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Heavy-Atom Effect in Photoisomerization of 4-Pyrones and 4-Pyridones

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Internal and external heavy-atom effects were applied to determine the excited state involved in photoisomerization of 2,6-dimethyl-3,5-bis(para-substituted phenyl)-4-pyrones to 3,6-bis(para-substituted phenyl)-4,5-dimethyl-2-pyrones. A similar method was used in the photorearrangement of 1,2,6-trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones to 1,4,6-trimethyl-3,5-bis(para-substituted phenyl)-2-pyridones. Both 4-pyrones and 4-pyridones phosphoresce at 77 K from the π,π^* triplet state and show a shorter phosphorescence lifetime with increasing atomic number of the halogen substituents. Quantum yields of both the photoisomerization and intersystem crossing of these 4-pyrones and 4-pyridones are not internally dependent on the atomic number of the substituent. Addition of the heavy-atom solvent (n-butyl bromide) decreases quantum yield of photoisomerization and increases intersystem crossing efficiency from the singlet to triplet excited states. This photoisomerization was not quenched by dienes, indicating that the photoisomerization of both 4-pyrones and 4-pyridones proceeds via their π,π^* singlet.

Although internal and external heavy-atom effects on photophysical processes have been extensively investigated using the spectroscopic and theoretical methods,[2-5] studies on a heavy-atom effect on a photochemical reaction have been relatively few until the discovery by Cowan and Drisco[6] that the photodimerization of acenaphthylene was beneficially perturbed when a heavy-atom solvent was present. Somewhat later, a heavy-atom effect was widely utilized in the photochemical cycloaddition of acenaphthylene to acrylonitrile,[7] pentadiene,[8] cyclopentadiene,[9] and maleic anhydride.[10] The effect was also observed in the photochemical isomerization of bicyclo[4.2.1]nona-2,4-dienes[11] and bromostilbenes[12] and in the photoabstraction–cyclization of methyl o-benzyloxyphenylglyoxylate.[13]

We recently reported the photoisomerization of 4-pyrones to 2-pyrones[14] and of 4-pyridones to 2-pyridones.[15] Evidence was given to support the idea that the photorearrangement of the 4-pyridone[15] occurred in the excited singlet state, although the photoexcited state responsible for the photoisomerization of 4-pyrones[14] was not determined and further study has remained.

We now wish to report a study illustrating an application of a heavy-atom effect in determining the excited state involved in the photoisomerization of 4-pyrones. Emission spectra of 2,6-dimethyl-3,5-bis(para-substituted phenyl)-4-pyrones (I) were measured and the quantum yield in the photoisomerization of I, perturbed internally or externally by a heavy atom, was also determined. A similar study was extended to the photorearrangement of 1,2,6-trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones (II). Comparison of the internal and external heavy-atom effects in the photoisomerization of I with those in the photorearrangement of II was anticipated to determine the nature of the excited state involved in the photoreaction of I, since the excited state re-

sponsible for the photoreaction of II was firmly established.[15]

Results and Discussion

2,6-Dimethyl-3,5-bis(para-substituted phenyl)-4-pyrones (I) were prepared by condensation of para,para′-disubstituted bibenzyl ketone (III) with acetic acid in the presence of polyphosphoric acid (PPA) as employed for the synthesis of Ia.[16,17] These 4-pyrones were condensed with methylamine in a sealed tube to form the corresponding 4-pyridones (II).[15b,18] The structures assigned to I and II rest on the
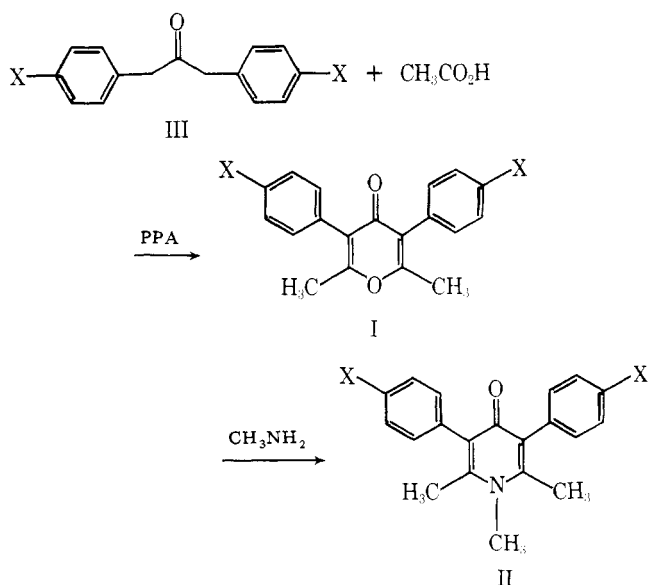
a, X = H; b, X = CH$_3$; c, X = F; d, X = Cl; e, X = Br

Table I. Spectral Data of Absorption and Phosphorescence of 4-Pyrones and 4-Pyridones in Ethanol

Substrate	Registry no.	λ_{max}, nm (Absorption, ϵ)	Phosphorescence	E_T,[b] kcal/mol	τ, s
Ia[a]	33731-54-3	221 (22600), 258 (12200)	454	62	0.29
Ib	65622-25-5	221 (22000), 261 (10600), 297 (860)	459	62	0.30
Ic	65622-26-6	255 (10100), 299 (320)	465	61.5	0.35
Id	65622-27-7	225 (30600), 256 (13800)	490	58	0.012
Ie	65622-28-8	229 (41900), 261 (sh, 21000)	492	58	0.0011
IIa[a]	42215-29-2	236 (19600), 275 (13500)	430	66.5	1.30
IIb	65622-29-9	236 (sh, 22000), 276 (13900)	430	66.5	1.40
IIc	65622-30-2	227 (24100), 274 (15200)	430	66.5	1.50
IId	65622-31-3	225 (26700), 275 (13200)	435	66	0.33
IIe	65622-32-4	228 (14600), 275 (14600)	435	66	0.045

[a] Reference 19. [b] Band maxima were taken as the triplet energy.

