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); ^1H NMR ($CDCl_3$) δ 1.78 (1 H, s, D_2O-exchangeable, NH), 7.83 (10 H, m, aromatic and formyl), 9.15 (1 H, s, D_2O-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}; ^1H NMR ($CDCl_3$) δ 2.21 (3 H, s, methyl), 5.53 (2 H, s, D_2O-exchangeable, NH_2), 5.73 (2 H, s, D_2O-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.

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

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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-

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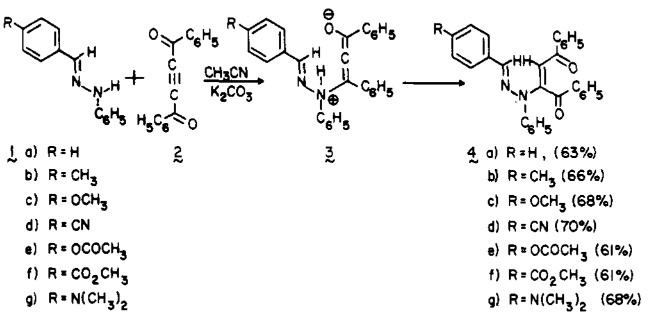
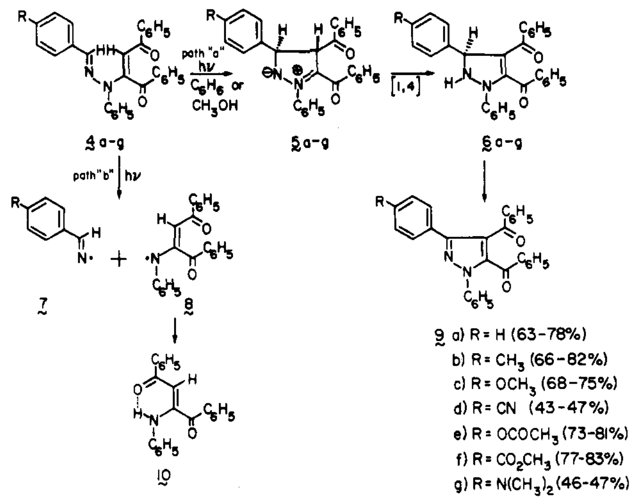
Scheme I



Scheme II



eral substrates containing 1,2-dibenzoylalkene moieties in order to study the mechanistic implications of these photoreactions and also their synthetic utility. Some of the substrates that we have studied include 1,4- and 1,2-epoxy compounds containing 1,2-dibenzoylalkene moieties,[9,10] dibenzobarrelenes,[10-12] 1-pyrazolyl-1,2-dibenzoylalkenes,[13-14] and 1-aziridinyl-1,2-dibenzoylalkenes.[15] It has been observed, in general, that the photoreactions of these substituted 1,2-dibenzoylalkenes are strongly influenced by the nature of the substituents present in them. Thus, the dibenzobarrelenes containing 1,2-dibenzoylalkene moieties undergo the di-π-methane rearrangement (Zimmerman rearrangement),[16] giving rise to dibenzoyl-substituted dibenzosemibullvalenes and not the 1,2-dibenzoylalkene rearrangement.[3-8] 1-Pyrazolyl-1,2-dibenzoylalkenes, on the other hand, undergo the 1,2-dibenzoylalkene rearrangement and also electrocyclic reactions involving aryl substituents present in the pyrazolyl ring.[13,14] In contrast to these, 1-aziridinyl-1,2-dibenzoylalkenes undergo facile ring-expansion reactions, yielding pyrroline derivatives, as well as extrusion of alkenes from the aziridine moieties forming nitrene fragments, which subsequently undergo ring-closure to give isoxazoles.[15]

