DIRECT ARYLATION OF 2-PYRIDONES; PHOTOSTIMULATED $S_{RN}1$ REACTION BETWEEN CESIUM PHENOXIDES AND CHLORO-2-PYRIDONES

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Abstract ----- 4-Hydroxyphenyl- (**3** and **4**) and 6-hydroxyphenyl-1-methyl-2-pyridones (**6** and **7**) were obtained by the photostimulated reaction of 4-chloro- (**1**) and 6-chloro-1-methyl-2-pyridone (**5**), respectively, with variously substituted cesium phenoxides (**2**). The reactions were proposed to proceed *via* an $S_{RN}1$ mechanism.

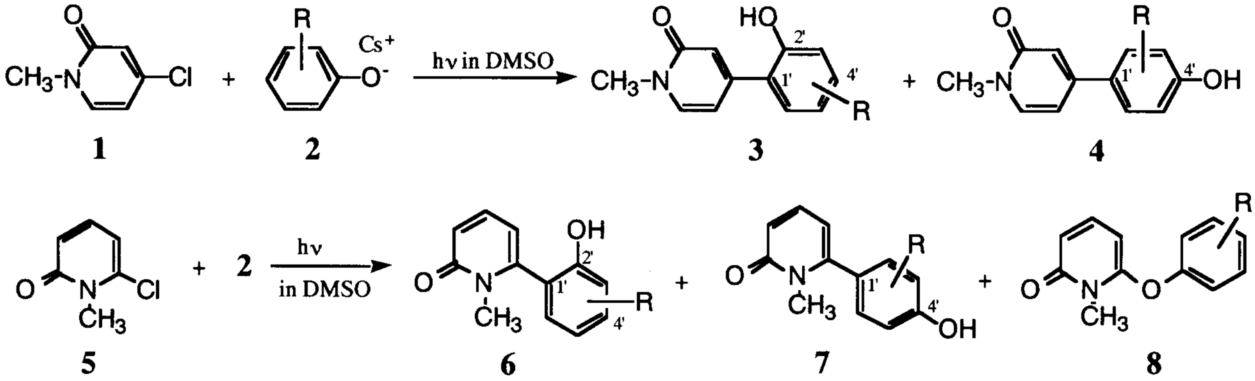
INTRODUCTION

The 2-pyridone ring is an important structural element of a number of biologically and structurally interesting molecules.[1] 2-Pyridones are versatile synthetic intermediates for many alkaloids.[2] We have recently reported that irradiation of 2-pyridones in the presence of electron donors such as aliphatic amines[3] or π-excessive heteroaromatic compounds (pyrroles and indoles)[4] causes a single electron transfer (SET) to yield addition products, 4-substituted 3,4-dihydropyridin-2(1*H*)-ones and 6-substituted 3,6-dihydropyridin-2(1*H*)-ones. As part of our investigations on the photochemistry of 2-pyridones *via* a SET process, we have studied the photostimulated substitution reaction of halo-2-pyridones with phenoxides under the intention of synthesizing aryl-2-pyridone derivatives, some of which are known to have biological activities such as elastase inhibitor,[1b] cardiac,[5] and anti-inflammatory.[6] There is no literature precedent for a direct arylation of 2-pyridones to our knowledge though the syntheses of this class of compounds have been investigated extensively.[2a] We now report the photosubstitution reaction of 4-chloro- (**1**) and 6-chloro-1-methyl-2-pyridone (**5**) with the cesium salts (**2**) of phenol and its derivatives having an electron-withdrawing (EWG) or an electron-donating group (EDG). Preliminary experiments revealed that 3-chloro-1-methyl-2-pyridone did not take place any reaction and 5-chloro-1-methyl-2-pyridone gave the substitution products only in low yields though the starting 2-pyridone was completely consumed.

RESULTS AND DISCUSSION

The photoreaction was carried out by irradiation of a deaerated solution of chloro-1-methyl-2-pyridone (**1**) or

(**5**) and cesium phenoxides (**2**) in dimethyl sulfoxide (DMSO) with a 400W high-pressure mercury lamp through a Pyrex filter at room temperature. The reaction mixture was separated by column chromatography on silica gel with CH_2Cl_2-MeOH solvent systems. The structures of the products obtained were established by spectroscopic methods.