Table II. Quantum Yield and Intersystem Crossing Efficiency of 2,6-Dimethyl-3,5-bis(*p*-substituted phenyl)-4-pyrones and 1,2,6-Trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones at Ambient Temperature
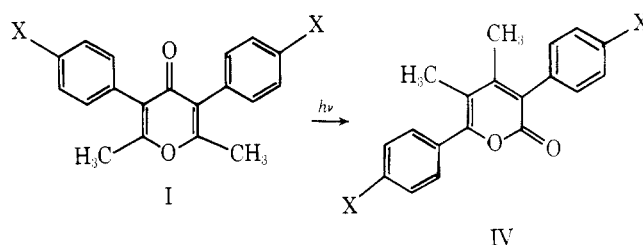
Substrate[a]	Quantum yield Φ	Φ_{rel}[b]	Intersystem crossing efficiency, ϕ_{isc}	$\phi_{rel\ isc}$[c]
Ia	0.40	(1)	0.36	(1)
Ib	0.48	1.2	0.25	0.69
Ic	0.44	1.1	0.27	0.75
Id	0.35	0.87	0.38	1.05
Ie	0.20[d]	0.5	0.38	1.05
IIa	0.21	(1)	0.074	(1)
IIb	0.18	0.84	0.080	1.1
IIc	0.22	1.0	0.065	0.87
IId	0.23	1.1	0.097	1.3
IIe	0.23[d]	1.1	0.10	1.35

[a] Solvents were dioxane for I and methanol for II. [b] Quantum yield relative to Ia for I and IIa for II. [c] Intersystem crossing efficiency relative to Ia for I and to IIa for II. [d] Because of the fast formation of by-products, quantum yield could not be determined as accurately as that of other compounds.

spectral (IR, NMR, and mass) and elemental analysis data which are detailed in the Experimental Section.

Electronic absorption spectra of 4-pyrones (Ib–e) and 4-pyridones (IIb–e) were measured in ethanol, and their band maxima and molar extinction coefficients are given in Table I together with those of each parent compound, Ia and IIa.[19] The 4-pyrones except Ic exhibit two intense π,π^* absorption bands at 220–230 and 255–261 nm. In addition to the strong π,π^* absorptions two 4-pyrones, Ib and Ic, show a weak n,π^* absorption band at 297–299 nm. This spectral pattern is similar to the spectrum of Ia.[19] 4-Pyridones (IIb–e) also show two intense π,π^* bands at 225–236 and 274–276 nm but no n,π^* band is observed, the pattern being similar to the spectrum of IIa.[19] Both 4-pyrones and 4-pyridones show no fluorescence at room temperature and 77 K. All 4-pyrones and 4-pyridones studied phosphoresce in rigid media at 77 K, and their triplet energies, band maxima, and phosphorescence lifetimes are listed in Table I. A similar pattern is observed in phosphorescence spectra of the substituted heteroaromatics (Ib–e and IIb–e) and the parent compounds (Ia and IIa), suggesting that the lowest triplet state of these compounds is mainly of π,π^* character.[19] The substituent effect (halogen atoms and the methyl group) on the excitation energy is not apparently observed in the absorption and phosphorescence spectra. On the other hand, the phosphorescence lifetime of 4-pyrones and 4-pyridones decreases with increasing atomic number of a halogen atom (Table I). This is in line with expectation based on the internal heavy-atom effect upon the phosphorescence rate from the π,π^* triplet,[2b,20] although this internal heavy-atom effect on the intersystem crossing efficiency from singlet to triplet states is not observed at room temperature. (See Table II and the following discussion.)

Preparative photochemical reaction was carried out with a medium-pressure mercury lamp in an immersion apparatus using a Vycor filter. Irradiation of 4-pyrones (Ib–e) in aceto-

nitrile gave 2-pyrones (IVb–e) and the structural assignment was based on the spectral data. (Firm structural evidence was obtained in the parent compound IVa.[14b]) Photolysis of 4-pyridones (IIb–e) in methanol afforded 2-pyridones (Vb–e and VIb–e[21]). The structure of V was confirmed by no depression of melting point in a mixture of the photoproduct with an authentic sample and by agreement of NMR in IR spectra of the photoproduct with those of the authentic sample. Each authentic sample was independently prepared by N-methylation of 4,6-dimethyl-3,5-bis(para-substituted phenyl)-2-pyridones (Vb-e), which were synthesized from the reaction of α-acetyl para-substituted benzylcyanides (VIIb–e) with para-substituted phenylacetones (IXb–e). (For X = H the preparative procedure was reported.)[15b,22]

Quantum yield for appearance of IV from I or of V from II was determined in order to study the internal heavy-atom effect. Degassed and sealed quartz tubes containing a solution of I or II and an aqueous solution of potassium ferrioxalate for actinometry[23] were irradiated with 253.7-nm light in a rotating photochemical assembly. Reaction was controlled at low conversion to prevent appreciable light absorption by a photoproduct. Yield of the product was determined by an UV method. The results are given in Table II.

