New Aspects of the Aromatic Photosubstitution with Iodopyridines[1)]

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Reactive entities in the photoreaction of 2-, 3- and 4-iodopyridines with substituted benzenes were investigated; 3- and 4-pyridylation could be explained in terms of radical reaction, while the 2-pyridyl cation was an important intermediate in the 2-pyridylation. The importance of the unshared electron pair of the nitrogen adjacent to the radical carbon for the conversion of the 2-pyridyl radical initially produced into the cation is discussed on the basis of molecular orbital (MO) calculations.

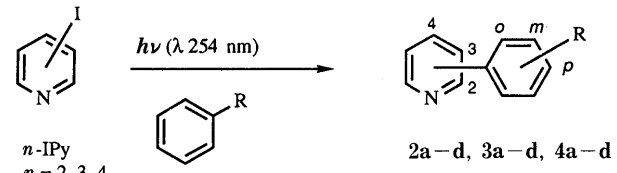
Keywords aromatic photosubstitution; iodopyridine; pyridylation; pyridyl radical; 2-pyridyl cation

As well as the Gomberg reaction and the thermal reaction with benzoyl peroxide,[3)] photoreaction of aryl[4)] and heteroaryl iodides[5)] with aromatic compounds has been studied intensively not only from a synthetic point of view but also to explore the reactivity of the intermediate radicals[6)]; it is now recognized that the heteroaryl radicals are electrophilic in character, especially in the case of the radicals having a radical carbon adjacent to the hetero atom.[3)] The electrophilicity has been interpreted in terms of the inductive effect of the hetero atoms.[3,6)] Meanwhile, photolyses of alkyl halides[7)] and vinyl halides[8)] were reported to generate the cationic species *via* homolysis of the C-halogen bond followed by electron transfer within the resulting radical pair. This opened up a new aspect of photolytic behavior of organic halides; their reaction mechanism had previously been discussed only in terms of homolysis or heterolysis. We have recently reported that the direct photolysis of 2-halopyridines in various nucleophilic solvents gave ionic products by way of the reaction of the intermediate 2-pyridyl cation with the nucleophilic solvent, while the photolysis of 3- and 4-halopyridines exclusively furnished the radical product pyridine.[9)] To explore the reactive entities in the photo-pyridylation of benzenes, we have investigated the photoreaction of *n*-iodopyridines (*n*-IPy; $n=2$, 3, 4) with monosubstituted benzenes (RPh, **1a—d**: **a**, R=OCH_3; **b**, R=CH_3; **c**, R=Cl; **d**, R=CO_2CH_3). In the present paper we present our findings that the cationic species participates significantly in the 2-pyridylation, whereas the reactive entities of 3- and 4-pyridylations are the radical species.

UV-irradiation of *n*-IPy in **1** with a low-pressure mercury lamp afforded a mixture of *ortho*, *meta* and *para* isomers of *n*-(*x*-aryl)pyridines [$\mathbf{2}_x$ ($n=2$), $\mathbf{3}_x$ ($n=3$), $\mathbf{4}_x$ ($n=4$); $x=o$ for *ortho*, *m* for *meta*, *p* for *para*] in varying yields depending on the substituents of the benzene ring (Chart 1). The results are summarized in Table I.

The reaction with benzenes having electron-donating substituents (*i.e.*, **1a**, **1b**) afforded arylpyridines in higher efficiencies than with those bearing electron-withdrawing groups (Cl, CO_2CH_3). The patterns of the isomer distributions of 3-arylpyridines (**3**) and 4-arylpyridines (**4**) are comparable to each other, whereas that of the 2-isomers (**2**) seems characteristically different from those of **3** and **4**: For example, a) with anisole (**1a**), the isomer ratios of **3a** ($o:m:p=72:13:15$) and **4a** ($o:m:p=71:14:15$) are closely similar, while the *ortho* ratio of the 2-isomer (**2a**) decreases to 52% and the *para* ratio increases to 35%; b) with methyl benzoate (**1d**), 3- and 4-pyridylation occurred predominantly at the *ortho* position, whereas the 2-pyridylation proceeded preferentially at the *meta* position.