The object of the present investigation has been to explore the photochemical transformations of some selected substrates containing *cis*-1,2-dibenzoylalkene moieties and having structural features which could significantly alter the course of the dibenzoylalkene type of rearrangement. In this context, we have examined the reactions of several substituted (*E*)-1-(2′-arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkenes to study the nature of products formed in these reactions and also the reaction pathways followed in these cases. The substrates that we have studied include (*E*)-1-(2′-benzylidine-1′-phenylhydrazinyl)-1,2-dibenzoylalkene (**4a**), (*E*)-1-(2′-methylbenzylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkene (**4b**), (*E*)-1-(2′-*p*-methoxybenzylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkene (**4c**), (*E*)-1-(2′-*p*-cyanobenzylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkene (**4d**), (*E*)-1-(2′-*p*-acetoxybenzylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkene (**4e**), (*E*)-1-(2′-(*p*-carbomethoxybenzylidene)-1′-phenyl-hydrazinyl)-1,2-dibenzoylalkene (**4f**), and (*E*)-1-(2′-((dimethylamino)-benzylidene)-1′-phenylhydrazinyl)-1,2-dibenzoylalkene (**4g**). Examination of the structural features of **4a–g** reveals that these substrates, in principle, should be capable of undergoing the 1,2-dibenzoylalkene type of rearrangement[3-8] and also the pentadienyl anion mode of cyclization, leading to five-membered heterocycles.[17]

Results and Discussion

(1) Preparation of Starting Materials. We have prepared the 1-(2′-arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkenes **4a–g** in yields ranging between 61 and 70% through the reaction of the appropriate benzaldehyde phenylhydrazones **1a–g** with dibenzoylacetylene (DBA, **2**) in refluxing acetonitrile and in the presence of anhydrous potassium carbonate (Scheme I). The structures of the adducts **4a–g** have been established on the basis of analytical results and spectral data. The geometry of the carbon–carbon double bond in these adducts (**4a–g**) has been assigned the *E* configuration on the basis of their electronic spectra[13,18,19] and literature precedents.[20,21]

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(2) Preparative Photochemistry and Product Identification. Irradiation of a benzene solution of **4a** for 2 h gave a mixture of 4,5-dibenzoyl-1,3-diphenylpyrazole (**9a**, 78%) and 1-anilino-1,2-dibenzoylalkene (**10**, 6%), along with a small amount (5%) of the unchanged starting material, **4a** (Scheme II). The irradiation of **4a** in methanol, likewise, under analogous conditions gave a mixture of **9a** (63%), **10** (5%), and **4a** (28%). Similarly, the irradiation of the starting 1,2-dibenzoylalkenes **4b–g** in solvents such as benzene and methanol gave the corresponding pyrazoles **9b** (66–82%), **9c** (68–75%), **9d** (43–47%), **9e** (73–81%), **9f** (77–83%), and **9g** (46–47%), respectively, along with small amounts of **10** (1–6%) in each case. The structure of the pyrazoles **9a–g** was established as the basis of analytical results and spectral data.

To ascertain whether the transformations of **4a–g** to the corresponding pyrazoles **9a–g** occur through true photoreactions or not, blank runs were carried out in each case. Thus, the stirring of benzene and methanol solutions of **4a–g** for periods ranging from 5 to 15 h around 30 °C in the dark and workup in the usual manner resulted in the recovery of the starting materials (**4a–g**), in nearly quantitative yield, in each case. Also, in a representative run, a benzene solution of **4a** was refluxed (~80 °C) for 5 h and worked up to give a nearly quantitative yield of the unchanged starting material (**4a**). These results clearly indicate that the formation of the pyrazoles **9a–g** in the reactions under study is proceeding through photochemical pathways.

The formation of the pyrazoles **9a–g** in the photolysis of **4a–g** could be understood in terms of the pathway "a" shown in Scheme II. It is assumed that the initial step in the reaction involves a photochemical, electrocyclic, conrotatory ring-closure of the six-electron system present in the substrates **4a–g** to give the zwitterionic intermediates, **5a–g**. Subsequent hydrogen migration through either a [1,4] or two [1,2] shifts will lead to the pyrazolines **6a–g**, which, on air-oxidation under the conditions of workup will give rise to the pyrazoles **9a–g**, ultimately. It may be pointed out here that numerous examples[17] of such photocyclizations of six-electron systems as in the case of diarylamines, arylvinylamines, diaryl ethers, aryl vinyl ethers, aryl vinyl sulfides, and miscellaneous divinyl systems are reported in the literature. On the basis of the product yields (Scheme II), both electron-donating and electron-withdrawing groups appear compatible with such photocyclizations.