Table II also shows intersystem crossing efficiencies of I and II, which were measured by comparing the cis–trans conversion of *cis*-piperylene in the sensitized reaction by I or II with
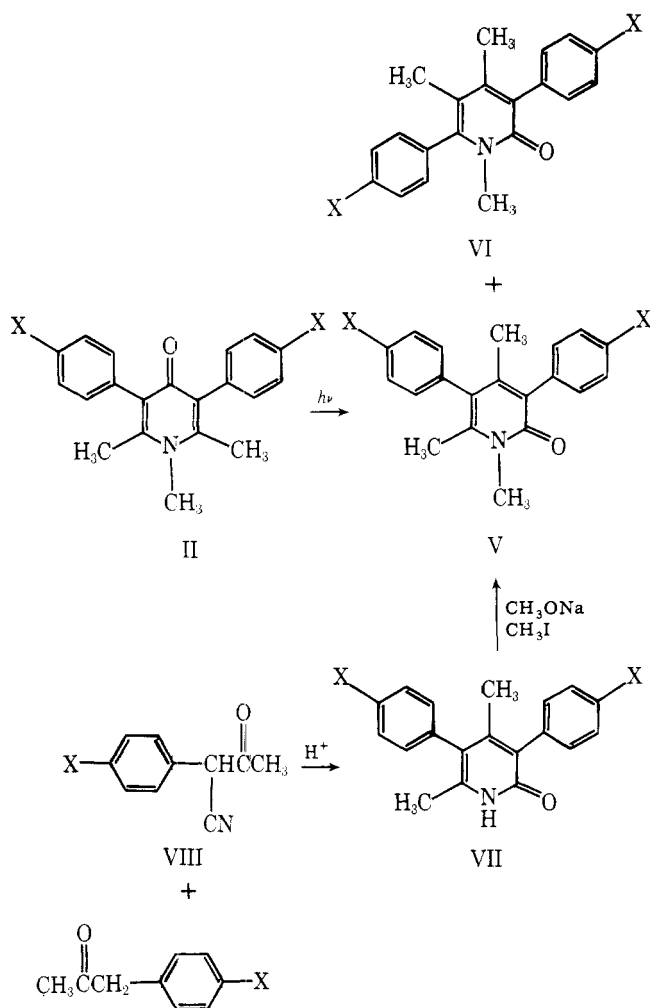
Table III. External Heavy-Atom Effect on Intersystem Crossing Efficiency and Quantum Yields of Ia, Id, IIa, and IId at Ambient Temperature

Substrate[a]	n-Butyl bromide, %	Quantum yield Φ	Intersystem crossing efficiency, ϕ_{isc}
Ia	0	0.40	0.36
	10	0.33	
	50	0.27	0.47
	90	0.11	0.62
	100	0.095	0.68
Id	0	0.35	0.38
	10	0.25	
	50	0.23	0.40
	100	0.097	
IIa	0	0.21	0.074
	10	0.21	
	50	0.11	0.15
	90[b]	0.030	0.29
IId	0	0.23	0.097
	10	0.20	
	50	0.046	0.24
	90[b]	0.023	0.44

[a] Dioxane for Ia and Id. Methanol for IIa and IId. [b] Both IIa and IId are not soluble in neat n-butyl bromide.

Table IV. Quantum Yields for Formation of 2-Pyrones and 2-Pyridones

4-Pyrones or 4-pyridones[a]	Additive	Quantum yield, Φ
Ia	None	0.40
	trans-Piperylene (0.15 M)	0.38
	cis-Piperylene (0.15 M)	0.37
Id	None	0.35
	trans-Piperylene (0.2 M)	0.35
	cis-Piperylene (0.2 M)	0.33
IIa	None	0.21
	trans-Piperylene (0.15 M)	0.21
	cis-Piperylene (0.15 M)	0.19
IId	None	0.23
	trans-Piperylene (0.2 M)	0.21
	cis-Piperylene (0.2 M)	0.20

[a] The concentration was $1-3 \times 10^{-3}$ M for I and $3-7 \times 10^{-3}$ M for II. Solvents were dioxane for I and methanol for II.

that of the bezophenone-sensitized reaction.[24] Degassed and sealed quartz tubes containing the solutions of benzophenone and cis-piperylene were irradiated with 253.7-nm light for actinometry. The intersystem crossing efficiency for benzophenone at 253.7 nm was determined as 1.02 using potassium ferrioxalate actinometry.[23] The intersystem crossing efficiency was determined by extrapolating to infinite concentration of cis-piperylene. The results in Table II show that the presence of heavier atoms tends to slightly decrease quantum yield of the photoisomerization of I and II with slight increase of the intersystem crossing efficiency, although the internal heavy-atom effect is clearly observed in the phosphorecence lifetime at 77 K as shown in Table I. On the other hand, the external heavy-atom effect evidently increases intersystem crossing efficiencies of Ia, Id, IIa, and IId at room temperature and, then, decreases quantum yield of the photorearrangement (Table III). The intersystem crossing efficiency increases with higher concentration of n-butyl bromide as observed in the photodimerization of acenaphthylene.[6d] We cannot explain at the present time why the external heavy-atom effect on ϕ_{isc} and Φ is more effective than the internal one.[25]

Both cis- and trans-piperylene did not quench the photoisomerization of 4-pyrones (Ia and Id) to 2-pyrones.[26] Similarly the photoreaction of 4-pyridones (IIa and IId) was not quenched by cis- and trans-piperylene (Table IV). This quenching experiment suggests that the singlet state is responsible for the photoisomerization of both I and II. It was previously established that the photorearrangement of 4-pyridones to 2-pyridones proceeded via the π,π^* singlet.[15]

As shown in Table III for IIa and IId, use of high concentration of the heavy-atom solvent increases ϕ_{isc} for the S_1-T_1 process and, then, decreases quantum yield of the photoisomerization of II. A similar trend is observed in the external

heavy-atom effect on the photorearrangement of Ia and Id (Table III).

