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ATMOSPHERE DEPENDENT PHOTOREACTION OF METHYL 4-PYRIDINECARBOXYLATE IN METHANOL. METHOXYLATION AT 3-POSITION UNDER O_2 AND METHOXYLATION AND HYDROXYMETHYLATION AT 2-POSITION UNDER N_2

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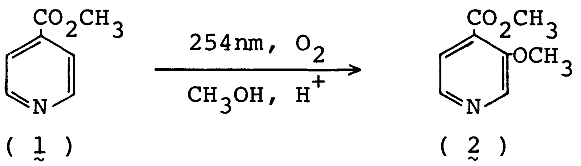
The UV-Irradiation of methyl 4-pyridinecarboxylate in methanol under oxygen in the presence of H_2SO_4 brings about methoxylation at the 3-position of the pyridine ring, while under nitrogen methoxylation and hydroxymethylation occur at the 2-position.

In previous papers[1-4] we have reported pronounced photoreactivities of 2- and 3-pyridinecarboxylic esters: parallel occurrence of radical reaction (alkylation) and ionic reaction (alkoxylation), different paths to give the same product, and the coexistence of several different excited states of the same multiplicity. The photoreactions of pyridinecarboxylic esters depend on the reaction conditions, especially, the acidity of the solutions and polarity of the solvent alcohol.

We report here a remarkable atmosphere dependence of photoreactions of methyl 4-pyridinecarboxylate(**1**): the presence of oxygen changes dramatically the position of methoxylation.

The irradiation of methyl 4-pyridinecarboxylate (nomally 50 cm^3 solution containing 0.02 mol dm^{-3} of **1**) in the presence of H_2SO_4 in methanol under oxygen atmosphere with a low pressure mercury lamp for 25 min at 30°C gave methyl 3-methoxy-4-pyridinecarboxylate(**2**)[5] quantitatively (Table 1).



(**1**) (**2**)

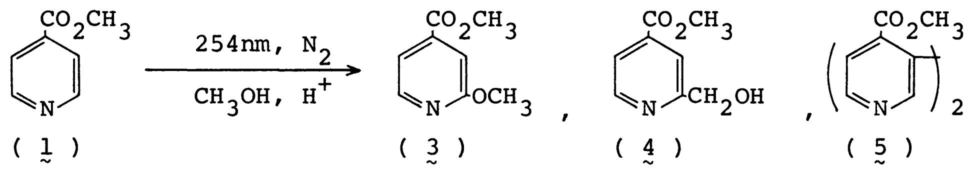


Table 1. Photoreactions of methyl 4-pyridinecarboxylate(1) in acidic methanolic solutions. [1] = 0.02 mol dm^{-3}; Irradiation time, 25 min; Temp., 30°C.

[H_2SO_4] / mol dm^{-3}	Atmosphere	Conversion of 1 / %	(Yield of product)$^{a)}$/%			
			2	3	4	5
0.25	O_2	14	88	trace	-	-
0.25	N_2	47.5	trace	14	5.5	trace

a) Yields were determined by means of GLC and/or HPLC, and were calculated on the basis of 1 consumed.

On the other hand, in the irradiation under nitrogen atmosphere, methyl 2-methoxy-4-pyridinecarboxylate(3),$^{5)}$ methyl 2-hydroxymethyl-4-pyridinecarboxylate (4),$^{5)}$ and a trace of 3,3'-dimer(5)$^{5)}$were obtained.

The photoreaction of 1 is characterized by the fact that the presence of oxygen causes a dramatic change of photoreaction. Such a remarkable oxygen effect was not observed in the photoreactions of 2- and 3-pyridinecarboxylic esters.

The effects of anthracene on the two methoxylations are different, as shown in the Stern-Volmer plots (Figs. 1 and 2).$^{6)}$ These figures indicate that methoxylation under N_2 is inhibited by anthracene effectively, while that under O_2 is not inhibited by anthracene at all.

Although the photo-methoxylation at the 2-position under N_2 is inhibited by anthracene, benzene, and triphenylene, it is slightly affected by *trans*-1,3-pentadiene (Table 2). The inhibition of photo-methoxylation under N_2 by aromatic hydrocarbons could be explained not by the triplet energy transfer, but by an electron transfer from the aromatic hydrocarbons to the excited 1. A similar result has been obtained in the photo-methoxylation of methyl 2-pyridinecarboxylate.$^{3)}$ Thus, methoxylation under N_2 should originates from a singlet state.

For the photo-methoxylation at the 3-position under O_2, the contribution of an comlex between 1 and oxygen can be postulated because the absorbance of the 1 - O_2 system in 235 - 255 nm region is greater than that of 1 under N_2 in CH_3CN.

A feature of the photoreaction is that oxygen promotes an ionic reaction.

A few reports on the similar promotion of photochemical ionic reactions by oxygen have appeared except for alcoholyses of benzotrichloride[7)] and for alcoholyses of trihaloacetyl groups.[8)]

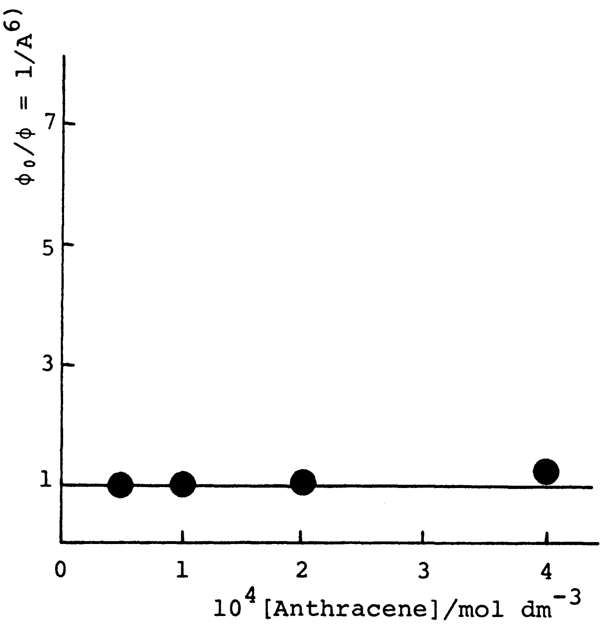


Fig. 1. Stern-Volmer plot for an effect of anthracene on the photoreaction of **1** in methanol under O_2 atmosphere.