Interestingly the patterns of the isomer distributions for **3** and **4** correspond to that reported for photochemical phenylation with iodobenzene (IPh),[10)] while that of **2** seems similar to the findings in cationic phenylation (Table II).[11)] In fact, the cationic 2-pyridylations conducted in **1a**



a : R=OCH_3
b : R=CH_3
c : R=Cl
d : R=CO_2CH_3

Chart 1

TABLE I. Photoreaction of Iodopyridines with Substituted Benzenes (**1**)

1	2-Arylpyridine (**2**)				3-Arylpyridine (**3**)				4-Arylpyridine (**4**)			
	Yield (%) (Consumed 2-IPy)	Isomer ratio			Yield (%) (Consumed 3-IPy)	Isomer ratio			Yield (%) (Consumed 4-IPy)	Isomer ratio		
		o	*m*	*p*		*o*	*m*	*p*		*o*	*m*	*p*
1a	29 (29)	52	13	35	34 (39)	72	13	15	27 (33)	71	14	15
1b	30 (33)	54	21	25	27 (40)	63	19	18	21 (36)	64	20	16
1c	7 (22)	41	31	28	6 (7)	69	16	15	5 (11)	58	23	19
1d	3 (5)	28	38	34	3 (4)	57	13	30	0.5 (2)	50	21	29

TABLE II. Reported Isomer Distributions of Arylbenzenes Obtained by Homolytic[10] and Cationic[11] Phenylation

1	Homolytic phenylation Arylbenzene			Cationic phenylation Arylbenzene		
	o	*m*	*p*	*o*	*m*	*p*
1a	71.5	15.0	13.5	56.4	12.2	31.4
1b	65.5	20.0	14.5	47.3	21.1	31.6
1c	58.0	26.5	15.5	48.2	24.0	27.8
1d	54.0	19.0	27.0	43.1	43.5	13.4

TABLE III. Isomer Distributions of 2-Arylpyridines Obtained by Cationic Pyridylation

1	Method[a]	2-Arylpyridine		
		o	*m*	*p*
1a	A	53	14	33
1a	B	53	17	30
1d	A	40	44	16
1d	B	45	35	20

a) Method A, reaction with 2-aminopyridine and isoamylnitrite. B, thermal decomposition of thiatriazolopyridineoxide.

and **1d** with 2-aminopyridine and isoamyl nitrite in the presence of a strong acid[12] or with thiatriazolopyridine oxide,[13] showed isomer distributions comparable to that obtained from 2-IPy (Table III).

Furthermore, the isomer distribution of **2d** obtained from the thermolysis of benzoyl peroxide in the presence of 2-IPy in **1d**[14] was similar to those of **3d** and **4d** obtained photochemically from 3- and 4-IPy's (Chart 2), suggesting that the characteristic pattern of the isomer distribution obtained from the photolysis of 2-IPy could not be ascribed to the participation of the electrophilic 2-pyridyl radical, but to that of the 2-pyridyl cation (2-Py$^+$) as the reactive entity.

The photolysis of 2-IPy in **1a** and **1d** at low temperature (−9 °C) gave isomer distributions of **2a** and **2d** closer to those of cationic pyridylation, while at high temperature (50 °C) they approximated more closely to the typical pattern of the radical reaction (Table IV). In accordance with the results observed in the direct solvolysis of 2-IPy, though less markedly,[9] these findings seem to suggest that 2-Py$^+$ may be derived from the initially produced 2-pyridyl radical (2-Py$^\cdot$).

In order to obtain insight into the mechanism of formation of 2-Py$^+$, molecular orbital (MO) calculations for 2-, 3- and 4-pyridyl radicals (2-, 3- and 4-Py$^\cdot$) were performed.[15] According to the frontier molecular orbital theory, electrophilicity of the radicals should depend on the energy level (eigen value) of the singly occupied molecular orbitals (SOMO) and the net charge on the radical carbon.[16] As shown in Fig. 1, the eigen values of the SOMO's of 3- and 4-Py$^\cdot$ (−11.49 eV, −11.50 eV) are lower, whereas that of 2-Py$^\cdot$ (−9.94 eV) is higher than that of the phenyl radical (Ph$^\cdot$) (−10.54 eV). These results reveal that 3- and 4-Py$^\cdot$'s may be more electrophilic than Ph$^\cdot$, while 2-Py$^\cdot$ should be more nucleophilic in character. The radical carbon of 2-Py$^\cdot$ is charged more negatively (−0.088) (Fig. 1) than that of Ph$^\cdot$ (−0.079). Thus, these results did not account for the electrophilicity of 2-Py$^\cdot$.

