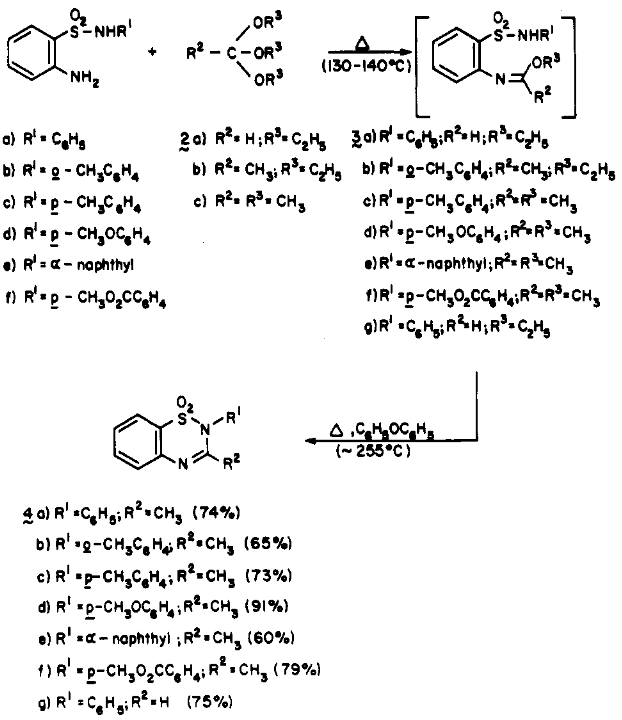
Several examples of the photochemical and thermal transformations of heterohexa-1,3,5-trienes are reported in the literature.[3] Heterohexa-1,3,5-trienes containing heteroatoms such as oxygen, nitrogen, and sulfur can, in principle, undergo electrocyclic reaction leading to heterocyclohexa-1,3-dienes or intramolecular cycloaddition, leading to heterobicyclo[3.1.0]hexenes.[3] In addition, heterohexa-1,3,5-trienes can give rise to five-membered ring systems through a pentadienyl anion mode of cyclization.[4] There has been no report so far on the photochemical or thermal transformations of 2*H*-1,2,4-benzothiadiazines, which are potential precursors of heterohexa-1,3,5-trienes containing one sulfur and two nitrogen atoms. In this context, we have examined the photochemical transformations of a few 2*H*-1,2,4-benzothiadiazine 1,1-dioxides. Laser flash photolysis studies have also been carried out to characterize the transients involved in these photoreactions. The substrates that we have examined include 2*H*-1,2,4-benzothiadiazine 1,1-dioxides **4a–g** (Scheme I).

Results and Discussion

(1) Preparative Photochemistry and Product Identification. The thiadiazine dioxides **4a–g** were prepared by a slight modification of the earlier procedure,[5] as shown in Scheme I.

Irradiation of **4a** in benzene gave a 25% yield of 6-methyl-5*H*-dibenzo[*b*,*g*][1,4,6]thiadiazocine 12,12-dioxide (**6a**) and a 50% recovery of the starting material (**4a**) (Scheme II), whereas in methanol the corresponding yields of **6a** and **4a** were 44% and 40%, respectively. Similarly, the irradiation of **4b–f** in benzene and methanol gave the corresponding thiadiazocine dioxides **6b–e** in yields ranging between 25–70% and 14–50%, respectively, together with significant amounts of the starting material (**4b–f**), in each case. When the irradiation of **4d** was carried out under acetophenone sensitization in benzene, under conditions wherein the sensitizer absorbed most of the light, a 40% yield of **6d** was obtained, along with a 30% recovery of the starting material (**4d**). The irradiation of **4g** in benzene, on the other hand, gave a 68% yield of *N*-(2′-formamidobenzenesulfonyl)aniline (**10**), whereas the irradiation in methanol gave a mixture of **10** (8%) and *N*-(2′-aminobenzenesulfonyl)aniline (**1a**, 72%) (Scheme III). The structures of all the products were confirmed on the basis of analytical results, spectral data, and chemical evidence. Acid hydrolysis of **6a**, for example, gave a 74% yield of 2,2′-diaminobiphenyl sulfone (**8a**), in agreement with the assigned structure **6a**. Similarly, acid hydrolysis of **6c** gave a 64% yield of 2,2′-diamino-5-methyldiphenyl sulfone (**8b**) (Scheme IV). The structure **10** was confirmed through its photolysis in methanol to give **1** (71%) and also through the formylation of **1** by treatment with formic acid to give back **10** (71%).

Scheme I



The formation of the different benzothiadiazocine dioxides **6a–f** from **4a–f** could be rationalized in terms of either a diradical pathway (path "a") or through a concerted mechanism (path "b"), shown in Scheme II. The formation of **10** from **4g**, on the other hand, could be

---

[1] Document No. NDRL-2781 from the Notre Dame Radiation Laboratory.

[2] (a) Indian Institute of Technology. (b) University of Notre Dame.

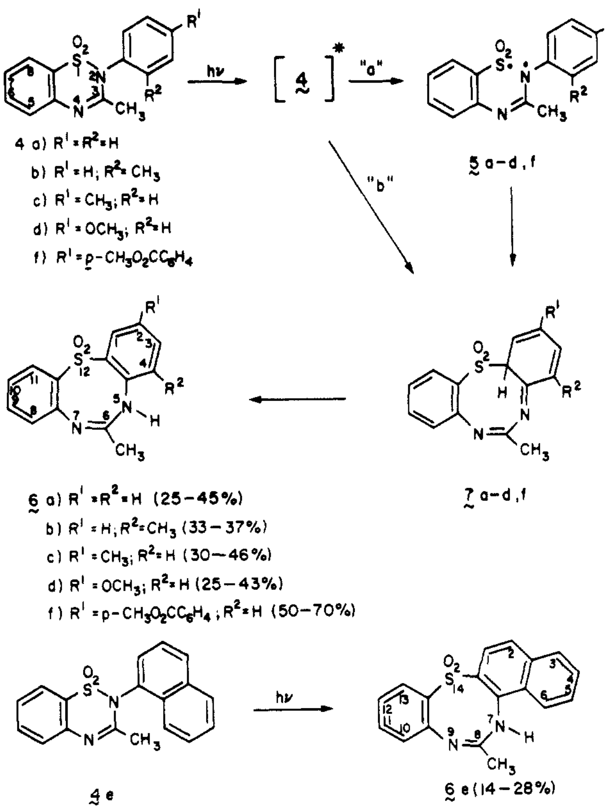
[3] For some examples of heterohexa-1,3,5-triene transformations, see: (a) Marvell, E. N. In *Thermal Electrocyclic Reactions*; Academic Press: New York, 1980; pp 305–342. (b) Jutz, J. C. In *Topics in Current Chemistry*; Springer-Verlag: Berlin Heidelberg, 1978; Vol. 73, pp 125–230. (c) George, M. V.; Mitra, A.; Sukumaran, K. B. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 973–983.