Ineffectiveness of quenching by dienes and decrease of quantum yield in the heavy-atom solvent indicate that the photoisomerization proceeds via π,π^* singlet state,[27] since the n,π^* excited state is expected to be relatively insensitive to the heavy-atom perturbation[2,28] and since the n,π^* excitation of Ia did not produce IIa.[14b] These results suggest that the formation of IV involves the singlet excited states of both I and a 4,5-epoxycyclopent-2-en-1-one intermediate, because the photochemical rearrangement of the 4-pyrone to the latter intermediate and, then, to the 2-pyrone was recently established in UV irradiation of 3,5-dimethyl-4-pyrone in trifluoroethanol.[29]

This work illustrates an application of the heavy-atom effect in elucidating the nature of the excited state of the photoisomerization, in which care must be taken with evaluation of both internal and external heavy-atom effects.

Experimental Section

Microanalyses were conducted by Microanalytical Laboratories, Kyoto University. Infrared spectra were measured on a Jasco DS-

Table V. Preparation of 2,6-Dimethyl-3,5-bis(para-substituted phenyl)-4-pyrones

Substituent	Bibenzyl ketone, wt in g	Product, wt in g (%)	Mp, °C	% Calcd, Found			
				C	H	Cl	Br
CH₃	IIIb,ᵃ 0.3	Ib, 0.23 (77)	162–163	82.86	6.62		
				82.71	6.56		
Cl	IIId,ᵇ 5	Id, 1.0 (20)	197–198.5	56.10	4.09	20.54	
				66.33	4.09	20.26	
Br	IIIe,ᶜ 0.3	Ie, 0.028 (10)	210–212	52.57	3.25		36.81
				52.75	3.44		36.95

ᵃ S. B. Cowan, D. E. Trucker, and E. I. Becker, *J. Am. Chem. Soc.*, **77**, 60 (1955). ᵇ F. J. Thaller, D. E. Trucker, and E. I. Becker, *ibid.*, **73**, 228 (1951). ᶜ E. J. Corey and M. F. Semmelhack, *ibid.*, **89**, 2755 (1967); E. Yoshisato and S. Tsutsumi, *J. Org. Chem.*, **33**, 869 (1968).

Table VI. Preparation of 1,2,6-Trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones

Substituent	4-Pyrones, wt in g	4-Pyridones, wt in g (%)	Mp, °C	% Calcd, Found				
				C	H	N	Cl	Br
CH₃	Ib, 0.4	IIb, 0.2 (50)	>300	83.24	7.30	4.41		
				83.18	7.15	4.37		
Cl	Id, 2.0	IId, 1.25 (63)	296–298	67.05	4.78	3.91	19.79	
				67.26	4.90	3.61	19.89	
Br	Ie, 1.5	IIe, 1.0 (66)	275–276	53.72	3.82	3.13		35.74
				53.54	3.84	3.11		35.82

402G grating spectrophotometer. Ultraviolet absorption spectra were obtained on a Hitachi 323 spectrophotometer. Phosphorescence excitation and emission spectra were measured on a Hitachi MPF-4 spectrofluorometer equipped with a Hitachi phosphoroscope attachment. Phosphorescence spectra (uncorrected) were measured by photographing the decay of emmission signals (displayed on an oscilloscope screen), following excitation of the exciting light. Lifetimes were calculated from the exponential decay curves obtained. NMR spectra were obtained at 60 MHz (Varian T-60A) or 100 MHz (Joel PS-100) using tetramethylsilane as internal standard. Chemical shifts were reported in parts per million (δ) from Me₄Si. Mass spectra were obtained by direct insertion on a Hitachi RMU-6L spectrometer. Melting points were uncorrected.

Preparation of 2,6-Dimethyl-2,5-bis(para-substituted phenyl)-4-pyrones. In general procedure 5 g of 4,4'-diflurobibenzyl ketone was added to a mixture of 31.5 g of acetic acid and 50 g of polyphosphoric acid at 70 °C. The mixture was stirred at 110–130 °C for 3 h and poured into 1000 mL of ice-cooled water. The reaction mixture was extracted with 200 mL of ether five times. The combined extracts were neutralized with aqueous sodium bicarbonate, washed thoroughly with water, and dried over anhydrous sodium sulfate. After removal of the solvent in vacuo the residual solid was chromatographed on silica gel with chloroform as eluent. Recrystallization of crude crystals from methanol gave 3.5 g (70%) of 2,6-dimethyl-3,5-bis(p-fluorophenyl)-4-pyrone (Ic): mp 212.0–214.0 °C; IR (KBr) 1640, 1600, 1500, 1430, 1415, 1400, 1325, 1295, 1220, 1155, 1145, 1095, 990, 840, 820 cm⁻¹; NMR (CDCl₃) δ 2.23 (s, 6 H), 6.80–7.40 (m, 8 H); mass spectrum (*m/e*) 313 (17), 312 (M⁺, 87), 311 (100), 136 (15), 134 (21), 133 (40), 43 (71). Anal. Calcd for C₁₉H₁₄O₂F₂: C, 73.07; H, 4.52; F, 12.17. Found: C, 73.15; H, 4.28; F, 12.25.