The formation of small amounts of 1-anilino-1,2-dibenzoylalkene (**10**) in the photoreactions of **4a–g** may be understood in terms of the pathway "b", shown in Scheme II. The starting 1,2-dibenzoylalkenes **4a–g** could undergo a photofragmentation to give the radicals **7a–g** and **8**. Subsequent reaction of **8**, involving hydrogen atom abstraction from either **7** or from the medium, will give **10**. It may be pointed out that similar photofragmentation reactions involving carbon–nitrogen bond cleavage have been observed in the case of several arylvinylamines.[22]

In continuation, we have examined the thermal cyclization of two representative examples of 1-(2′-arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkenes such as **4a** and **4c**. Neat heating of **4a** around 215 °C for 1 h in a sealed tube gave a mixture of **9a** (82%) and **10** (5%). Similarly, **4c** on heating around 215 °C for 1 h gave 83% of **9c** and 5% of **10**. The formation of the pyrazoles **9a** and **9c** from **4a** and **4c**, respectively, may be proceeding through an analogous pathway (path "a"), as shown in Scheme II, except that the initial step in these thermal reactions would involve a disrotatory cyclization, leading to isomeric zwitterionic intermediates, which will ultimately lead to the pyrazoles **9a** and **9c**.

Laser Flash Photolysis Studies. The major absorption–spectral change upon laser flash photolysis (337.1 or 355 nm) of **4a–g** in benzene or methanol is the bleaching of the ground-state absorption at 320–450 nm. Beyond and below the spectral region of ground-state depletion, small positive absorbance changes due to photoproducts are observed. The monitoring of the photoproduct absorptions at the longest time scale (~150 μs) shows very little (≤15%) or no decay. The presence of oxygen (~2 mM) in the solutions does not affect the yields or decay kinetics of the photoproducts. This rules out their assignments in terms of substrate triplets and makes the intermediacy of long-lived triplets unlikely (under direct excitation). The absorbance changes in the course of laser flash photolysis are best explained in part by cis → trans photoisomerization and in part by the formation of zwitterion **5** (Scheme II). Details of the time-resolved study will be presented elsewhere.

Experimental Section

All melting points are uncorrected and were determined on a Melt-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 377 or Model 580 infrared spectrophotometers. The electronic spectra were recorded on Cary 17D or Cary 219 spectrophotometers. The ^{1}H NMR spectra were recorded on a Brucker WH-90 or Varian EM-390 NMR spectrometers with tetramethylsilane as internal standard. The mass spectra were recorded on a Hitachi RMU-GE single-focusing mass spectrometer. Steady-state irradiations were carried out by using a Hanovia 450-W medium pressure mercury lamp in a quartz-jacketed immersion well with a Pyrex filter.

Starting Materials. Dibenzoylacetylene (**2**), mp 110–111 °C,[23,24] benzaldehyde phenylhydrazone (**1a**), mp 158 °C,[25] *p*-tolualdehyde phenylhydrazone (**1b**), mp 112 °C,[25] *p*-methoxybenzaldehyde phenylhydrazone (**1c**), mp 121 °C,[25] *p*-cyanobenzaldehyde phenylhydrazone (**1d**), mp 144 C,[26] *p*-acetoxybenzaldehyde phenylhydrazone (**1e**), mp 121 °C, *p*-carbomethoxybenzaldehyde phenylhydrazone (**1f**), mp 115 °C,[26] and *p*-(dimethylamino)benzaldehyde phenylhydrazone (**1g**), mp 148 °C,[25] were prepared by reported procedures. Solvents for steady-state photolysis 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 (*E*)-1-(2′-Arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkenes 4a–g. A general procedure for the preparation of **4a–g** was to reflux a mixture of the appropriate aldehyde phenylhydrazone (**1a–g**, 10 mmol), DBA (10 mmol), and anhydrous potassium carbonate (10 mmol) in acetonitrile (30 mL) for about 3 h. Removal of the solvent under reduced pressure gave a residual solid, which was treated with methanol and kept overnight at room temperature. The 1-(2′-arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkenes that separated were purified by recrystallization from a mixture (2:1) of methanol and chloroform.

Compound 4a: (63%); mp 206–207 °C; IR ν_{max} (KBr) 3045 (CH), 1685 (C=O), 1620, 1585, and 1514 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 263 nm (ϵ 32800), 374 (34000); ^{1}H NMR (CDCl$_3$) δ 6.00 (1 H, s, vinylic), 7.70 (21 H, m, Ar and benzylidenic); MS, *m/e* (rel intensity) 430 (M^+, 6), 325 ($M^+ - COC_6H_5$, 30), 297 ($M^+ - COC_6H_5$, CO, 1) and other peaks. Anal. Calcd for

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$C_{29}H_{22}N_2O_2$: C, 80.9; H, 5.12; N, 6.51. Found: C, 81.0; H, 4.90; N, 6.80.

