

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 942-946 (1973)

The Photochemistry of 2-Quinolinecarbonitriles. I. The Photochemical Reactions of 2-Quinolinecarbonitriles with Alcohols, Ethers, or Carboxylic Acids

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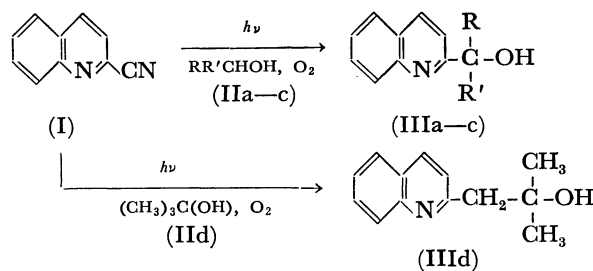
(Received August 19, 1972)

The photochemical reactions of 2-quinolinecarbonitriles with alcohols, diethyl ether, or aliphatic carboxylic acids in an atmosphere of oxygen or nitrogen were found to result in the replacement of the cyano group by 1-hydroxyalkyl, 1-ethoxyethyl, or alkyl group. However, the irradiation of 2-quinolinecarbonitrile in an alcoholic solvent except for the case of *tert*-butyl alcohol under a nitrogen atmosphere gave an unidentified substance (probably, a certain triazapentaphene) in addition to the photosubstitution product. The photoinduced substitution reaction found in the present experiment was revealed to proceed through the excited singlet state of 2-quinolinecarbonitrile, whereas the lowest triplet state was responsible for the formation of an unidentified substance in a deaerated alcohol.

Photoalkylation reactions of *N*-heterocyclic compounds have been extensively studied from both a synthetic and mechanistic point of view during the past few years.¹⁾ In order to investigate the effect of an electron-withdrawing group on such photo-induced reactions, the present authors have started photochemical studies of cyano-substituted *N*-hetero-aromatics. As has been briefly reported in a preliminary communication,²⁾ 2-quinolinecarbonitrile in an alcoholic solvent has been found, interestingly, to be converted into 2-(1-hydroxyalkyl)quinoline upon irradiation by ultraviolet light longer than 300 nm under an oxygen atmosphere. The purpose of the present paper is to present the experimental data on the photochemical reactions of 2-quinolinecarbonitriles with alcohols, ethers, or carboxylic acids.

Photochemical Reactions of 2-Quinolinecarbonitriles with Alcohols. A 2×10^{-2} M solution of 2-quinolinecarbonitrile (I) in an alcoholic solvent (II) (350 ml of ethanol, 1-propanol, 2-propanol, or *tert*-butyl alcohol) was irradiated with ultraviolet light longer than 300 nm in an atmosphere of oxygen at room temperature. As a result, white, crystalline solids (III) depending on the reaction medium were isolated as the main product. The UV absorption spectra of

the photoproducts (III) were quite similar to that of quinaldine. The IR spectra of III in KBr showed absorptions at about 3250 cm^{-1} (O-H stretching) and $\sim 2900\text{ cm}^{-1}$ (aliphatic C-H stretching), while the peak at 2230 cm^{-1} characteristic of the $\text{C}\equiv\text{N}$ group was completely missing. The NMR spectra in CDCl_3 indicated the presence of a 1-hydroxyalkyl group, which corresponds to the alcohol used as a reaction medium, at the 2-position of a quinoline. In addition to the UV, IR, and NMR spectra, the structural determinations of the products (III) were made on the basis of the mass spectra as well as by means of elemental analysis; the results are summarized in Table I. It was concluded from these results that the 2-quinolinecarbonitrile (I) changed photochemically in an alcoholic solvent (IIa-d) to yield 2-(1-hydroxyalkyl)quinoline (IIIa-d). In the case of 4-methylquinoline-2-carbonitrile, also a similar photosubstitution reaction was found to take place to afford 2-(1-hydroxyalkyl)-4-methylquinoline in a good yield; the analytical data for 2-(1-hydroxyethyl)-4-methylquinoline (III'a) are listed in Table 1.