The preparative condition and analytical results for other 4-pyrones are given in Table V. The spectral data for these compounds are as follows.

2,6-Dimethyl-3,5-bis(p-tolyl)-4-pyrone (Ib): IR (KBr) 1630, 1600, 1500, 1400, 1325, 1230, 1100, 1020, 980, 910, 800, 745 cm⁻¹; NMR (CDCl₃) δ 2.26 (s, 6 H), 2.40 (s, 6 H), 7.20 (s, 8 H); mass spectrum (*m/e*) 305 (15), 304 (M⁺, 80), 303 (100), 151 (7), 132 (7), 130 (7), 129 (9), 128 (6), 115 (11), 43 (13).

2,6-Dimethyl-3,5-bis(p-chlorophenyl)-4-pyrone (Id): IR (KBr) 1645, 1620, 1590, 1490, 1410, 1390, 1330, 1295, 1230, 1090, 990, 845, 825, 790 cm⁻¹; NMR (CDCl₃) δ 2.22 (s, 6 H), 7.30 (q, J = 8.0 Hz, 8 H); mass spectrum (*m/e*) 347 (6), 346 (8), 345 (8), 344 (M⁺, 10), 121 (7), 120 (6), 107 (7), 106 (30), 90 (27), 89 (21), 78 (27).

2,6-Dimethyl-3,5-bis(p-bromophenyl)-4-pyrone (Ie): IR (KBr) 1645, 1610, 1580, 1490, 1385, 1225, 1065, 1010, 985, 810, 780 cm⁻¹; NMR (CDCl₃) δ 2.22 (s, 6 H), 7.33 (q, J = 8.0 Hz, 8 H); mass spectrum (*m/e*) 437 (9), 436 (43), 435 (57), 434 (M⁺, 100), 433 (93), 432 (52), 431 (43), 355 (11), 354 (21), 353 (11), 352 (20), 202 (18), 198 (13), 196 (25), 194 (14), 149 (71), 137 (21), 105 (86), 89 (16), 57 (61), 43 (43).

Preparation of 1,2,6-Trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones. A typical procedure follows with the results

for the remaining cases tabulated in Table VI. A mixture containing 1 g of 2,6-dimethyl-3,5-bis(p-fluorophenyl)-4-pyridone and 30 g of 40% aqueous methylamine in 100 mL of ethanol was heated in a stainless steel pressured bottle at 90 °C for 30 h. After evaporation of the solvent and excess methylamine under reduced pressure, the residual solid was recrystallized from benzene to yield 0.8 g (80%) of 1,2,6-trimethyl-3,5,-bis(p-fluorophenyl)-4-pyridone (IIc): mp 292.5–293.5 °C; IR (KBr) 1610, 1555, 1510, 1395, 1300, 1225, 1160, 1100, 830 cm⁻¹; NMR (CCl₄) δ 2.23 (s, 6 H), 3.55 (s, 3 H), 6.8–7.4 (m, 8 H); mass spectrum (*m/e*) 326 (8), 325 (M⁺, 45), 324 (100), 312 (6), 311 (7), 297 (6), 296 (8), 162 (7), 133 (9), 78 (11), 56 (19). Anal. Calcd for C₂₀H₁₇NOF₂: C, 73.82; H, 5.27; N, 4.31, F, 11.68. Found: C, 73.55; H, 5.14; N, 4.49; F, 11.52.

Spectral Data. 1,2,6-Trimethyl-3,5-bis(p-tolyl)-4-pyridone (IIb): IR (KBr) 1610, 1545, 1490, 1300, 1175, 1150, 1105, 990, 960, 800, 750 cm⁻¹; NMR (CCl₄) δ 2.26 (s, 6 H), 2.35 (s, 6 H), 3.60 (s, 3 H), 7.0–7.4 (m, 8 H); mass spectrum (*m/e*) 318 (9), 317 (M⁺, 46), 316 (100), 301 (5), 300 (4(= 2—9 (4), 158 (7), 157 (14), 56 (16).

1,2,6-Trimethyl-3,5-bis(p-chlorophenyl)-4-pyridone (IId): IR (KBr) 1615, 1595, 1495, 1390, 1300, 1155, 1095, 990, 960, 940, 850, 815, 790 cm⁻¹; NMR (CCl₄) δ 2.29 (s, 6 H), 3.60 (s, 3 H), 7.0–7.6 (m, 8 H); mass spectrum (*m/e*) 361 (6), 360 (15), 359 (29), 358 (M⁺, 70), 357 (45), 356 (100), 321 (12), 143 (9), 141 (12), 56 (23).

1,2,6-Trimethyl-3,5-bis(p-bromophenyl)-4-pyridone (IIe): IR (KBr) 1615, 1595, 1485, 1390, 1300, 1070, 1010, 990, 960, 810, 785, 690 cm⁻¹; NMR (CCl₄) δ 2.23 (s, 6 H), 3.57 (s, 3 H), 7.0–7.6 (m, 8 H); mass spectrum (*m/e*) 449 (23), 448 (55), 447 (M⁺, 48), 446 (100), 445 (27), 444 (51), 434 (6), 433 (6), 419 (4), 418 (4), 367 (12), 366 (9), 365 (10), 184 (10), 183 (12), 143 (27), 136 (14), 115 (19), 78 (64), 56 (40).

