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The Photoinduced Substitution Reaction of 4-Quinolinecarbonitrile

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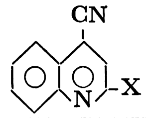
Synopsis. The photochemical reactions of 4-quinolinecarbonitrile with alcohol (ethanol, 1-propanol, 2-propanol, or *t*-butyl alcohol) resulted in the substitution of the 1- and/or 2-hydroxyalkyl group at the 2-position of a quinoline nucleus.

As has been reported previously,[1–3] 2-quinolinecarbonitrile in alcoholic solvents undergoes a photochemical replacement of the cyano group at the 2-position of a quinoline nucleus by a hydroxyalkyl group in an atmosphere of oxygen, while, under a nitrogen atmosphere, a certain triazapentaphene is also produced in addition to the photosubstitution product. On the other hand, 3-quinolinecarbonitrile in methanol has been reported by Natsume and Wada to undergo the addition of methanol to afford 1,2-dihydro-2-hydroxymethylquinoline.[4] From the synthetic and mechanistic points of view, therefore, it is of interest to investigate whether 4-quinolinecarbonitrile is photochemically susceptible to the replacement of the cyano group by the hydroxyalkyl one or to the addition of alcohol to give 1,2-dihydro-2-hydroxyalkylquinoline.

4-Quinolinecarbonitrile[5] (0.5 g) dissolved in 350 ml of alcohol (ethanol, 1-propanol, 2-porpanol, or *t*-butyl alcohol) in a Pyrex vessel was irradiated with a 100W high-pressure immersion mercury lamp (Riko Kagaku Sangyo Co.) for 3 to 4 hr while oxygen was being bubbled in. After the removal of the solvent under reduced pressure, the residue was chromatographed on a slica-gel column by elution with dichloromethane to separate the products. As a result, as is shown in Table 1, white crystalline solids (Ia, Ic, Id, IIb, and IIc) and a colorless liquid (Ib) were isolated as the main products. The UV absorption spectra of these products were quite similar to that of 4-quinolinecarbonitrile; also, the IR spectra in KBr showed absorptions at 3200 cm^{-1} (O–H stretching), ~2900 cm^{-1} (aliphatic C–H stretching), and 2230 cm^{-1} (C≡N stretching).[6] The NMR spectra in CDCl$_3$ indicated the presence of a 1-hydroxyalkyl (Products Ia—Id) or 2-hydroxyalkyl group (Products IIb and IIc), which corresponds to the alcohol used as a reaction medium, at the 2-position of a quinoline nucleus.[7] In addition, the products were identified on the basis of the mass spectra[8] as well as by means of elemental analyses;

