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Photo-Arylation. VIII.[1)] Photosubstitution Reaction of 2-Fluoropyridine with Indoles[2)]

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Photoreaction of 2-fluoropyridine with indoles gave 1-(2-pyridyl)indoles regioselectively. The yields of the coupling products were improved significantly by using the indole anion derivatives. A reaction mechanism involving charge-transfer excitation is proposed for the latter, while the former reaction was concluded to be caused by local excitations.

Keywords——1-(2-pyridyl)indole; photo-arylation; photosubstitution; nucleophilic aromatic photosubstitution; photolysis; 2-fluoropyridine; indole; indole 1-anion; charge-transfer complex; frontier molecular orbital theory

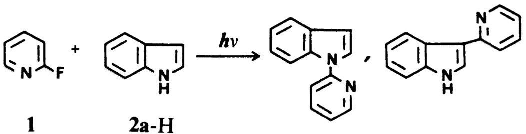
In our continuing studies on the photoreaction of halopyridines with aromatic compounds, we have recently reported that the photoreaction of 2-halopyridine (halogen; Cl, Br, I) and indole afforded substituted (2-pyridyl)indoles as a mixture of possible regioisomers.[1)] This reaction was considered to involve the coupling of the indole 1-radical and the 2-pyridyl radical generated *via* electron transfer from indole to a 2-halopyridine, followed by the elimination of the halide anion from the latter. To explore the synthetic utility of the present reaction, we have extended our investigation to the photolysis of 2-fluoropyridine and indole derivatives. In this paper, we present our findings that the photoreaction of indole with 2-fluoropyridine afforded 1-(2-pyridyl)indole as a major product, and that, by using the indole 1-anion, 1-(2-pyridyl)indole was obtained as a sole product in greatly increased yields *via* charge-transfer excitation.

Photolysis of a solution of 2-fluoropyridine (**1**) and indole (**2a**-H) in acetonitrile afforded 1-(2-pyridyl)indole (**3a**) in 14% yield (based on **2a**-H consumed) as a sole product with 86% recovery of **2a**-H by gas liquid chromatography (GLC). Similarly, the photoreaction was conducted in various solvents (hexane, cyclohexane, ether, and acetone) and the results are summarized in Table I. The best result was obtained in ether solution. Under the conditions used, 3-(2-pyridyl)indole (**4**) was detected by GLC as a minor product (3.9%). The photoreaction was slow in ether with a 500 W high-pressure mercury lamp, but afforded **3a**. A similar photoreaction with a high-pressure mercury lamp in acetone solution failed to afford **3a**.

The photoreaction of **1** with 3-methylindole (**2b**-H), and tetrahydrocarbazole (**2c**-H), in ether with a low-pressure mercury lamp furnished 3-methyl-1-(2-pyridyl)indole (**3b**) and 9-(2-pyridyl)-1,2,3,4-tetrahydrocarbazole (**3c**) as sole products in 32% and 19% yields, respectively, but no coupling product was obtained from the reaction with carbazole (**2d**-H) (Table II).

In contrast to the photoreaction of **2a**-H with other 2-halopyridines (halogen = Cl, Br, I),

TABLE I. The Photoreaction of 2-Fluoropyridine (**1**) with Indole (**2a**-H) in Various Solvents (10 h)

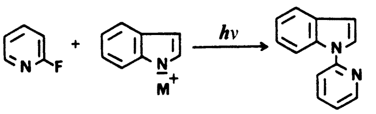


1 **2a**-H **3a** **4**

Solvent	Yield of **3a** (%)[a]	Consumed **2a**-H (%)
Hexane	8	32
Cyclohexane	8	25
Ether	19.5	52
Ether[b,c]	10	25
CH_3CN	14	14
Acetone[b]	0	10

a) Based on **2a**-H consumed. *b*) Irradiated with a high-pressure mercury lamp. *c*) 5 h.