IIa and IIIa: R = CH₃, R' = H
 IIb and IIIb: R = C₂H₅, R' = H
 IIc and IIIc: R = CH₃, R' = CH₃

1) (a) M. Ochiai and K. Morita, *Tetrahedron Lett.*, **1967**, 2349; M. Ochiai, E. Mizuta, Y. Asahi, and K. Morita, *Tetrahedron*, **24**, 5861 (1968). (b) H. Nozaki, M. Kato, R. Noyori, and M. Kawanishi, *Tetrahedron Lett.*, **1967**, 4259; R. Noyori, M. Kato, M. Kawanishi, and H. Nozaki, *Tetrahedron*, **25**, 1125 (1969). (c) F. R. Stermitz, R. P. Seiber and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968). (d) F. R. Stermitz, C. C. Wei, and G. M. O'Donnell, *J. Amer. Chem. Soc.*, **92**, 2745 (1970). (e) E. F. Travecedo and V. I. Stenberg, *Chem. Commun.*, **1970**, 609.

2) N. Hata, I. Ono, and S. Ogawa, *This Bulletin*, **44**, 2286 (1971).

TABLE 1. ANALYTICAL DATA FOR THE PHOTOPRODUCTS III AND VIII

Product	Mp (°C)	Yield (%) ^{a)}	Mass (M ⁺)	NMR ^{b)} (δ , ppm)	Elemental analysis	
					Found (%)	Calc (%)
IIIa	79—80	35 (54) ^{c)}	173	7.2—8.2 (m, 6H, aromatic)	C 76.22	C 76.30
				6.15 (s, 1H, -OH, deuterium exchangeable)	H 6.44	H 6.36
				5.08 (q, $J=7$ Hz, 1H, -CH(CH ₃)OH)	N 8.07	N 8.09
				1.55 (d, $J=6.5$ Hz, 3H, -CH(CH ₃)OH)		(for C ₁₁ H ₁₁ NO)
IIIb	68—69	45 (30) ^{c)}	187	7.4—8.3 (m, 6H, aromatic)	C 76.57	C 77.01
				4.90 (t, $J=4.5$ Hz, 1H, -CH(OH)C ₂ H ₅)	H 6.49	H 6.95
				4.82 (s, 1H, -OH, deuterium exchangeable)	N 7.83	N 7.49
				1.6—2.2 (m, 2H, -CH(OH)CH ₂ CH ₃)		(for C ₁₂ H ₁₃ NO)
				0.98 (t, $J=7$ Hz, 3H, -CH(OH)CH ₂ CH ₃)		
IIIc	69—70	40 (20) ^{c)}	187	7.3—8.3 (m, 6H, aromatic)	C 76.75	C 77.01
				4.75 (s, 1H, -OH, deuterium exchangeable)	H 6.85	H 6.95
				1.62 (s, 6H, -C(CH ₃) ₂ OH)	N 8.06	N 7.49
						(for C ₁₂ H ₁₃ NO)
IIId	49—50 ^{d)}	14 (35) ^{c)}	201	7.5—8.2 (m, 6H, aromatic)	C 77.36	C 77.58
				5.95 (s, 1H, -OH, deuterium exchangeable)	H 7.46	H 7.51
				3.10 (s, 2H, -CH ₂ C(CH ₃) ₂ OH)	N 6.78	N 6.95
				1.30 (s, 6H, -CH ₂ C(CH ₃) ₂ OH)		(for C ₁₃ H ₁₅ NO)
III'a	82.5	41 (62) ^{c)}	187	7.4—8.2 (m, 5H, aromatic)	C 77.08	C 77.01
				5.22 (s, 1H, -OH, deuterium exchangeable)	H 6.98	H 6.95
				4.99 (q, $J=6.5$ Hz, 1H, -CH(OH)CH ₃)	N 7.77	N 7.49
				2.62 (s, 3H, -CH ₃)		(for C ₁₂ H ₁₃ NO)
				1.55 (d, $J=6.8$ Hz, 3H, -CH(OH)CH ₃)		
VIII	109—110 ^{e)}	32 (59) ^{c)}	201	7.4—8.3 (m, 6H, aromatic)	C 52.74 ^{e)}	C 53.03 ^{e)}
				4.74 (q, $J=7$ Hz, 1H, -CH(CH ₃)O-)	H 4.24 ^{e)}	H 4.22 ^{e)}
				3.48 (q, $J=7.3$ Hz, 2H, -OCH ₂ CH ₃)	N 12.70 ^{e)}	N 13.02 ^{e)}
				1.56 (d, $J=6.7$ Hz, 3H, -CH(CH ₃)O-)		(for C ₁₉ H ₁₈ N ₄ O ₈)
				1.23 (t, $J=7$ Hz, 3H, -OCH ₂ CH ₃)		

a) Represents the yield in an oxygen atmosphere. b) Measured in CDCl₃ solution using a TMS as an internal standard. c) The value in bracket represents the yield in HCl acidified solution. d) Mp of the picrate: 141—142°C. e) The picrate.

