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Substitution of Cyano Group by Hydroxyalkyl Group and of Ring Hydrogen by Alkoxyl Group in UV-Irradiation of 2-Pyridinecarbonitrile in Alcohols

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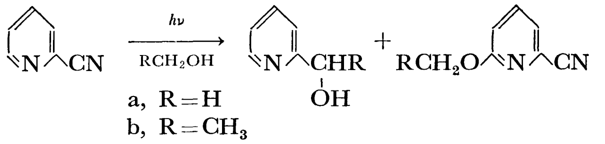
The UV-irradiation of 2-pyridinecarbonitrile(**1**) in methanol and in ethanol brings about the replacement of the cyano group by the hydroxyalkyl groups and the replacement of the ring hydrogen by the alkoxyl group. Free base-form of **1** in ethanol undergoes exclusively photo-hydroxyethylation, while the pyridinium form of **1** in ethanol undergoes both photo-hydroxyethylation *via* a singlet excited state and -ethoxylation *via* a singlet-excited state complex, which is quenched by the electron transfer from the aromatic hydrocarbons to the excited complex.

Photochemical reactions of aromatic carbonitriles have been extensively investigated, especially from the viewpoint of the photoreactions *via* charge transfer complexes either in the ground state or in the excited state.[1,2] Concerning the photoreactions of quinolinecarbonitriles in alcohols, Hata *et al.* reported the substitution of the cyano group by the hydroxyalkyl groups derived from the solvent alcohols.[3] A similar photosubstitution has been reported for 4-pyridinecarbonitrile–triethylamine system.[4] Most of the reported photoreactions of aromatic and heteroaromatic nitriles are the substitution of CN in radical processes.

Another photoreactivity is expected for pyridinecarbonitriles: As a member of pyridinecarboxylic acid derivatives,[5,6] they are expected to undergo ionic type reactions. The main concern of our present study is to clarify in the photoreactions of pyridinecarbonitriles whether ionic processes similar to those of pyridinecarboxylic esters occur actually in parallel with radical processes or not and further what kinds of excited states are responsible for photoreactions.[7]

Results and Discussion

The UV-irradiation of 2-pyridinecarbonitrile (**1**) in alcohols brings about the replacement of the cyano group by the hydroxyalkyl group and the replacement of the ring hydrogen by the alkoxyl group (Table 1).



1 **2** **3**

The former reaction is similar to that reported for quinolinecarbonitriles[3] and the latter to that reported for 2-pyridinecarboxylic ester.[6]

A detailed study was done mainly on the **1**–ethanol system. Which of the reactions is dominant is dependent on the reaction conditions: 1) the presence or the absence of the added acids, 2) the nature of the added acids, and 3) the concentration of **1**. Additives (quenchers) affect photo-ethoxylation and -hydroxyethylation differently.

Table 1 and Fig. 1 show the effect of sulfuric acid on the photoreaction. In the absence of sulfuric acid, hydroxyethylation occurs exclusively. However, ethoxylation becomes significant as the concentration of sulfuric acid increases.

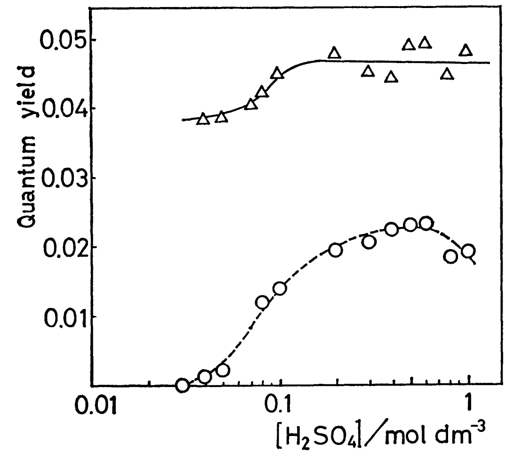


Fig. 1. Dependence of photo-hydroxyethylation and -ethoxylation of **1** on the concentration of sulfuric acid.
[1]=0.04 mol dm^{-3}, —△—: **2b**, --○--: **3b**.