[4] For some examples of pentadienyl anion cyclizations, see: (a) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 947–973. (b) Taylor, E. C.; Turchi, I. J. *Chem. Rev.* **1979**, *79*, 181–231. (c) Staley, S. W. In *Pericyclic Reactions*; Lehr, R. E., Marchand, A. P., Eds.; Academic Press: New York, 1977, Vol. 1, pp 199–264.

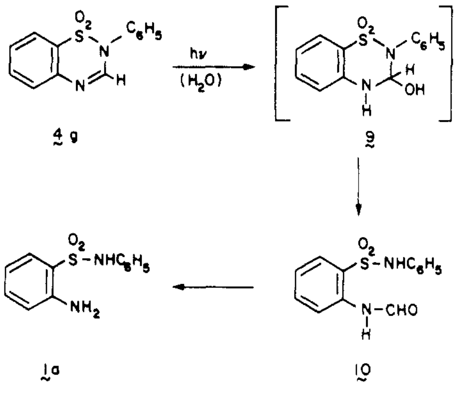
[5] Freeman, J. H.; Wagner, E. C. *J. Org. Chem.* **1951**, *16*, 815–837.

0022-3263/86/1951-1967$01.50/0

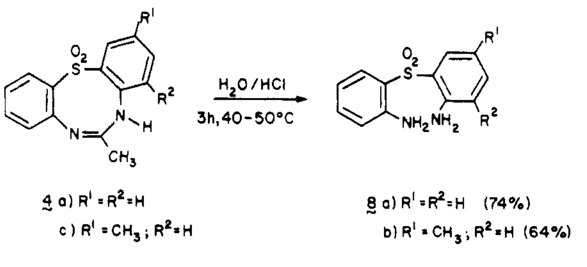
Scheme II



Scheme III



Scheme IV



through the addition of water (from the moisture present in the solvent) to **4g** and involving the hydroxy derivative **9**, as shown in Scheme III. Further transformation of **9** will lead to **10**, which in turn will be converted to **1a**, through its interaction with the solvent. In support of this view, it has been observed that the irradiation of **10**, in methanol, for example, gave a 71% yield of **1a**.

From our studies, it is evident that when the 3-position of the starting benzothiazine dioxide does not have a substituent, excepting a hydrogen atom as in **4g**, facile addition of water across the C=N bond is observed. However, when the 3-position is substituted with a methyl group, as in **4a–f**, then water addition is not observed; instead the substrate undergoes photorearrangement to give the corresponding ring-enlargement products. When the phenyl group at the 2-position of the thiadiazine moiety carries either electron-donating or -withdrawing substituents as in **4b–f**, facile ring enlargement reactions leading to the corresponding dibenzothiazocines, **6b–f**, are observed. When an α-naphthyl group is present at the 2-position as in **4e**, then the photoreaction leading to **6e** is considerably slowed down and steric factors may be responsible for the poor yield of the photoproduct (**6e**) in this case. The exact role of the substituents in these rearrangements is not very clear.

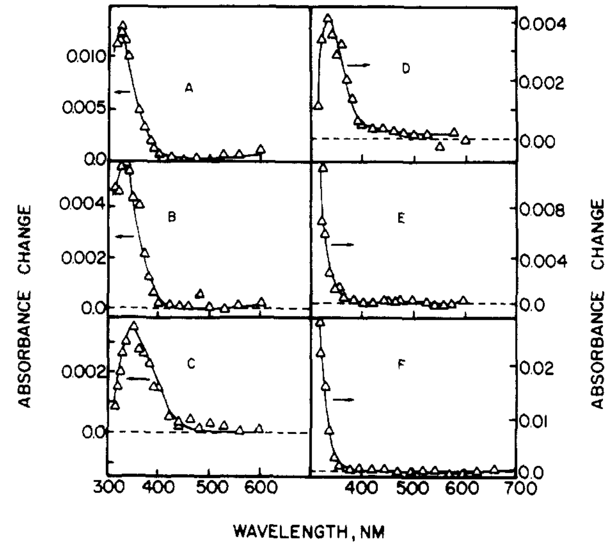


Figure 1. Photoproduct absorption spectra observed at 3–5 μs following 308 nm laser flash photolysis of (A) **4a**, (B) **4c**, (C) **4d**, (D) **4e**, (E) **4f**, and (F) **4g** in methanol. The ground-state absorbances of the solutions at 308 nm were 0.55–0.60 in 2-mm cells.

Unlike the photoreactions of **4a–f**, leading to products **6a–f**, attempted thermal transformation of **4a–f** by refluxing in diphenyl ether (~255 °C) did not give any isolable product; most of the starting material could be recovered, in each case. In contrast, the refluxing of **4g** in diphenyl ether for 10 h gave a 87% yield of **10** and this reaction may be proceeding through the intermediate **9**, as shown in Scheme III.

(2) Laser Flash Photolysis Studies. The benzothiadiazine dioxides **4a–g** were subjected to laser flash photolysis under direct excitation at 308 nm (in benzene and methanol) and 266 nm (in methanol) as well as under sensitization by benzophenone and *p*-methoxyacetophenone (in benzene and acetonitrile). At millimolar concentrations these substrates have negligible absorptions at >320 nm; this renders the sensitization experiments feasible under 337.1 nm and 355 nm laser excitation. However, in the latter experiments the short-wavelength spectral region remains inaccessible for the purpose of the monitoring of photoproduct absorption because of laser scatter and/or sensitizer and substrate ground-state absorptions.

Upon 308 nm laser flash photolysis in methanol, substrates **4a–e** produce long-lived transient photoproducts absorbing weakly at 315–420 nm ($\lambda_{max}{}^{P}$ = 325–350 nm).[6] The transient absorption spectra are illustrated in Figure 1, parts A–D. Compared to **4a–c,e**, $\lambda_{max}{}^{P}$ in the case of **4d** is conspicuously red-shifted (350 nm). The photoproduct spectra in the case of **4f** and **4g** (Figure 1, parts E and F)

---

[6] These maxima correspond to *difference* absorption spectra and are not necessarily the true absorption maxima.

