Substituent Effect on Selectivity in Photoisomerization of 4-Pyrones and 4-Pyridones

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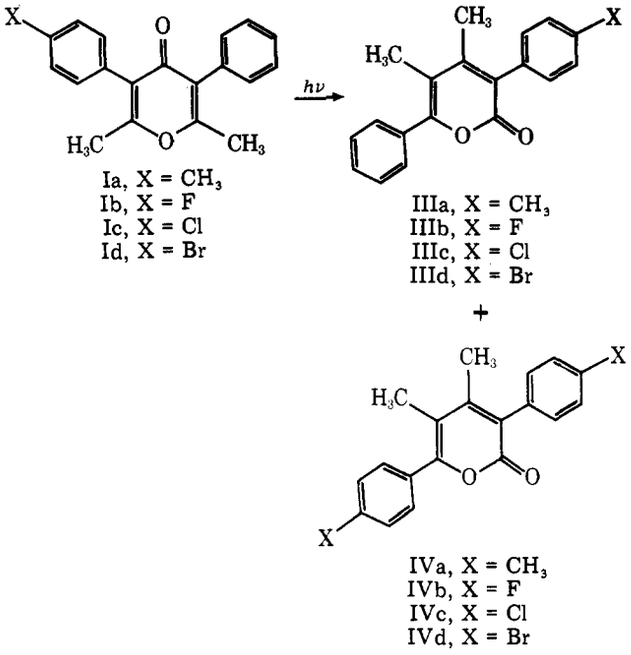
Received March 21, 1977

Ultraviolet irradiation of 2,6-dimethyl-3-phenyl-5-(*p*-X-phenyl)-4-pyrones (X = Me, F, Cl, and Br) gave both 3-phenyl-6-(*p*-X-phenyl)-4,5-dimethyl-2-pyrones and 3-(*p*-X-phenyl)-6-phenyl-4,5-dimethyl-2-pyrones. Similarly 1,2,6-trimethyl-3-phenyl-5-(*p*-X-phenyl)-4-pyridones (X = Me, F, Cl, and Br) were photoisomerized to both 1,4,6-trimethyl-3-phenyl-5-(*p*-X-phenyl)-2-pyridones and 1,4,6-trimethyl-3-(*p*-X-phenyl)-5-phenyl-2-pyridones. Effect of para substituents on selectivity in this photoisomerization was discussed.

In the past the study of the substituent effect on the photochemical reaction of ketones has provided much information concerning the electronic nature of species undergoing rearrangement.[3] Such an approach was found to be useful in interpreting photochemistry of the di-π-methane[4] and sigmatropic rearrangements[5] and of lactones.[6] In a hope that such a study would prove to be similarly informative in understanding the photorearrangement of 4-pyrones[7] and 4-pyridones,[8] we have examined the effect of para substituents on selectivity in the photoisomerization of 2,6-dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones and 1,2,6-trimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyridones to the 2-pyrones and 2-pyridones, respectively. In the preceding paper[9] the quenching effect by dienes and the external heavy-atom effect on quantum yield indicated that the π,π^* singlet state was responsible for the photorearrangement of 4-pyrones to 2-pyrones and that of 4-pyridones to 2-pyridones. Involvement of the π,π^* singlet state can be reflected in selectivity in the formation of 2-pyrones and 2-pyridones. Recently, Pavlik et al.[10] suggested the formation of two isomeric 2-hydroxypyrylium cations in the photolysis of 2,6-dimethyl-3-phenyl-4-hydroxypyrylium cation but could not isolate their isomeric 2-pyrones.



Results and Discussion

2,6-Dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones (I) were synthesized from 1-(para-substituted phenyl)-3-phenylacetones by polyphosphoric acid-catalyzed condensation with acetic acid. The corresponding 4-pyridones (II) were obtained by the condensation of 4-pyrones with methylamine in a sealed tube as described in the preceding paper.[9,11] The structures assigned to I and II are based on their spectral (IR, NMR, and mass) data and elemental analyses which were described in the Experimental Section.

Preparative scale photolysis of I was carried out on solutions of 4-pyrones in acetonitrile using Vycor-filter light from a Taika 300-W medium-pressure mercury arc. Irradiation of I gave two isomeric 2-pyrones, III and IV, which were separated by careful column or thick-layer chromatography. The structure assignment to 2-pyrones rests on the spectral data. Three strong absorptions characteristic of the 2-pyrone are observed at 1700, 1630, and 1550 cm^{-1} in the infrared spectra and two nonequivalent methyl protons are detected at δ 2.00–2.08 and 2.05–2.12 in the NMR spectra, the pattern being similar to that of the parent 2-pyrone, 3,6-diphenyl-4,5-dimethyl-2-pyrone.[7]

Mass spectra of the photoproduct obtained at low voltage bombardment were particularly relevant to determine which substituent (either the phenyl or para-substituted phenyl group) is located on C-6 of the 2-pyrone ring, because the favorable fragmentation of 2-pyrones involves loss of the substituent at C-6 of the 2-pyrone ring as acyl radical from the fragment ion $[M - CO]^+$.[12,13] Their mass spectra are summarized in Table I. At the low bombarding electron energies (15–30 eV) the presence of the fragment ion corresponding to $[M - CO - Ph]^+$ indicates the presence of the phenyl group at C-6, whereas the formation of fragment ion corresponding