TABLE III. Photoreaction of 2-Fluoropyridine (**1**) with Sodium and Lithium Salts of Indole (**2a**$^-$M$^+$)



1 **2a**$^-$M$^+$ **3a**

M$^+$	Solvent	Yield of **3a** (%)[a]	Consumed **2a**$^-$M$^+$ (%)
Na	DME	51	26
Na	DMSO	46	45
Na	DMF	85	59
Na	DMF[b]	74	36
Li	Ether–DME	28	17

a) Based on **2a**$^-$M$^+$ consumed. *b*) Irradiated with a high-pressure mercury lamp.

TABLE II. Photoreaction of 2-Fluoropyridine (**1**) with Indoles (**2**-H)

2*x*-H (*x*)	Yield of **3** (%)[a]	Consumed **2**-H (%)
a	19.5	52
b	32	28
c	19	35
d	0	5

a) Based on **2**-H consumed.

TABLE IV. Photoreaction of 2-Fluoropyridine (**1**) with Sodium Salts of Indoles (**2**$^-$Na$^+$)

2*x*$^-$Na$^+$ (*x*)	Yield of **3** (%)[a]	Consumed **2**$^-$Na$^+$ (%)
a	85	59
b	93	40
c	62	44
d	83	44

a) Based on **2**$^-$Na$^+$ consumed.

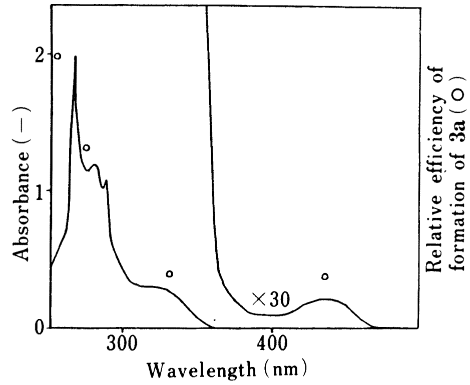


Fig. 1. UV Absorption Spectrum of the Equimolar Mixture of **1** and **2a**$^-$Na$^+$ in DMF (1.1×10^{-4} M) and the Efficiency of Photolysis of the Solution at Various Wavelengths

in which (2-pyridyl)indoles were produced as a mixture of all of the possible regioisomers, the present photoreaction of **1** proceeded in the manner of nucleophilic aromatic photosubstitution[3] to afford **3a** as a major product, indicating that this reaction is a potentially useful method for the synthesis of 1-(2-pyridyl)indole derivatives (**3**). In view of the report that fluoride and chloride are satisfactory leaving groups in the nucleophilic photosubstitution of suitably activated haloarenes by alkoxide or hydroxide anion,[3a] we then examined the photoreaction of **1a** with the indole 1-anion (**2a**$^-$) in place of a neutral indole (**2a**-H).

Photolysis of a mixture of **1** and the sodium salt (**2a**$^-$Na$^+$) or the lithium salt (**2a**$^-$Li$^+$) of **2a**-H in various solvents, 1,2-dimethoxyethane (DME), dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), gave **3a** as a sole product in distinctly higher yields. As shown in Table III, the reaction with **2a**$^-$Na$^+$ in DMF gave **3a** in the best yield.[4] Irradiation of

TABLE V. The Frontier Orbital Coefficients of Indole (**2a**-H) and Indole Anion (**2a**$^-$)

	2a-H		**2a**$^-$	
	HOMO	LUMO	HOMO	LUMO
Eigen value (eV)	−11.19	3.25	−3.49	9.02
Coefficient				
Site 1	0.477	0.136	0.666	0.092
2	−0.301	−0.396	0.019	−0.320
3	−0.458	0.220	−0.476	0.104
4	0.419	−0.514	0.239	−0.545
5	0.193	0.132	0.286	0.205
6	−0.293	0.400	−0.159	0.333
7	−0.401	−0.474	−0.330	−0.535

TABLE VI. Coefficients of Frontier Orbitals for 2-Fluoropyridine (**1**)

	HOMO	LUMO	NLUMO
Eigen value (eV)	−13.75	3.19	3.87
Coefficient			
Site 1	−0.193	0.520	0.169
2	−0.461	−0.156	−0.579
3	−0.438	−0.410	0.352
4	0.084	0.572	0.178
5	0.539	−0.082	−0.544
6	0.377	−0.448	0.413

2a$^-$Na$^+$ with a high-pressure mercury lamp also afforded **3a** in satisfactory yields.