Scheme

Irradiation of 4-chloro-1-methyl-2-pyridone (**1**) with variously substituted phenoxides (**2**) underwent substitution reaction to yield 4-hydroxyphenyl-1-methyl-2-pyridones (**3** and **4**) in which the hydroxyl group on the benzene ring was located either *ortho* (*ortho*-substitution) or *para* (*para*-substitution) to the newly formed C-C bond. Similarly, 6-hydroxyphenyl-1-methyl-2-pyridones (**6** and/or **7**) were formed by the photoreaction of 6-chloro-1-methyl-2-pyridone (**5**) with the phenoxides (**2**) (*C*-substitution). The latter reactions were accompanied by the formation of 6-phenoxy-1-methyl-2-pyridones (**8**) (*O*-substitution) except for the case with *p*-cyanophenoxide (**2g**). The results are summarized in Table 1.

The common features of the photoreaction of chloro-2-pyridones (**1** and **5**) with cesium phenoxides in DMSO are as follows: 1) the *ortho*-substitution was preferable to the *para*-substitution irrespective of the species (EWG or EDG) of a substituent on the phenoxides; 2) the presence of an EWG at the *ortho* position of phenoxides significantly reduced the formation of the substitution product; 3) in the photoreaction with 6-chloro-2-pyridone (**5**), the presence of an EWG on the phenoxides increased the ratio of *C*-substitution/*O*-substitution.

When a solution of phenoxide (**2d**) and 4-chloro-2-pyridone (**1**) in DMSO, which gave *C*-substitution product (**3d**) on irradiation, was treated in the dark, no reaction occurred. On the other hand, only the *O*-substitution product (**8d**) was obtained in 80% yield in the dark reaction of 6-chloro-2-pyridone (**5**) with **2d**. The above results demonstrate that the *C*-substitution proceeded *via* a photochemical process and the *O*-substitution *via* a thermal process. Irradiation of phenoxy-2-pyridone (**8d**) in DMSO did not cause any reaction, indicating that the phenoxy-2-pyridone derivatives might not be an intermediate for the *C*-substitution. It has recently been reported that hydroxybiaryls are synthesized both photochemically[7] and electrochemically[8] starting from haloarenes and phenoxides or naphthoxides. These substitution reactions are proved to proceed *via* $S_{RN}1$ mechanism. The photostimulated reaction of **1** with **2f** was significantly inhibited in the presence of *p*-dinitrobenzene (*p*-DNB, 0.1 eq. to **1**), a well-known inhibitor of $S_{RN}1$

reactions (Table 1), in analogy with those of haloarenes and phenoxides.[7,8] The formation of *C*-substitution product (**6d**) also decreased, in contrast to a significant increase of the *O*-substitution product (**8d**) by addition of the inhibitor to the photoreaction of **5** with **2d**. All these results let us to propose an $S_{RN}1$ mechanism for the photostimulated substitution reaction leading to the formation of hydroxyphenyl-2-pyridone derivatives.

Table 1. Photostimulated Reaction of Chloro-2-pyridones (**1** and **5**) with Phenoxides (**2**) in DMSO

2-pyridones	phenoxides	products (yields %)[a]					
1	**2a**; R=H[c]						
	2b; R=2-OMe	**3b**; R=3'-OMe	(40)	**4b**; R=3'-OMe	(19)		
	2c; R=3-OMe	**3c**; R=4'-OMe	(8)	**4c**; R=2'-OMe	(8)		
		3c'; R=6'-OMe	(12)				
	2d; R=4-OMe	**3d**; R=5'-OMe	(27)				
	2e; R=2-CN	**3e**; R=3'-CN	(5)	**4e**; R=3'-CN	(5)		
	2f; R=3-CN	**3f**; R=4'-CN	(20)	**4f**; R=2'-CN	(12)		
			(10)[b]		(6)[b]		
	2g; R=4-CN	**3g**; R=5'-CN	(18)				
5	**2a**	**6a**; R=H	(32)	**7a**; R=H	(10)	**8a**; R=H	(10)
	2b			**7b**; R=3'-OMe	(5)	**8b**; 2'-OMe	(50)
	2c	**6c**; 4'-OMe	(20)			**8c**; 3'-OMe	(20)
	2d	**6d**; 5'-OMe	(22)			**8d**; 4'-OMe	(28)
			(8)[b]				(82)[b]
	2e[c]						
	2f	**6f**; R=6'-CN	(40)			**8f**; R=3'-CN	(25)
	2g	**6g**; R=5'-CN	(54)				

a, Isolated yields. Products (**3** and **4**, and **6a** and **7a**) were obtained as an inseparable mixture of regioisomers, ratios of which were estimated by ^{1}H-NMR spectra.
b, In the presence of *p*-dinitrobenzene (10 mol %).
c, Complex mixture.