Like the photo-methoxylation of methyl 2-pyridinecarboxylate[6] and 2-pyridinecarboxylic acid,[8] the photo-ethoxylation of 2-pyridinecarbonitrile shows a remarkable concentration dependence (Fig. 2). Such behavior, *i.e.*, that alkoxylation is efficient at higher concentrations of the substrates, is an important common feature of 2-pyridinecarboxylic acid derivatives. A kinetic analysis for photo-methoxylation of methyl 2-pyridinecarboxylate shows that the concentration dependence is due to the formation of an excimer which undergoes alkoxylation.[6] A similar mechanism can be applied to the photo-ethoxylation of **1**.

An attempt to obtain direct evidence for the exsistence of an excimer by means of emission spectral measurement was unsuccessful because no fluorescence from **1** was observed either in lower or higher concentration of **1**.

In order to identify the excited species responsible for hydroxyethylation and ethoxylation, the effects of *trans*-1,3-pentadiene, anthracene, naphthalene, fluorene, and azulene were analyzed. Because some additives

TABLE 1. YIELDS OF PRODUCTS IN PHOTOREACTION OF 2-PYRIDINECARBONITRILE(**1**) IN ALCOHOLS

Alcohol	$\frac{[\mathbf{1}]}{\text{mol dm}^{-3}}$	$\frac{[H_2SO_4]}{\text{mol dm}^{-3}}$	$\frac{\text{Irr. time}^{a)}}{\text{h}}$	Yield of product$^{b)}$ / % **2**	Yield of product$^{b)}$ / % **3**	$\frac{\text{Recovery of } \mathbf{1}}{\%}$
Methanol	5×10^{-2}	5×10^{-2}	24	9	9	41
	1×10^{-2}	1×10^{-1}	24	8	15	52
Ethanol	4×10^{-2}	—	1	15	0	57
	4×10^{-2}	5×10^{-1}	1	15	7	82

a) Different light sources were used for the reactions in methanol and in ethanol.

b) $\text{Yield} = 100 \times \frac{\text{Amount of product formed}}{\text{Amount of } \mathbf{1} \text{ consumed}}$.

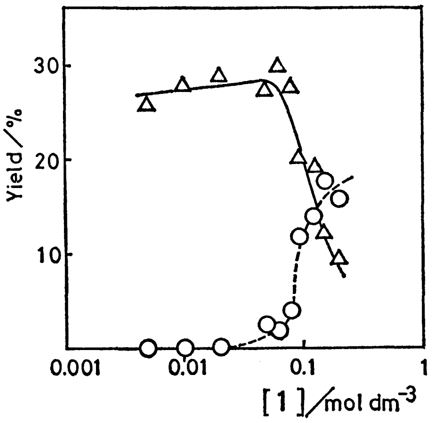
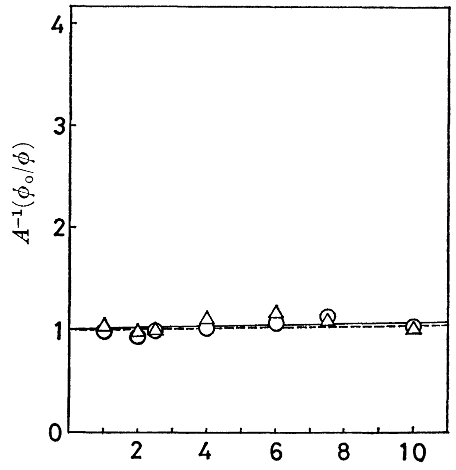
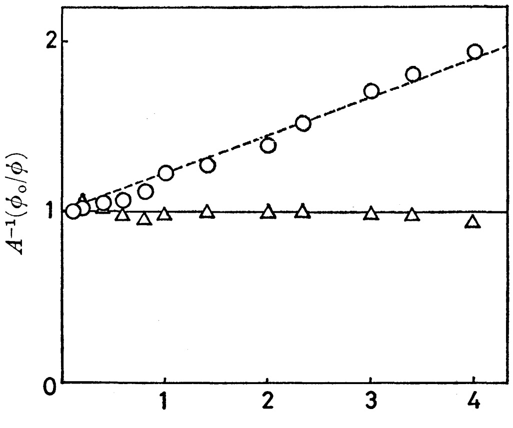