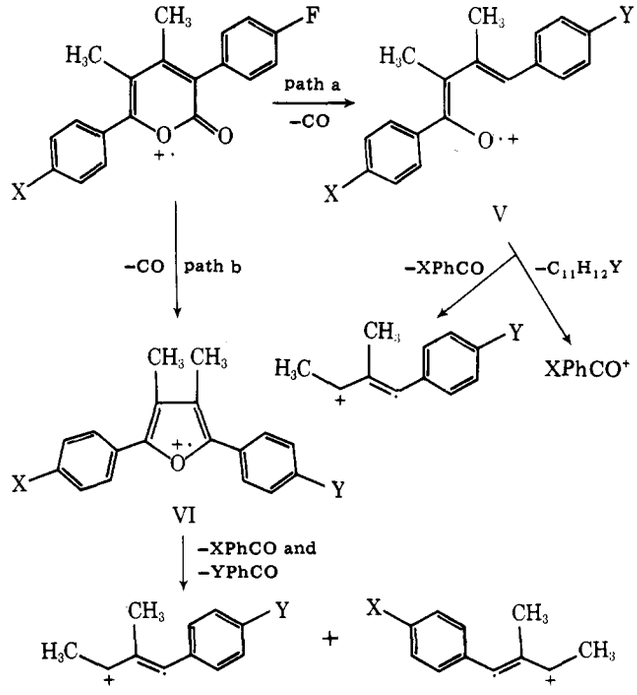


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Table I. Mass Spectral Fragmentation of 2-Pyrones

2-Pyrone[a]	Registry no.	Bombardment voltage, eV	Fragment *m/e* (rel intensity)
IIIa	65636-01-3	25	291 (6), 290 (M^+, 36), 263 (21), 262 (100), 157 (25), 143 (3), 105 (8)
IIIb	65636-02-4	30	295 (5), 294 (M^+, 29), 267 (15), 266 (100), 258 (9), 161 (13), 143 (5), 105 (21)
IVb	65636-03-5	30	295 (4), 294 (M^+, 26), 267 (16), 266 (100), 161 (3), 143 (19), 105 (5)
IIIc	65636-04-6	24	312 (16), 311 (9), 310 (M^+, 46), 285 (7), 284 (33), 283 (21), 282 (100), 179 (4), 177 (13), 143 (2), 105 (21)
IVc	65636-05-7	24	312 (10), 311 (5.5), 310 (M^+, 30), 285 (4), 284 (33), 283 (20), 282 (100), 177 (4), 143 (22), 139 (9)
IIId	65636-06-8	22.5	357 (3), 356 (22), 355 (5), 354 (M^+, 24), 329 (17), 328 (98), 327 (21), 326 (100), 223 (10), 221 (11), 143 (9), 105 (41)
IVd	65636-07-9	15	357 (20), 356 (100), 355 (23), 354 (M^+, 97), 329 (20), 328 (87), 327 (20), 326 (80), 185 (10), 183 (10), 143 (15)

[a] Pure IVa could not be isolated by column or thick-layer chromatography.

Table II. Selectivity in Photorearrangement of 2,6-Dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones and 1,2,6-Trimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyridones

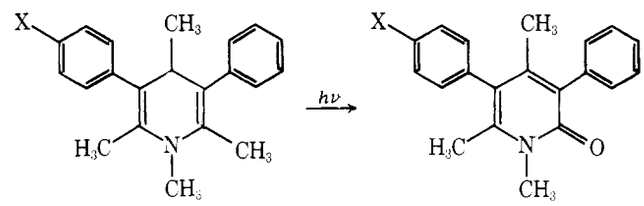
Substrate	Registry no.	Substituent	Yield, %	Ratio[b]
Ia	65636-08-0	CH_3	61	IIIa/IVa = 0.62[c]
Ib	65636-09-1	F	83	IIIb/IVb = 1.8
Ic	65636-10-4	Cl	76	IIIc/IVc = 2.2
Id	65636-11-5	Br	51[a]	IIId/IVd = 2.5
IIa	65636-12-6	CH_3	64	VIIIa/VIIa = 0.43
IIb	65636-13-7	F	64	VIIIb/VIIb = 1.9
IIc	65636-14-8	Cl	68	VIIIc/VIIc = 3.0
IId	65636-15-9	Br	32[a]	VIIId/VIId = 3.0

[a] The prolonged irradiation decreased yield because of formation of a tarry material. [b] Estimated maximum analytical error was within 5% except for that in Ib and IIb ranging ±9%. [c] Although pure IVa was not isolated, the 220 MHz NMR spectra of the isomeric mixture showed the different chemical shift for the methyl protons and the integration then gave the relative ratio of the isomers.

to $[M - CO - XPhCO]^+$ indicates the presence of the para-substituted phenyl group at C-6. The 2-pyrone, III, possessing the phenyl group instead of the para-substituted phenyl group at C-6 shows no or a very weak fragment corresponding to the para-substituted benzoyl cation but exhibits a strong peak of the benzoyl cation. On the other hand, the isomer of 2-pyrone, IV, produces a much more intense fragment of the para-substituted benzoyl cation relative to a fragment of the benzoyl cation. These results together with the fragmentation pathway of the substituent at C-6 of the 2-pyrone support our structural assignment of the photoproduct. As shown in Table I the elimination of the substituent at C-6 in 2-pyrones predominates over that at C-3 as the most favorable fragmentation pathway from the fragment ion $[M - CO]^+$, suggesting that the elimination of carbon monoxide gives the intermediate V (path a)[13] rather than VI (path b),[12] the latter being anticipated to eliminate both benzoyl and para-substituted benzoyl groups from $[M - CO]^+$.