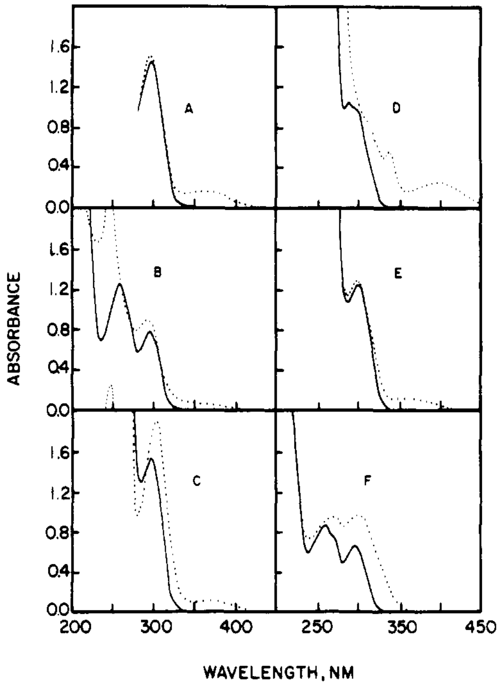


Figure 2. Absorption spectral changes (permanent) observed upon irradiation (5 min) of (A) **4a** in benzene, (B) **4a** in methanol, (C) **4d** in benzene, (D) **4e** in benzene, (E) **4f** in benzene, and (F) **4g** in methanol, by repetitive 308 nm laser pulses (10 Hz, ca. 5 × 10^{-7} einsteins s^{-1} cm^{-2}) in 2 mm × 10 mm cells (path length 2 mm). The continuous and dotted curves represent absorption spectra before and after irradiation, respectively. Irradiation for longer and shorter periods (2–10 min) in each case showed the isosbestic nature of the points of intersection of each pair of curves.

keep on rising, on going to shorter wavelengths and fail to show any maxima in the spectral region 315–700 nm. The photoproducts undergo slight decay ($\lesssim$20%) on the longest time scale (~150 μs). Their decay kinetics and as well as yields remain unaffected in the presence of oxygen (~2 mM). Laser flash photolysis at 308 nm in benzene and at 266 nm in methanol gave essentially similar results, except that the photoproduct spectra in benzene are more extended into the visible ($\lesssim$500 nm). One interesting difference in the behavior of **4g**, relative to other substrates, was that if the photolysis solution under 308 nm laser excitation was not disturbed by shaking (in a static cell) or not allowed to drain out and replenished (in the flow cell), negative absorbance changes (bleaching) were observed at 320–350 nm as a result of the action of subsequent laser shots. This points to the lack of photostability of the initial product accumulated in the case of **4g**.

The insensitivity of the yields and decay kinetics of photoproducts toward oxygen strongly suggests that these are not the triplets of the substrates and that the latter, if long-lived, are not involved as intermediates for the photoproducts under direct excitation. In view of the long-lived character (τ > 500 μs) of the transient absorptions, it was important to examine critically if there were substantial contributions from the final isolated products (i.e., **6a–e**) formed via a fast route. For this purpose, we have recorded the permanent absorption spectral changes upon partial photolysis of the substrates **4a–g** using 308 nm laser pulses (repetitive, 10 Hz). A few representative cases are presented in Figure 2. Except for **1g**, the product spectra are characterized by long-wavelength band systems (λ_{max}'s in benzene ≈ 365 nm for products from **4a–d,f** and 338 and 392 nm for product from **4e**). A comparison with the absorption spectra of the isolated, ring-expanded products (benzothiadiazocine dioxides) reveals that these compounds and the unreacted substrates are the principal components of the partially photolyzed mixtures from 308 nm laser irradiation. Although the existence of the long-wavelength absorption band-systems at 330–460 nm for the ring-expanded products and the observation of absorptions due to laser-flash-photolytic, long-lived photoproducts in the same region suggest a link between the two, a close scrutiny shows that they are not related. For example, the substituents (OCH_3 vs. $COOCH_3$) at the 2-position of dibenzothiadiazocine dioxides do not make any difference in the location of the low-energy λ_{max} of the products of photolysis (365 nm in benzene); however, the transient photoproduct spectra seen upon laser flash photolysis show a substantial difference ($\lambda_{max}{}^{P}$ = 350 nm vs. <315 nm for **4d** vs. **4f** in methanol). Similarly, in the case of the α-naphthyl derivative (**4e**), the two-band feature of the spectrum of the isolated product (**6e**) is absent in the laser-pulse-induced transient spectra. In view of this spectral dissimilarity as well as the transient nature of the absorption, we are led to the conclusion that the final ring-expanded products are not responsible for the absorption changes at $\lesssim$150 μs following laser flash photolysis. Plausible assignments for the latter may be sought in terms of the diradical **5** or the intermediate **7** (based on the predominant photochemistry observed under steady-state irradiation). In view of the insensitivity of the decay of the transients toward oxygen, the diradical assignment appears unlikely.

Table I. Transient Photoproduct Maxima ($\lambda_{max}{}^{P}$) upon 308 nm Laser Excitation of 4a–f in Methanol and Bimolecular Rate Constants ($k_q{}^{T}$) for the Quenching of Benzophenone (BP) and *p*-Methoxyacetophenone (PMA) Triplets by 4a–f in Benzene and Acetonitrile

		$k_q{}^{T}$,[b] 10^9 M^{-1} s^{-1}			
quencher	d$\lambda_{max}{}^{P}$,[a] nm	^{3}BP*/-Bz	^{3}PMA*/-Bz	^{3}BP*/-MeCN	^{3}PMA*/-MeCN
4a	325	0.67	3.4	1.2	3.8
4b	330	0.58	3.0	0.85	3.4
4c	330	0.68	3.3	1.2	3.5
4d	350	0.81	3.5	1.2	3.8
4e	330	4.3	5.6	6.1	7.8
4f	<315	0.57	3.3	1.3	3.9
4g	<315	1.3	3.5	2.1	4.2

[a] ± 5 nm. [b] Ca. ± 15%.