Under similar conditions, photoreaction of **1** with the sodium salts of **2b**-H (**2b**$^-$Na$^+$), **2c**-H (**2c**$^-$Na$^+$), and **2d**-H (**2d**$^-$Na$^+$) gave the corresponding **3b**, **3c**, and **3d**[5] in satisfactory yields (93%, 62%, and 83%, respectively) (Table IV).

The products **3a** and **3d** were identical with **3a** and **3d** prepared according to the reported method.[1,5] The structural assignments of **3b** and **3c** were made on the basis of their mass spectra (MS), proton nuclear magnetic resonance (^{1}H-NMR) spectra and elemental analyses.

An equimolar mixture of **1** and **2a**$^-$Na$^+$ in DMF displayed a new absorption band over the region of 430—440 nm that was shown by neither individual component, and is ascribable to the formation of a charge-transfer complex. The formation of **3a** was observed upon selective excitation of the charge-transfer complex of **1** and **2a**$^-$Na$^+$ in DMF at 436 nm with a diffraction grating spectroscope (Fig. 1). These results suggest that the reaction of **1** with **2a**$^-$Na$^+$ was essentially initiated by excitation of the charge-transfer complex.[6]

On the other hand, the ultraviolet (UV) spectrum of the starting mixture of **1** and **2a**-H exhibited the sum of the individual absorption bands of both components, and no charge-transfer absorption band in the ground state was observed. Selective irradiation of **2a**-H in a mixture of **2a**-H and **1** in ether with filtered light (Pyrex filter, >300 nm), to which **1** is transparent, gave rise to the formation of **3a** as shown in Table I, suggesting that the formation of **3a** in the reaction with neutral indole (**2a**-H) was initiated by the local excitation of **2a**-H.

No significant quenching effect on the reaction of **1** with **2a**-H in ether was observed by the addition of piperylene, while the addition of acetone to the solution completely suppressed the formation of **3a** (Table I). Moreover, the fluorescence of **2a**-H was efficiently quenched by **1** with a Stern–Volmer rate constant of $k_q\tau = 86\ \mathrm{l \cdot mol^{-1}}$, suggesting that the reaction with **2a**-H proceeds *via* the excited singlet state.

Recently, Mutai *et al.* have clearly demonstrated that the frontier orbital treatment is a useful method for interpreting the regioselectivities and the mechanisms of nucleophilic aromatic photosubstitutions.[7] According to their treatment, we have conducted molecular orbital (MO) calculations for **1**, **2a**-H, and **2a**$^-$, by using the CNDO/2 method,[8] to elucidate the factors causing regioselective substitutions in this reaction. The results are summarized in Tables V and VI.

The highest occupied MO of **2a**$^-$ (HOMO$_{\mathbf{2a}^-}$) is largely located on the nitrogen atom (N-1). Upon irradiation of the charge-transfer complex, an electron is transferred from the HOMO$_{\mathbf{2a}^-}$ to the unoccupied MO of **1**. In this stage, the lowest unoccupied MO of **1** (LUMO$_{\mathbf{1}}$) that extends slightly to C-2 attached to the fluorine atom could not be an important frontier MO (FMO). Therefore, the next lowest unoccupied MO of **1** (NLUMO$_{\mathbf{1}}$), which lies