EXPERIMENTAL

General Procedures

Melting points were determined on a Yanagimoto micro melting apparatus and are uncorrected. ^{1}H NMR spectra were measured in DMSO-d_6 unless otherwise noted, with a JEOL JNM-GX 400 or a JEOL JNM-GSX 270 spectrometer, and chemical shifts (δ) are given in parts per million (ppm) down field from tetramethylsilane as an internal standard. Coupling constants (*J*) are given in Hertz (Hz). EI-MS were taken on

JEOL D-300 instrument. IR spectra were measured with Hitachi 215 spectrophotometer at KBr discs. Analytical GLC was carried out with Hitachi 263-30 gas chromatograph equipped with a column (0.3 x 200 cm) of silicon OV-17 on Gas Chrom Q. GLCEI-MS were measured with the same instrument as used for EI-MS, and GLC conditions were the same as in the analytical GLC except for the use of He instead of N_2 as a carrier gas. A Riko 400W high-pressure mercury lamp was used as the irradiation sources. 6-Chloro-2-pyridinol and phenols were obtained from commercial sources and purified by distillation or recrystallization before use. 4-Chloro-2-pyridinol was synthesized by the reported method.[9] **1** and **5** were prepared in 92% and 82% yields, respectively, by stirring a solution of the chloro-2-pyridinols (0.65 g, 5.0 mmol), methyl iodide (2.13 g, 15.0 mmol) and tetrabutylammonium iodide(0.18 g, 0.5 mmol) in benzene (10 mL) in the presence of anhydrous K_2CO_3 (2.07 g, 15.0 mmol) for 24 h at rt: **1**; mp 74-75 °C (sublimation); ^{1}H-NMR ($CDCl_3$) δ: 6.61 (1H, d, *J* = 2.4, 3-H), 6.19 (1H, dd, *J* = 7.3 and 2.4, 5-H), 7.23 (1H, d, *J* = 7.3, 6-H). **5**: needles from *n*-C_5H_{12}-Et_2O, mp 63-65 °C, that was identical with the reported value.[10] The cesium salts of phenoles were prepared analogously to the reported procedure.[11] DMSO was purified by distillation after being dried with CaH_2 and stored on molecular sieves (4Å).

General procedure for the photochemical reactions. A solution of the chloro-2-pyridones (0.6 mmol) and the cesium salts (3.0 mmol) in dry DMSO (6 mL) was flushed with N_2 for 15 min and then sealed under reduced pressure. The solution was irradiated externally for 7 h through a Pyrex filter with a 400W high-pressure mercury lamp. After removal of the solvent under reduced pressure, the residue was treated with water, 5% HCl and then extracted with CH_2Cl_2 several times. The combined extracts were dried on Na_2SO_4 and evaporated to dryness *in vacuo*. The residue was separated by repeated column chromatography on silica gel using CH_2Cl_2-MeOH solvent systems.

Photoreaction of 1 with 2b. Products (**3b** and **4b**) were obtained as an inseparable mixture (74 mg, 59%) of the ratio of 2:1. *4-(2-Hydroxy-3-methoxyphenyl)-1-methyl-2-pyridone* (**3b**); GLC-MS *m/z*: 231 (M^+, 100), 230, 214; ^{1}H-NMR δ: 3.58 (3H, s, NCH_3), 6.78 (1H, d, *J* =1.8, 3-H), 6.44 (1H, dd, *J* =7.3 and 1.8, 5-H), 7.28 (1H, d, *J* =7.3, 6-H), 10.32 (1H, br, 2'-OH), 3.93 (3H, s, 3'-OCH_3), 6.91 (1H, d, *J* =8.6, 4'-H), 6.93 (1H, dd, *J* =8.6 and 8.6, 5'-H), 6.95 (1H, d, *J* =8.6, 6'-H). Irradiation at the singlet (δ 3.93) due to the OCH_3 group caused enhancement of the doublet at δ 6.91 (4'-H). *4-(4-Hydroxy-3-methoxyphenyl)-1-methyl-2-pyridone* (**4b**); GLC-MS *m/z*: 231 (M^+, 100), 230, 214; ^{1}H-NMR δ: 3.56 (3H, s, NCH_3), 6.86 (1H, d, *J* =1.8, 3-H), 6.58 (1H, dd, *J* =7.3 and 1.8, 5-H), 7.34 (1H, d, *J* =7.3, 6-H), 7.07 (1H, d, *J* =1.8, 2'-H), 3.94 (3H, s, 3'-OCH_3), 10.4 (1H, br, 4'-OH), 6.98 (1H, d, *J* =8.6, 5'-H), 7.13 (1H, dd, *J* =8.6 and 1.8, 6'-H). Irradiation at the singlet (δ 3.94) due to the OCH_3 group induced enhancement of the doublet at δ 7.07 (2'-H).