The substrates **4a–g** prove to be moderate to efficient quenchers for benzophenone (BP) and *p*-methoxyacetophenone (PMA) triplets. The bimolecular rate constants ($k_q{}^{T}$) for quenching, obtained from the linear dependence of the pseudo-first-order rate constants (for ketone triplet decay) on substrate concentrations are compiled in Table I. The BP and PMA triplets were produced by excitation with 337.1 nm laser pulses and monitored by their absorptions 520–530 nm and 370–380 nm, respectively. From the kinetic data, it is not obvious if the mechanism of the quenching is charge transfer or energy transfer. However, the lack of observation of ketyl radical (λ_{max} = 545 nm) or radical anion (600–700 nm) in the course of the quenching of BP triplet in benzene and acetonitrile points against a charge-transfer mechanism with the substrates acting as electron donors. On the other hand, the fact that $k_q{}^{T}$ increases on going from BP (E_T = 69 kcal mol^{-1})[7] to PMA (E_T = 72 kcal mol^{-1})[7] is compatible with an energy-transfer mechanism.

As evident from Table I, $k_q{}^{T}$'s in both benzene and acetonitrile are much higher for 4e than for other substrates. Understandably, the naphthyl group (E_T for

---

[7] Murov, S. L. *Handbook of Organic Photochemistry*; Marcel-Dekker: New York, 1973.

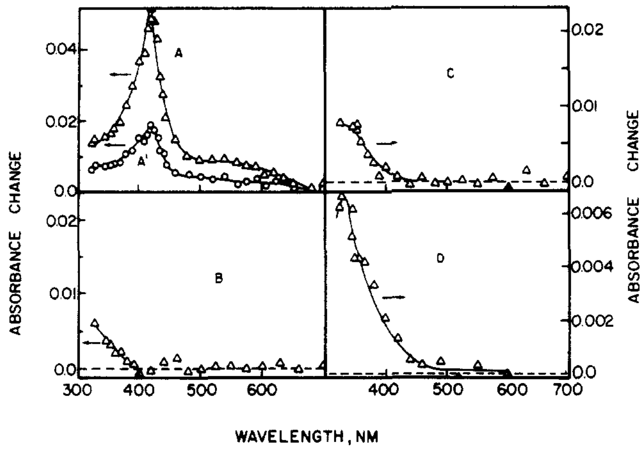


Figure 3. Transient absorption spectra at (A) 1, (A′) 7, (B) 3 and (C & D) 5 μs following 337.1 nm laser excitation of *p*-methoxyacetophenone in the presence of (A, A′) **4e**, (B) **4d**, (C) **4b** and (D) **4d** in benzene (each substrate at 5 mM).

naphthalene = 61 kcal mol^{-1})[7] provides an exothermic energy-transfer pathway for quenching. The transient absorption spectrum (Figure 3, parts A and A′) of the product of quenching of the ketone triplets by **4e** has its maximum at 420 nm (in benzene) and resembles, in both appearance and location, the triplet–triplet absorption spectrum of naphthalene (λ_{max} = 423 nm in benzene).[8] It is quenched by oxygen with a rate constant of 8.1 × 10^8 M^{-1} s^{-1} (in benzene). The most reasonable assignment for the 420 nm species is that it is the triplet of **4e** with the excitation energy localized primarily on the naphthyl moiety. The fact that this transient is not observed as a result of the direct laser excitation (266 or 308 nm) of **4e** in methanol suggests that the intersystem crossing quantum yield is negligible for this system. While the relatively short lifetime (5.6 μs in benzene) of the triplet of **4e** suggests its photoactive nature (see below), no growth component concomitant with its decay is observed at short wavelengths (Figure 3, parts A and A′).

The decay of PMA triplet under efficient quenching by **4a–d,f** leads to weak, but nonnegligible, residual absorptions with spectral and kinetic features reminiscent of those seen under direct laser excitation. The transient spectra in three cases are shown in Figure 3, parts B–D. The insensitivity of decay of these transient absorptions toward oxygen rules out their assignments in terms of triplets of **4a–d** or ketyl radical derived from PMA. It is possible that these correspond to the same species seen under direct laser excitation. It is worthwhile to note that the photolysis of PMA in benzene containing 1 mM **4d** and **4e** by repetitive 355 nm laser pulses leads to accumulation of the photoproducts **6d,e**. This is evident from the development of the characteristic long-wavelength band systems of the latter at 330–400 nm. This establishes that the triplets of **4d,e**, as well as those of the other substrates (by analogy), are photoreactive as far as the ring-enlargement reaction is concerned. A similar conclusion has also been arrived at on the basis of acetophenone-sensitized, steady-state photolysis of **4d** in benzene (vide supra).

In order to ascertain if long-lived triplets participate in the photochemistry under direct excitation, steady-state photolysis experiments were carried out by using **4a** and **4d** as substrates in the presence and absence of 2,5-dimethyl-2,4-hexadiene (DMHD) in benzene. From the triplet quenching rate data (Table I) it appears that the triplet energies of **4a–d,f,g** are close to or higher than the triplet energy of benzophenone (E_T = 69 kcal mol^{-1}).[7] Thus the triplets of **4a** and **4d** should be quenched by the diene (E_T = 59 kcal mol^{-1})[7] with rate constants in the limit of diffusion control. The photolysis (310 nm) of deaerated benzene solutions of **4a** and **4d** in the presence of DMHD (≤0.15 M) gave photoprodut absorptions (340–430 nm), the intensities of which were practically identical with those observed under similar conditions of irradiation in the absence of the diene. This result suggests that if the triplets of **4a** and **4d** are important intermediates for the observed photochemistry under direct excitation they must have very short lifetimes (subnanosecond). Alternatively, the photoreactions are predominantly singlet-mediated. We should note that prolonged photolysis of **4a** and **4d** in the presence of excess of DMHD (~0.2 M) led to the formation of additional photoproducts (λ_{max}'s = 344 and 363 nm) which were not characterized.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The ^{1}H NMR spectra were recorded by using tetramethylsilane as an internal standard. Steady-state irradiations were carried out in a Srinivasan–Griffin Rayonet photochemical reactor (2537 or 3000 Å) or using a Hanovia 450-W medium-pressure mercury lamp in a quartz-jacketted immersion well.

Starting Material. Triethyl orthoformate (**2a**) (Aldrich) was freshly distilled (bp 145–146 °C) before use. Triethyl orthoacetate (**2b**),[9] bp 144–146 °C, trimethyl orthoacetate (**2c**)[10] bp 107–109 °C, *N*-(2′-aminobenzenesulfonyl)aniline (**1a**),[5] mp 121–122 °C, *N*-(2′-aminobenzenesulfonyl)-2-methylaniline (**1b**),[5] mp 115–116 °C, *N*-(2′-aminobenzenesulfonyl)-4-methylaniline (**1c**),[5] mp 125–126 °C, and *N*-(2′-aminobenzenesulfonyl)-1-naphthylamine (**1e**),[5] mp 128–129 °C, were prepared by reported procedures. Solvents for steady-state photolysis studies were purified and distilled before use, whereas Aldrich Gold Label solvents were used for laser studies. Petroleum ether used was the fraction with bp 60–80 °C.

