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PHOTOREACTIONS OF HETEROAROMATIC COMPOUNDS V*[1]
PHOTOCHEMICAL ALKOXYLATION OF METHYL 2-PYRIDINECARBOXYLATE VIA EXCIMER

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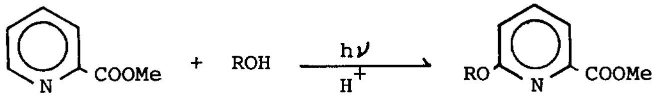
In the previous paper,[1)] we reported that 2-pyridinecarboxylic acid undergoes photo-alkoxylation in acidic alcohol solutions and that the photo-alkoxylation occurs only at higher concentration of the substrate (above 10^{-4} M*[2]). In the present paper, we report a similar photoreaction of methyl 2-pyridinecarboxylate in alcohol solutions and some evidences for the participation of the excimer in the photo-alkoxylation.

Methyl 2-pyridinecarboxylate gives methyl 6-methoxy-, 6-ethoxy and 6-(2-propoxy)-2-pyridinecarboxylate in the irradiation at 254 nm under nitrogen in methanol, ethanol and 2-propanol each containing 5 x 10^{-2}M of sulfuric acid, respectively. The physical data of the photo-products are summarized in Table 1.



R = Me, Et and 2-Pr

The photoreaction is almost quantitative, no other products being obtained (Table 2). The photo-alkoxylation does not occur in the absence of mineral acids.

Similar to 2-pyridinecarboxylic acid, the photo-alkoxylation occurs at higher concentration of methyl 2-pyridinecarboxylate as is seen in Fig. 1. The concentration dependence suggests the participation of a sort of dimer of the substrate (either in the ground state or in the excited state) in the photoreaction. The mechanism involving the excimer (Scheme 1) gives the following kinetic relationship;

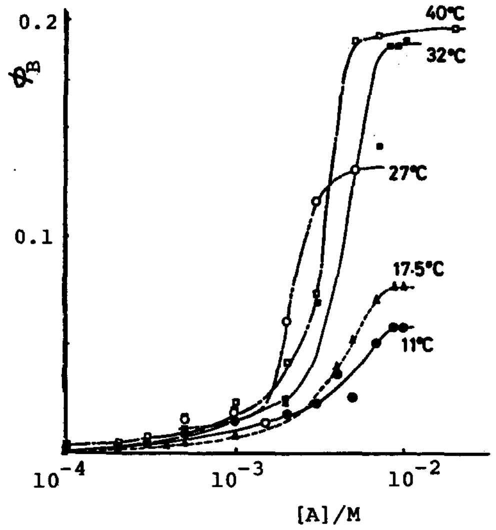
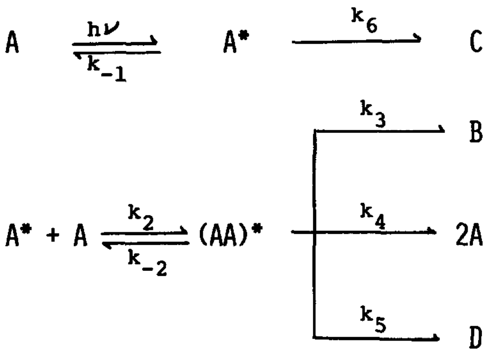
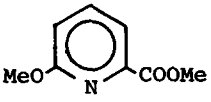
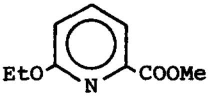
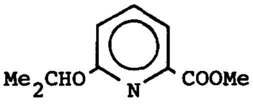


Fig. 1 Dependence of the quantum yield of photo-methoxylation on the concentration of methyl 2-pyridinecarboxylate



Scheme 1 The mechanism of photo-alkoxylation
A, Reactant; B, Alkoxylated compound; C and D, Products of side reactions; (AA)*, Excimer

Table 1 Photo-products in the irradiation of methyl 2-pyridinecarboxylate with 254 nm light in alcohol solutions each containing 0.05 M of H_2SO_4

Solvent	Metanol	Ethanol	2-Propanol
Product			
Mp/°C	34.5-35	liquid	liquid
λ_{max}/nm	287	289	291
NMR spectra (δ)			
H at 3 position H at 5 position	7.65(d) or 7.66(d)	7.60(d)	7.60(d)
H at 4 position	6.90(q)	6.83(t)	6.74(t)
PyO-$\underline{CH}_n$-	3.95(s)	4.40(q)	5.35(septet)

Elemental analysis of methyl 6-methoxy-2-pyridinecarboxylate. Found: C, 57.32; H, 5.51; N, 8.37%. Calcd. for $C_8H_9NO_3$: C, 57.40; H, 5.38; N, 8.38%.

Methyl 6-ethoxy-2-pyridinecarboxylate was identified by comparing IR and NMR spectra with those of 6-ethoxy-2-pyridinecarboxylic acid after hydrolysis with sodium hydroxide.