Irradiation of 2,6-Dimethyl-3,5-bis(para-substituted phenyl)-4-pyrones. A typical preparative photoirradiation of 2,6-dimethyl-3,5-bis(para-substituted phenyl)-4-pyrones follows with the results for the remaining cases summarized in Table VII.

A solution containing 0.2 g of 1,2,6-trimethyl-3,5-bis(p-fluorophenyl)-4-pyrone in 250 mL of acetonitrile was irradiated under nitrogen for 3 h using a 500-W Taika medium-pressure mercury lamp equipped with a Vycor filter. Removal of the solvent in vacuo left a pale yellow solid, which was chromatographed on silica gel with chloroform as eluent. The 1000-mL collection afforded colorless crystals, which, after recrystallization from cyclohexane–chloroform, gave 0.092 g (46%) of 3,6-bis(p-fluorophenyl)-4,5-dimethyl-2-pyrone (IVc): mp 161.0–162.5 °C; UV (CH₃CN) λ_{max} 233 (ϵ 9300), 325 nm (10400); IR (KBr) 1685, 1625, 1600, 1545, 1500, 1380, 1340, 1215, 1160, 1090, 1025, 1010, 955, 945, 840, 825 cm⁻¹; NMR (CDCl₃) δ 2.03 (s, 3 H), 2.06 (s, 3 H), 7.0–7.8 (m, 8 H); mass spectrum (*m/e*) 313 (7), 312 (M⁺, 36), 285 (15), 284 (100), 161 (86), 123 (33), 95 (31). Anal. Calcd for C₁₉H₁₄O₂F₂: C, 73.07; H, 4.52; F, 12.17. Found: C, 73.26; H, 4.62; F, 12.34.

Spectral Data. 3,6-Bis(p-tolyl)-4,5-dimethyl-2-pyrone (IVb): UV (CH₃CN) λ_{max} 242 (ϵ 13500), 325 nm (16700); IR (KBr) 1700, 1630, 1540, 1500, 1445, 1380, 1335, 1185, 1080, 1030, 1010, 950, 935, 815, 715

Table VII. Irradiation of 2,6-Dimethyl-3,5-bis(para-substituted phenyl)-4-pyrones

Substituent	4-Pyrone, wt in g	Solvent mL	Irradiation time, h	2-Pyrone, wt in g (%)	Mp, °C	% Calcd, Found			
						C	H	Cl	Br
CH₃	Ib, 0.3	CH₃CN 250	1.5	IVb, 0.23 (77)	148–149	82.86 82.67	6.62 6.47		
Cl	Id, 0.9	CH₃CN 900	5	IVd, 0.19 (21)	156–157	66.10 65.82	4.09 3.88	20.54 20.26	
Br	Ie, 0.3	CH₃CN 250	0.5	IVe, 0.03^a (10)	193–194	52.57 52.50	3.25 3.08		36.81 36.95

^{a} Prolonged irradiation produced tarry materials and reduced yield of IVe further.

Table VIII. Irradiation of 1,2,6-Trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones

Substituent	4-Pyridones, wt in g	Solvent mL	Irradiation time, h	2-Pyridones, wt in g (%)	Mp, °C	% Calcd, Found				
						C	H	N	Cl	Br
CH₃	IIb, 0.2	CH₃CN 250	2	Vb, 0.038 (19)	207–209	83.25 83.27	7.30 7.18	4.41 4.50		
				VIb, 0.006 (3)	160–162	83.25 83.08	7.30 7.20	4.41 4.31		
Cl	IId, 0.6	CH₃OH 600	7	Vd, 0.073 (14)^a	166–168	67.05 67.21	4.78 5.06	3.91 3.78	19.79 19.66	
Br	IIe, 0.5	CH₃CN 250	0.5^b	Ve, 0.049 (5)^b	189–191	53.72 53.73	3.83 3.69	3.13 3.27		35.74 35.48

^{a} An isomer of Vd appeared to be formed on the basis of TLC as in the case of IIb, but an amount of isolated product could not permit its identification. ^{b} Prolonged irradiation produced tarry materials and reduced yield of Ve further.

cm⁻¹; NMR (CDCl₃) δ 2.02 (s, 3 H), 2.06 (s, 3 H), 2.35 (s, 6 H), 7.0–7.5 (m, 8 H); mass spectrum (*m/e*) 305 (7), 304 (M⁺, 26), 277 (24), 276 (100), 157 (48), 141 (14), 119 (21), 115 (13), 91 (27), 65 (16).

3,6-Bis(*p*-chlorphenyl)-4,5-dimethyl-2-pyrone (IVd): UV (CH₃CN) λ_max 242 (ε 12700), 325 nm (16700); IR (KBr) 1700, 1630, 1585, 1530, 1445, 1390, 1375, 1330, 1180, 1080, 1000, 945, 930, 870, 835, 825 cm⁻¹; NMR (CDCl₃) δ 2.05 (s, 3 H), 2.10 (s, 3 H), 7.0–7.6 (m, 8 H); mass spectrum (*m/e*) 348 (5), 347 (6), 346 (28), 345 (9), 344 (M⁺, 48), 320 (12), 319 (13), 318 (65), 317 (20), 316 (100), 179 (13), 177 (40), 159 (8), 158 (12), 141 (25), 139 (25), 115 (9), 111 (15).

