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PHOTOREACTIONS OF HETEROAROMATIC COMPOUNDS VII*
PROMOTION AND INHIBITION OF PHOTO-METHOXYLATION OF METHYL 2-PYRIDINECARBOXYLATE IN ACIDIC METHANCLIC SOLUTIONS BY ADDITIVES. SPECIFIC PROMOTION BY 4-SUBSTITUTED PYRIDINES

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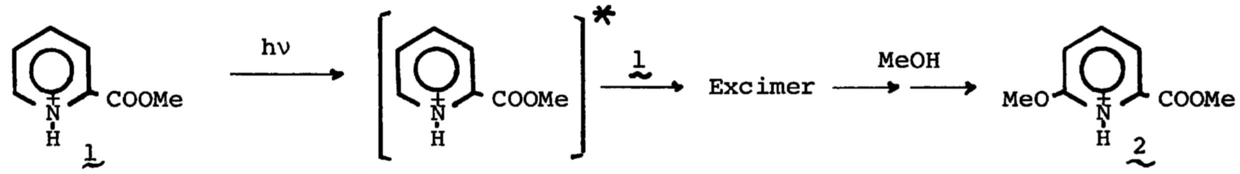
Photo-methoxylation of methyl 2-pyridinecarboxylate at 6-position is promoted specifically by 4-substituted pyridines. Substituted pyridines at 2- or 3-position have no effect or inhibit the process. Many other substances including sensitizers (singlet or triplet), electron donors and acceptors do not promote the photo-methoxylation.

We have reported that 2-pyridinecarboxylic acid derivatives undergo concentration dependent photo-alkoxylation in alcoholic solutions acidified with sulfuric acid and have proposed the mechanism via an excimer.[1-3]



We report here the specific promotion of photo-methoxylation of methyl 2-pyridinecarboxylate (**1**) by substituted pyridines.

Effect of additives on the photoreaction of **1** was examined in the lower concentration range of **1**, $2.5 - 10 \times 10^{-4}$ mol dm^{-3}, where the self promotion of **1** is low. Methanolic solutions of **1** acidified with sulfuric acid (5×10^{-2} mol dm^{-3}) were irradiated by 254 nm light from a low pressure mercury lamp at 32°C under nitrogen in the presence of additives ($2 - 100 \times 10^{-4}$ mol dm^{-3}) or in their absence.

Aliquots of solution were taken out at regular time intervals. The formation of methyl 6-methoxy-2-pyridinecarboxylate(**2**) was measured by means of UV-spectra or gas-chromatography. To avoid errors resulting from the intensity fluctuations of the light source, the solutions with and without additives were irradiated at the same time.

The effect of additives can be represented by an index A defined in Table 1. As the molar absorption coefficient of **1** at 254 nm is 4150 $(\mathrm{mol/dm^3})^{-1}\cdot\mathrm{cm}^{-1}$, 90 % of the incident 254 nm light is absorbed by 2.4 mm of light pass through

Table 1. Effect of additives on the formation of methyl 6-methoxy-2-pyridinecarboxylate(**2**) from methyl 2-pyridinecarboxylate (**1**)

$$L = \frac{\text{Quantity of light absorbed by } \mathbf{1}}{\text{Quantity of light absorbed by } \mathbf{1} \text{ and additive}}$$

$$Y = \frac{\text{Yield of } \mathbf{2} \text{ in the presence of additive}}{\text{Yield of } \mathbf{2} \text{ in the absence of additive}}$$

$A = Y/L$ ($A > 1$, promotion; $0 < A < 1$, inhibition)

Additive	$\frac{[\text{Additive}]\cdot 10^3}{\text{mol dm}^{-3}}$	$\frac{[\mathbf{1}]\cdot 10^3}{\text{mol dm}^{-3}}$	L	Y	A
Benzene	1.0	1.0	0.96	0.83	0.86
	10	1.0	0.68	0.62	0.91
Naphthalene	6.0	1.0	0.16	0.055	0.34
Acetophenone	1.0	1.0	0.45	0.44	1.0
	3.0	1.0	0.21	0.21	1.0
Anisole	1.0	1.0	0.74	0.72	0.97
Ferrocene	1.0	1.0	0.64	0	0
1,2,4,5-Tetracyanobenzene	1.0	0.25	0.17	0	0
Nitrobenzene	1.0	0.25	0.27	0	0
2-Pyridinecarbonitrile	1.0	1.0	0.62	0.56	0.90
2-Pyridinecarboxamide	0.2	1.0	0.85	0.77	0.91
	1.0	1.0	0.53	0.44	0.83
2-Hydroxypyridine	0.2	1.0	0.92	0.73	0.79
2-Aminopyridine	0.2	1.0	0.98	1.10	1.1
	1.0	1.0	0.90	0.97	1.1
3-Pyridinecarbonitrile	1.0	1.0	0.61	0.59	0.97
3-Pyridinecarboxamide	1.0	1.0	0.22	0	0
3-Hydroxypyridine	0.2	1.0	0.98	0.64	0.65
	1.0	1.0	0.90	0.58	0.64
3-Aminopyridine	0.2	1.0	0.67	0.58	0.87
	1.0	1.0	0.29	0.26	0.89
3-Methylpyridine	1.0	1.0	0.23	0	0