Preparative photolysis of II was performed on a methanol solution of II under nitrogen using a Taika 300-W medium-pressure mercury lamp fitted with a Vycor filter. Two major products[14] were carefully separated by column chromatography on silica gel. Their structures were assigned as 1,4,6-trimethyl-3-phenyl-5-(para-substituted phenyl)-2-pyridones, VII, and 1,4,6-trimethyl-3-(para-substituted phenyl)-5-phenyl-2-pyridones, VIII, respectively. These assignments were established by comparison of their spectral (IR, NMR, and mass) data with those of authentic samples independently prepared from *N*-methylation of the corresponding 2-pyridones, which were synthesized by condensation–cyclization of either para-substituted phenylacetones with α-acetyl benzylcyanide or phenylacetone with α-acetyl para-substituted benzylcyanide.

After irradiation of I in acetonitrile and II in methanol for the same period of time and after drying of the reaction mixture under vacuum, the products were analyzed by a 100 or 220 MHz NMR spectrometer in which the integration gave the ratio of the isomers. The results are given in Table II.



IIa, X = CH_3
IIb, X = F
IIc, X = Cl
IId, X = Br

VIIa, X = CH_3
VIIb, X = F
VIIc, X = Cl
VIId, X = Br

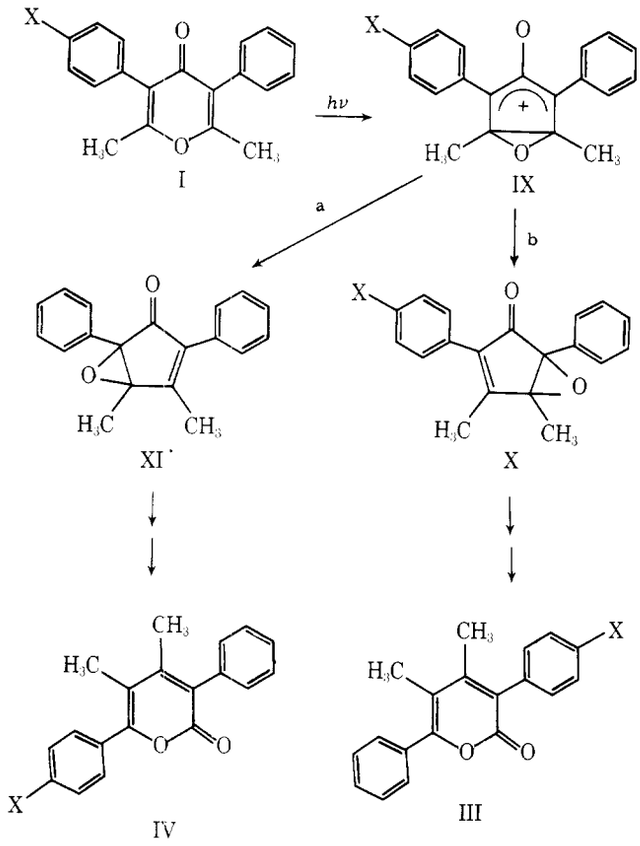
+

VIIIa, X = CH_3
VIIIb, X = F
VIIIc, X = Cl
VIIId, X = Br

It is immediately clear that the polar substituents exert an evident effect on selectivity in the formation of both 2-pyrones and 2-pyridones. The presence of the electron-withdrawing group in 4-pyrones enhances the preferable formation of III over IV and conversely increasing the electron density at C-5 (Ia) favors the formation of IV over III. The mechanism consistent with the rearrangement of 4-pyrones is shown in Scheme I.

Assuming conjugation of the phenyl group with the heterocyclic ring to some extent, the electron-withdrawing sub-

Scheme I



stituent decreases the electron density at the 1-phenylpropenyl terminus (C-3 in IX) so that the nucleophilic oxygen attacks preferably at C-3 (path b). Involvement of this zwitterionic 2,6-bonded intermediate in 4-pyrone photochemistry was recently established.[15] The 4,5-epoxycyclopent-2-en-1-one intermediate, X, formed further rearranges to III.[16] The pattern of the substituent effect observed in the photorearrangement of I[17] appears to be analogous to that predicted for ground-state rearrangement of the epoxy oxygen atom where the rearrangement is predicted to become less favorable at the rearrangement terminus going from cationic to radical-like to anionic.