Photoreaction of 1 with 2c. Products (**3c**, **3c'** and **4c**) were obtained as an inseparable mixture (40 mg, 28%) of the ratio of 2:3:2. *4-(2-Hydroxy-4-methoxyphenyl)-1-methyl-2-pyridone* (**3c**); GLC-MS *m/z*: 21 (M^+, 100), 230, 214; ^{1}H-NMR δ: 3.41 (3H, s, NCH_3), 6.42 (1H, d, *J* =1.8, 3-H), 6.33 (1H, dd,

J =7.3 and 1.8, 5-H), 7.58 (1H, d, J =7.3, 6-H), 9.81 (1H, br, 2'-OH), 6.48 (1H, d, J =1.8, 3'-H), 3.75 (3H, s, 4'-OCH_3), 6.53 (1H, dd, J =7.9 and 1.8, 5'-H), 7.26 (1H, d, J =7.9, 6'-H). *4-(2-Hydroxy-6-methoxyphenyl)-1-methyl-2-pyridone* (**3c'**): GLC-MS *m/z*: 231 (M^+, 100), 230, 214; ^{1}H-NMR δ: 3.43 (3H, s, NCH_3), 6.23 (1H, d, J =1.8, 3-H), 6.08 (1H, dd, J =7.3 and 1.8, 5-H), 7.56 (1H, d, J =7.3, 6-H), 9.55 (1H, br, 2'-OH), 6.57 (1H, d, J =7.9, 3'-H), 7.15 (1H, dd, J =7.9 and 6.7, 4'-H), 6.55 (1H, d, J =6.7, 5'-H), 3.68 (3H, s, 6'-OCH_3). *4-(4-Hydroxy-2-methoxyphenyl)-1-methyl-2-pyridone* (**4c**); GLC-MS *m/z*: 231 (M^+, 100), 230, 214; ^{1}H-NMR δ: 3.38 (3H, s, NCH_3), 6.46 (1H, d, J =1.8, 3-H), 6.43 (1H, dd, J =7.3 and 1.8, 5-H), 7.60 (1H, d, J =7.3, 6-H), 3.73 (3H, s, 2'-OCH_3), 6.49 (1H, d, J =1.8, 3'-H), 9.85 (1H, br, 4'-OH), 6.48 (1H, dd, J =7.9 and 1.8, 5'-H), 7.11 (1H, d, J =7.9, 6'-H).

Photoreaction of 1 with 2d. Product (**3d**) (38 mg, 27%) was obtained. *4-(2-Hydroxy-5-methoxyphenyl)-1-methyl-2-pyridone* (**3d**); colorless crystals from EtOH-C_6H_6, mp 237-239 ℃ (Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.25; H, 5.61; N, 5.96); MS *m/z*: 231 (M^+, 100%), 230, 214; IR (KBr): 3000(OH), 1645(C=O); ^{1}H-NMR δ: 3.58 (3H, s, NCH_3), 6.82 (1H, d, J =1.8, 3-H), 6.42 (1H, dd, J =7.3 and 1.8, 5-H), 7.35 (1H, d, J =7.3, 6-H), 10.45 (1H, br, 2'-OH), 6.93 (1H, d, J =8.3, 3'-H), 6.85 (1H, dd, J =8.3 and 2.9, 4'-H), 3.78 (3H, s, 5'-OCH_3), 7.30 (1H, d, J =2.9, 6'-H). Irradiation of the singlet at δ 3.78 (5'-OCH_3) caused enhancements of the double doublet at δ 6.85 (4'-H) and the doublet at δ 7.30 (6'-H).