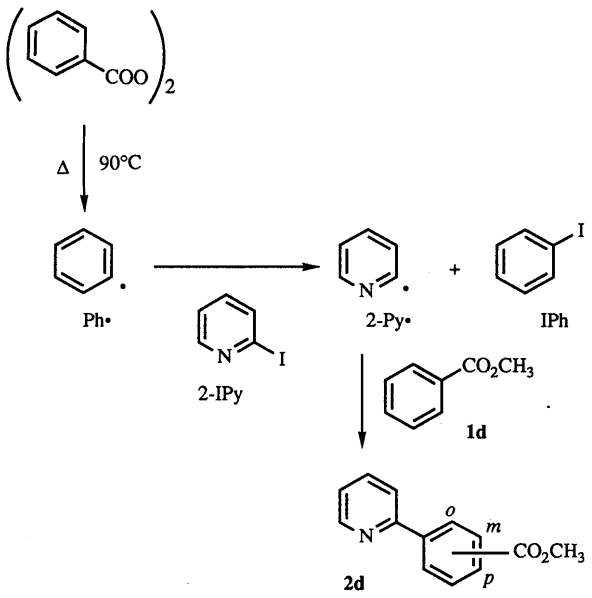


Chart 2

TABLE IV. Photolysis of 2-IPy in **1a** and **1d** at Various Temperatures

1	Reaction temp. (°C)	2-Arylpyridine				Consumed 2-IPy (%)
		o	*m*	*p*	Yield (%)	
1a	50	56	18	26	35	41
1a	22	52	13	35	29	29
1a	−9	52	13	35	19	22
1d	50	35	29	36	3	15
1d	22	28	38	34	3	5
1d	−9	23	45	32	2	9

Interestingly the energy levels of the SOMO's of 3-Py$^\cdot$ and 4-Py$^\cdot$ are lower than their highest occupied molecular orbitals (HOMO's) corresponding to the unshared electron pair of the nitrogen, while the SOMO of 2-Py$^\cdot$ is energetically higher than the MO corresponding to the unshared electron pair of the nitrogen; the SOMO of 2-Py$^\cdot$ is higher than the HOMO's of 3- and 4-Py$^\cdot$, and the MO corresponding to the unshared electron pair of the nitrogen of 2-Py$^\cdot$ is lower in energy than the SOMO's of 3- and 4-Py$^\cdot$ (Fig. 1[17]).

Moreover, in the cases of 3-Py$^\cdot$ and 4-Py$^\cdot$, the MO's related to the unshared electron pair (=HOMO's) have large coefficients over the nitrogen atoms and the SOMO's have large coefficients over the radical carbons, while in the case of 2-Py$^\cdot$, the MO's corresponding to the unshared electron pair and the unpaired electron both have large coefficients at both the nitrogen and the adjacent radical carbon (C-2) with the same sign for the former and with the opposite sign for the latter (Fig. 1). This indicates that the unshared electron pair of the nitrogen in the exocyclic orbital and the unpaired electron in the sp^2 orbital of the radical carbon of 2-Py$^\cdot$ interact either in a bonding or in an antibonding way to make up the energetically lowered orbital and the raised orbital (Fig. 2). Two of the electrons would be accommodated in the former MO and the other one in the latter MO.[18] Thus, 2-Py$^\cdot$ would readily release