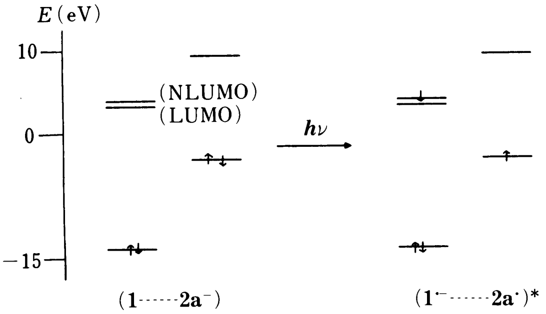


Fig. 2. Frontier Orbital Interaction for the Charge-Transfer Excitation of **1** and **2a**⁻

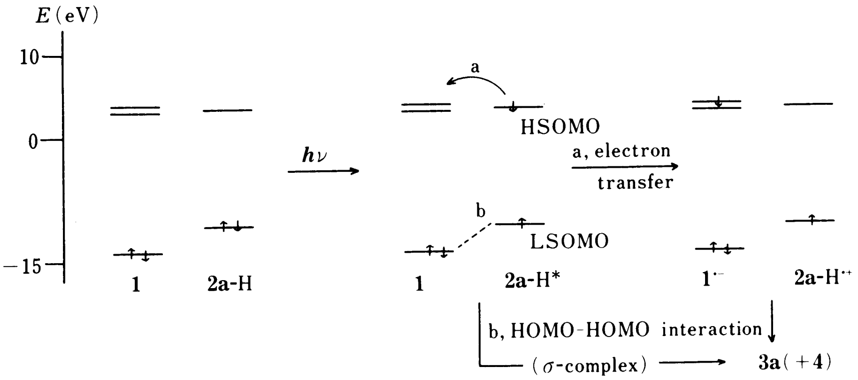


Fig. 3. Frontier Orbital Interaction for the Photoreaction of **1** and **2a**-H

very close to the $LUMO_1$, with a large extension over C-2, is considered as an important FMO to accept the electron. Then the bonding interaction develops between the $HOMO_{2a^-}$ and the $NLUMO_1$, giving rise to the formation of **3a** (Fig. 2). This procedure can be taken as "rule 2" of Mutai *et al.*[7,9] Thus, the regioselective formation of **3a** can be rationalized on the basis of the FMO method.

Selective bonding of **1** at C-2 attached to the fluorine atom but not to C-5, on which the HOMO is largely extended as well, can be reasonably explained by taking into consideration the superiority of the fluoride anion (F^-) over the hydride anion (H^-) as a leaving group in nucleophilic aromatic substitution.[10]

On the other hand, in the case of **2a**-H, the extension of the HOMO is greatest over the N-1, as it is for **2a**⁻, though less marked. The local excitation of **2a**-H produces the singlet excited state, in which one electron is promoted from the $HOMO_{2a\text{-}H}$ to the $LUMO_{2a\text{-}H}$. If an electron is transferred from the resulting high-energy singly occupied MO (SOMO) of **2a**-H ($HSOMO_{2a\text{-}H}$) ($LUMO_{2a\text{-}H}$ before excitation) to the $NLUMO_1$ (Fig. 3), radical coupling would take place between the resulting radical cation of **2a**-H (**2a**-H$^{\cdot +}$) and the radical anion of **1** (**1**$^{\cdot -}$), which might be regarded as substantially analogous to what should have been generated from the excitation of the charge-transfer complex of **1** with **2a**⁻, affording mainly **3a** and a small amount of 3-(2-pyridyl)indole (**4**).