Such a photochemical hydroxyalkylation of 2-quinolinecarbonitrile was demonstrated to take place in an HCl-acidified alcoholic solution as well, although the yield of III was appreciably different from that in the solution without acid. On the other hand, Stermitz *et al.*^{1d)} have reported that the irradiation of quinoline in HCl-acidified ethanol resulted in the ethylation of the 2- or 4-position of a quinoline, indicating that there exists a striking difference in the photoreactivity between 2-quinolinecarbonitrile and quinoline in an acidified alcohol.

When the irradiation of 2-quinolinecarbonitrile in alcohols different from *tert*-butyl alcohol was carried out, with nitrogen being bubbled in instead of oxygen, the solution became reddish-violet³⁾ and two products were separated; one was the product (III) depending on the reacting solvent, while the other was a compound (IV) with a mp of 215°C (decomp), irrespective of the alcohol used as a reaction medium. The yields of III and IV in various alcohols are as follows: 36% and 17% in ethanol, 30% and 25% in 1-propanol, and 26% and 20% in 2-propanol. However, the product (IV) was not formed in an acidified alcohol,

nor was it in the case of 4-methylquinoline-2-carbonitrile. When the *tert*-butyl alcohol was used as a reaction medium, only the product (IIId) was isolated as the major product in a 14% yield, while the formation of the product (IV) was not observed. The IR spectrum of the photoproduct (IV) in KBr indicated that the peak at 2230 cm⁻¹ characteristic of a C≡N group was absent, whereas absorptions around 3060 cm⁻¹ (aromatic C-H stretching), 1505, 1590 cm⁻¹ (ring vibration), and 830, 755 cm⁻¹ (aromatic C-H out-of-plane) were observed. The NMR spectrum showed only multiplet signals due to aromatic protons around 7.5—8.5 ppm (CDCl₃, TMS); also, the predominantly strong peaks corresponding to M⁺=281 and (M-1)⁺=280 were observed in the mass spectrum. Figure 1 shows the UV absorption spectrum of the product (IV), which is interestingly very similar to that of pentaphene in maximum wavelength and in molar extinction coefficient.⁴⁾ In addition to these data, the elemental analysis led to a conclusion that the product (IV) might be a certain triazapentaphene; Found, C 80.22, H 3.96; N 14.99%, Calcd for C₁₉H₁₁N₃, C 81.22, H 3.92, N 14.95%.

3) The reddish-violet color disappeared rapidly by the introduction of air (or oxygen) or the addition of DPPH into the irradiated solution.

4) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy", John Wiley & Sons Inc., London, (1962) Chapter 13.

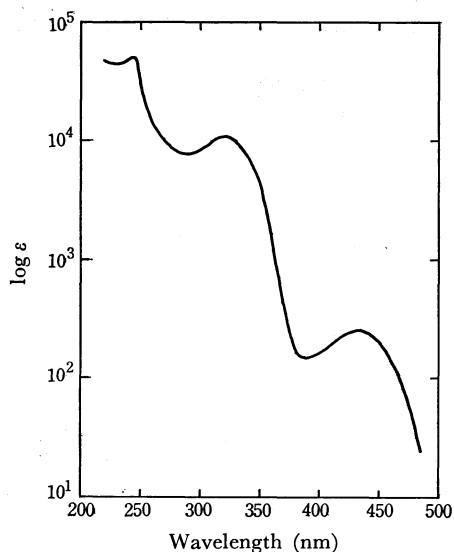
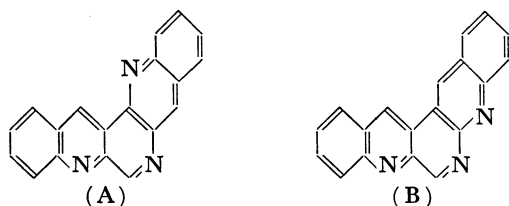
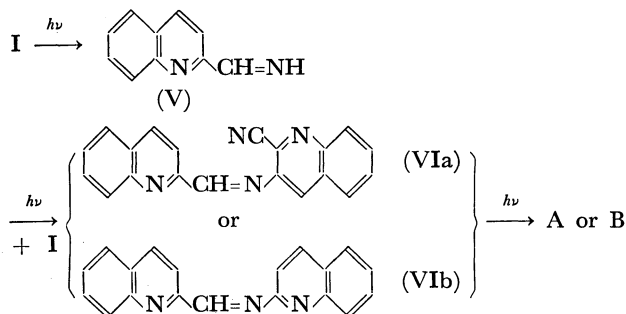