3,6-Bis(*p*-bromophenyl)-4,5-dimethyl-2-pyrone (IVe): UV (CH₃CN) λ_max 248 (ε 7500), 325 nm (15900); IR (KBr) 1705, 1625, 1585, 1535, 1485, 1380, 1340, 1185, 1085, 1070, 1005, 950, 935, 840, 830, 810 cm⁻¹; NMR (CDCl₃) δ 2.07 (s, 3 H), 2.12 (s, 3 H), 7.1–7.7 (m, 8 H); mass spectrum (*m/e*) 436 (18), 434 (M⁺, 39), 432 (18), 408 (47), 407 (18), 406 (100), 404 (51), 223 (33), 221 (35), 203 (16), 185 (23), 183 (26), 155 (15), 141 (30), 115 (10), 77 (6).

Irradiation of 1,2,6-Trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones. A typical procedure for the preparative irradiation of 1,2,6-trimethyl-3,5-bis(para-substituted phenyl)-4-pyridones is as follows. The irradiation conditions and results for the remaining compounds are summarized in Table VIII.

A solution of 0.3 g of 1,2,6-trimethyl-3,5-bis(*p*-fluorophenyl)-4-pyridone in 250 mL of acetonitrile was irradiated under nitrogen with a 500-W medium-pressure mercury lamp using Vycor filter at 29 °C for 2 h. The solvent was removed under reduced pressure and the residual solid was chromatographed on silica gel with chloroform–ether (8:2) as eluent. The first 600-mL collection afforded colorless crystals, which, after recrystallization from benzene–ligroin, gave 0.009 g (3.5%) of 1,4,5-trimethyl-3,6-bis(*p*-fluorophenyl)-2-pyridone (VIc): mp 215–217 °C; IR (KBr) 1630, 1605, 1580, 1540, 1505, 1420, 1390, 1280, 1220, 1210, 1155, 1090, 1010, 910, 880, 845, 825 cm⁻¹; NMR (CDCl₃) δ 1.80 (s, 3 H), 2.03 (s, 3 H), 3.23 (s, 3 H), 7.0–7.5 (m, 8 H); mass spectrum (*m/e*) 326 (18), 325 (M⁺, 86), 324 (100), 298 (5), 297 (23), 296 (24), 162 (8), 136 (13), 133 (9), 95 (12). Anal. Calcd for C₂₀H₁₇NOF₂: C, 73.83; H, 5.27; N, 4.31; F, 11.68. Found: C, 73.55; H, 5.24; N, 4.29; F, 11.62.

The next 500-mL fraction furnished a solid, which, after recrystallization from benzene–ligroin, gave 0.10 g (36%) of 1,4,6-trimethyl-3,5-bis(*p*-fluorophenyl)-2-pyridone (Vc): mp 128–129 °C; UV (MeOH) λ_max 240 (ε 8700), 317 nm (9800); IR (KBr) 1625, 1600, 1585, 1525, 1500, 1420, 1300, 1215, 1150, 1085, 1010, 950, 865, 820, 785 cm⁻¹; NMR (CCl₄) δ 1.62 (s, 3 H), 2.05 (s, 3 H), 3.52 (s, 3 H), 6.8–7.4 (m, 8 H); mass spectrum (*m/e*) 326 (23), 325 (M⁺, 99), 324 (100), 298 (7), 297 (33), 296 (33), 162 (11), 78 (20), 57 (23), 56 (52). Anal. Calcd for C₂₀H₁₇NOF₂: C, 73.83; H, 5.27; N, 4.31; F, 11.68. Found: C, 73.60; H, 5.42; N, 4.12, F, 11.41.

Spectral Data. **1,4,6-Trimethyl-3,5-bis(*p*-tolyl)-2-pyridone (Vb):** UV (MeOH) λ_max 240 (ε 13000), 315 nm (11700); IR (KBr) 1625, 1580, 1530, 1510, 1420, 1370, 1355, 1300, 1235, 1200, 1175, 1105, 1095, 1015, 950, 865, 805, 780, 735 cm⁻¹; NMR (CCl₄) δ 1.60 (s, 3 H), 2.03 (s, 3 H), 2.33 (s, 6 H), 3.50 (s, 3 H), 6.8–7.2 (m, 8 H); mass spectrum (*m/e*) 318 (25), 317 (M⁺, 100), 316 (96), 290 (8), 289 (34), 288 (22), 158 (11), 157 (18), 149 (16), 91 (14), 56 (17).

1,4,5-Trimethyl-3,6-bis(*p*-tolyl)-2-pyridone (VIb): IR (KBr) 1625, 1585, 1545, 1510, 1440, 1420, 1280, 1175, 1105, 1090, 1010, 905, 880, 805, 735, 715 cm⁻¹; NMR (CCl₄) δ 1.78 (s, 3 H), 2.03 (s, 3 H), 2.40 (s, 3 H), 2.45 (s, 3 H), 3.22 (s, 3 H), 7.0–7.4 (m, 8 H); mass spectrum (*m/e*) 318 (21), 317 (M⁺, 87), 316 (100), 290 (7), 289 (74), 288 (17), 136 (7), 132 (9), 119 (14), 115 (8), 105 (6), 91 (19), 78 (28), 77 (10), 57 (14), 56 (11).