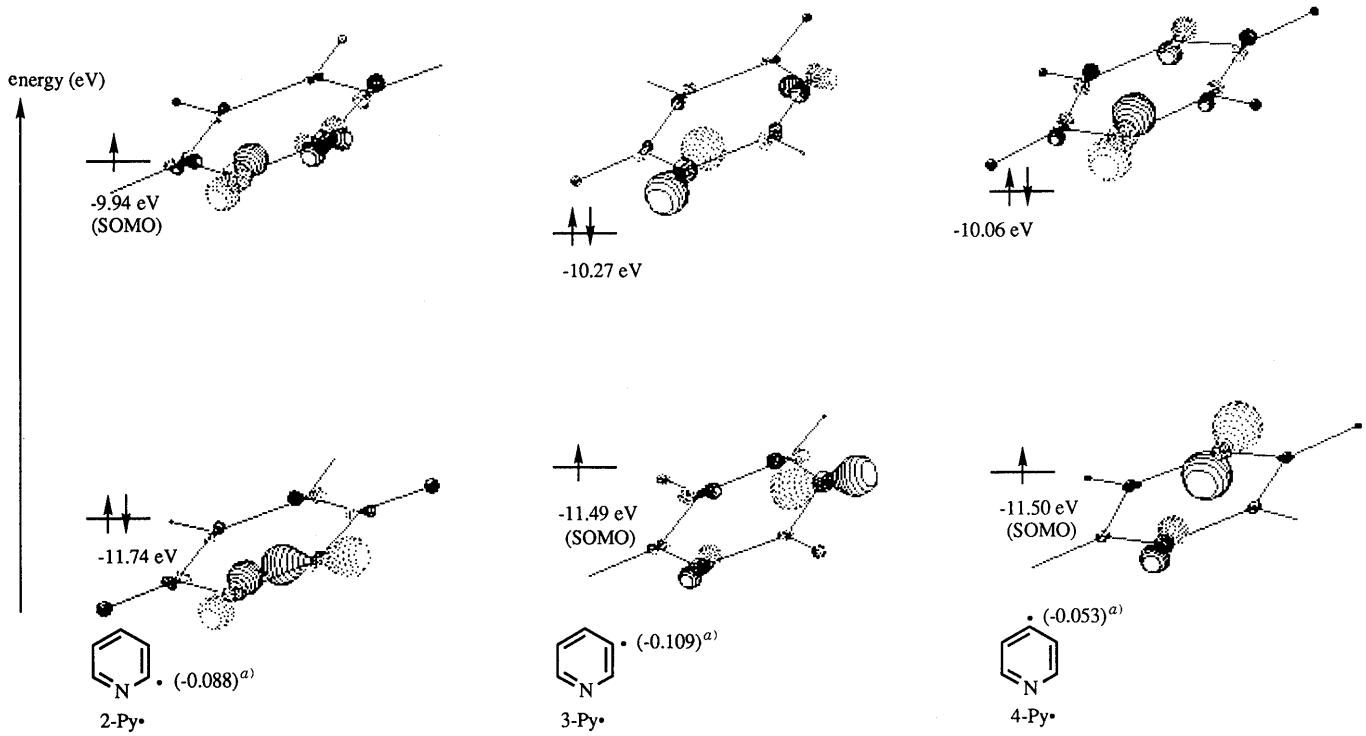


Fig. 1. Energies of the SOMO's and the MO's Corresponding to the Unshared Electrons of Nitrogens of 2-, 3-, and 4-Pyridyl Radicals

a) Net charges of the radical carbons are given in parentheses.

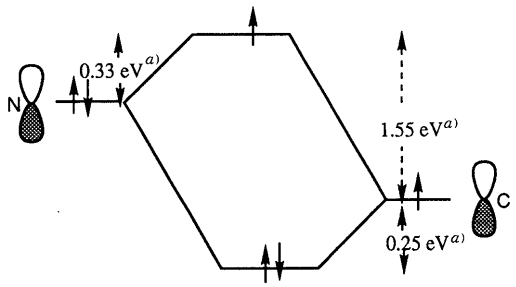


Fig. 2. Orbital Interaction of the Unpaired Electron of the Radical Carbon and the Unshared Electron Pair of the Nitrogen of the 2-Pyridyl Radical

a) Estimated on the basis of the MO's due to the SOMO and the HOMO of the 3-pyridyl radical.

an electron from the energetically raised SOMO to an appropriate electron acceptor to form 2-Py^+.

In direct solvolysis of 2-halopyridines, the halogen atom generated by the simple homolysis of a 2-halopyridine serves as the electron acceptor.[9] The same process might apply to the present 2-pyridylation. However, taking into consideration the fact that most of the incident light (254 nm) (97—99%) is absorbed by the substituted benzenes used as solvents and the report on the photosubstitution of substituted benzenes by halobenzenes,[19] it is reasonable to presume that an energy transfer process involving electron transfer may participate in the present reaction. In the case of electron transfer, the radical cation of substituted benzenes should serve as the electron acceptor.[20] Detection of anisole formed in photolyses of solutions of 2-, 3-, and 4-IPy's in an equivolume mixture of benzene and methanol suggested the generation of the benzene radical cation ($Ph^{\cdot +}$) in the reaction (Chart 3).

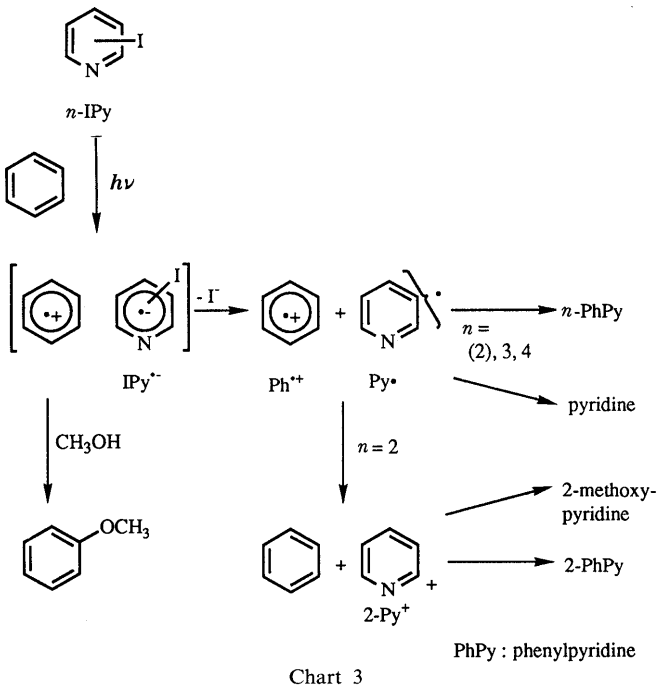


Chart 3

Addition of nitrobenzene (0.3 mmol) to a solution of *n*-IPy ($n=2$, 3, 4) (10 mM) in **1a** (10 ml) suppressed the formation of *n*-(methoxyphenyl)pyridine (**2a**, **3a**, or **4a**) with similar efficiencies (*ca.* 50%). Similarly, the photoreaction of 2-IPy (2 mM) and anisole (**1a**) (0.184 M) in acetonitrile was quenched efficiently by the addition of acrylonitrile with a Stern-Volmer rate constant of $k_q\tau = 150\,dm^3 \cdot mol^{-1}$. These results may support the above considerations.