In view of the low-energy $SOMO_{2a\text{-}H}$ ($LSOMO_{2a\text{-}H}$) ($HOMO_{2a\text{-}H}$ before excitation) and $HOMO_1$ lying closely in energy and the latter being extended largely on C-2, there is another conceivable mechanism involving direct formation of a σ-complex through the interaction between the MOs, according to the procedure referred to as "rule 1" by Mutai *et al.*[7,9]

Although the precise mechanism of the reaction of **1** and **2** still remains unclear, it may be assumed that the regiospecific formation of **3a** in the photoreaction using **1** is caused by the

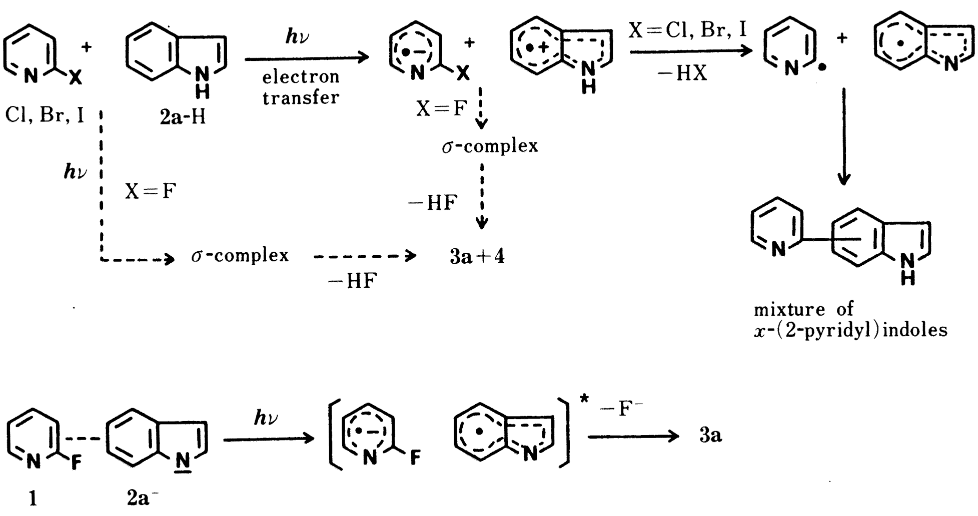


Chart 1

formation of σ-bonding with the indole molecule prior to the elimination of the fluoride anion, while the other 2-halopyridines lose the halide anion prior to linking to the indole ring, thus producing (2-pyridyl)indoles as a mixture of all possible isomers (Chart 1).[11] It is noteworthy that the present reaction provides a preparative method for 1-(2-pyridyl)indoles.

Experimental

All melting points are uncorrected. ^{1}H-NMR spectra were measured with a JNM-GX 270 (270 MHz) spectrometer in $CDCl_3$, and chemical shifts are given on the δ (ppm) scale with tetramethylsilane as an internal standard. Abbreviations are used as follows: s, singlet; d, doublet; t, triplet; m, multiplet. MS were determined on a JEOL QH-100 mass spectrometer. UV spectra and fluorescence spectra were taken on a Shimadzu UV-240 instrument and a Hitachi 650-60 fluorescence spectrometer at room temperature, respectively. GLC was performed on a Shimadzu GC-7A gas chromatograph equipped with a hydrogen flame-ionization detector using nitrogen as a carrier gas (30 ml/min). Glass columns (1.5 m, 3 mm i.d.) of 3% OV-17 on Shimalite W (80—100 mesh) were used. Column chromatography was conducted with a Shimadzu LC-5A apparatus on a prepacked silica gel column (Lobar column, Lichroprep Si-60, Merck). Thin layer chromatography (TLC) was carried out on Kieselgel 60 F_{254} (Merck) TLC plates. UV-irradiation was carried out with a 60 W low-pressure mercury lamp (Eiko-sha), unless otherwise stated. For irradiation of the region at >300 nm, a high-pressure mercury lamp was used with a Pyrex filter. External irradiation was conducted for analytical-scale photoreaction in a quartz tube (low-pressure mercury lamp) or in a Pyrex tube (high-pressure mercury lamp, Eiko-sha) under an argon atmosphere using a merry-go-round apparatus (Eiko-sha) at room temperature, while internal irradiation was carried out in a Pyrex vessel under argon for preparative-scale photoreaction. The yields of the products given in tables were determined by GLC. The effect of wavelength on the photoreaction was examined by using a JASCO diffraction grating spectroscope (CRM-FA).