In the photorearrangement of 4-pyridones, II, to 2-pyridones the electron-withdrawing group (IIb–d) increases the formation of VIII relative to VII and conversely the electron-donating group (IIa) favors the formation of VII over VIII. Assuming that this selectivity is determined by the formation of either the C_3–C_6 or C_2–C_5 bond in the mechanism proposed previously,[8] the electron-withdrawing group decreases the electron density at C-6 of II, resulting in favorable bonding between C-3 and C-6. On the other hand, the electron-donating substituent increases the charge density at C-6 of II, leading to the preferential formation of IX, although the ring-closured intermediate has to isomerize further to 2-pyridones.[17]

Experimental Section

Microanalyses were conducted by Microanalytical Laboratories, Kyoto University, Kyoto, Japan. Infrared spectra were recorded on a Jasco DS-402G spectrophotometer. Ultraviolet absorption spectra were obtained on a Hitachi 323 spectrophotometer. NMR spectra were measured at 60 MHz (Varian T-60A) or 100 MHz (Varian HA-100) or 220 MHz (Varian HR-220) using tetramethylsilane as internal standard. Chemical shifts were reported in parts per million (δ) from Me_4Si. Mass spectra were obtained by direct insertion on a Hitachi RMU-6L spectrometer at 70 eV unless otherwise cited. Melting points were uncorrected.

Preparation of 2,6-Dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones. In the general procedure 5 g of 1-phenyl-3-(*p*-fluorophenyl)-2-propanone was added to a mixture of 32 g of acetic acid and 51 g of polyphosphoric acid at room temperature. The mixture was stirred at 120–130 °C for 2 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 the crude crystals from methanol gave 3.5 g (70%) of 2,6-dimethyl-3-phenyl-5-(*p*-fluorophenyl)-4-pyrone (Ib): mp 196–198 °C; IR (KBr) 1640, 1600, 1500, 1430, 1410, 1365, 1320, 1310, 1295, 1275, 1220, 1175, 1150, 1090, 1070, 1020, 985, 910, 845, 815, 800, 780, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.23 (s, 6 H), 6.9–7.5 (m, 9 H); mass spectrum (*m/e*) 295 (14), 294 (M^+, 80), 293 (100), 276 (12), 275 (17), 251 (13), 233 (10), 223 (16), 149 (22), 147 (28), 136 (25), 134 (27), 133 (52), 118 (38), 116 (31), 115 (52), 108 (13), 90 (17), 89 (14), 43 (52). Anal. Calcd for $C_{19}H_{15}O_2F$: C, 77.54; H, 5.14; F, 6.46. Found: C, 77.24; H. 5.29; F, 6.30.

Preparative conditions and analytical results for other 4-pyrones are summarized in Table III. All values for the elemental analyses (C, H, and halogen) were within 0.3% of those calculated.

Spectral data for these compounds are as follows.

2,6-Dimethyl-3-phenyl-5-(*p*-tolyl)-4-pyrone (Ia): IR (KBr) 1645, 1620, 1600, 1500, 1440, 1415, 1370, 1310, 1235, 990, 920, 800, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.225 (s, 6 H), 2.35 (s, 3 H), 7.16 (s, 5 H), 5.30 (d, J = 8.2 Hz, 4 H); mass spectrum (*m/e*) 291 (8), 290 (M^+, 55), 289 (42), 288 (57), 275 (6), 246 (11), 219 (9), 204 (7), 203 (11), 202 (11), 145 (20), 144 (35), 132 (25), 130 (30), 129 (28), 128 (19), 127 (11), 116 (11), 115 (67), 104 (14), 103 (12), 90 (10), 83 (28), 77 (17), 56 (39), 55 (19), 43 (100), 42 (24).

2,6-Dimethyl-3-phenyl-5-(*p*-chlorophenyl)-4-pyrone (Ic): IR (KBr) 1640, 1620, 1585, 1560, 1490, 1435, 1410, 1395, 1370, 1330, 1315, 1230, 1150, 1085, 985, 920, 855, 830, 795, 755, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.23 (s, 6 H), 7.1–7.4 (m, 9 H); mass spectrum (*m/e*) 312 (34), 311 (57), 310 (M^+, 93), 309 (100), 275 (12), 274 (16), 267 (14), 249 (11), 232 (14), 204 (16), 203 (24), 155 (24), 152 (34), 150 (22), 149 (14), 137 (17), 124 (14), 119 (14), 118 (45), 116 (46), 115 (71), 90 (24), 89 (31), 63 (27), 43 (71).

2,6-Dimethyl-3-phenyl-5-(*p*-bromophenyl)-4-pyrone (Id): IR (KBr) 1640, 1610, 1480, 1415, 1390, 1325, 1230, 1145, 1090, 1055, 1035, 1005, 985, 915, 840, 830, 800, 790, 745, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.60 (s, 6 H), 7.1–7.7 (m, 9 H); mass spectrum (*m/e*) 357 (14), 256 (72), 355 (100), 354 (72), 353 (89), 275 (8), 274 (17), 203 (8), 202 (8), 196 (8), 118 (8), 117 (9), 116 (18), 115 (58), 90 (8), 89 (18), 43 (89).

Preparation of 1,2,6-Trimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyridones. A typical procedure follows with the result for the remaining cases tabulated in Table III. All C, H, N, and halogen (Cl and Br) were within 0.2% of calculated.