Fig. 2. Dependence of the yields of **2b** and **3b** on the concentration of **1**.
$[H_2SO_4] = ([\mathbf{1}]+0.05)$ mol dm^{-3},
$\text{Yield} = 100 \times \frac{\text{Amount of product formed}}{\text{Amount of } \mathbf{1} \text{ consumed}}$,
—△—: **2b**, --○--: **3b**.



10^4[*trans*-1,3-Pentadiene]/mol dm^{-3}

Fig. 3. Effects of *trans*-1,3-pentadiene on photo-hydroxyethylation and -ethoxylation of **1**.
$[\mathbf{1}]=0.04$ mol dm^{-3}, $[H_2SO_4]=0.2$ mol dm^{-3}, —△—: **2b**, --○--: **3b**.



10^3[Fluorene]/mol dm^{-3}

Fig. 4. Effects of fluorene on photo-hydroxyethylation and -ethoxylation of **1**.
$[\mathbf{1}]=0.04$ mol dm^{-3}, $[H_2SO_4]=0.2$ mol dm^{-3}, —△—: **2b**, --○--: **3b**.

absorb the 254 nm light competitively with the substrate, the effects of the additives were analyzed by means of an index, A, the relative quantum yield calculated on the basis of the light absorbed by the substrate:

$$A = Y/L$$

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

$$L = \frac{\varepsilon_1 c_1}{\varepsilon_1 c_1 + \varepsilon_Q c_Q},$$

where ε_1 and ε_Q are the molar absorption coefficients of **1** and the additive at 254 nm, respectively. Symbols c_1 and c_Q are the concentrations of **1** and the additive. A^{-1} corresponds to ϕ_0/ϕ for the Stern-Volmer equation in the quenching experiment (ϕ_0, quantum yield in the absence of a quencher; ϕ, quantum yield in the presence of a quencher).

trans-1,3-Pentadiene, an effective triplet quencher, (E_T=244 kJ/mol[9]), inhibits neither the photo-hydroxyethylation nor the photo-ethoxylation (Fig. 3). However, the quenching by fluorene (Fig. 4) shows a different feature from that by *trans*-1,3-pentadiene. Fluorene, the triplet energy of which is higher (E_T for fluorene, 284 kJ/mol[9]) than that of *trans*-1,3-pentadiene, inhibits photo-ethoxylation of **1**. On the other hand, fluorene exhibits no quenching during the photo-hydroxyethylation.

This characteristic of the quenching by fluorene is common for those by aromatic hydrocarbons, as are shown in the Stern-Volmer plots for the quenching by anthracene (Fig. 5), naphthalene (Fig. 6), and benzene (Fig. 7). Even benzene, which can be used as

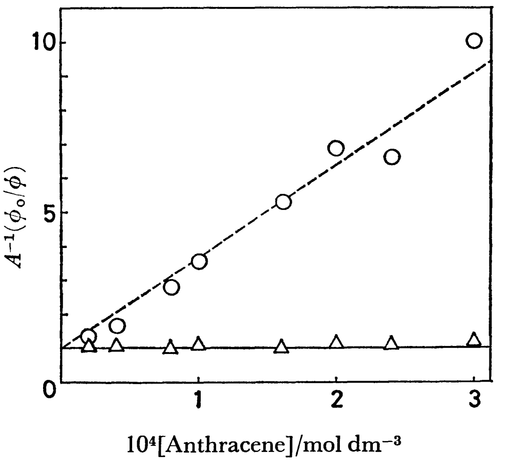


Fig. 5. Effects of anthracene on photo-hydroxyethylation and -ethoxylation of **1**.
[**1**]=0.04 mol dm^{-3}, [H_2SO_4]=0.2 mol dm^{-3}, —△—: **2b**, --○--: **3b**.