Compound 4b: (66%); mp 186 °C; IR ν_{max} (KBr) 3050, 2910 (CH), 1680 (C=O), 1625, 1590, and 1520 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 254 nm (ϵ 25 200), 378 (41 000); ^{1}H NMR ($CDCl_3$) δ 2.27 (3 H, s, methyl), 5.96 (1 H, s, vinylic), 7.51 (20 H, m, Ar and benzylidenic); MS, *m/e* (rel intensity) 444 (M$^+$, 26), 442 (M$^+$ − 2 H, 37), 365 (M$^+$ − 2 H, C_6H_5, 15), 339 (M$^+$ − COC_6H_5, 65), and other peaks. Anal. Calcd for $C_{30}H_{24}N_2O_2$: C, 81.08; H, 5.41; N, 6.31. Found: C, 81.32; H, 5.40; N, 6.25.

Compound 4c: (68%); mp 209 °C; IR ν_{max} (KBr) 3060, 2960, 2920 (CH), 1685 (C=O), 1620, 1600, and 1525 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 258 nm (ϵ 23 800), 385 (42 000); ^{1}H NMR ($CDCl_3$) δ 3.72 (3 H, s, methoxy), 5.95 (1 H, s, vinylic) 7.21 (20 H, m, Ar and benzylidenic); MS, *m/e* (rel intensity) 460 (M$^+$, 39), 458 (M$^+$ − 2 H, 91), 381 (M$^+$ − 2 H, C_6H_5, 60), 353 (M$^+$ − 2 H, COC_6H_5, 100), and other peaks. Anal. Calcd for $C_{30}H_{24}N_2O_3$: C, 78.26; H, 5.22; N, 6.09. Found: C, 77.92; H, 5.51; N, 6.10.

Compound 4d: 70%; mp 232 °C; IR ν_{max} (KBr) 3060 (CH), 2215 (C≡N), 1685 (C=O), 1620, 1590, 1560, and 1520 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 259 nm (ϵ 26 700), 384 (49 000); ^{1}H NMR ($CDCl_3$) δ 6.00 (1 H, s, vinylic), 7.61 (20 H, m, Ar and benzylidenic). Anal. Calcd for $C_{30}H_{22}N_3O_4$: C, 79.12; H, 4.62; N, 9.23. Found: C, 78.73; H, 4.60; N, 9.51.

Compound 4e: (61%); mp 202 °C; IR ν_{max} (KBr) 3060, 3010 (CH), 1760, 1685 (C=O), 1620, 1590, 1565, and 1520 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 252 nm (ϵ 42 400), 374 (42 000); ^{1}H NMR ($CDCl_3$) δ 2.22 (3 H, s, acetoxy), 6.0 (1 H, s, vinylic), 7.49 (20 H, m, Ar and benzylidenic). Anal. Calcd for $C_{31}H_{24}N_2O_4$: C, 76.03; H, 4.93; N, 5.74. Found: C, 76.41; H, 5.05; N, 5.70.

Compound 4f: (61%); mp 181 °C; IR ν_{max} (KBr) 3060, 2950 (CH), 1725, 1685 (C=O), 1630, 1595, and 1550 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 246 nm (ϵ 30 100), 384 (45 000); ^{1}H NMR ($CDCl_3$) δ 3.84 (3 H, s, carbomethoxy), 5.96 (1 H, s, vinylic), 7.67 (20 H, m, Ar). Anal. Calcd for $C_{31}H_{24}N_2O_4$: C, 76.03; N, 4.92; N, 5.74. Found: C, 76.25; H, 4.48; N, 5.78.

Compound 4g: (68%); mp 234 °C; IR ν_{max} (KBr) 3050, 2980 (CH), 1680 (C=O), 1610, 1590, and 1560 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 253 nm (ϵ 27 400), 414 (43 000); ^{1}H NMR ($CDCl_3$) δ 2.89 (6 H, s, (dimethylamino)) 6.0 (1 H, s, vinylic), 7.37 (20 H, m, Ar and benzylidenic); MS; *m/e* (rel intensity) 473 (M$^+$, 20), 471 (M$^+$ − 2 H, 100), 368 (M$^+$ − COC_6H_5, 15), 366 (M$^+$ − 2 H, COC_6H_5, 15), and other peaks. Anal. Calcd for $C_{31}H_{27}N_3O_2$: C, 78.65; H, 5.71; N, 8.88. Found: C, 79.05; H, 5.70; N, 8.82.