Photoreaction of 1 with 2e. An inseparable 1:1 mixture (14 mg, 10%) of **3e** and **4e** was obtained. *4-(3-Cyano-2-hydroxyphenyl)-1-methyl-2-pyridone* (**3e**); GLC-MS *m/z*: 226 (M^+, 100%), 225, 209; ^{1}H-NMR δ: 3.47 (3H, s, NCH_3), 6.47 (1H, d, J =1.8, 3-H), 6.32 (1H, dd, J =6.7 and 1.8, 5-H), 7.75 (1H, d, J =6.7, 6-H), 10.45 (1H, br, 2'-OH), 7.68 (1H, dd, J =7.3 and 1.8, 4'-H), 7.08 (1H, dd, J =7.3 and 7.3, 5'-H), 7.56 (1H, dd, J =7.3 and 1.8, 6'-H). *4-(3-Cyano-4-hydroxyphenyl)-1-methyl-2-pyridone* (**4e**); GLC-MS *m/z*: 226 (M^+, 100%), 225, 209; ^{1}H-NMR δ: 3.53 (3H, s, NCH_3), 6.67 (1H, d, J =1.8, 3-H), 6.58 (1H, dd, J =6.7 and 1.8, 5-H), 7.77 (1H, d, J =6.7, 6-H), 8.03 (1H, d, J =1.8, 2'-H), 10.78 (1H, br, 4'-OH), 7.08 (1H, d, J =7.3, 5'-H), 7.89 (1H, dd, J =7.3 and 1.8, 6'-H).

Photoreaction of 1 with 2f. An inseparable 5:3 mixture (43 mg, 32%) of **3f** and **4f** was obtained. *4-(4-Cyano-2-hydroxyphenyl)-1-methyl-2-pyridone* (**3f**); GLC-MS *m/z*: 226 (M^+, 100%), 225, 209; ^{1}H-NMR δ: 3.40 (3H, s, NCH_3), 6.40 (1H, d, J =1.8, 3-H), 6.22 (1H, dd, J =7.3 and 1.8, 5-H), 7.70 (1H, d, J =7.3, 6-H), 10.30 (1H, br, 2'-OH), 7.25 (1H, d, J =1.8, 3'-H), 7.34 (1H, dd, J =7.9 and 1.8, 5'-H), 7.38 (1H, d, J =7.9, 6'-H). *4-(2-Cyano-4-hydroxyphenyl)-1-methyl-2-pyridone* (**4f**); GLC-MS *m/z*: 226 (M^+, 100%), 226, 209; ^{1}H-NMR δ: 3.38 (3H, s, NCH_3), 6.57 (1H, d, J =1.8, 3-H), 6.42 (1H, dd, J =7.3 and 1.8, 5-H), 7.68 (1H, d, J =7.3, 6-H), 7.35 (1H, d, J =1.8, 3'-H), 10.70 (1H, br, 4'-OH), 7.23 (1H, dd, J =7.9 and 1.8, 5'-H), 7.48(1H, d, J =7.9, 6'-H). The mixture was treated with an ethereal solution of CH_2N_2 to give an 1:1 mixture of the methyl ethers of **3f** and **4f**, which was also inseparable. *4-(4-Cyano-*

2-methoxyphenyl)-1-methyl-2-pyridone; ^{1}H-NMR ($CDCl_3$) δ: 3.57 (3H, s, NCH_3), 6.65 (1H, d, J =1.8, 3-H), 6.42 (1H, dd, J =6.7 and 1.8, 5-H), 7.23 (1H, d, J =6.7, 6-H), 3.88 (3H, s, 2'-OCH_3), 7.23 (1H, d, J =2.4, 3'-H), 7.36 (1H, dd, J =7.3 and 2.4, 5'-H), 7.43 (1H, d, J =7.3, 6'-H). Irradiation of the singlet due to the OCH_3 group at δ 3.88 induced enhancement of the doublet at δ 7.23(3'-H). *4-(2-Cyano-4-methoxyphenyl)-1-methyl-2-pyridone*; ^{1}H-NMR ($CDCl_3$) δ: 3.55 (3H, s, NCH_3), 6.72 (1H, d, J =1.8, 3-H), 6.38 (1H, dd, J =6.7 and 1.8, 5-H), 7.28 (1H, d, J =6.7, 6-H), 7.19 (1H, d, J =2.4, 3'-H), 3.86 (3H, s, 4'-OCH_3), 7.17 (1H, dd, J =7.3 and 2.4, 5'-H), 7.41 (1H, d, J =7.3, 6'-H). Irradiation of the singlet at δ 3.86 (4'-OCH_3) induced enhancement of the doublet at δ 7.19 (3'-H) and the double doublet at δ 7.17 (5'-H).