Fig. 1. The UV absorption spectrum of photoproduct (IV) in ethanol.

Although the location of nitrogen atoms on the pentaphene nucleus is entirely ambiguous at present, (A) or (B) seems to be a plausible structure for the reason to be discussed below.



Judging from the fact that the photochemical conversion $I \rightarrow IV$ did not occur in *tert*-butyl alcohol or benzene, the light absorption of 2-quinolinecarbonitrile (I) appears first to cause a hydrogen-atom abstraction from an alcohol to give V. If V thus formed reacts photochemically with I to yield an azomethine compound (VIa) or (VIb), followed by photochemical cyclization, A or B may be expected to be formed.



As has been described above, the product (III) was formed under an oxygen or nitrogen atmosphere, while the product (IV) resulted only in an atmosphere of nitrogen. This implies that the reactive state responsible for the formation of the product (III) is probably the excited singlet state of 2-quinolinecarbonitrile, whereas the triplet state is involved in the formation of the product (IV). In order to make this clear, a quenching experiment on the lowest triplet state of 2-quinolinecarbonitrile was thus undertaken

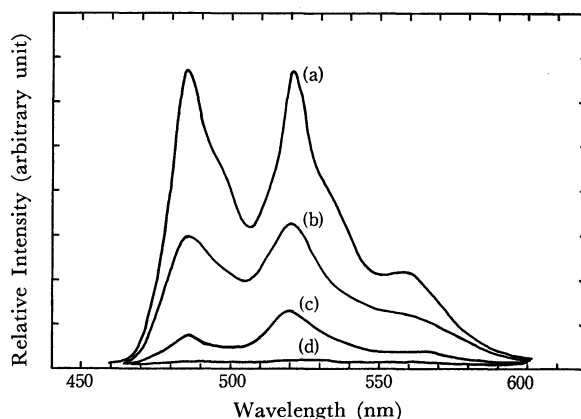


Fig. 2. The phosphorescence spectrum of 2-quinolinecarbonitrile in ethanol at 77K (concentration of 2-quinolinecarbonitrile: 5.0×10^{-4} M). (a) [Piperylene]: 0 M, (b) [Piperylene]: 5.0×10^{-2} M, (c) [Piperylene]: 4.0×10^{-1} M, (d) [Piperylene]: 1.0 M

in deaerated ethanol. Figure 2 shows the phosphorescence spectrum of 2-quinolinecarbonitrile in ethanol at 77K. It was estimated, from the first maximum of the phosphorescence spectrum (484 nm), that the lowest triplet state of 2-quinolinecarbonitrile has an excitation energy of about $59 \text{ kcal} \cdot \text{mol}^{-1}$. Accordingly, the piperylene ($E_T = 57 \text{ kcal} \cdot \text{mol}^{-1}$) may be expected to be usable as a triplet quencher for 2-quinolinecarbonitrile. As is shown in Fig. 2, the addition of piperylene to an ethanol solution of 2-quinolinecarbonitrile in amounts much greater than the molar equivalence led to the complete disappearance of the phosphorescence of 2-quinolinecarbonitrile. The photochemical reaction of 2-quinolinecarbonitrile in deaerated ethanol at room temperature was, therefore, carried out in the presence of varying amounts of piperylene. As can be seen from Fig. 3, the photochemical conversion from I to IIIa was not affected by the addition of piperylene, while the formation of the product (IV) decreased linearly with the in-