Irradiation of (*E*)-1-(2′-Arylidene-1′-phenylhydrazinyl)-1,2-dibenzoylalkenes, 4a–g. General Procedure. A general procedure was to irradiate a dilute solution of the appropriate 1,2-dibenzoylalkene in benzene or methanol (1–2 mmol in 175 mL) for varying periods of time and then remove the solvent under vacuum. The residual solid was chromatographed over silica gel and eluted with different solvents to give the products, which were finally purified, in each case, by recrystallization from suitable solvents.

Irradiation of 4a. A benzene solution of **4a** (430 mg, 1 mmol in 175 mL) was irradiated for 2 h and worked up to give 20 mg (6%) of **10**, mp 130 °C (mixture melting point)[27] (elution with a 1:4 mixture of benzene and petroleum ether), 350 mg (78%) of 4,5-dibenzoyl-1,3-diphenylpyrazole (**9a**), mp 136 °C (elution with a 3:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), and 22 mg (5%) of the unchanged starting material **4a**, mp 206–207 °C (mixture melting point).

9a: IR ν_{max} (KBr) 3060 (CH), 1660, 1645 (C=O), 1600, and 1580 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 255 nm (ϵ 39 700); ^{1}H NMR ($CDCl_3$) δ 7.3 (m, Ar). Anal. Calcd for $C_{29}H_{20}N_2O_2$: C, 81.31; H, 4.67; N, 6.54. Found: C, 81.30; H, 4.71; N, 6.51.

In a repeat run, a methanol solution of **4a** was irradiated for 2 h under analogous conditions and worked up to give 5% of **10**, 63% of **9a**, and 28% of **4a**.

Irradiation of 4b. A solution of **4b** in benzene (890 mg, 2 mmol in 175 mL) was irradiated for 4 h and worked up to give 30 mg (4%) of **10**, mp 130 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), and 735 mg (82%) of 4,5-dibenzoyl-1-phenyl-3-(*p*-tolyl)pyrazole (**9b**), mp 131 °C (elution with a 3:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether).

9b: IR ν_{max} (KBr) 3060, 3000, 2910 (CH), 1660, 1640, (C=O), 1590 and, 1580 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 253 nm (ϵ 53 000); ^{1}H NMR ($CDCl_3$) δ 2.27 (3 H, s, methyl), 7.31 (19 H, m, Ar). Anal. Calcd for $C_{30}H_{22}N_2O_2$: C, 81.45; H, 4.98; N, 6.33. Found: C, 81.80; H, 4.53; N, 6.35.

In a repeat run, a methanol solution of **4b** was irradiated for 4 h under analogous conditions to give a mixture of **10** (4%), **9b** (66%), and **4b** (19%).

Irradiation of 4c. A solution of **4c** in benzene (920 mg, 2 mmol in 175 mL) was irradiated for 5 h and worked up to give 40 mg (6%) of **10**, mp 130 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), 675 mg (75%) of 3-(*p*-anisyl)-4,5-dibenzoyl-1-phenylpyrazole (**9c**), mp 133 °C (elution with a 3:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), and 28 mg (3%) of **4c**, mp 209 °C (mixture melting point).

9c: IR ν_{max} (KBr) 3060, 2930, 2840 (CH), 1660, 1645 (C=O), 1610, 1595, and 1585 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 256 nm (ϵ 35 200); ^{1}H NMR ($CDCl_3$) δ 3.75 (3 H, s, methoxy), 7.32 (19 H, m, Ar). Anal. Calcd for $C_{30}H_{22}N_2O_3$: C, 78.60; H, 4.80; N, 6.11. Found: C, 78.71; H, 4.75; N, 6.00.

In a repeat experiment, a methanol solution of **4c** was irradiated for 5 h, under analogous conditions, to give a mixture of **10** (6%), **9c** (68%), and **4c** (15%).