Materials——2-Fluoropyridine (**1**) (Aldrich Chemical Company Inc.) and indoles (**2**-H) are commercially available (Wako Pure Chemical Industries Ltd., Japan for **2a**-H and **2b**-H and Kanto Chemical Co., Inc., Japan for **2d**-H). Compound **2c**-H was prepared according to the reported procedure.[12]

Photolysis of 1 and Indole (2a-H) in Various Solvents——A solution of **1** (0.11 mmol) and **2a**-H (0.1 mmol) in ether (10 ml) was irradiated externally in a quartz test tube under an argon atmosphere for 10 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. The results are listed in Table I. The residual reaction mixture was submitted to TLC with hexane–acetone (5 : 1) to furnish 1-(2-pyridyl)indole (**3a**) (2 mg, 10.3%) and 3-(2-pyridyl)indole (**4**) (0.2 mg, 1%), together with recovered **2a**-H (4.5 mg, 38.5%). The photoreactions in hexane, cyclohexane, acetonitrile and acetone were carried out and worked up as above.

Photoreaction of 1 with Various Indoles (2-H)——Photolysis in ether was carried out as described above, and a part of the reaction mixture was submitted to GLC with naphthalene (for **2b**-H) or anthracene (for **2c**-H and **2d**-H) as an internal standard. The residual reaction mixture was submitted to silica gel TLC.

3-Methyl-1-(2-pyridyl)indole (3b) by the Photoreaction of 1 with 3-Methylindole (2b-H)——Development of the reaction mixture on TLC with hexane–acetone (5 : 1) afforded **3b** (2.0 mg, 9.6%) as a colorless oil, together with recovered **2b**-H (9.2 mg, 70%). **3b**: mp of picrate 138—139 °C (plates from ethanol). *Anal.* Calcd for $C_{20}H_{15}N_5O_7$ (picrate): C, 54.92; H, 3.46; N, 16.01. Found: C, 55.03; H, 3.34; N, 16.23. ^{1}H-NMR: 2.37 (3H, d, J=1.1 Hz, CH_3), 7.10 (1H, ddd, J=7.3, 4.8, 0.7 Hz, H-5′), 7.21 (1H, td, J=7.7, 1.1 Hz, H-5), 7.30 (1H, ddd, J=8.1, 7.7, 1.5 Hz, H-6), 7.43 (1H, dt, J=8.1, 0.7 Hz, H-3′), 7.51 (1H, d, J=1.1 Hz, H-2), 7.59 (1H, dd, J=7.7, 1.5 Hz, H-4), 7.77 (1H, ddd, J=8.1, 7.3, 1.8 Hz, H-4′), 8.22 (1H, ddd, J=8.1, 1.1, 0.7 Hz, H-7), 8.53 (1H, ddd, J=4.8, 1.8, 0.7 Hz, H-6′). MS m/z (relative intensity): 208 (M^+, 100), 207 (82), 130 (40).

9-(2-Pyridyl)-1,2,3,4-tetrahydrocarbazole (3c) by the Photoreaction of 1 and 1,2,3,4-Tetrahydrocarbazole (2c-H)——Development of the reaction mixture on TLC with hexane–benzene (1 : 1) afforded **3c** (1.5 mg, 6%) as a colorless oil and recovered **2c**-H (8.0 mg, 46.8%). **3c**: mp of picrate 173—174 °C (needles from ethanol). *Anal.* Calcd for $C_{23}H_{19}N_5O_7$ (picrate): C, 57.86; H, 4.01; N, 14.67. Found: C, 57.92; H, 3.97; N, 14.58. ^{1}H-NMR[13]: 1.90 (4H, m, 2-H_2, 3-H_2), 2.80 (4H, m, 1-H_2, 4-H_2), 7.14 (1H, m, J=7.8, 7.1, 1.1 Hz, H-6), 7.15 (1H, m, J=8.1, 7.1, 0.8 Hz, H-7), 7.21 (1H, ddd, J=7.3, 4.8, 0.7 Hz, H-5′), 7.40 (1H, ddd, J=8.1, 1.1, 0.7 Hz, H-3′), 7.50 (1H, m, J=7.8, 0.8, 0.7 Hz, H-5), 7.55 (1H, m, J=8.1, 1.1, 0.7 Hz, H-8), 7.81 (1H, ddd, J=7.7, 7.4, 1.8 Hz, H-4′), 8.60 (1H, ddd, J=4.8, 1.8, 0.7 Hz, H-6′). MS m/z (relative intensity): 248 (M^+, 71), 247 (22), 220 (37), 219 (100).