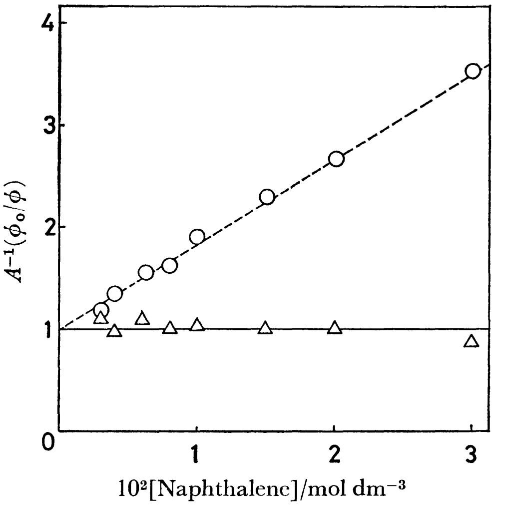


Fig. 6. Effects of naphthalene on photo-hydroxyethylation and -ethoxylation of **1**.
[**1**]=0.04 mol dm^{-3}, [H_2SO_4]=0.2 mol dm^{-3}, —△—: **2b**, --○--: **3b**.

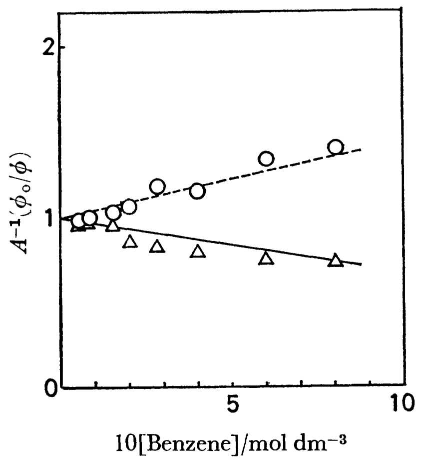


Fig. 7. Effects of benzene on photo-hydroxyethylation and -ethoxylation of **1**.
[**1**]=0.04 mol dm^{-3}, [H_2SO_4]=0.2 mol dm^{-3}, —△—: **2b**, --○--: **3b**.

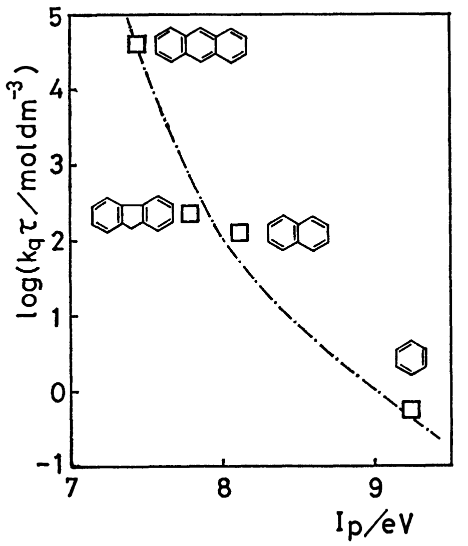


Fig. 8. Relation between $k_q\tau$ for the quenching of photo-ethoxylation and ionization potential of quencher.