A mixture containing 1.5 g of 2,6-dimethyl-3-phenyl-5-(*p*-fluorophenyl)-4-pyrone and 30 g of 40% methylamine in 100 mL of ethanol was heated in a stainless steel bomb at 90 °C for 48 h. After removal of the solvent and methylamine under reduced pressure, the residual solid was recrystallized from benzene to yield 0.9 g (60%) of 1,2,6-trimethyl-3-phenyl-5-(*p*-fluorophenyl)-4-pyridone (IIb): mp 276–278 °C; IR (KBr) 1615, 1565, 1555, 1440, 1390, 1305, 1225, 1100, 995, 960, 850, 815, 805, 755, 710 cm^{-1}; NMR ($CDCl_3$) δ 2.21 (s, 6 H), 3.53 (s, 3 H), 6.9–7.4 (m, 9 H); mass spectrum (*m/e*) 308 (8), 307 (M^+, 41), 306 (100), 277 (7), 56 (9). Anal. Calcd for $C_{20}H_{18}NOF$: C, 78.15; H, 5.90; N, 4.56; F, 6.18. Found: C, 77.91; H, 5.82; N, 4.73; F, 6.05.

Table III. Preparation of 2,6-Dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones and 1,2,6-Trimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyridones

Substituent	4-Pyrones[a] or 4-Pyridones, wt in g (%)	Mp, °C
CH_3	Ia, 0.92 (18)	121–122.5
Cl	Ic, 1.35 (27)	167.5–168
Br	Id, 1.85 (37)	169–170.5
CH_3	IIa (52)	267–269
Cl	IIc (63)	262–263
Br	IId (66)	228–230

[a] Five grams of 1-aryl-3-phenyl-2-propanones was used. These ketones were prepared according to the following literature: S. B. Coan and E. I. Becker, *J. Am. Chem. Soc.*, **76**, 501 (1954); R. C. Elderfield and K. L. Burgess, *ibid.*, **82**, 1975 (1960).

Table IV. Irradiation of 2,6-Dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones and 1,2,6-Trimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyridones

Substituent	4-Pyrones or 4-Pyridones, wt in g	Solvent (mL)	Irradiation time, h	2-Pyrones or 2-pyridones, wt in g (%)[a]	Mp, °C
CH_3	Ia, 0.45	CH_3CN (400)	20	IIIa, 0.030 (7)	158–160
F	Ib, 0.5	CH_3CN (600)	13	IIIb, 0.025 (5)	186–188
				IVb, 0.008 (1.7)	126–128
Br	Id, 0.5	CH_3CN (600)	5	IIId, 0.089 (10)	204–206
				IVd, 0.018 (2)	148–150
CH_3	IIa, 0.7	CH_3CN (400)	5	VIIIa[b]	164–166
				VIIa[b]	153–155
F	IIb, 0.5	CH_3OH (400)	3	VIIIb, 0.01 (8)	143–146
				VIIb, 0.003 (2.8)	130–131
Br	IId, 0.5	CH_3OH (400)	0.5	VIIId, 0.007 (5)	174–176
				VIId, 0.003 (1.2)	139–141

[a] Yield was based on an isolated amount of pure product. [b] Reference 19.

Table V. Synthesis of 2-Pyridones

Substituent	Phenylacetones,[a] wt in g	α-Acetyl benzylcyanides,[a] wt in g	2-Pyridones, wt in g (%)	Registry no.
CH_3	p-CH_3, 2.2	H, 2.5	VIIa, 0.95 (25)	65636-17-1
	H, 2.5	p-CH_3, 2.2	VIIIa, 0.75 (46)	65636-18-2
F	p-F, 5	H, 5	VIIb, 4.5 (50)	65636-19-3
	H, 5	p-F, 5	VIIIb, 2.0 (20)	65636-20-6
Cl	p-Cl, 5.4	H, 4.8	VIIc, 2.3 (26)	65636-21-7
	H, 5	p-Cl, 5	VIIIc, 3.5 (44)	65636-22-8
Br	p-Br, 5	H, 5	VIId, 5.0 (56)	65636-23-9
	H, 5	p-Br, 5	VIIId, 2.0 (20)	65636-24-0

[a] p-X = a substituent X on the para position of the benzene ring.

Spectral Data. 1,2,6-Trimethyl-3-phenyl-5-(p-tolyl)-4-pyridone (IIa): IR (KBr) 1610, 1550, 1490, 1440, 1385, 1300, 1150, 1105, 985, 955, 795, 740, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 6 H), 2.35 (s, 3 H), 3.50 (s, 3 H), 6.9–7.3 (m, 9 H); mass spectrum (*m/e*) 304 (9), 303 (M^+, 47), 302 (100), 274 (5), 129 (4), 115 (5), 105 (7), 91 (8), 78 (22), 77 (7), 56 (17).

1,2,6-Trimethyl-3-phenyl-5-(p-chlorphenyl)-4-pyridone (IIc): IR (KBr) 1615, 1545, 1490, 1440, 1430, 1390, 1300, 1155, 1105, 1085, 1070, 1010, 980, 960, 850, 825, 795, 755, 705 cm^{-1}; NMR ($CDCl_3$) δ 2.23 (s, 6 H), 3.60 (s, 3 H), 7.20–7.30 (m, 9 H); mass spectrum (*m/e*) 325 (15), 324 (41), 323 (M^+, 44), 322 (100), 294 (5), 287 (7), 150 (5), 136 (5), 125 (5), 119 (5), 115 (7), 91 (8), 81 (6), 77 (3), 69 (11), 56 (17).