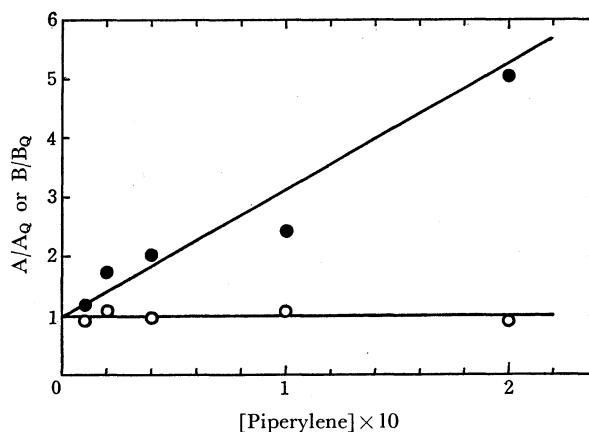
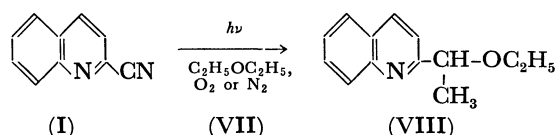


Fig. 3. The Effect of piperylene on the photochemical reaction of 2-quinolinecarbonitrile in ethanol under nitrogen atmosphere at 20°C . A (or B) and A_0 (or B_0) represent, respectively, the amounts of the product (IIIa) (or (IV)) in the absence and in the presence piperylene. Initial amount of 2-quinolinecarbonitrile: 100 mg (in 70 ml ethanol). Irradiation time: 60 min. A: 25 mg. B: 16 mg. ○: product (IIIa). ●: product (IV).

creased concentration of perylene. These results indicate that the photochemical substitution reaction I→III proceeds through the excited singlet state of 2-quinolinecarbonitrile, whereas the photochemical formation of IV involves the lowest triplet state.

Photochemical Reactions of 2-Quinolinecarbonitriles with Diethyl Ethers. In the same manner as in the case of an alcoholic solution, the ultraviolet irradiation of 2-quinolinecarbonitrile was carried out in diethyl ether under an oxygen or nitrogen atmosphere. As a result, an oily, colorless substance (VIII) was obtained as the main product; the yield was 32% in an oxygen atmosphere, while it was only 21% in a nitrogen atmosphere. The UV absorption spectrum of the product (VIII) was very similar to that of quinaldine. The IR spectrum in liquid showed peaks at about 3050 cm^{-1} (aromatic C-H stretching), 2960, 2930, 2850 cm^{-1} (aliphatic C-H stretching), 1100 cm^{-1} (C-O-C stretching), and 828 and 705 cm^{-1} (aromatic C-H out-of-plane), while a peak due to the C≡N group (2230 cm^{-1}) was missing. The analytical data of the product (VIII) are listed in Table 1. Consequently, the C≡N group of 2-quinolinecarbonitrile was revealed to be replaced by an 1-ethoxyethyl group as follows:



Differing from the case of an alcoholic solution, neither a deep coloration of the solution nor the formation of a triazapentaphene-like substance was detected in an atmosphere of nitrogen. The photosubstitution reaction also took place in the solution saturated with HCl gas; the yield was good (59%).

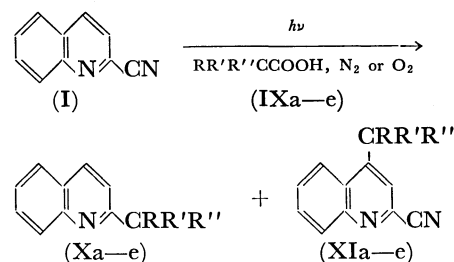
Photochemical Reactions of 2-Quinolinecarbonitriles with Aliphatic Carboxylic Acids. 2-Quinolinecarbonitriles (0.5 g) dissolved in 70 ml of benzene containing carboxylic acid (IX) (2 g of acetic acid, propionic acid, butyric acid, isobutyric acid, or trimethylacetic acid) in a Pyrex vessel were irradiated with ultraviolet

TABLE 2. YIELDS OF THE PHOTOPRODUCTS X AND XI

Products	Yield (%)				
	a	b	c	d	e
X	4	11	18	17	13
XI	trace	9	15	14	5

light under a nitrogen or oxygen atmosphere. As a result, two products, X and XI, were separated as the main products; the yields of these products in an atmosphere of nitrogen are shown in Table 2. On the basis of the UV, IR, and NMR spectra as well as the melting points of the picrates, the products (X) were identified as known 2-alkylquinolines^{1b)} corresponding to the carboxylic acid used in the photo-reaction. The UV absorption spectra of the products (XI) closely resembled that of 2-quinolinecarbonitrile (I), and the IR spectra in KBr showed peaks at about 3050 cm^{-1} (aromatic C-H stretching), 2220 cm^{-1} (C≡N stretching), and ~2900 cm^{-1} (aliphatic C-H stretching). Table 3 summarizes the analytical data for the products (XI).