Preparation of 2*H*-1,2,4-Benzothiadiazine 1,1-Dioxides 4a–e,g. A general procedure for the preparation of **4a–e,g** was to heat a mixture of the starting *N*-(2′-aminobenzenesulfonyl)aniline **1a–e,g** with an excess of the ortho ester **2** around 130–140 °C for 0.5 h and to remove the unchanged ortho ester under vacuum. The resultant residue was refluxed in diphenyl ether (25 mL) for 0.5 h and the solvent removed under vacuum. The product was purified by recrystallization from suitable solvents, in each case.

3-Methyl-2-phenyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (4a): mp 162–163 °C (chloroform) (74%) from the reaction of **1a** (5 mmol) and **2b** (7.5 mmol); IR ν_{max} (KBr) 3040, 2980, 2940 (CH), 1601 (C=N), 1575 (C=C), 1332 and 1060 (SO$_2$) cm^{-1}; UV λ_{max} (methanol) 260 nm (ε 14 100), 270 (11 900, sh), 297 (8700 sh); ^{1}H NMR (CDCl$_3$) δ 2.14 (3 H, s, methyl), 7.40 (8 H, m, aromatic), 7.82 (1 H, d, $J_{7,8}$ = 7 Hz, H-8). Anal. Calcd for $C_{14}H_{12}N_2O_2S$: C, 61.76; H, 4.41; N, 10.29. Found: C, 61.90; H, 4.44; N, 9.96.

3-Methyl-2-(2′-methylphenyl)-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (4b): mp 155–156 °C (lit.[5] mp 154–155 °C) (65%) from the reaction of **1b** (18 mmol) with **2b** (25 mmol).

3-Methyl-2-(4′-methylphenyl)-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (4c): mp 172–173 °C (chloroform) (73%) from the reaction of **1c** (10 mmol) with **2c** (15 mmol); IR ν_{max} (KBr) 3060, 3020, 2920, 2860 (CH), 1610 (C=N), 1585 (C=C), 1330 and 1160 (SO$_2$) cm^{-1}; UV λ_{max} (methanol) 260 nm (ε 15 000), 275 (11 000 sh), 300 (8500); ^{1}H NMR (CDCl$_3$) δ 2.1 (3 H, s, methyl), 2.4 (3 H, s, methyl), 7.6 (8 H, m, aromatic). Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.94; H, 4.90; N, 9.79. Found: C, 62.89; H, 4.62; N, 9.41.

3-Methyl-2-(4′-methoxyphenyl)-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (4d): mp 171–172 °C (1:1 mixture of benzene and

---

[8] Bensasson, R.; Land, E. J. *Photochem. Photobiol. Rev.* **1978**, *3*, 163–191.

[9] McElvain, S. M.; Nelson, J. W. *J. Am. Chem. Soc.* **1942**, *64*, 1825–1827.

[10] Sah, P. P. T. *J. Am. Chem. Soc.* **1928**, *50*, 516–518.

petroleum ether) from the reaction of **1d** (10 mmol) with **2c** (15 mmol); IR ν_{max} (KBr) 3040, 3000, 2955, 2820 (CH), 1600 (C=N), 1525 (C=C), 1320 and 1160 (SO_2) cm^{-1}; UV λ_{max} (methanol) 251 (ϵ 14 800), 266 (15 000), 295 (94 000); ^1H NMR ($CDCl_3$) δ 2.1 (3 H, s, methyl), 3.8 (3 H, s, methoxy), 7.3 (8 H, m, aromatic). Anal. Calcd for $C_{15}H_{14}N_2O_3S$: C, 59.68; H, 4.63; N, 9.27. Found: C, 59.52; H, 4.59; N, 9.23.

3-Methyl-2-(1-naphthyl)-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (4e): mp 152–153 °C (chloroform) (60%) from the treatment of **1e** (10 mmol) with **2c** (15 mmol); IR ν_{max} (KBr) 3060, 2930 (CH), 1610 (C=N), 1585 (C=C), 1230 and 1180 (SO_2) cm^{-1}; UV λ_{max} (methanol) 252 nm (ϵ 16 100), 262 (16 000), 271 (15 900), 284 (16 100), 297 (16 200); ^1H NMR ($CDCl_3$) δ 2.1 (3 H, s, methyl), 7.6 (11 H, m, aromatic). Anal. Calcd for $C_{18}H_{14}N_2O_2S$: C, 67.08; H, 4.34; N, 8.69. Found: C, 66.81; H, 4.23; N, 8.97.

2-Phenyl-2*H*-1,2,4-benzothiadiazine 1,1-dioxide (4g): mp 133–134 °C (lit.[5] mp 133–134 °C) (75%) from the reaction of **1a** (10 mmol) with **2a** (15 mmol).

Preparation of 2-(4′-Carbomethoxyphenyl)-3-methyl-2*H*-1,2,4-benzothiadiazine 1,1-Dioxide (4f). *N*-(2′-Nitrobenzenesulfonyl)-4-carbomethoxyaniline, mp 199–200 °C (methanol) was prepared in a 45% yield by the treatment of 2-nitrobenzenesulfonyl chloride (15 mmol) with methyl 4-aminobenzoate (15 mmol) in pyridine (20 mmol) (mixing at room temperature and stirring at 60–70 °C for 1 h, followed by workup by treatment with dilute (2 N) hydrochloric acid): IR ν_{max} (KBr) 3200 (NH), 3040, 3020, 2938, 2850 (CH), 1680 (C=O), 1600 (C=C), 1345 and 1150 (SO_2) cm^{-1}. *N*-(2-Aminobenzenesulfonyl)-4-carbomethoxyaniline (**1f**), mp 174–175 °C was prepared by the reduction of *N*-(2′-nitrobenzenesulfonyl)-4-carbomethoxyaniline (6.8 mmol) with zinc (4 g) and glacial acetic acid (50 mL) (addition of zinc in small portions at 80 °C for 0.5 h, followed by pouring over crushed ice): IR λ_{max} (KBr) 3430, 3340 (NH_2), 3205 (NH), 3040, 3000, 2935, 2850 (CH), 1685 (C=O), 1600 (C=C), 1310 and 1135 (SO_2) cm^{-1}.