Irradiation of 4d. A solution of **4d** in benzene (910 mg, 2 mmol in 175 mL) was irradiated for 2 h and worked up to give 20 mg (3%) of **10**, mp 130 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), 380 mg (43%) of 3-(*p*-cyanophenyl)-4,5-dibenzoyl-1-phenylpyrazole (**9d**), mp 146 °C (elution with a 4:1 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), and 200 mg (22%) of the unchanged starting material **4d** (elution with benzene), mp 232 °C (mixture melting point).

9d: IR ν_{max} (KBr) 3060, 3030 (CH), 2230 (C≡N), 1660, 1650 (C=O), 1610, 1590, and 1580 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 251 nm (ϵ 45 000); ^{1}H NMR ($CDCl_3$) δ 7.48 (m, Ar). Anal. Calcd for $C_{30}H_{19}N_3O_2$: C, 79.47; H, 4.19; N, 9.27. Found: C, 79.12; H, 4.55; N, 5.73.

Irradiation of 4e. A solution of **4e** (945 mg, 1.97 mmol) in benzene (175 mL) was irradiated for 2 h and worked up to give 5 mg (1%) of **10**, mp 130 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), 760 mg (81%), of 3-(*p*-acetoxyphenyl)-4,5-dibenzoyl-1-phenylpyrazole (**9e**), mp 154 °C (elusion with a 3:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), and 50 mg (5%) of the unchanged starting material **4e**, mp 202 °C (mixture melting point) (elution with benzene).

9e: IR ν_{max} (KBr) 3060 (CH), 1760, 1650 (C=O), 1590, and 1575 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 252 nm (ϵ 40 100); ^{1}H NMR ($CDCl_3$) δ 2.3 (3 H, s, acetoxy), 7.28 (19 H, m, Ar); MS, *m/e* (rel intensity) 486 (M$^+$, 92), 443 (M$^+$ − $COCH_3$, 100), 338 (M$^+$ − $COCH_3$, COC_6H_5, 10), and other peaks. Anal. Calcd for $C_{31}H_{22}N_2O_4$: C, 76.54; H, 4.53; N, 5.76. Found: C, 76.50; H, 4.53; N, 5.73.

In a repeat run, the irradiation of **4e** for 2 h, under analogous conditions, gave a mixture of **10** (1%), **9e** (73%), and **4e** (20%).

Irradiation of 4f. A solution of **4f** (490 mg, 1 mmol) in benzene (175 mL) was irradiated for 2 h and worked up to give 20 mg (6%) of **10**, mp 130 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), and 410 mg (83%) of 3-(*p*-carbomethoxyphenyl)-4,5-dibenzoyl-1-phenylpyrazole (**9f**), mp 201 °C (elution with a 3:2 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether).

9f: IR ν_{max} (KBr) 3050, 3000, 2930 (CH), 1715, 1650 (C=O), 1610, 1590, and 1580 (C=N and C=C) cm^{-1}; UV λ_{max} (methanol) 254 nm (ϵ 30 800); ^{1}H NMR ($CDCl_3$) δ 3.9 (3 H, s, carbomethoxy), 7.5 (19 H, m, Ar). Anal. Calcd for $C_{31}H_{22}N_2O_4$: C, 76.54; H, 4.53; N, 5.76. Found: C, 76.55; H, 4.68; N, 5.81.

In a repeat experiment, irradiation of a methanol solution of **4f** for 2 h, under analogous conditions, gave a mixture of **10** (6%),

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[27] Lahiri, S. Ph.D. Thesis, Indian Institute of Technology, Kanpur 1977.

9f (77%), and unchanged starting material **4f** (10%), mp 181 °C (mixture melting point).

Irradiation of 4g. A solution of **4g** (475 mmol) in benzene (175 mL) was irradiated for 12 h and worked up to give 20 mg (6%) of **10**, mp 130 °C (mixture melting point) (elution with a 1:4 mixture of benzene and petroleum ether), 215 mg (46%) of 4,5-dibenzoyl-3-(*p*-(dimethylamino)phenyl)-1-phenylpyrazole (**9g**), mp 156 °C (elution with a 1:4 mixture of benzene and petroleum ether and recrystallization from a 1:1 mixture of benzene and petroleum ether), and 145 mg (31%) of unchanged starting material **4g**, mp 234 °C (mixture melting point) (elution with a 9:1 mixture of benzene and ethyl acetate).