1,2,6-Trimethyl-3-phenyl-5-(p-bromophenyl)-4-pyridone (IId): IR (KBr) 1615, 1560, 1545, 1490, 1440, 1390, 1300, 1150, 1100, 1070, 1005, 985, 955, 845, 820, 790, 750, 700 cm^{-1}; NMR (CCl_4) δ 2.33 (s, 6 H), 3.75 (s, 3 H), 7.0–7.6 (m, 9 H); mass spectrum (*m/e*) 369 (44), 368 (98), 367 (M^+, 45), 366 (100), 287 (14), 144 (15), 115 (13), 56 (36).

Irradiation of 2,6-Dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones. A typical procedure for UV irradiation of 2,6-dimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyrones is as follows. The irradiation condition and the results for the remaining 4-pyrones are given in Table IV. All elemental analyses for C, H, and halogen (F and Br) gave the values within 0.25% of calculated.

A solution of 0.7 g of 2,6-dimethyl-3-phenyl-5-(*p*-chlorophenyl)-4-pyrone in 800 mL of acetonitrile was irradiated under nitrogen with a 500-W medium-pressure mercury lamp using a Vycor filter at ambient temperature for 6 h. The solvent was removed under vacuum and the residual solid was chromatographed on silica gel with chloroform–benzene (5:5) as eluent. Every 5-mL fraction was collected and the solvent was removed under vacuum. The residual solid melted within a short range of temperature was collected and recrystallized from methanol to give 0.142 g (20%) of 3-(*p*-chlorophenyl)-6-phenyl-4,5-dimethyl-2-pyrone (IIIc): mp 215–217 °C; IR (KBr) 1700, 1625, 1545, 1495, 1450, 1385, 1345, 1190, 1085, 1015, 960, 945, 830, 770, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.05 (s, 3 H), 2.10 (s, 3 H), 7.0–7.6 (m, 9 H). Anal. Calcd for $C_{19}H_{15}O_2Cl$: C, 73.43; H, 4.87; Cl, 11.41. Found: C, 73.07; H, 4.83; Cl, 11.34.

Further collection of solids from every 5-mL fraction gave 0.17 g of colorless crystals which melted at 110–170 °C, indicating a mixture of IIIc and IVc.

The next fraction, after recrystallization from methanol, gave 0.065 g (9%) of 3-phenyl-6-(*p*-chlorophenyl)-4,5-dimethyl-2-pyrone (IVc): mp 126.5–128 °C; IR (KBr) 1710, 1690, 1625, 1605, 1545, 1490, 1385, 1340, 1190, 1095, 1010, 950, 850, 790, 770, 710, cm^{-1}; NMR ($CDCl_3$) δ 2.05 (s, 3 H), 2.10 (s, 3 H), 7.1–7.6 (m, 9 H). Anal. Calcd for $C_{19}H_{15}O_2Cl$: C, 73.43; H, 4.87; Cl, 11.41. Found: C, 72.99; H, 4.79; Cl, 11.30.

Finally 0.275 g of the starting material was recovered.

Spectral Data. 3-(p-Tolyl)-6-phenyl-4,5-dimethyl-2-pyrone (IIIa): NMR ($CDCl_3$) δ 2.08 (s, 3 H), 2.12 (s, 3 H), 2.38 (s, 3 H), 7.1–7.6 (m, 9 H).

3-Phenyl-6-(p-tolyl)-4,5-dimethyl-2-pyrone[18] (IVa): NMR ($CDCl_3$) δ 2.09 (s, 3 H), 2.12 (s, 3 H), 2.37 (s, 3 H), 7.1–7.6 (m, 9 H).

3-(p-Fluorophenyl)-6-phenyl-4,5-dimethyl-2-pyrone (IIIb): NMR ($CDCl_3$) δ 2.06 (s, 3 H), 2.10 (s, 3 H), 7.0–7.7 (m, 9 H).

3-Phenyl-6-(p-fluorophenyl)-4,5-dimethyl-2-pyrone (IVb): NMR ($CDCl_3$) δ 2.06 (s, 3 H), 2.10 (s, 3 H), 7.0–7.7 (m, 9 H).

3-(p-Bromophenyl)-6-phenyl-4,5-dimethyl-2-pyrone (IIId): IR (KBr) 1700, 1625, 1540, 1475, 1445, 1380, 1335, 1185, 1090, 1070, 1005, 950, 940, 920, 825, 715, 700 cm^{-1}; NMR ($CDCl_3$) δ 2.06 (s, 3 H), 2.11 (s, 3 H), 7.1–7.6 (m, 9 H).

3-Phenyl-6-(p-bromophenyl)-4,5-dimethyl-2-pyrone (IVd): NMR ($CDCl_3$) δ 2.00 (s, 3 H), 2.05 (s, 3 H), 7.2–7.7 (m, 9 H).

Irradiation of 1,2,6-Trimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyridone. Typical photolysis of 1,2,6-trimethyl-3-phenyl-5-(para-substituted phenyl)-4-pyridones is described as follows with the remaining cases which are summarized in Table IV. All C, H, N, and halogen (F and Br) were within 0.3% of calculated values.