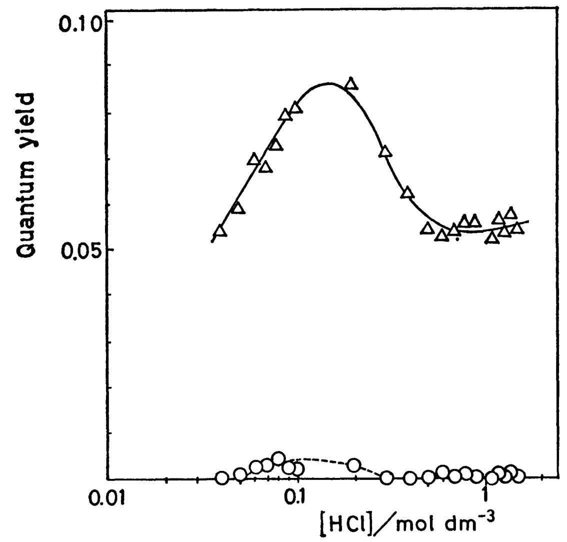


Fig. 9. Dependence of photo-hydroxyethylation and -ethoxylation of **1** on the concentration of hydrochloric acid.
[**1**]=0.04 mol dm^{-3}. —△—: **2b**, --○--: **3b**.

a triplet sensitizer because of its high triplet energy (E_T=347 kJ/mol[9)]), inhibits the photo-ethoxylation of **1**. In contrast with the photo-ethoxylation, photo-hydroxyethylation is independent on the quenchers.

These facts indicate that: 1) the substitution of the cyano group by the hydroxyethyl group is ascribed to a singlet excited state and 2) the substitution of the ring hydrogen by the ethoxyl group is ascribed not to a triplet excited state but to a certain singlet excited state. This singlet excited state should be different from the one which gives the hydroxyethylated product.

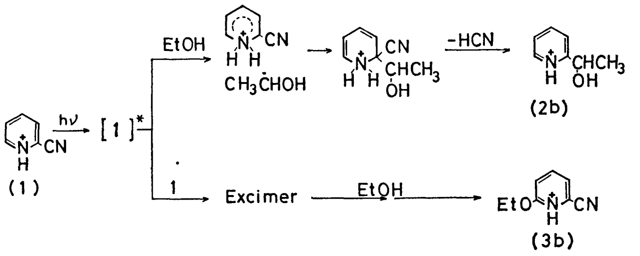
When the fact that the photo-ethoxylation has a significant concentration dependence is taken into consideration, the quenching of the photo-ethoxylation by aromatic hydrocarbons can be explained by the quenching of an excimer *via* the electron transfer mechanism proposed by Caldwell *et al.*[10]

The efficiencies for the quenching ($k_q\tau$ values obtained from the Stern-Volmer plots) of photo-ethoxylation by aromatic hydrocarbons correlate well with the ionization potentials of aromatic hydrocarbons[11] (Fig. 8). The lower the ionization potential, the higher the $k_q\tau$ value (k_q, rate constant for bimolecular quenching; τ, lifetime of the excited species). This shows that the excimer, which gives an ethoxylation product in the absence of quenchers, is quenched *via* the electron transfer from the quenchers. Alkoxylation is considered to involve a nucleophilic attack of alcohol to the electron-deficient moiety of the excited species. Therefore, the inhibition of ethoxylation by electron-rich aromatic hydrocarbons is reasonable. A similar quenching of photo-methoxylation by anthracene and benzene was observed for methyl 2-pyridinecarboxylate.[6]

Photo-ethoxylation is depressed by HCl (Fig. 9). A similar effect of HCl (or LiCl) on photo-methoxylation of 2-pyridinecarboxylic ester has been observed.[6] As in the case of 2-pyridinecarboxylic ester, the depression of photo-ethoxylation by HCl can be explained by the electron transfer from chloride ion to an electron-deficient excimer.

The conclusion that the hydroxyethylation occurs *via* a singlet excited state of **1** is similar to that reported by Hata *et al.* for the photo-hydroxyalkylation of quinolinecarbonitriles.[3] The mechanism proposed by Hata *et al.* can be applied to the corresponding reaction of 2-pyridinecarbonitrile.

The photoreactions of 2-pyridinecarbonitrile in acidic ethanolic solutions are summarized in Scheme 1.



Scheme 1.

Experimental

Materials. 2-Pyridinecarbonitrile (**1**) supplied by Yuki Gosei Yakuhin Co. was purified by vacuum distillation; mp 28—29 °C. Commercial naphthalene was purified by recrystallization; mp 80.5—81.5 °C. Commercial anthracene (analytical standard reagent of BDH Chemicals Co.), fluorene (zone-refined U.P. grade reagent of Tokyo Kasei Co.), and *trans*-1,3-pentadiene (GR grade reagent of Wako Junyaku Co.) were used without further purification.