To explore the participation of the radical cation of benzenes ($Ar^{\cdot +}$) in the formation of 2-Py^+, 2-IPy and **1a**

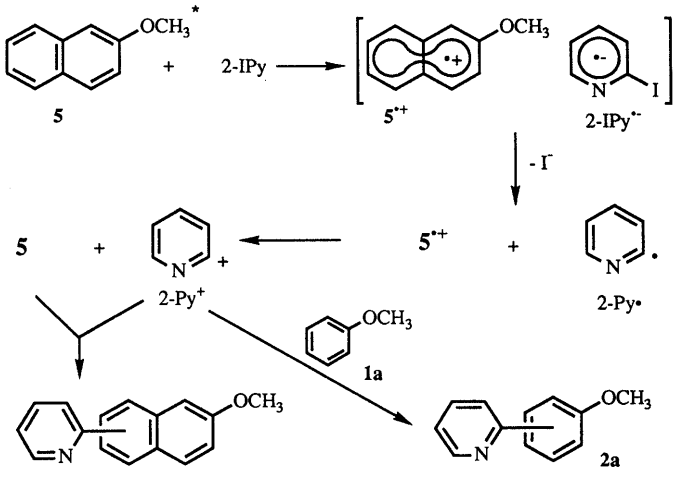


Chart 4

were irradiated with λ 327 nm light in the presence of electron-donating 2-methoxynaphthalene (**5**) to produce **2a** (14%, together with 2-(methoxynaphthyl)pyridines in 6.1% yield and unreacted 2-IPy in 72.5% yield) in an isomer ratio (*o*:*m*:*p*=52:14:34) close to that of the cationic pyridylation of anisole, shown in Table III. Photoreaction under similar conditions but in the absence of **5** afforded **2a** only in low yields (5%, *o*:*m*:*p*=56:16:28, together with unreacted 2-IPy in 89.1% yield), suggesting that **5** served as a sensitizer. Since the incident light is absorbed exclusively by **5** under the present conditions, and energy transfer from the excited **5** in the singlet states to 2-IPy seems unlikely, excitation of **5** would cause the electron transfer to 2-IPy to form the pair of the radical cation of **5** ($\mathbf{5}^{\cdot+}$) and the radical anion of 2-IPy (2-IPy$^{\cdot-}$), followed by the spontaneous elimination of iodide from the latter. Electron transfer from the resulting 2-Py$^{\cdot}$ to $\mathbf{5}^{\cdot+}$ would lead to the formation of 2-Py^{+} (Chart 4). Although the reaction mechanisms, including the excited states, of the present reaction remain unelucidated,[21] the present study provides new aspects to the heteroarylation of benzenes, the mechanism of which has been hitherto explained in terms of the electrophilic radicals due to the inductive effect of the adjacent hetero atoms.

Experimental

All melting points are uncorrected. ^{1}H-NMR spectra were measured with a JEOL JNM-EX400 (400 MHz) spectrometer, and chemical shifts are given on the δ (ppm) scale with tetramethylsilane as an internal standard. Mass spectra (MS) were determined on a Shimadzu GCMS 9100-MK spectrometer at 70 eV. Infrared (IR) spectra were recorded on a Hitachi 270-30 IR spectrophotometer. UV and fluorescence spectra were taken on a Shimadzu UV-240 and a Shimadzu RF-540, respectively. Products were analyzed by gas-liquid chromatography (GLC) with a glass column (PEG20M 20% Celite545U, 3 mm × 1.5 m i.d., for the detection of anisole) and a capillary column (ULBON HR-1, Shinwa-kako) on a Shimadzu GC-7A gas chromatograph equipped with a hydrogen flame-ionization detector using nitrogen for the former and helium for the latter as the carrier gas. High-performance liquid chromatography (HPLC) was performed on a Hibar Lichrosorb Si60 (Merck) (25 cm × 4.6 mm i.d.), using a Shimadzu LC-6A apparatus with monitoring at 254 nm. UV-irradiation was carried out externally with a 60 W low-pressure mercury (1-p Hg) lamp (Eiko-sha) in an argon-filled quartz test tube (254 nm) on a merry-go-round apparatus at room temperature.