Photoreaction of 1 with 2g. Product (**3g**) (24 mg, 18%) was obtained. *4-(5-Cyano-2-hydroxyphenyl)-1-methyl-2-pyridone* (**3g**); colorless crystals from EtOH-C_6H_6, mp >300°C; (M^+, *m/z* 226.0743. $C_{13}H_{10}N_2O_2$ requires 226.0743); MS *m/z*: 226 (100 %), 225, 209; IR (KBr): 3000, 2215(CN), 1650(C=O); ^{1}H-NMR δ: 3.33 (3H, s, NCH_3), 6.58 (1H, d, J =1.8, 3-H), 6.43 (1H, dd, J =8.5 and 1.8, 5-H), 7.69 (1H, d, J =8.5, 6-H), 11.20 (1H, br, 2'-OH), 7.07 (1H, d, J =8.5, 3'-H), 7.68 (1H, dd, J =8.5 and 1.8, 4'-H), 7.78 (1H, d, J =1.8, 6'-H).

Photoreaction of 5 with 2a. An inseparable 3:1 mixture (50 mg, 42%) of **6a** and **7a**, and **8a** (12 mg, 10%) was obtained. *6-(2-Hydroxyphenyl)-1-methyl-2-pyridone* (**6a**); GLC-MS *m/z*: 201 (M^+), 200 (100%), 172; ^{1}H-NMR δ: 3.40 (3H, s, NCH_3), 6.62 (1H, dd, J =9.0 and 1.2, 3-H), 7.39 (1H, dd, J =9.0 and 6.8, 4-H), 6.23 (1H, dd, J =6.8 and 1.2, 5-H), 7.95 (1H, br, 2'-OH), 7.05 (1H, d, J =8.1, 3'-H), 7.35 (1H, ddd, J =8.1, 7.6 and 1.7, 4'-H), 6.97 (1H, dd, J =7.6 and 7.6, 5'-H), 7.16 (1H, dd, J =7.6 and 1.7, 6'-H). *6-(4-Hydroxyphenyl)-1-methyl-2-pyridone* (**7a**); GLC-MS *m/z*: 201 (M^+), 200 (100%), 172; ^{1}H-NMR δ: 3.40 (3H, s, NCH_3), 6.58 (1H, dd, J =9.0 and 1.2, 3-H), 7.39 (1H, dd, J =9.0 and 6.8, 4-H), 6.13 (1H, dd, J =6.8 and 1.2, 5-H), 6.95 (2H, d, J =8.6, 2'-H and 6'-H), 7.20 (2H, d, J =8.6, 3'-H and 5'-H), 7.80 (1H, br, 4'-OH). *1-Methyl-6-phenoxy-2-pyridone* (**8a**); colorless columns from *n*-hexane-C_6H_6, mp 82-84 °C (Anal. Calcd for $C_{12}H_{11}NO_2$: C, 71.62; H, 5.51; N, 6.96. Found: C, 71.83; H, 5.47; N, 6.93); MS *m/z*: 201 (M^+, 100%), 108; IR (KBr): 1655(C=O); ^{1}H-NMR ($CDCl_3$) δ: 3.63 (3H, s,), 6.27 (1H, dd, J =9.0 and 1.2, 3-H), 7.19 (1H, dd, J =9.0 and 6.8, 4-H), 5.03 (1H, dd, J =6.8 and 1.2, 5-H), 7.12 (2H, d, J =8.6, 2'-H and 6'-H), 7.44 (2H, dd, J =8.6 and 7.3, 3'-H and 5'-H), 7.29 (1H, dd, J =7.3 and 7.3, 4'-H).

Photoreaction of 5 with 2b. Products (**7b**) (3.5 mg, 3%) and (**8b**) (68 mg, 50%) were obtained. *6-(4-Hydroxy-3-methoxyphenyl)-1-methyl-2-pyridone* (**7b**); pale yellow plates from C_6H_6-EtOH, mp 194-196 °C (M^+ *m/z* 231.0893. $C_{13}H_{13}NO_3$ requires 231.0896); MS *m/z*: 231 (100 %), 230, 214; ^{1}H-NMR δ: 3.35 (3H, s, NCH_3), 6.58 (1H, dd, J =9.2 and 1.8, 3-H), 7.37 (1H, dd, J =9.2 and 6.7, 4-H), 6.10 (1H, dd, J =6.7 and 1.8, 5-H), 6.80 (1H, d, J =1.8, 2'-H), 3.92 (3H, s, 3'-OCH_3), 5.86 (1H, br, 4'-OH), 6.99 (1H, d, J =7.9, 5'-H), 6.85 (1H, dd, J =7.9 and 1.8, 6'-H). Irradiation of the singlet at δ 3.92 (3'-OCH_3)