In a repeat run, irradiation of a methanol solution of **4g**, under analogous conditions, gave a mixture of **10** (6%), **9g** (47%), and unchanged starting material **4g** (32%).

Attempted Thermal Transformations of 4a–g in Benzene and Methanol (Blank Runs). Blank runs were carried out by stirring solutions of **4a–g** in benzene and methanol (4 mmol) around 30 °C for 5–15 h. Workup in the usual manner gave back the starting material (**4a–g**), in each case, in nearly quantitative yield.

Attempted Thermal Transformation of 4a in Refluxing Benzene. A solution of **4a** in benzene (430 mg, 1 mmol in 175 mL) was refluxed in the dark for 5 h. Workup of the mixture of the usual manner resulted in the recovery of 410 mg (95%) of the unchanged starting material **4a**, mp 206–207 °C (mixture melting point).

Thermal Transformation of 4a (Neat Heating at 215 °C). A sample of **4a** (860 mg, 2 mmol) was heated around 215 °C in a sealed tube for 1 h. The reaction mixture, on cooling, was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 35 mg (5%) of **10**, mp 130 °C (mixture melting point). Further elution and petroleum ether gave 695 mg (82%) of **9a**, mp 136 °C (mixture melting point).

Thermal Transformation of 4c (Neat Heating at 215 °C). A sample of **4c** (460 mg, 1 mmol) was heated around 215 °C in a sealed tube for 1 h. The reaction mixture was chromatographed on silica gel, and elution with a mixture (1:4) of benzene and petroleum ether gave 15 mg (5%) of **10**, mp 130 °C (mixture melting point). Further elution with a mixture (3:2) of benzene and petroleum ether yielded 382 mg (83%) of **9c**, mp 133 °C (mixture melting point).

Laser Flash Photolysis. The laser flash photolysis experiments were carried out in a computer-controlled setup by using pulse excitation at 337.1 nm (Molectron UV-400 nitrogen, 2–3 mJ, ~8 ns) or 355 nm (Quanta-Ray DCR-1 Nd-YAG, ≤ 10 mJ, ~6 ns). Details of the apparatus and procedures are described elsewhere.[28–30]

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 U.S. Department for financial support of this work.

Registry No. **1a**, 588-64-7; **1b**, 2829-25-6; **1c**, 622-73-1; **1d**, 100726-23-6; **1e**, 101773-48-2; **1f**, 87829-01-4; **1g**, 2829-28-9; **2**, 1087-09-8; **4a**, 101773-49-3; **4b**, 101773-50-6; **4c**, 101773-51-7; **4d**, 101773-52-8; **4e**, 101773-53-9; **4f**, 101773-54-0; **4g**, 101773-55-1; **9a**, 78830-57-6; **9b**, 101773-56-2; **9c**, 101773-57-3; **9d**, 101773-58-4; **9e**, 101773-59-5; **9f**, 101773-60-8; **9g**, 101773-61-9; **10**, 29954-08-3.

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Amines as Leaving Groups in Nucleophilic Aromatic Substitution Reactions

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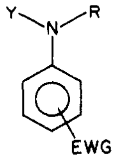
Received September 19, 1985

The hydrolysis reactions of *N*-(2,4-dinitrophenyl)piperidine (**7**) and *N*-(2,4-dinitrophenyl)morpholine (**8**) were studied. Both reactions lead quantitatively to the formation of 2,4-dinitrophenol. They are second order toward the HO^- concentration and are strongly catalyzed by the amine leaving group. The catalysis is interpreted in terms of the formation of 1,3-σ complexes with the amine or the HO^-, which then react with another hydroxide ion to give the final product. The reactivity of the 1,3-σ complexes toward HO^- is higher than that of the substrates themselves.

Aromatic amines with general structure **1** are quite resistant to elimination of the amino group.



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In the presence of bases, compounds of type **1** can react in several forms.[1,2] In Scheme I they are summarized for the case of a trinitro substituted compound, reacting with a base Z^-.

The formation of intermediate **3** eventually leads to the replacement of the amino group,[3] but this reaction has only been studied in a few instances as a primary reaction. Most rate data regarding reactions where an amino group in an aromatic ring is displaced by a nucleophile were obtained as secondary reactions in other studies.[4]

The low reactivity of compounds of the type **2** toward attack at carbon 1 is considered to be a consequence of the interaction of the lone pair of electrons on the nitrogen

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