[**1**] = 0.01 mol dm^{-3}, $[H_2SO_4]$ = 0.05 mol dm^{-3}; Irradiation time, 1 h; Temp., 20°C.

-●- : **2**

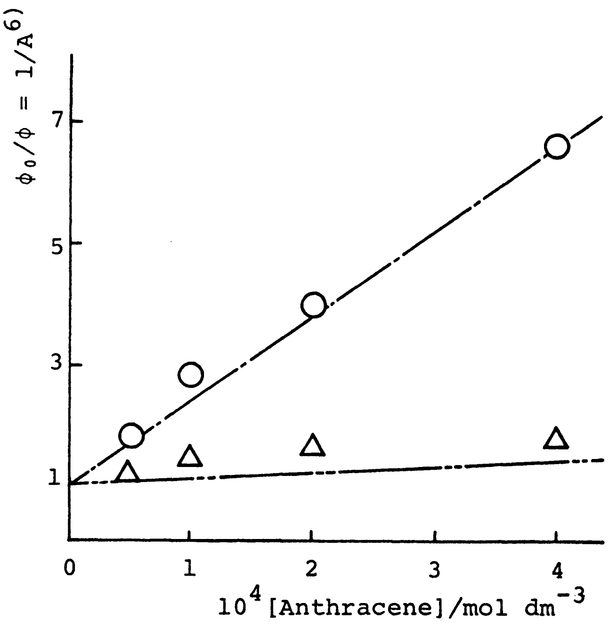


Fig. 2. Stern-Volmer plots for effects of anthracene on the photoreaction of **1** in methanol under N_2 atmosphere.

[**1**] = 0.01 mol dm^{-3}, $[H_2SO_4]$ = 0.05 mol dm^{-3}; Irradiation time, 1 h; Temp., 20°C.

-○-- : **3**, -△-- : **4**

Table 2. Effects of additives on the photo-methoxylation of **1**

Atmosphere	Additive	[Additive] / mol dm^{-3}	Ratio of light absorbed by **1**(=L)[6)]	Relative Yield(=A)[6)]	
				2	**3**
O_2	*trans*-1,3-Pentadiene	4×10^{-4}	1.00	1.24	-
N_2	*trans*-1,3-Pentadiene	4×10^{-4}	1.00	-	0.90
N_2	Benzene	1×10^{-1}	0.69	-	0.96
N_2	Triphenylene	3×10^{-4}	0.69	-	0.32

[**1**] = 1×10^{-2} mol dm^{-3}; [H_2SO_4] = 5×10^{-2} mol dm^{-3}; Irradiation time, 1 h; Temp., 20°C.

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5) **2**: mp, 55-56.5°C; IR(KBr), 1720(ester C=O) and 1220cm^{-1}(C-O-C); ^{1}H NMR($CDCl_3$) δ = 8.44(1H,s), 8.29(1H,d,J=4Hz), 7.55(1H,d,J=4Hz), 4.02(3H,s) and 3.91(3H,s); MS(70eV), m/z (rel intensity) 167(M^+;77), 152(14), 138(18), 136(100), 135(18), 133(31), Found: m/z 167.0585. Calcd for $C_8H_9NO_3$:M, 167.0583.

   3: mp, 33-34.5°C; ^{1}H NMR spectra are in accord with those obtained by Deady *et al.* (L.W.Deady, P.M.Harrison, and R.D.Topsom, *Org. Magn. Reson.*, 7, 41 (1975); L.W.Deady, private communication).

   4: mp, 67.5-68°C (lit,68-69°C); The spectral data are in accord with those obtained by Ninomiya (I.Ninomiya, private communication).

   5: mp, 184-187°C(sub); IR(KBr), 1720cm^{-1}(ester C=O); ^{1}H NMR($CDCl_3$) δ = 8.95 (1H,d,J=1.6Hz), 8.85(1H,d,J=5Hz), 7.87(1H,dd,J=1.6 and 5Hz), and 4.00(3H,s); Found: C, 61.7; H, 4.7; N, 10.2 %;M^+, 272. Calcd for $C_{14}H_{12}N_2O_4$: C, 61.76; H, 4.44; N, 10.29 %;M, 272.

6) In this case, the effects of additives were analyzed by means of an index A, the relative quantum yield calculated on the basis of the light absorbed by **1**, because the additives absorb the 254 nm light competitively with **1**. A^{-1} corresponds to ϕ_0/ϕ in the Stern-Volmer plots for the quenching experiment.
   A = Y/L, Y = (Yield in the presence of additive(**Q**))/(Yield in the absence of additive(**Q**)), $L = \varepsilon_{\mathbf{1}}[\mathbf{1}]/(\varepsilon_{\mathbf{1}}[\mathbf{1}] + \varepsilon_{\mathbf{Q}}[\mathbf{Q}])$, where $\varepsilon_{\mathbf{1}}$ and $\varepsilon_{\mathbf{Q}}$ are the molar absorption coefficients of **1** and **Q** at 254 nm, respectively.

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