A solution containing 0.6 g of 1,2,6-trimethyl-3-phenyl-5-(*p*-chlorophenyl)-4-pyridone in 950 mL of methanol was irradiated under nitrogen for 6 h using a 500-W Taika medium-pressure mercury lamp equipped with a Vycor filter. Removal of the solvent in vacuo left solid which was chromatographed on silica gel with chloroform–ether (4:1) as eluent. Every 10-mL fraction was evaporated to remove the solvent and the residual solids which showed a similar range of the melting point were combined together. Recrystallization from benzene gave 0.109 g (31%) of 1,4,6-trimethyl-3-(*p*-chlorophenyl)-5-phenyl-2-pyridone (VIIIc): mp 166–167 °C; IR (KBr) 1625, 1580, 1525, 1485, 1435, 1425, 1300, 1235, 1095, 1080, 1010, 945, 815, 810, 765, 700 cm^{-1}; NMR (CCl_4) δ 1.80 (s, 3 H), 2.25 (s, 3 H), 3.75 (s, 3 H), 7.0–7.5 (m, 9

H); mass spectrum (*m/e*) 325 (30), 324 (50), 323 (M^+, 95), 322 (100), 297 (10), 296 (14), 295 (31), 294 (26), 244 (11), 202 (10), 115 (19), 77 (11), 56 (90). Anal. Calcd for $C_{20}H_{18}NOCl$: C, 74.18; H, 5.60; N, 4.33; Cl, 10.95. Found: C, 74.08; H, 5.29; N, 4.03; Cl, 10.66.

Further collection of crystals from every 10-mL fraction yielded, after recrystallization from benzene, 0.15 g of colorless crystals which melted at 138–160 °C, indicating a mixture of VIIc and VIIIc.

Further careful column chromatography gave, after recrystallization from benzene, 0.036 g (10%) of 1,4,6-trimethyl-3-phenyl-5-(*p*-chlorophenyl)-2-pyridone (VIIc): mp 150–152 °C; IR (KBr) 1630, 1600, 1540, 1490, 1440, 1420, 1300, 1240, 1094, 1085, 1015, 955, 830, 820, 760, 705, 700 cm^{-1}; NMR (CCl_4) δ 1.66 (s, 3 H), 2.06 (s, 3 H), 3.56 (s, 3 H), 7.0–7.5 (m, 9 H); mass spectrum (*m/e*) 325 (32), 324 (49), 323 (M^+, 89), 322 (100), 296 (13), 295 (24), 223 (14), 205 (16), 167 (14), 150 (34), 149 (44), 122 (14), 121 (10), 115 (10), 105 (25), 99 (26), 92 (20), 91 (38), 83 (16), 81 (20), 77 (19), 71 (23), 70 (20), 69 (42), 57 (99), 56 (43), 43 (40), 41 (53). Anal. Calcd for $C_{20}H_{18}NOCl$: C, 74.18; H, 5.60; N, 4.33; Cl, 10.95. Found: C, 74.17; H, 5.72; N, 4.28; Cl, 10.73.

Finally 0.25 g of the starting material was recovered by further elution.

Spectral Data. 1,4,6-Trimethyl-3-(*p*-tolyl)-5-phenyl-2-pyridone[19] (VIIIa): IR (KBr) 1570, 1545, 1515, 1450, 1415, 1390, 1375, 1335, 1285, 1235, 1220, 1170, 1090, 1025, 995, 810, 740, 725 cm^{-1}; NMR (CCl_4) δ 1.60 (s, 3 H), 2.08 (s, 3 H), 2.39 (s, 3 H), 3.55 (s, 3 H), 6.9–7.4 (m, 9 H); mass spectrum (*m/e*) 304 (23), 303 (M^+, 100), 302 (97), 289 (23), 288 (25), 275 (29), 274 (22), 56 (48).

1,4,6-Trimethyl-3-phenyl-5-(*p*-tolyl)-2-pyridone[18] VIIa: IR (KBr) 1620, 1580, 1530, 1495, 1445, 1425, 1375, 1360, 1300, 1100, 950, 810, 770, 710 cm^{-1}; NMR (CCl_4) δ 1.63 (s, 3 H), 2.07 (s, 3 H), 2.39 (s, 3 H), 3.55 (s, 3 H), 6.8–7.4 (m, 9 H); mass spectrum (*m/e*) 304 (22), 303 (M^+, 100), 302 (98), 275 (31), 274 (25), 56 (36).

1,4,6-Trimethyl-3-(*p*-fluorophenyl)-5-phenyl-2-pyridone (VIIIb): IR (KBr) 1620, 1600, 1580, 1525, 1500, 1425, 1375, 1300, 1215, 1155, 1085, 950, 865, 825, 810, 770, 700 cm^{-1}; NMR (CCl_4) δ 1.63 (s, 3 H), 2.12 (s, 3 H), 3.68 (s, 3 H), 6.9–7.4 (m, 9 H); mass spectrum (*m/e*) 308 (20), 307 (M^+, 99), 306 (100), 279 (28), 278 (29), 56 (46), 41 (12).