Photolysis of 1 and the Indole 1-Anion (2a$^-$) in Various Solvents——A solution of **1** (0.17 mmol) and the sodium salt of indole (**2a**$^-$Na$^+$), prepared by treatment of **2a**-H with 60% NaH in oil (0.1 mmol; previously washed with hexane), in DMF, DMSO, or DME (10 ml) was irradiated externally for 5 h. The reaction mixture was submitted to GLC with naphthalene as an internal standard.

Similarly, a solution of **1** with the lithium salt of **2a**-H (**2a**$^-$Li$^+$), prepared from **2a**-H by treatment with *n*-butyl lithium at −80 °C under argon, in an equivolume mixture of ether and DME (10 ml) was photolyzed, and worked up in the same manner as described above.

General Procedure for the Photoreaction of 1 with the Sodium Salts of Indole Derivatives (2$^-$Na$^+$)——Photolysis in DMF was carried out as described above. The reaction mixture was acidified with 20% hydrochloric acid (0.5 ml), and the solvent was evaporated under reduced pressure. The residual oil was neutralized with 30% aqueous K_2CO_3 (2 ml), followed by extraction with ethyl acetate (5 ml × 3). The extract was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting oil was submitted to TLC.

9-(2-Pyridyl)carbazole (3d) by the Photoreaction of 1 with the Sodium Salt of Carbazole (2d$^-$Na$^+$)——Development of the reaction mixture on TLC with hexane–benzene (1 : 2) afforded **3d** and **2d**-H (8.6 mg, 51.5%). The former, upon treatment with petroleum ether, afforded crystalline **3d** (7.9 mg, 32.4%). **3d**: mp 69—70 °C (colorless plates from petroleum ether) (lit. 90—92 °C).[5] A mixture of **3d** and the product (mp 68—69 °C) prepared alternatively by the procedure of Khan and Polya[5] showed no melting point depression. *Anal.* Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.72; H, 4.96; N, 11.41. ^{1}H-NMR: 7.31 (1H, dd, J=7.3, 1.0 Hz, H-5′), 7.32 (2H, ddd, J=8.1, 7.7, 1.1 Hz, H-3, H-6), 7.44 (2H, td, J=7.7, 1.5 Hz, H-2, H-7), 7.64 (1H, ddd, J=7.90, 1.0, 0.7 Hz, H-3′), 7.84 (2H, ddd, J=8.1, 1.5, 0.7 Hz, H-4, H-5), 7.92 (1H, ddd, J=7.9, 7.3, 1.8 Hz, H-4′), 8.12 (2H, ddd, J=7.7, 1.1, 0.7 Hz, H-1, H-8), 8.73 (1H, ddd, J=5.0, 1.8, 0.7 Hz, H-6′). MS m/z (relative intensity): 244 (M^+, 100), 243 (91).

Preparative-Scale Photoreaction of 1 with 2a$^-$Na$^+$——A solution of **1** (2 mmol) and the sodium salt of indole (**2a**$^-$Na$^+$) (2 mmol) in DMF (100 ml) was irradiated for 15 h. The reaction mixture was worked up in the same manner as described above. The residual oil was developed on TLC with hexane–acetone (5 : 1) to afford **3a** together with recovery of **2a**-H (30 mg, 13%) (150 mg, 64% by GLC analysis). Further treatment of the crude **3a** on a short column of alumina (Aluminum oxide 90 active neutral, Merck) gave **3a** (128 mg, 33%) as a colorless oil.