induced enhancement of the doublet at δ 6.80. *1-Methyl-6-(2-methoxyphenoxy)-2-pyridone* (**8b**): colorless columns from hexanes-C_6H_6, mp 99-101 °C (Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.46; H, 5.63; N, 6.01); *m/z* 231 (M^+), 108 (100%); IR (KBr): 1660(C=O); ^{1}H-NMR ($CDCl_3$) δ: 3.19 (3H, s, NCH_3), 6.24 (1H, dd, *J* =9.2 and 1.2, 3-H), 7.20 (1H, dd, *J* =9.2 and 8.0, 4-H), 5.13 (1H, dd, *J* =8.0 and 1.2, 5-H), 3.67 (3H, s, 2'-OCH_3), 7.26 (1H, dd, *J* =7.3 and 1.8, 3'-H), 7.04 (2H, m, 4'-H and 5'-H), 7.15 (1H, dd, *J* =7.3 and 1.8, 6'-H).

Photoreaction of 5 with 2c. Products (**6c**) (28 mg, 20%) and (**8c**) (28 mg, 20%) were obtained. *6-(2-Hydroxy-4-methoxyphenyl)-1-methyl-2-pyridone* (**6c**): colorless needles from C_6H_6-EtOH, mp 250-252 °C (Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.50; H, 5.66; N, 6.01); MS *m/z*: 231 (M^+, 100%), 230, 214; IR (KBr): 2950(OH), 1640(C=O); ^{1}H-NMR δ: 3.25 (3H, s, NCH_3), 6.57 (1H, dd, *J* =9.2 and 1.8, 3-H), 7.37 (1H, dd, *J* =9.2 and 6.7, 4-H), 6.14 (1H, dd, *J* =6.7 and 1.8, 5-H), 7.98 (1H, br, 2'-OH), 6.64 (1H, d, *J* =1.8, 3'-H), 3.78 (3H, s, 4'-OCH_3), 6.55 (1H, dd, *J* =8.6 and 1.8, 5'-H), 7.02 (1H, d, *J* =8.6, 6'-H). Irradiation of the singlet at δ 3.78 (4'-OCH_3) caused enhancements of the signals at δ 6.64 (3'-H) and 6.55 (5'-H). *6-(3-methoxyphenoxy)-1-methyl-2-pyridone* (**8c**); colorless plates from C_6H_6-*n*-hexane, mp 99 °C (Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5,67; N, 6.06. Found: C, 67.74; H, 5.70; N, 6.06); MS *m/z*: 231 (M^+), 108 (100); IR (KBr): 1660(C=O); ^{1}H-NMR ($CDCl_3$) δ: 3.60 (3H, s, NCH_3), 6.29 (1H, dd, *J* =9.2 and 1.2, 3-H), 7.20 (1H, dd, *J* =9.2 and 7.3, 4-H), 5.37 (1H, dd, *J* =7.3 and 1.2, 5-H), 6.65 (1H, dd, *J* =2.4 and 2.4, 2'-H), 3.82 (3H, s, 3'-OCH_3), 6.68 (1H, dd, *J* =8.5 and 2.4, 4'-H), 7.32 (1H, dd, *J* =8.5 and 8.5, 5'-H), 6.82 (1H, dd, *J* =8.5 and 2.4, 6'-H).