UV-Irradiation. The alcoholic solutions containing **1**, sulfuric or hydrochloric acid, and the additive if necessary, were deaerated by bubbling nitrogen or argon for 40 min before irradiation. For the quenching experiment with *trans*-1,3-pentadiene or benzene, the quencher was added after the deaeration of the substrate solutions in order to avoid the evaporation of the quenchers during the bubbling of inert gas.

The solutions were irradiated with a low pressure mercury lamp in a merry-go-round type photoreactor. For the normalization, standard and sample solutions were irradiated at the same time.

Isolation and Identification of Photo-products. After the irradiation the solution was concentrated under reduced pressure. The solution was neutralized with sodium carbonate and the products were extracted with dichloromethane. The products were separated by means of TLC (plate, GF_{254} (Type 60) of E. Merck Co.; developing solvent, ethyl acetate–dichloromethane 1:1 for the reaction products in methanol, hexane–dichloromethane–diethyl ether 2:20:3 for the reaction products in ethanol).

2-Pyridylmethanol (**2a**) was identified by the accordance of its spectral properties with those of the commercially available authentic specimen. 1-(2-Pyridyl)ethanol (**2b**) was identified by the accordance of its spectral and gas-chromatographic properties with those of the authentic sample prepared by the hydrogenation of 2-acetylpyridine over Raney nickel catalyst.

6-Methoxy-2-pyridinecarbonitrile (**3a**): mp 58.0—58.5 °C; IR (KBr disk) 3000, 2950, 2915, 2850, 2225 (C≡N), 1603, 1465, 1130, and 1030 cm^{-1}; NMR (CCl_4) $\delta=7.60$ (1H, dd, $J=8.4$ and 7.4 Hz, H at 4-position), 7.16 (1H, dd, $J=7.4$ and 1.2 Hz, H at 3- or 5-position), 6.84 (1H, dd, $J=8.4$ and 1.2 Hz, H at 3- or 5-position), and 3.88 (3H, s, CH_3). Found: C, 61.6; H, 4.4; N, 20.4%. Calcd for $C_7H_6N_2O$: C, 62.7; H, 4.5; N, 20.9%.

6-Ethoxy-2-pyridinecarbonitrile (**3b**): mp 67.0—69.0 °C; IR (KBr disk) 3050, 2970, 2900, 2840, 2210 (C≡N), 1600, 1450, 1330, 1270, 1030, and 800 cm^{-1}; NMR ($CDCl_3$) $\delta=$ 7.66 (1H, dd, $J=8$ and 6 Hz, H at 4-position), 7.21 (1H, dd, $J=6$ and 1 Hz, H at 3- or 5-position), 6.86 (1H, dd, $J=8$ and 1 Hz, H at 3- or 5-position), 4.34 (2H, q, $J=7$ Hz, CH_2), and 1.30 (3H, t, $J=7$ Hz, CH_3). Found: C, 64.9; H, 5.6; N, 19.4%. Calcd for $C_8H_8N_2O$: C, 64.9; H, 5.4; N, 18.9%.

Quantitative Analysis of Photoproducts. After the irradiation the reaction mixture was concentrated under reduced pressure and was neutralized with sodium hydroxide and/or sodium hydrogencarbonate. The products were extracted repeatedly with dichloromethane and submitted to GLC analysis (column, 2 m column of Triton QS 11 (15%) on Uniport B (60/80 mesh); column temperature, 160 °C).

Actinometry. Actinometry was performed with a potassium trioxalatoferrate(III) actinometer.[12]

Spectral Measurements. NMR spectra were recorded on a Hitachi R 22 NMR spectrometer (90 MHz), and IR spectra were recorded on a Hitachi 260-50 IR spectrometer.

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