It was concluded from these results that the 2- or 4-alkylquinolines were formed as a result of the photochemical reaction of 2-quinolinecarbonitrile with an aliphatic carboxylic acid in benzene as follows:



IXa, Xa and XIa: R=H, R'=H, R''=H
 IXb, Xb and XIb: R=CH₃, R'=H, R''=H
 IXc, Xc and XIc: R=C₂H₅, R'=H, R''=H
 IXd, Xd and XIc: R=CH₃, R'=CH₃, R''=H
 IXe, Xe and XIe: R=CH₃, R'=CH₃, R''=CH₃

TABLE 3. ANALYTICAL DATA FOR THE PHOTOPRODUCTS XI

Product	Mp (°C)	Mass (M ⁺)	NMR ^{a)} (δ, ppm)	Elemental analysis	
				Found (%)	Calcd (%)
XIb	121	182	7.5—8.3 (m, 5H, aromatic) 3.15 (q, J=7 Hz, 2H, -CH ₂ CH ₃) 1.40 (t, J=7.5 Hz, 3H, -CH ₂ CH ₃)	C 78.26 H 5.26 N 15.27	C 79.12 H 5.49 N 15.38 (for C ₁₂ H ₁₀ N ₂)
XIc	66	196	7.4—8.2 (m, 5H, aromatic) 3.72 (h, J=6.5 Hz, 1H, -CH(CH ₃) ₂) 1.39 (d, J=6.8 Hz, 6H, -CH(CH ₃) ₂)	C ₁₃ H ₁₂ N ₂ ^{b)}	
XId	107	196	7.5—8.3 (m, 5H, aromatic) 3.10 (t, J=7.5 Hz, 2H, -CH ₂ CH ₂ CH ₃) 1.5—2.2 (m, -CH ₂ CH ₂ CH ₃) 1.06 (t, J=7 Hz, 3H, -CH ₂ CH ₂ CH ₃)	C 78.85 H 5.96 N 13.97	C 79.59 H 6.12 N 14.29 (for C ₁₃ H ₁₂ N ₂)
XIe	104	210	7.6—8.6 (m, 5H, aromatic) 1.64 (s, 9H, -C(CH ₃) ₃)	C ₁₄ H ₁₄ N ₂ ^{b)}	

a) Measured in CDCl₃ solution using a TMS as an internal standard. b) Estimated from the result of the mass analysis performed with a JEOL JMS-01SG-2 mass spectrometer.

Such a photochemical alkylation was not inhibited by the addition of perylene.

Further studies for the elucidation of the primary photochemical process as well as the reaction mechanism are now in progress and will be reported soon.

Experimental

The UV absorption and the phosphorescence spectra were respectively, measured with a Hitachi recording spectrophotometer EPS-3T and a Hitachi fluorescence spectrophotometer MPF-2A with a phosphorescence accessory attached. The IR spectra were determined with a JASCO infrared spectrophotometer IR-G. The NMR spectra were taken in deuteriochloroform with a Hitachi-Perkin Elmer NMR spectrometer R-20 at 60 MHz, using a TMS as the internal standard. The mass spectra were obtained with a Hitachi RMU-6L or a JEOL JMS-O1SG-2 mass spectrometer.

Materials. The 2-quinolinecarbonitrile and 4-methylquinoline-2-carbonitrile used in this experiment were prepared according to the method given in the literature;⁵⁾ these compounds were purified by recrystallization from ethanol several times. The aliphatic carboxylic acids and all the solvents for the irradiation experiments were reagent-grade products of Wako Pure Chemical Industries, all of which were used without further purification. Reagent-grade perylene was purified by distillation several times.