Heating of a mixture of **1f** (5 mmol) and **2c** (10 mmol) around 115–125 °C for 0.5 h, followed by removal of the unchanged **2c** under vacuum and recrystallization of the residue from a mixture (1:1) of chloroform and petroleum ether, gave a 99% yield of **3f**, mp 148–149 °C: IR λ_{max} (KBr) 3235 (NH), 3040, 3015, 2970, 2920 (CH), 1680 (C=O), 1660 (C=N), 1590 (C=C), 1280 and 1150 (SO_2) cm^{-1}.

Refluxing of **3f** (4.8 mmol) in dry xylene (15 mL) for 2.5 h, followed by workup in the usual manner, gave a 79% yield of **4f**, mp 193–194 °C (recrystallization from a mixture (1:1) of methanol and petroleum ether): IR ν_{max} (KBr) 3075, 3025, 3000, 2935 (CH), 1710 (C=O), 1600 (C=N), 1570 (C=C), 1320 and 1170 (SO_2) cm^{-1}; UV λ_{max} (methanol) 258 nm (ϵ 18 800), 263 (21 700), 296 (11 700); ^1H NMR ($CDCl_3$) δ 2.16 (3 H, s, methyl), 3.93 (3 H, s, carbomethoxy), 7.71 (8 H, m, aromatic). Anal. Calcd for $C_{16}H_{14}N_2O_4S$: C, 58.18; H, 4.24; N, 8.48. Found: C, 58.01, H, 4.32; N, 8.50.

Irradiation of 2*H*-1,2,4-Benzothiadiazine 1,1-Dioxides 4a–e. A general procedure was to irradiate a 5–10 mM solution of the starting benzothiadiazine dioxides **4a–d** in benzene or methanol for 2–16 h. After removal of the solvent under reduced pressure, the residual solid was chromatographed over alumina. Elution with a mixture (1:9) of benzene and petroleum ether gave the unchanged starting material. Subsequent elution of the column with a mixture (3:1) of benzene and petroleum ether gave the photoproduct, in each case, which could be purified by recrystallization from suitable solvents.

Irradiation of 4a. **4a** (1.47 mmol) in C_6H_6 (300 mL) (2.5 h, RPR 2537 Å) gave a mixture of **4a** (50%) and 6-methyl-5*H*-dibenzo[*b*,*g*][1,4,6]thiadiazocine 12,12-dioxide (**6a**), mp 214–215 °C (acetone) (25%); **4a** (0.68 mmol) in CH_3OH (180 mL) (2 h) gave **4a** and **6a** in 40% and 44% yields, respectively. **6a**: IR ν_{max} (KBr) 3320 (NH), 3060 (CH), 1690 (C=N), 1330 and 1150 (SO_2) cm^{-1}; UV λ_{max} (ethanol) 254 nm (ϵ 17 000), 300 (6700), 350 (250); ^1H NMR ($CDCl_3$) δ 2.36 (3 H, s, methyl), 5.0 (1 H, broad s, D_2O-exchangeable, NH), 7.25 (6 H, m, aromatic), 7.78 (2 H, doublet of doublets, H-1 and H-11, $J_{1,2} = J_{11,10} = 8$ Hz, $J_{1,3} = J_{11,9} = 2$ Hz). Anal. Calcd for $C_{14}H_{12}N_2O_2$,s: C, 61.76; H, 4.44; N, 10.29; mol wt. 272. Found: C, 61.30; H, 4.79; N, 10.02; mol wt, 272 (mass spectrometry).

Irradiation of 4b. **4b** (0.67 mmol) in C_6H_6 (180 mL) (3 h, RPR, 2537 Å) gave a mixture of **4b** (35%) and 4,6-dimethyl-5*H*-dibenzo[*b*,*g*][1,4,6]thiadiazocine 12,12-dioxide (**6b**), mp 238–239 °C (acetone) (37%); **4b** (0.7 mmol) in CH_3OH (180 mL) (4 h) gave **4b** and **6b** in 42% and 33% yields, respectively. **6b**: IR ν_{max} (KBr) 3364 (NH), 2916 (CH), 1684 (C=N), 1564 (C=C), 1535 and 1164 (SO_2) cm^{-1}; UV λ_{max} (ethanol) 254 nm (ϵ 17 200), 301 (6800), 350 (200); ^1H NMR ($CDCl_3$) δ 2.19 (3 H, s, methyl), 2.40 (3 H, s, methyl), 7.05 (5 H, m, aromatic), 7.65 (2 H, doublet of doublets, H-1 and H-11, $J_{1,2} = 8$ Hz; $J_{1,3} = 2$ Hz; $J_{10,11} = 7$ Hz; $J_{9,11} = 2$ Hz), 9.05 (1 H, s, D_2O-exchangeable, NH). Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.94; H, 4.89; N, 9.79; mol wt, 286. Found: C, 62.58; H, 4.59; N, 9.68; mol wt, 286 (mass spectrometry).

Irradiation of 4c. **4c** (3.5 mmol) in C_6H_6 (350 mL) (16 h, RPR, 2537 Å) gave a mixture of **4c** (40%) and 2,6-dimethyl-5*H*-dibenzo[*b*,*g*][1,4,6]thiadiazocine 12,12-dioxide (**6c**), mp 225–226 °C (acetone) (46%); **4c** (3.5 mmol) in CH_3OH (350 mL) (16 h) gave **4c** and **6c** in 45% and 30% yields, respectively. **6c**: IR ν_{max} (KBr) 3340 (NH), 3070, 3040, 2980, 2930 (CH), 1680 (C=N), 1310 and 1170 (SO_2) cm^{-1}; UV λ_{max} (methanol) 250 nm (ϵ 39 800), 300 (10 100), 350 (900); ^1H NMR ($CDCl_3$) δ 2.26 (3 H, s, methyl), 2.36 (3 H, s, methyl), 5.3 (1 H, s, D_2O-exchangeable, NH), 7.23 (6 H, m, aromatic), 7.46 (1 H, s, H-1), 7.66 (1 H, doublet of doublets, H-11, $J_{10,11} = 8$ Hz; $J_{9,11} = 2$ Hz). Anal. Calcd for $C_{15}H_{14}N_2O_2S$: C, 62.94; H, 4.89; N, 9.79; mol wt, 286. Found: C, 63.39; H, 4.76; N, 9.77; mol wt, 286 (mass spectrometry).