1,4,6-Trimethyl-3-phenyl-5-(*p*-fluorophenyl)-2-pyridone (VIIb): IR (KBr) 1625, 1600, 1585, 1525, 1505, 1420, 1355, 1300, 1215, 1155, 1090, 950, 835, 815, 785, 765, 750, 700 cm^{-1}; NMR (CCl_4) δ 1.67 (s, 3 H), 2.11 (s, 3 H), 3.63 (s, 3 H), 7.0–7.4 (m, 9 H); mass spectrum (*m/e*) 308 (16), 307 (M^+, 83), 306 (81), 289 (18), 288 (34), 279 (36), 278 (41), 260 (14), 92 (47), 91 (78), 83 (16), 78 (13), 77 (16), 71 (28), 70 (22), 65 (19), 63 (16), 57 (44), 56 (94), 55 (38), 50 (13), 43 (100), 42 (38), 41 (81).

1,4,6-Trimethyl-3-(*p*-bromophenyl)-5-phenyl-2-pyridone (VIIId): IR (KBr) 1625, 1580, 1530, 1485, 1440, 1420, 1380, 1300, 1240, 1100, 1070, 1010, 950, 865, 815, 770, 705 cm^{-1}; NMR (CCl_4) δ 1.63 (s, 3 H), 2.03 (s, 3 H), 3.47 (s, 3 H), 7.0–7.6 (m, 9 H); mass spectrum (*m/e*) 370 (21), 369 (98), 368 (91), 367 (M^+, 100), 366 (76), 341 (26), 340 (26), 339 (27), 338 (23), 288 (12), 244 (11), 203 (12), 202 (14), 144 (38), 136 (21), 135 (10), 115 (17), 101 (14), 89 (11), 77 (10), 56 (88), 41 (10).

1,4,6-Trimethyl-3-phenyl-5-(*p*-bromophenyl)-2-pyridone (VIId): IR (KBr) 1630, 1595, 1530, 1485, 1440, 1420, 1200, 1100, 1070, 1010, 950, 820, 790, 755, 700 cm^{-1}; NMR (CCl_4) δ 1.64 (s, 3 H), 2.07 (s, 3 H), 3.55 (s, 3 H), 7.0–7.5 (m, 9 H); mass spectrum (*m/e*) 370 (14), 369 (66), 368 (74), 367 (M^+, 63), 366 (56), 341 (18), 340 (16), 339 (18), 338 (13), 323 (10), 322 (11), 289 (47), 288 (50), 261 (14), 260 (14), 244 (13), 78 (62), 77 (19), 56 (43), 52 (14), 51 (16).

NMR Determination of the Relative Ratio of Isomeric Photoproduct. A solution of 4-pyridone (0.05–0.1 g) in methanol (100 mL) was irradiated under nitrogen with a 100-W medium-pressure mercury lamp equipped with a Vycor filter. After irradiation for 2–3 h, the solvent was removed under vacuum and the residual solid was quickly passed through a short column packed with dry silica gel to eliminate a polymeric compound. After drying either $CDCl_3$ or CCl_4 containing 1% tetramethylsilane was added to the mixture and a NMR spectrum was recorded. The relative ratio of the photoproduct and the percent reactivity were determined by monitoring change of the methyl proton integration. Two or three runs were carried out for each sample. The average results were given in Table II.

Independent Synthesis of 1,4,6-Trimethyl-3-phenyl-5-(para-substituted phenyl)-2-pyridones and 1,4,6-Trimethyl-3-(para-substituted phenyl)-5-phenyl-2-pyridones. 1,4,6-Trimethyl-3-(para-substituted phenyl)-5-phenyl-2-pyridones were prepared by condensation of α-acetyl-para-substituted benzylcyanides with phenylacetone to 4,6-dimethyl-3-(para-substituted phenyl)-5-phenyl-2-pyridones, followed by *N*-methylation. 1,4,6-Trimethyl-3-phenyl-5-(para-substituted phenyl)-2-pyridones were also synthesized by a similar method using α-acetyl benzylcyanide and para-substituted phenylacetones. The preparative condition was similar to that described in the preceding report.[9] The results are summarized in Table V.

Registry No.—IVa, 65636-24-0; 1-phenyl-3-(*p*-fluorophenyl)-2-propanone, 330-97-2; 1-phenyl-3-(*p*-tolyl)-2-propanone, 35730-02-0; 1-phenyl-3-(*p*-chlorophenyl)-2-propanone, 35730-03-1; 1-phenyl-3-(*p*-bromophenyl)-2-propanone, 65636-25-1.

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(17) A referee pointed out the possibility that the substituent effect observed was a heavy atom rather than inductive and/or resonance effect. Lack of quenching data cannot exclude this possibility, but yield of the photoproduct in Table II does not correlate well with the atomic number of the substituent. The preceding paper also shows no internal heavy-atom effect in the photorearrangement. These results strongly suggest that an electronic rather than heavy-atom effect plays a major role in determining selectivity.
(18) A pure compound was not isolated. The 220 MHz NMR spectra of the isomeric mixture gave the different chemical shifts for the C-methyl proton.
(19) Conventional column or thick-layer chromatography could not separate the mixture. Spectral data were given for the authentic sample prepared by the chemical method.