Photolysis of Iodopyridines (*n*-IPy; *n*=2, 3, 4) and Substituted Benzenes (1a—d) A solution of *n*-IPy (*n*=2, 3, 4; 0.1 mmol) in a substituted benzene (**1a—d**) (10 ml) or an equivolume mixture of benzene and methanol (10 ml) was irradiated for 1 h. The reaction mixture was neutralized with 30% aqueous K_2CO_3 and dried over anhydrous Na_2SO_4, followed by GLC analysis with naphthalene as an internal standard; in the case of methyl benzoate (**1d**), the reaction mixture was extracted with 10% HCl and the aqueous extract was neutralized with K_2CO_3, followed by extraction with ether. After drying over Na_2SO_4, the organic extract was submitted to GLC analysis. In the case of chlorobenzene (**1c**), the isomer ratio was determined by column chromatography on silica gel pretreated with formic acid (hexane : ethyl acetate = 10 : 1).

The photoproducts were identified by chromatographic and spectroscopic comparison with authentic samples prepared as follows. 2-Arylpyridines (**2a—d**) were prepared by the reported procedure.[22] The *ortho* and the *para* isomers of 3-[23] and 4-arylpyridines[24] (**3a—d**, **4a—d**) were synthesized according to the reported methods. The *meta* isomers ($\mathbf{4a}_m$—$\mathbf{d}_m$) were obtained analogously from *meta*-substituted halobenzenes.[25]

3-(*o*-Methoxyphenyl)pyridine ($\mathbf{3a}_o$): Oil. Picrate, mp 184—185 °C (from acetone) (lit.[26] 182 °C).

3-(*p*-Methoxyphenyl)pyridine ($\mathbf{3a}_p$): Colorless crystals, mp 64 °C (from hexane) (lit.[27] 64—65 °C).

3-(*o*-Methylphenyl)pyridine ($\mathbf{3b}_o$): Colorless oil. MS *m*/*z* (%): 169 (M^+, 100), 168 (90). Picrate, mp 169—171 °C (from ethanol). *Anal.* Calcd for $C_{18}H_{14}N_4O_7$ (picrate): C, 54.27; H, 3.54; N, 14.07. Found: C, 54.21; H, 3.46; N, 14.06. ^{1}H-NMR ($CDCl_3$) δ: 2.27 (3H, s, CH_3), 7.18—7.42 (5H, m, aromatic H), 7.66 (1H, d, *J*=7.8 Hz, 4-H), 8.60 (2H, br s, 2- and 6-H).

3-(*p*-Methylphenyl)pyridine ($\mathbf{3b}_p$): Colorless crystals, mp 39—40 °C (from hexane). MS *m*/*z* (%): 169 (M^+, 100), 168 (77). *Anal.* Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.15; H, 6.54; N, 8.30. ^{1}H-NMR ($CDCl_3$) δ: 2.41 (3H, s, CH_3), 7.29 (2H, d, *J*=7.8 Hz, 3′- and 5′-H), 7.34 (1H, dd, *J*=7.8, 4.9 Hz, 5-H), 7.48 (2H, d, *J*=7.8 Hz, 2′- and 6′-H), 7.85 (1H, d, *J*=7.8 Hz, 4-H), 8.56 (1H, d, *J*=4.9 Hz, 6-H), 8.83 (1H, d, *J*=2.4 Hz, 2-H).

3-(*o*-Chlorophenyl)pyridine ($\mathbf{3c}_o$): Colorless oil. MS *m*/*z* (%): 191 (M^+, 34), 189 (M^+, 100), 154 (72). Picrate, mp 174—176 °C (from ethanol). *Anal.* Calcd for $C_{17}H_{11}ClN_4O_7$ (picrate): C, 48.76; H, 2.65; Cl; 8.47; N, 13.38. Found: C, 48.70; H, 2.60; Cl, 8.46; N, 13.33. ^{1}H-NMR ($CDCl_3$) δ: 7.30—7.40 (3H, m, aromatic H), 7.37 (1H, dd, *J*=7.8, 4.4 Hz, 5-H), 7.48—7.52 (1H, m, aromatic H), 7.80 (1H, d, *J*=7.8 Hz, 4-H), 8.63 (1H, d, *J*=4.4 Hz, 6-H), 8.69 (1H, br s, 2-H). IR (neat) cm^{-1}: 1464, 1433, 754, 714.

3-(*p*-Chlorophenyl)pyridine ($\mathbf{3c}_p$): Colorless oil. MS *m*/*z* (%): 191 (M^+, 35), 189 (M^+, 100), 154 (68). Picrate, mp 170—171 °C (from ethanol). *Anal.* Calcd for $C_{17}H_{11}ClN_4O_7$ (picrate): C, 48.76; H, 2.65; Cl 8.47; N, 13.38. Found: C, 48.85; H, 2.65; Cl, 8.59; N, 13.32. ^{1}H-NMR ($CDCl_3$) δ: 7.36 (1H, dd, *J*=8.3, 4.9 Hz, 5-H), 7.45 (2H, d, *J*=8.3 Hz, 3′- and 5′-H), 7.51 (2H, d, *J*=8.3 Hz, 2′- and 6′-H), 7.82 (1H, d, *J*=8.3 Hz, 4-H), 8.60 (1H, d, *J*=4.9 Hz, 6-H), 8.81 (1H, d, *J*=2.4 Hz, 2-H). IR (neat) cm^{-1}: 1472, 1092, 837, 712.