Irradiation of 4d. **4d** (1 mmol) in C_6H_6 (180 mL) (3 h, RPR, 3000 Å) gave a mixture of **4d** (33%) and 2-methoxy-6-methyl-5*H*-dibenzo[*b*,*g*][1,4,6]thiadiazocine 12,12-dioxide (**6d**), mp 243–244 °C (acetone) (43%); **4d** (1 mmol) in CH_3OH (220 mL) (3 h) gave **4d** and **6d** in 41% and 25% yields, respectively. **6d**: IR ν_{max} (KBr) 3515 (NH), 3090, 3020, 2980, 2950 (CH), 1665 (C=N), 1570 (C=C), 1300 and 1155 (SO_2) cm^{-1}; UV λ_{max} (methanol) 257 nm (ϵ 15 000), 300 (12 600), 354 (1200); ^1H NMR (acetone-d_6) δ 2.25 (3 H, s, methyl), 3.75 (3 H, s, methoxy), 7.3 (6 H, m, aromatic), 7.6 (1 H, doublet of a doublet, H-11, $J_{10,11} = 7$ Hz; $J_{9,11} = 2$ Hz), 8.16 (1 H, br s, D_2O-exchangeable, NH). Anal. Calcd for $C_{15}H_{14}N_2O_3S$: C, 59.60; H, 4.63; N, 9.26; mol wt, 302. Found: C, 59.68; H, 4.65; N, 9.13; mol wt; 302 (mass spectrometry).

Acetophenone-Sensitized Irradiation of 4d. **4d** (0.16 mmol) in C_6H_6 (40 mL) containing acetophenone (4.2 mmol) was photolyzed in a Pyrex vessel (2 h, RPR, 3500 Å, 2 mM naphthalene in benzene as filter) to give a mixture of **4d** (30%) and **6d** (40%). In a blank run, **4d** (0.16 mmol) in C_6H_6 (40 mL) without acetophenone was photolyzed for 2 h, under conditions identical with the previous run to give a 80% yield of **4d** of none of **6d**.

Irradiation of 4e. **4e** (1.86 mmol) in C_6H_6 (440 mL) (4 h, RPR, 3000 Å) gave a mixture of **4e** (54%) and 7*H*-benzo[*g*]naphtho[2,1-*b*][1,4,6]thiadiazocine 14,14-dioxide (**6e**), mp 234–235 °C (acetone) (28%); **4e** (0.93 mmol) in CH_3OH (220 mL) (5 h) gave **4e** and **6e** in 60% and 14% yields, respectively. **6e**: IR ν_{max} (KBr) 3305 (NH), 3090, 3030, 2990 (CH), 1660 (C=N), 1575 (C=C), 1295 and 1160 (SO_2) cm^{-1}; UV λ_{max} (methanol) 256 nm (ϵ 27 800), 262 (34 200), 307 (6100), 333 (4300); ^1H NMR ($CDCl_3$) δ 2.5 (3 H, s, methyl), 7.45 (9 H, m, aromatic), 8.23 (1 H, doublet of doublets, H-13; $J_{12,13} = 8$ Hz; $J_{11,13} = 2$ Hz), 8.4 (1 H, s, D_2O-exchangeable, NH). Anal. Calcd for $C_{18}H_{14}N_2O_2S$: C, 67.08; H, 4.35; N, 8.70; mol wt, 322. Found: C, 66.93; H, 4.35; N, 8.70; mol wt, 322 (mass spectrometry).

Irradiation of 2-(4′-Carbomethoxyphenyl)-3-methyl-2*H*-1,2,4-benzothiadiazine 1,1-Dioxide (4f). **4f** (0.33 mmol) in C_6H_6 (180 mL) (10 h, RPR, 3000 Å) gave a 70% yield of 2-carbomethoxy-6-methyl-5*H*-dibenzo[*b*,*g*][1,4,6]thiadiazocine 12,12-dioxide, mp 231–232 °C (acetone); **4f** (0.166 mmol) in CH_3OH (100 mL) (10 h) gave a 50% yield of **6f**. **6f**: IR ν_{max} (KBr) 3335 (NH), 3075, 3020, 2940 (CH), 1715 (C=O), 1665 (C=N), 1285 and 1150 (SO_2) cm^{-1}; UV λ_{max} (methanol) 225 nm (ϵ 13 000), 252 (18 300), 300 (7600), 361 (1900); ^1H NMR (acetone-d_6) δ 2.3 (3 H, s, methyl), 3.8 (3 H, s, carbomethoxy), 7.6 (8 H, m, aromatic and NH). Anal. Calcd for $C_{16}H_{14}N_2O_4S$: C, 58.18; H, 4.24; N, 8.48. Found: C, 57.79; H, 3.87; N, 8.90.

Irradiation of 2-Phenyl-2*H*-1,2,4-benzothiadiazine 1,1-Dioxide (4g). In Benzene. A solution of **4g** (444 mg, 1.72 mmol) in benzene (400 mL) was irradiated (RPR, 2537 Å) for 1.5 h in two batches. Removal of the solvent under vacuum gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (4:1) of petroleum ether and benzene gave 43 mg (10%) of the unchanged starting material, **4g**, mp 133–134 °C (mixture melting point). Further elution with a mixture (4:1) of petroleum ether and ethyl acetate gave 323 mg (68%) of *N*-(2′-formamidobenzenesulfonyl)aniline (**10**), mp 151–152 °C, after recrystallization from chloroform: IR ν_{max} (KBr) 3325 (NH), 3160 (NH), 3080, 2900 (CH), 1680 (C=O), 1340 and 1150 (SO$_2$) cm^{-1}; UV λ_{max} (methanol) 246 nm (ϵ 21 900), 280 (5250); ^{1}H NMR (CDCl$_3$) δ 1.78 (1 H, s, D$_2$O-exchangeable, NH), 7.83 (10 H, m, aromatic and formyl), 9.15 (1 H, s, D$_2$O-exchangeable, NH). Anal. Calcd for $C_{13}H_{12}N_2O_2S$: C, 56.52; H, 4.35; N, 10.14; mol wt, 276. Found: C, 56.39; H, 4.30; N, 10.38; mol wt, 276 (mass spectrometry).

Reaction of 1a with Formic Acid. A mixture of **1a** (250 mg, 1 mmol) and formic acid (85%, 2 mL) was heated around 75–80 °C for 3 h and poured over crushed ice. The solid that separated out was washed with water and recrystallized from chloroform to give 195 mg (71%) of **10**, mp 151–152 °C (mixture melting point).