1,4,6-Trimethyl-3,5-bis(*p*-chlorophenyl)-2-pyridone (Vd): UV (MeOH) λ_max 246 (ε 6400), 318 nm (6700); IR (KBr) 1615, 1550, 1490, 1390, 1300, 1105, 1085, 1015, 990, 960, 850, 815, 790, 695 cm⁻¹; NMR (CDCl₃) δ 1.66 (s, 3 H), 2.10 (s, 3 H), 3.60 (s, 3 H), 7.0–7.4 (m, 8 H); mass spectrum (*m/e*) 361 (12), 360 (22), 359 (63), 358 (M⁺, 81), 357 (100), 356 (95), 331 (19), 330 (22), 329 (28), 328 (22), 324 (14), 323 (22), 322 (26), 295 (10), 278 (10), 202 (11), 115 (11), 101 (11), 56 (10).

1,4,6-Trimethyl-3,5-bis(*p*-bromophenyl)-2-pyridone (Ve): UV (MeOH) λ_max 255 (ε 10200), 318 nm (10400); NMR (CCl₄) δ 1.67 (s, 3 H), 2.12 (s, 3 H), 3.60 (s, 3 H), 7.0–7.6 (m, 8 H); mass spectrum (*m/e*) 449 (47), 448 (52), 447 (M⁺, 100), 446 (80), 445 (62), 444 (36), 419 (16), 418 (13), 369 (39), 368 (42), 367 (46), 366 (37), 339 (10), 202 (15), 144 (54), 143 (60), 137 (16), 135 (21), 122 (10), 105 (14), 56 (8).

Preparation of 1,4,6-Trimethyl-3,5-bis(para-substituted phenyl)-2-pyridones. 1,4,6-Trimethyl-3,5-bis(para-substituted phenyl)-2-pyridones were prepared by condensation of α-acetyl para-substituted benzylcyanides with para-substituted arylacetones to 4,6-dimethyl-3,5-bis(para-substituted phenyl)-2-pyridones[15b,22] followed by *N*-methylation.

A mixture of 2 mmol of α-acetyl *p*-fluorobenzylcyanide and 4 mmol of *p*-fluorophenyl acetone in 6 mL of glacial acetic acid and 2 mL of concentrated sulfuric acid was heated until evolution of carbon dioxide began. If the reaction tended to become vigorous, the mixture was cooled with water. After about 1 h, the mixture was gently heated again until evolution of carbon dioxide ceased. After cooling, the mixture was poured into water and neutralized with a sodium carbonate solution. The precipitate obtained was filtered off and washed with water and acetone. This crude product, after drying, was dissolved into a solution of a slight excess of sodium methylate in methanol. Methyl iodide was added dropwise to this solution at 5 °C. The reaction mixture was extracted with ether, washed with water, and dried over anhydrous sodium sulfate. After evaporation of the solvent, column chromatography of the residual solid on silica gel with

chloroform–ether (5:1) gave a solid, which, after recrystallization from a ligroin–benzene mixture, afforded 1,4,6-trimethyl-3,5-bis(*p*-fluorophenyl)-2-pyridone. No depression of melting point in admixture of this product with the photoproduct, Vc, was observed. Its IR and NMR spectra were identical with those of Vc.

Quantum Yield Determination. Dilute solutions of I ($2–5 \times 10^{-3}$ M) in dioxane and of II ($1–3 \times 10^{-3}$ M) in methanol in quartz test tubes were irradiated in a merry-go-round apparatus with four Taika 15W low-pressure mercury lamps. The samples in photolysis tubes were degassed using three freeze–pump (to about 10^{-2} Torr)–thaw cycles and then sealed under vacuum. These samples were irradiated to less than 3% conversion. Potassium ferrioxalate actinometer[23] provided light intensities in the order of 6.0×10^{-3} mEinstein/min (10 cm^3). After irradiation, the concentration of the photoproduct was determined by quantitative ultraviolet spectroscopy. Absorption due to the starting material was corrected to determine the degree of reaction.

The quantum yield of photoreaction of I or II in a heavy-atom solvent (*n*-butyl bromide) was determined similarly.[27]

Determination of Intersystem Crossing Efficiency. *cis*- and *trans*-piperylenes (99.5%) were obtained from the Chemical Sample Co. and used as received. Dohjin Chemical Spectrograde solvents (methanol, dioxane, and *tert*-butyl alcohol) were used without further purification. Benzophenone was purified by recrystallization. The cis–trans isomers ratio was determined by vapor-phase chromatography using a Yanagimoto GCG-500T equipped with a hydrogen-flame ionization detector on a 20×0.125 in. column packed with 15% 1,2-bis(cyanoethoxy)ethane on Chromosorb P (40–60 mesh) at room temperature. Irradiation with 253.7-nm light was carried out in a merry-go-round apparatus similar to the case of the quantum yield determination mentioned above. The method developed by Lamola and Hammond[24] was employed for determining the intersystem crossing efficiency. Potassium ferrioxalate actinometry[23] was used in the determination of ϕ_{isc} for benzophenone. For actinometry at 253.7 nm the benzophenone ($\phi_{isc} = 1.02$) sensitized isomerization of *cis*-piperylene was employed. At the photostationary state [cis]$_s$/[trans]$_s$ = 0.82 (lit. value 0.81[24]). Each sensitizer ($1–4 \times 10^{-3}$ M for I and II) was run at least twice in the presence of *cis*-piperylene at different concentrations (0.01–0.1 M). The value of ϕ_{isc} was obtained by extrapolating to infinite concentration of *cis*-piperylene.

The value of ϕ_{isc} of I and II in the heavy-atom solvent (*n*-butyl bromide) was similarly determined.

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