Photoreaction of 5 with 2d. Products (**6d**) (30 mg, 22%) and (**8d**) (39 mg, 28%) were obtained. *6-(2-Hydroxy-5-methoxyphenyl)-1-methyl-2-pyridone* (**6d**); colorless plates from AcOEt-EtOH, mp 196 °C (Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.54; H, 5,67; N, 6.01); MS *m/z*: 231 (M^+, 100%), 230, 214; IR (KBr): 3080(OH), 1640(C=O); ^{1}H-NMR δ: 3.41 (3H, s, NCH_3), 6.58 (1H, dd, *J* =8.3 and 1.2, 3-H), 7.37 (1H, dd, *J* =8.3 and 6.7, 4-H), 6.23 (1H, dd, *J* =6.7 and 1.2, 5-H), 8.95 (1H, br, 2'-OH), 7.02 (1H, d, *J* =8.6, 3'-H), 6.88 (1H, dd, *J* =8.6 and 3.1, 4'-H), 3.81 (3H, s, 5'-OCH_3), 6.68 (1H, d, *J* =3.1, 6'-H). Irradiation of the singlet at δ 3.81 (5'-OCH_3) induced enhancements of the signals at δ 6.88 (4'-H) and 6.68 (6'-H). *6-(4-Methoxyphenoxy)-1-methyl-2-pyridone* (**8d**); colorless needles from C_6H_6-*n*-hexane, mp 132-134 °C (Anal. Calcd for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.70; H, 5.68; N, 5.94); MS *m/z*: 231 (M^+), 108 (100%); IR (KBr): 1655(C=O); ^{1}H-NMR ($CDCl_3$) δ: 3.63 (3H, s, NCH_3), 6.23 (1H dd, *J* =9.2 and 1.2, 3-H), 7.23 (1H, dd, *J* =9.2 and 7.3, 4-H), 5.23 (1H, dd, *J* =7.3 and 1.2, 5-H), 7.05 (2H, d, *J* =9.2, 2'-H and 6'-H), 6.92 (2H, d, *J* =9.2, 3'-H and 5'-H), 3.83 (3H, s, 4'-OCH_3).

Photoreaction of 5 with 2f. Products (**6f**) (54 mg, 40%) and (**8f**) (34 mg. 25%) were obtained. *6-(2-Cyano-6-hydroxyphenyl)-1-methyl-2-pyridone* (**6f**); colorless plates from AcOEt-EtOH, mp 231-233 °C

(Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.46; N, 12.38. Found: C, 68.72; H, 4.33; N, 12.37); MS *m/z*: 226 (M^+, 100%), 225, 209; IR (KBr): 3000(OH), 2220(CN), 1640(C=O); ^{1}H-NMR δ: 3.25 (3H, s, NCH_3), 6.65 (1H, dd, *J*= 9.2 and 1.2, 3-H), 7.58(1H, dd, *J* =9.2 and 6.7, 4-H), 6.38 (1H, dd, *J* =6.7 and 1.2, 5-H), 7.23 (1H, dd, *J* =8.6 and 1.2, 3'-H), 7.51 (1H, dd, *J* =8.6 and 8.6, 4'-H), 7.38 (1H, dd, *J* =8.6 and 1.2, 5'-H), 10.21 (1H, br, 6'-OH). *6-(3-Cyanophenoxy)-1-methyl-2-pyridone* (**8f**); colorless plates from C_6H_6, mp 115-117 °C (Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.46; N, 12.38. Found: C, 68.86; H, 4.36; N, 12.37); MS *m/z*: 226 (M^+), 108 (100%); IR (KBr): 1655(C=O); ^{1}H-NMR ($CDCl_3$) δ: 3.53 (3H, s, NCH_3), 6.27 (1H, dd, *J* =9.2 and 1.2, 3-H), 7.16 (1H, dd, *J* =9.2 and 6.7, 4-H), 5.25 (1H, dd, *J* =6.7 and 1.2, 5-H), 7.32 (1H, dd, *J* =3.1 and 2.4, 2'-H), 7.53 (1H, dd, *J* =7.5 and 2.4, 4'-H), 7.35 (1H, m, 5'-H), 7.54 (1H, dd, *J* =8.5 and 3.1, 6'-H).

Photoreaction of 5 with 2g. Product (**6g**) (74 mg, 54%) was obtained. *6-(5-Cyano-2-hydroxyphenyl)-1-methyl-2-pyridone* (**6g**); colorless needles from EtOH, mp 280-282 °C (Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.46; N, 12.38. Found: C, 68.77; H, 4.30; N, 12.41); MS *m/z*: 226 (M^+, 100%), 225, 209; IR (KBr): 3000(OH), 2210(CN), 1640(C=O); ^{1}H-NMR δ: 3.32 (3H, s, NCH_3), 6.42 (1H, dd, *J* =9.2 and 1.2, 3-H), 7.24 (1H, dd, *J* =9.2 and 6.7, 4-H), 6.11 (1H, dd, *J* =6.7 and 1.2, 5-H), 11.34 (1H, br, 2'-OH), 7.10 (1H, d, *J* =8.6, 3'-H), 7.79 (1H, dd, *J* =8.6 and 2.4, 4'-H), 7.72 (1H, d, *J* =2.4, 6'-H).

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