Table 2 Yield of methyl 6-methoxy-2-pyridinecarboxylate in the irradiation with 254 nm in acidic methanol solution at 32 °C at various concentrations

Conc. of starting material (M)	Irradiation time (min)	Decrease in conc. of reactant (M)	Increase in conc. of product (M)	Yield [a)]
10^{-4}	4	1.16×10^{-4}	9.4×10^{-5}	81
2×10^{-3}	4	1.42×10^{-4}	1.39×10^{-4}	98
3×10^{-3}	2	2.08×10^{-4}	1.97×10^{-4}	95
7×10^{-3}	2	4.45×10^{-4}	4.03×10^{-4}	90

a) Yield = 100 x (Amount of product)/(Amount of reactant consumed)

$$\Phi_B = \frac{k_3[A]/(k_3 + k_4)}{k_{-1}(k_{-2} + k_3 + k_4 + k_6)/k_2(k_3 + k_4) + [A]}$$

where Φ_B is the quantum yield of the product via excimer and [A] is the initial concentration of methyl 2-pyridinecarboxylate.

The plot of $1/\Phi_B$ against $1/[A]$ in the photoreaction in methanol at 11 °C resulted in a straight line (Fig. 2) as predicted by the above equation and the mechanism via excimer is kinetically supported. A similar linearity may result, if a mechanism involving the excitation of the dimer formed in the ground state is assumed. The latter mechanism is, however, not as much plausible, because

1) the UV-spectra of methyl 2-pyridinecarboxylate in higher concentration, where photo-alkoxylation occurred effectively, were identical with those in lower concentrations and
2) the exciting light of 254 nm is thus absorbed mostly by monomeric methyl 2-pyridinecarboxylate. The considerably high quantum yield of 0.2 for alkoxylation (methoxylation at 40 °C) can not be explained by the dimer formation in the ground state.

Since methyl 2-pyridinecarboxylate is not fluorescent, independently of concentration even at liquid nitrogen temperature, no direct evidence for the excimer obtained. However, the excimer of quinoline and isoquinoline have been established on the basis of emmission spectra.[2)] These facts support the mechanism via excimer.

The photo-alkoxylation is dependent on temperature. The limitting quantum yield (α) of photo-methoxylation increased with temperature (Fig. 1), whereas the threshold concentration for photo-methoxylation was slightly dependent on temperature.

The fact that the photo-alkoxylation is quantitative indicates that k_5 and k_6 are negligible under this condition. It follows from the above Equation that

$$\alpha = k_3/(k_3 + k_4)$$
$$\beta = k_{-1}(k_{-2} + k_3 + k_4)/k_2(k_3 + k_4)$$

where α is the limitting quantum yield, $\lim_{[A]\to\infty} \phi_B$, and β is the concentration at which $\phi_B = \alpha/2$. It is reasonable to assume $k_{-2} \gg k_3, k_4$. Hence

$$(1 - \alpha)/\alpha = k_4/k_3$$

$$\beta/\alpha = (k_{-2}/k_2)(k_{-1}/k_3)$$

The slope of the Arrhenius plot of $(1 - \alpha)/\alpha$ corresponds to the difference in activation energies of Reaction(4) and (3); $\Delta H_4^{\ddagger} - \Delta H_3^{\ddagger}$. Fig. 3 indicates that this value is -9 kcal/mol. Since the activation energy of radiationless transition such as Reaction(-1) and (4) is less than a few kcal/mol,3) Reaction(3) in which the excimer is converted to the methoxylated compound requires activation energy of about 10 kcal/mol.

Arrhenius plot of β/α gave $-\Delta H + \Delta H_{-1}^{\ddagger} - \Delta H_3^{\ddagger} = -10$ kcal/mol, where ΔH is the enthalpy change in the excimer formation. Considering the above $\Delta H_3^{\ddagger}$ value, the energy of excimer formation would be small.

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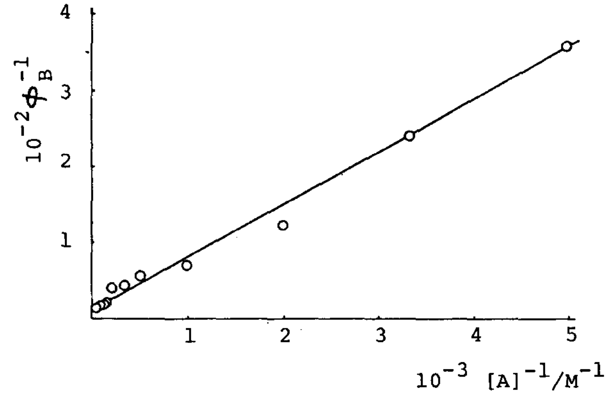

Fig. 2 Relation between $1/\phi_B$ and $1/[A]$ in the photo-methoxylation at 40 °C

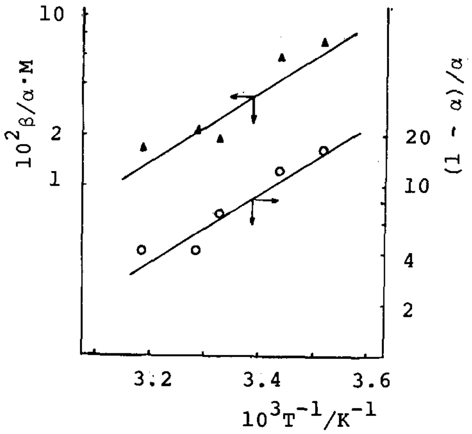

Fig. 3 Arrhenius plots of $(1 - \alpha)/$ and β/α

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*2 M = mol/dm^{-3}

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