Photochemical Reactions of 2-Quinolinecarbonitriles with Alcohols under an Oxygen Atmosphere. 2-Quinolinecarbonitrile (1.0 g) dissolved in 350 ml of alcohol (ethanol, 1-propanol, 2-propanol or *tert*-butyl alcohol in a Pyrex vessel was irradiated with a 100 W high-pressure immersion mercury lamp (Riko Kagaku Sangyo Co.) for 10 hr while oxygen was being bubbled in. After the removal of the solvent under reduced pressure, the residue was chromatographed on a silica-gel column by elution with a mixture of *n*-hexane and diethyl ether (1 : 1). A white, crystalline solid (III) was isolated as the main product. When the HCl-acidified alcohol was used as the reaction medium, a 350-ml alcoholic solution with 2-quinolinecarbonitrile (1.0 g), dissolved in it, to which 3.0 ml of concentrated HCl had been added, was irradiated for 10 hr under an oxygen atmosphere. The irradiated solution was concentrated *in vacuo*, and the concentrate was neutralized with a sodium carbonate aqueous solution. The aqueous solution was then extracted with chloroform, dried with anhydrous sodium sulfate, and the inorganic salts were removed by filtration. The chloroform solution was then concentrated under reduced pressure to afford a crystalline mass, which was subsequently chromatographed over silica gel to isolate the product (III).

Photochemical Reactions of 2-Quinolinecarbonitriles with Al-

cohols under a Nitrogen Atmosphere. A solution of 1.0 g 2-quinolinecarbonitrile in 350 ml of alcohol (ethanol, 1-propanol, or 2-propanol) was irradiated with a 100W high-pressure immersion mercury lamp, where half an hour before the irradiation was started nitrogen had been bubbled through the solution; this was continued constantly during the irradiation. When the irradiation was performed for *ca.* 15 min, the solution became reddish-violet. After the solution had been irradiated for 5 hr, the solvent was evaporated to dryness *in vacuo*. The residue was subjected to silica-gel chromatography (with dichloromethane used as the eluent) to afford the starting material, the products (III) and (IV). III or IV was purified by silica-gel chromatography using a mixture of *n*-hexane and diethyl ether (1 : 1) or a mixture of dichloromethane, *n*-hexane, and diethyl ether (10 : 1 : 1) as the eluent. The product (IV) thus obtained was further purified for the analysis by recrystallization from ethanol several times.

Photochemical Reactions of 2-Quinolinecarbonitriles with Diethyl Ether under a Nitrogen or Oxygen Atmosphere.

A solution of 1.0 g of 2-quinolinecarbonitrile in 350 ml of diethyl ether was irradiated in a Pyrex vessel under cooling at 5–10°C in an ice-bath, and with a 100W high-pressure immersion mercury lamp in an atmosphere of oxygen or nitrogen. After having been irradiated for 10 hr, the solution was concentrated under reduced pressure; the residue was chromatographed on a silica-gel column by elution with dichloromethane to isolate the product (VIII). The product (VIII) thus obtained was further purified by using a mixture of *n*-hexane and diethyl ether (1 : 1) as the eluent.

Photochemical Reactions of 2-Quinolinecarbonitriles with Aliphatic Carboxylic Acids in Benzene under a Nitrogen or Oxygen Atmosphere.

A solution of 2-quinolinecarbonitrile (0.5 g) and carboxylic acid (2 g of acetic acid, propionic acid, butyric acid, isobutyric acid, or trimethylacetic acid) in 70 ml of benzene was irradiated in a Pyrex vessel with a 100W high-pressure immersion mercury lamp for 6 hrs while nitrogen or oxygen was being bubbled in. After the removal of the solvent under reduced pressure, a 30-ml portion of water was added to the residue; the solution was then neutralized with sodium carbonate. After the extraction with chloroform or dichloromethane, the solution was concentrated *in vacuo*. The concentrate was chromatographed on a silica-gel column by elution with a mixture of *n*-hexane and ethyl acetate (9 : 1) to separate the starting material, the products (X) and (XI). These products were then further purified by alumina chromatography using the same eluent as before.

In conclusion, the authors wish to thank Professor Juji Yoshimura of Tokyo Institute of Technology for his kind discussions and Dr. Teiki Iwaoka of Sankyo Co. for his mass-spectral measurement of the photo-product (IV).

5) H. Menze, *Ber.*, **69**, 1566 (1936).