3-(*o*-Carbomethoxyphenyl)pyridine ($\mathbf{3d}_o$): Colorless oil. MS *m*/*z* (%): 213 (M^+, 14), 183 (54), 182 (100). Picrate, mp 187—188 °C (from ethanol). *Anal.* Calcd for $C_{19}H_{14}N_4O_9$ (picrate): C, 51.59; H, 3.19; N, 12.67. Found: C, 51.57; H, 3.14; N, 12.64. ^{1}H-NMR ($CDCl_3$ at 50 °C) δ: 3.66 (3H, s, CO_2CH_3), 7.25—7.35 (2H, m, 4- and 5-H), 7.46 (1H, t, *J*=7.8 Hz, 5′-H), 7.57 (1H, t, *J*=7.8 Hz, 4′-H), 7.64 (1H, d, *J*=7.8 Hz, 3′-H), 7.94 (1H, d, *J*=7.8 Hz, 6′-H), 8.55 (1H, d, *J*=1.5 Hz, 2-H), 8.60 (1H, d, *J*=4.4 Hz, 6-H). IR (neat) cm^{-1}: 1727 (C=O).

3-(*p*-Carbomethoxyphenyl)pyridine ($\mathbf{3d}_p$): Colorless crystals, mp 105—107 °C (from hexane). MS *m*/*z* (%): 213 (M^+, 56), 182 (100). *Anal.* Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.12; H, 5.19; N, 6.53. ^{1}H-NMR ($CDCl_3$) δ: 3.96 (3H, s, CO_2CH_3), 7.40 (1H, dd, *J*=7.8, 4.9 Hz, 5-H), 7.67 (2H, d, *J*=8.3 Hz, 3′- and 5′-H), 7.92 (1H, ddd, *J*=7.8, 2.4, 1.5 Hz, 4-H), 8.15 (2H, d, *J*=8.3 Hz, 2′- and 6′-H), 8.65 (1H, dd, *J*=4.9, 1.5 Hz, 6-H), 8.89 (1H, d, *J*=2.4 Hz, 2-H). IR (Nujol) cm^{-1}: 1721 (C=O).

The structural assignments of 3-(*m*-aryl)pyridines ($\mathbf{3}_m$) were made on the bases of the similarity of their mass spectra to those of the other isomers ($\mathbf{3}_o$ and $\mathbf{3}_p$), and their GLC retention times, which were intermediate between those of the *ortho* ($\mathbf{3}_o$) (shorter retention time) and the *para* isomers ($\mathbf{3}_p$) (longer retention time), typical behavior for a *meta* isomer.

3-(*m*-Methoxyphenyl)pyridine ($\mathbf{3a}_m$): MS *m*/*z* (%): 185 (M^+, 100), 155 (31), 154 (30).

3-(*m*-Methylphenyl)pyridine ($\mathbf{3b}_m$): MS *m*/*z* (%): 169 (M^+, 100), 168 (51).

3-(*m*-Chlorophenyl)pyridine ($\mathbf{3c}_m$): MS *m*/*z* (%): 191 (M^+, 29), 189 (M^+, 100), 154 (30).

3-(*m*-Carbomethoxyphenyl)pyridine ($\mathbf{3d}_m$): MS *m*/*z* (%): 213 (M^+, 69), 182 (100), 154 (54), 127 (32).

Isolation of 4-(*m*-Aryl)pyridines ($4a_m$—d_m) After the photoreaction and neutralization, the reaction mixture was submitted to HPLC, using hexane–ethyl acetate (5 : 2 for **4a** and 1 : 1 for **4c**) and CH_2Cl_2–ethyl acetate (10 : 1 for **4b** and **4d**), to give the pure $4a_m$, $4c_m$, $4b_m$ and $4d_m$, respectively, together with their *ortho* and *meta* isomers.

4-(*m*-Methoxyphenyl)pyridine ($4a_m$): Colorless oil. MS *m/z* (%): 185 (M^+, 100). Picrate, mp 206—208 °C (from ethanol). *Anal.* Calcd for $C_{18}H_{14}N_4O_8$ (picrate): C, 52.18; H, 3.41; N, 13.52. Found: C, 52.35; H, 3.25; N, 13.67.