Table 1 continued

Additive	$\frac{[\text{Additive}]\cdot 10^3}{\text{mol dm}^{-3}}$	$\frac{[\mathbf{1}]\cdot 10^3}{\text{mol dm}^{-3}}$	L	Y	A
Methyl 4-pyridine-carboxylate	0.1	1.0	0.93	4.2	4.5
	0.3	1.0	0.81	4.0	4.9
4-Pyridinecarbonitrile	0.1	1.0	0.96	1.9	2.0
	1.0	1.0	0.73	4.0	5.5
4-Pyridinecarboxamide	0.2	1.0	0.83	1.6	1.9
	1.0	1.0	0.49	1.2	2.4
4-Hydroxypyridine	1.0	1.0	0.87	2.8	3.2
4-Aminopyridine	0.1	1.0	0.76	0.93	1.2
4-Methylpyridine	0.2	0.4	0.50	0.75	1.5
	1.0	0.4	0.17	0.75	4.4

10^{-3} mol dm^{-3} solution of **1**. Considering that the diameter of the quartz cell used is 3 cm, the absorption of 254 nm light is complete even in the absence of additives. When the mixture of **1** and an additive is illuminated, the incident 254 nm light is distributed between **1** and the additive according to $\varepsilon \cdot c$ (ε, molar absorption coefficient at 254 nm; c, concentration). Index L represents the fraction of 254 nm light absorbed by **1**. Index Y is the ratio of the yield of **2** in the presence of an additive to that in its absence. Index A (=Y/L) is the relative quantum yield of **2** calculated on the basis of the light absorbed by **1**. The value A is the ratio of the observed quantum yield of **2** in the presence of additives to the one expected under the assumption that the light absorbed by **1** gives **2** without any interaction with additives. When A is greater than unity, the additives promote the formation of **2**, while when A is smaller than unity the additives inhibit the formation of **2**. A = 1 means that the additives have no effect.

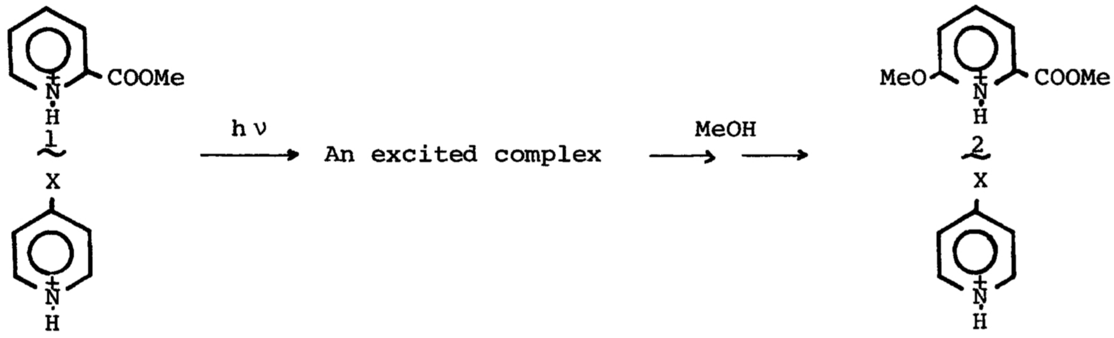
The effects of some aromatic compounds including representative sensitizers are listed in Table 1. Benzene and naphthalene, which have been reported to behave as singlet sensitizers,[4)] have no effect or an inhibiting effect. Acetophenone, an effective triplet sensitizer, has no effect. Electron donor-acceptor interactions do not promote photo-methoxylation of **1**. Strong electron donors (anisole, naphthalene, and ferrocene) and strong electron acceptors (1,2,4,5-tetracyanobenzene and nitrobenzene) have no effect or an inhibiting effect.

Among the additives examined, 4-substituted pyridines promote effectively the formation of **2**. The effect is very specific for 4-substituted pyridines. All the tested 4-substituted pyridines, with either electron donating or accepting groups, showed a promoting effect, while 2- and 3-substituted pyridines have no effect or an inhibiting one.

The promotion due to 4-substituted pyridines are generally more effective than the promotion due to the increase in the concentration of **1** itself.[2)] For example, 10^{-3} mol dm^{-3} of 4-pyridinecarbonitrile(**3**) in 10^{-3} mol dm^{-3} solution of **1** gives 5.5 times the yield of **2** which is obtained in the absence of **3** . By comparison, the formation of **2** in the absence of **3** at [**1**] = 2×10^{-3} mol dm^{-3} (a concentration of which is equal to [**1**] + [**3**] in the former case) is only 1.2 times greater than that at [**1**] = 10^{-3}mol dm^{-3}.

The effect of 4-substituted pyridines is catalytic. In **1** - **3** system, the recovery of **3** was almost quantitative after the photoreaction (97 % in the case of 7×10^{-4} mol dm^{-3} of **3**).

Considering that the photo-methoxylation of **1** in the absence of **3** proceeds via an excimer,[2)] it should be reasonable to postulate an excited state complex between **1** and 4-substituted pyridine, which is formed by the interaction of the excited **1** with an additive and/or by the interaction of the excited additive with **1** . The complex would finally give **2** .



X = CN, COOMe, $CONH_2$, OH, NH_2, CH_3

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