Photolysis of 1 and Indole (2a-H) in the Presence of Additives——A solution of **1** (0.11 mmol) and **2a**-H (0.1 mmol) in ether (10 ml), containing *trans*-piperylene (0.01—0.4 M) was irradiated with a 60 W low-pressure mercury lamp under argon for 5 h. The formation of **3a** was quenched by *trans*-piperylene at the Stern-Volmer rate constant of $k_q\tau = 5.9\,l \cdot mol^{-1}$.[14] Similarly, the photolysis of the solution containing acetone (0.034 M) was conducted with a 500 W high-pressure mercury lamp for 5 h. The yield of **3a** and the recovery of **2a**-H determined by GLC were 0.01% (based on **2a**-H used) and 82%, respectively: the photoreaction in the absence of acetone afforded **3a** in 2.5% yield together with recovery of **2a**-H in 75% yield.

Fluorescence Quenching of 2a-H by 1——Ethereal solutions of **2a**-H (1.1×10^{-4} M) containing various amounts of **1** (2.0×10^{-3}—2.8×10^{-2} M) were prepared. Excitation was induced at 287 nm, and the fluorescence emission of **2a**-H at 302 nm was measured.

MO Calculations——MO calculations were performed on an NEC personal computer (9801E) using the reported geometries of **1** optimized by *ab initio* calculations[15] and of **2a**-H obtained from X-ray data.[16]

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4) The starting mixture kept in the dark for 5 h at room temperature afforded **3a** in only 5% yield.

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6) The high efficiency of formation of **3a** at the shorter wavelength region (<300 nm) suggests that another reaction pathway initiated by the local excitation of **2a**$^-$Na$^+$ or **1** may participate in the reaction.

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8) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); Revised program for personal computer on the basis of QCPE program #0438 by W. Thiel (Quantum Chemistry Program Exchange; Chemistry Department, Room 204, Indiana University, Bloomington, Indiana 47401, U.S.A.).

9) The present photoreaction of **1** and **2a**-H or **2a**$^-$, should be distinguished in a strict sense from the nucleophilic aromatic substitution reaction, to which "rule 1" and "rule 2" are applied, in that the former reaction is caused by the excitation of the nucleophile **2a**-H or the charge-transfer complex containing **2a**$^-$, while the latter reaction involves photoexcited aromatic species and nucleophiles in the ground states.

10) J. B. Hendrickson, D. J. Cram, and G. S. Hammond, "Organic Chemistry" third ed., McGraw-Hill Inc., New York, 1970, pp. 542—545.

11) The photoreaction of 2-chloropyridine with **2a**$^-$Na$^+$, in place of **2a**-H, afforded a mixture of all possible isomers of x-(2-pyridyl)indole ($x=1$, 2, 3, 4, 5, 6, and 7) in similar isomer ratios.

12) C. U. Rogers and B. B. Corson, "Organic Synthesis," Coll. Vol. 4, ed. by N. Rabjohn, John Wiley & Sons Inc., New York, 1963, p. 884.

13) Determined by the modified program based on LAOCN3 (QCPE 111); Quantum Chemistry Program Exchange, Chemistry Department, Room 204, Indiana University, Bloomington, Indiana 47401, U.S.A.

14) The inefficient quenching was due to the formation of the addition product of piperylene and indole, appearing as a new peak on GLC. The MS of this product showed a molecular ion peak at m/z (M^+)$=185$.

15) J. E. Boggs and F. Pang, *J. Heterocycl. Chem.*, **21**, 1801 (1984).

16) I. L. Karle, K. Britts and P. Gum, *Acta Cryst.*, **17**, 496 (1964).