4-(*m*-Methylphenyl)pyridine ($4b_m$): Colorless oil. MS *m/z* (%): 169 (M^+, 100), 168 (51). Picrate, mp 214—216 °C (from ethanol). *Anal.* Calcd for $C_{18}H_{14}N_4O_7$ (picrate): C, 54.27; H, 3.54; N, 14.07. Found: C, 54.32; H, 3.56; N, 14.13.

4-(*m*-Chlorophenyl)pyridine ($4c_m$): mp 44—45 °C (from hexane). MS *m/z* (%): 191 (M^+, 47), 189 (M^+, 100), 154 (43), 127 (39). Picrate, mp 215—216 °C (from ethanol). *Anal.* Calcd for $C_{17}H_{11}ClN_4O_7$ (picrate): C, 48.76; H, 2.65; Cl, 8.47; N, 13.38. Found: C, 48.78; H, 2.74; Cl, 8.35; N, 13.14.

4-(*m*-Carbomethoxyphenyl)pyridine ($4d_m$): mp 63—64 °C (from ether–hexane). MS *m/z* (%): 213 (M^+, 74), 182 (100), 154 (36), 127 (30). *Anal.* Calcd for $C_{13}H_{11}NO_2$: C, 73.22; H, 5.20; N, 6.57. Found: C, 73.26; H, 5.17; N, 6.62.

Cationic Pyridylation of Anisole (1a) and Methyl Benzoate (1d) Method A: Isoamyl nitrite (0.39 mmol) was added to a solution of 2-aminopyridine (0.3 mmol) and an acid (42% tetrafluoroboric acid 6.0 mmol or trifluoroacetic acid 0.59 mmol) in acetonitrile (3 ml) at 0 °C, then a 50% solution of **1a** or **1d** in acetonitrile (4 ml) was added and the whole was kept at 42—45 °C for 5 h to give **2a** in 1 or 14% yield as a mixture of the *ortho*, *meta*, and *para* isomers (ratio of $2a_o$, $2a_m$, $2a_p$ (%) = 53 : 14 : 33) and **2d** in 1% yield (trifluoroacetic acid) in the ratio of *o*, *m* and *p* = 40, 45, and 16, respectively. Method B: A solution of 1,2,3,5-thiatriazolo[5,4-*a*]pyridine-3-oxide (0.19 mmol) in **1a** and **d** (1 ml) was kept at 110 °C for 2 h to afford **2a** in 10% yield (*o* : *m* : *p* = 53 : 17 : 30) and **2d** in 1.5% yield (*o* : *m* : *p* = 45 : 35 : 20), respectively.

Thermal Reaction of 2-IPy with Benzoylperoxide in Methyl Benzoate (1d) A solution of 2-IPy (0.2 mmol) and benzoyl peroxide (0.1 mmol) in **1d** (1 ml) was kept at 90 °C for 3 h to afford a regioisomeric mixture of **2d** in 11% total yield (*o* : *m* : *p* = 50 : 13 : 37).

Photolysis of 2-IPy in Anisole (1a) and Methyl benzoate (1d) at Various Temperatures Photoreaction was performed in the manner described above but in a water bath (22 °C, 50 °C) or in an ethanol bath (−9 °C).

MO Calculations Molecular orbital calculations by the PM3 method were performed with MOPAC Ver. 5.1 (JCPE program; #P028) on a personal computer, PC-9801 RA (NEC).[15]

Photoreaction of IPy's in a Mixture of Benzene and Methanol Photolysis of a solution of *n*-IPy (*n* = 2, 3, 4) in an equivolume mixture of benzene and methanol gave anisole (2, 2, 1.5%), *n*-phenylpyridine (*n*-PhPy) (27, 26, 33%), pyridine (15, 29, 30%), and 2-methoxypyridine (3%) in the case of 2-IPy, together with unreacted *n*-IPy (55, 44, 41%) in respective yields.

Photoreaction of IPy's and Anisole (1a) in the Presence of Additives (Nitrobenzene, Acrylonitrile) A solution of *n*-IPy (*n* = 2, 3, 4) (0.1 mmol) in **1a** or a solution of 2-IPy (2×10^{-2} mmol) and **1a** (1.84 mmol) in acetonitrile (10 ml) was irradiated for 20 min in the presence of an additive (nitrobenzene, 0.3 mmol, for the former and acrylonitrile, 10^{-2}—8×10^{-2} mmol, for the latter) or in the absence of an additive. The reaction mixture was worked up according to the previously described procedure and submitted to GLC analyses.

Photoreaction of 2-IPy and Anisole (1a) in the Presence of 2-Methoxynaphthalene (5) A solution of 2-IPy (7.26 mg, 0.035 mmol) and **5** (150 mg, 0.95 mmol) in anisole (**1a**) (3 ml) was irradiated with λ 327 nm light using a JASCO diffraction grating spectroscope (CRM-FA) for 3.5 h under an argon atmosphere.

References and Notes

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