Irradiation of 4g in Methanol. A solution of **4g** (888 mg, 3.4 mmol) in methanol (660 mL) was irradiated (450-W Hanovia medium-pressure lamp) for 1 h in three batches and worked up by removal of the solvent under vacuum. The residual solid was chromatographed over silica gel. Elution with a mixture (1:1) of petroleum ether and benzene gave 605 mg (72%) of **1a**, mp 121–122 °C (mixture melting point), after recrystallization from chloroform. Further elution with a mixture (4:1) of petroleum ether and ethyl acetate gave 75 mg (8%) of **10**, mp 151–152 °C (mixture melting point).

Irradiation of 10 in Methanol. A solution of **10** (220 mg, 0.8 mmol) in methanol (220 mL) was irradiated for 1 h (450-W Hanovia medium-pressure lamp, with Pyrex filter). Removal of the solvent under vacuum and recrystallization of the residual solid from chloroform gave 140 mg (71%) of **1a**, mp 121–122 °C (mixture melting point).

Acid Hydrolysis of 6a. A mixture of **6a** (50 mg, 0.18 mmol) and dilute hydrochloric acid (25%, 1 mL) was heated around 40–50 °C for 3 h. The mixture, on cooling, was neutralized with aqueous ammonia and the solid that precipitated out was filtered and recrystallized from acetone to give 33 mg (74%) of 2,2′-diaminodiphenyl sulfone (**8a**), mp 145 °C (lit.[8] mp 146 °C).

Acid Hydrolysis of 6c. Heating of a mixture of **6c** (60 mg, 0.21 mmol) and dilute hydrochloric acid (25%, 2 mL) around 40–60 °C for 3 h and workup as in the earlier case gave 35 mg (64%) of 2,2′-diamino-5-methyldiphenyl sulfone (**8b**), mp 184 °C, after recrystallization from acetone: IR ν_{max} (KBr) 3480, 3380, 3220 (NH), 3050, 2920 (CH), 1310 and 130 (SO$_2$) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 2.21 (3 H, s, methyl), 5.53 (2 H, s, D$_2$O-exchangeable, NH$_2$), 5.73 (2 H, s, D$_2$O-exchangeable, NH$_2$), 6.98 (5 H, m, aromatic), 7.58 (1 H, s, H-6), 7.78 (1 H, d, H-6′, $J_{5',6'}$ = 8 Hz). Anal. Calcd for $C_{13}H_{14}N_2O_2S$: C, 59.54; H, 5.34; N, 10.69; mol wt, 262. Found: C, 59.78; H, 5.40; N, 10.12; mol wt, 262 (mass spectrometry).

Attempted Thermolyses of 4a and 4b in Diphenyl Ether. A solution of **4a** (300 mg, 1.1 mmol) in diphenyl ether (4 mL) was refluxed (~255 °C) for 9 h. Removal of the solvent under vacuum gave a residual solid, which was recrystallized from chloroform, to give 250 mg (83%) of the unchanged starting material, **4a**, mp 161–162 °C (mixture melting point).

Similarly, refluxing of a solution of **4b** (400 mg, 1.4 mmol) in diphenyl ether (4 mL) for 10 h, followed by workup as in the earlier case, gave back 360 mg (90%) of **4b**, mp 155–156 °C (mixture melting point).

Laser Flash Photolysis. For laser flash photolysis, the pulse excitation was carried out at 337.1 nm (2–3 mJ, ~8 ns, Molectron UV-400 nitrogen laser), 355/266 nm (≲10 mJ, ~6 ns, Quanta-Ray DCR-1 Nd-YAG, 3rd/4th harmonic) or 308 nm (≲20 mJ, ~20 ns, Lambda-Physik EMG 101 MSC Excimer). The transient phenomena were observed in terms of absorption in 2–3-mm quartz cells using a kinetic spectrophotometer described in earlier papers.[12] The solvents employed were benzene and methanol and the solutions were deoxygenated by purging with argon or nitrogen, except in cases where oxygen effects were to be studied. In the experiments requiring a large number of laser shots (e.g., for wavelength-by-wavelength measurements of transient absorption spectra), a flow system was used in which the solution for photolysis was allowed to drain from a reservoir through the cell.

The absorption spectral changes due to photoproducts under controlled photolysis were measured in 1 cm × 1 cm quartz cells using a Cary 219 spectrophotometer (band pass 1 nm). The photolysis was carried out with either repetitive laser pulses (308 and 355 nm, see above) or steady output (310 nm) from a xenon lamp (500 W, coupled with a B&L monochromator, 33-88-07). The solutions were magnetically stirred during irradiation.

Acknowledgment. We thank the Department of Science and Technology, Government of India, Indian Institute of Technology, Kanpur, and the Office of Basic Energy Sciences of the U.S. Department of Energy for financial support of this work.

---

(11) Evans, W. J.; Smiles, S. *J. Chem. Soc.* **1935**, 181–188.

(12) (a) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965–6970. (b) Das, P. K.; Bobrowski, K. *J. Chem. Soc., Faraday* Trans. *2*, **1981**, *77*, 1009–1027. (c) Chattopadhyay, S. K.; Das, P. K.; Hug, G. *J. Am. Chem. Soc.* **1982**, *104*, 4507–4515. (d) Nagarajan, V.; Fessenden, R. W. *J. Phys. Chem.* **1985**, *89*, 2330–2335.

Photochemical Transformations of (*E*)-1-(2′-Arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkenes[1]

S. Pratapan,[2a] P. M. Scaria,[2a] K. Bhattacharyya,[2b] P. K. Das,*[2b] and M. V. George*[2a,b]

Department of Chemistry, Indian Institute of Technology, Kanpur-208016, India, and Radiation Laboratory
and Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

Received October 29, 1985

The photochemistry of several (*E*)-1-(2′-arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylethylenes has been studied by steady-state photolysis, product analysis, and laser flash photolysis. Exhaustive photolysis in benzene and methanol gives 3-aryl-4,5-dibenzoyl-1-phenylpyrazoles as the major products isolated in high yields (40–80%). The formation of the pyrazoles can be understood in terms of photochemical electrocyclic ring-closure to zwitterionic intermediates which undergo intramolecular hydrogen shifts to give pyrazolines. The latter give rise to pyrazoles upon air-oxidation during workup. (*Z*)-1-Anilino-1,2-dibenzoylethylene is obtained as a minor photoproduct in all cases; its formation is explainable in terms of the photocleavage of the N–N bond.

Dibenzoylethylenes are known to undergo interesting photorearrangements, leading to ketene derived products and lactones, in addition to cis–trans isomerization.[3-8] We have recently examined the phototransformations of sev-