TABLE 1. ANALYTICAL DATA FOR THE PHOTOPRODUCTS

Solvent	Product 	Mp (°C) Yield (%) Mass m/e (M^+)	NMR[a)] (δ, ppm)	Elemental analysis Found (%)	 Calcd (%)
Ethanol	(Ia) X=-CH(CH$_3$)OH	88 46 198	7.50—8.15 (m, 5H, aromatic) 5.00 (q, *J*=6.0 Hz, -C*H*(CH$_3$)OH) 3.85 (s, 1H, -O*H*)[c)]	C 73.00 H 5.27 N 3.89	C 72.71 H 5.09 N 4.06 (for $C_{12}H_{10}N_2O$)
1-Propanol	(Ib) X=-CH(C$_2$H$_5$)OH	125—126[b)] 24 212	7.41—8.30 (m, 5H, aromatic) 4.85 (q, *J*=4.8 Hz, 1H, -C*H*(OH)CH$_2$CH$_3$) 4.10 (s, 1H, -O*H*)[c)] 1.45—2.30 (m, 2H, -CH(OH)C*H*$_2$CH$_3$) 0.99 (t, *J*=4.7 Hz, 3H, -CH(OH)CH$_2$C*H*$_3$)	$C_{13}H_{12}N_2O$[d)]	
	(IIb) X=-CH(CH$_3$)CH$_2$OH	114—116 16 212	7.29—8.20 (m, 5H, aromatic) 3.96 (d, *J*=5.8 Hz, 2H, -CH(CH$_3$)C*H*$_2$OH) 2.90—3.50 (m, 1H, -C*H*(CH$_3$)CH$_2$OH) 1.35 (d, *J*=7 Hz, 3H, -CH(C*H*$_3$)CH$_2$OH)	$C_{13}H_{12}N_2O$[d)]	
2-Propanol	(Ic) X=-C(CH$_3$)$_2$OH	110—111 25 212	7.45—8.25 (m, 5H, aromatic) 4.80 (s, 1H, -O*H*)[c)] 1.65 (s, 6H, -C(C*H*)$_2$OH	C 73.20 H 5.73 N 13.00	C 73.58 H 5.66 N 13.21 (for $C_{13}H_{12}N_2O$)
	(IIc) X=-CH$_2$CH(CH$_3$)OH	100—103 19 212	7.34—8.22 (m, 5H, aromatic) 4.09—4.56 (m, 1H, -CH$_2$C*H*(CH$_3$)OH) 3.80 (s, 1H, -O*H*)[c)] 1.34 (d, *J*=6.5 Hz, -CH$_2$CH(C*H*$_3$)OH)	C 73.31 H 5.73 N 13.23	C 73.58 H 5.66 N 13.21 (for $C_{13}H_{12}N_2O$)
t-Butyl alcohol	(Id) X=-CH$_2$C(CH$_3$)$_2$OH	94— 95 55 226	7.60—8.20 (m, 5H, aromatic) 4.10 (s, 1H, -O*H*)[c)] 3.18 (s, 2H, -C*H*$_2$C(CH$_3$)$_2$OH) 1.32 (s, 6H, -CH$_2$C(C*H*$_3$)$_2$OH)	C 74.34 H 6.31 N 12.37	C 74.31 H 6.29 N 12.29 (for $C_{14}H_{14}N_2O$)

a) Measured in CDCl$_3$ solution using TMS as an internal standard. b) The picrate. c) Deuterium exchangeable. d) Estimated from the result of the mass analysis performed with a JEOL JMS-O1SG-2 mass spectrometer.

the analytical data are summarized in Table 1. The results definitely indicate that the 4-quinolinecarbonitrile in alcoholic solvents undergoes photochemically 1-hydroxyalkyl and/or 2-hydroxyalkyl substitution at the 2-position of a quinoline nucleus. Quite a similar photoreaction also occurred in an atmosphere of nitrogen.

The photoinduced-substitution reaction of 4-quinolinecarbonitrile is probably initiated by a hydrogen-atom abstraction from the alcoholic solvent by the ring nitrogen, just as in the case of 2-quinolinecarbonitrile.[3] It should be noticed that, in a 1- or 2-propanol solution, the product (IIb or IIc) arising from the β-hydrogen abstraction was obtained in addition to that from the α-hydrogen abstraction, quite unlike the case of 2-quinolinecarbonitrile. This could be interpreted as follows. In the case of 2-quinolinecarbonitrile, as has been discussed in a pervious paper,[3] the β-hydrogen abstraction from the alcohol hydrogen-bonded with the nitrogen of the quinoline nucleus is quite difficult because of the steric effect of a cyano group. On the other hand, such a steric hindrance does not exist in the case of 4-quinolinecarbonitrile, so the α- and β-hydrogen abstraction from 1- or 2-propanol by the ring nitrogen are considered to be possible, thus resulting in the IIb or IIc in addition to the Ib or Ic product.[9] In this respect, the present experimental results seem to support the idea that the photochemical hydroxyalkyl substitution reaction of 2- or 4-quinolinecarbonitrile in alcohol is initiated by a hydrogen-atom abstraction from the alcohol hydrogen-bonded with the nitrogen atom of the quinoline nucleus.[3]

References

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

2) N. Hata, I. Ono, S. Matono, and H. Hirose, *ibid.*, **46**, 942 (1973).

3) N. Hata and T. Saito, *ibid.*, **47**, 942 (1974).

4) M. Natsume and M. Wada, *Tetrahedron Lett.*, **1971**, 4503.

5) The 4-quinolinecarbonitrile used in this expreiment was synthesized by treating 4-bromoquinoline with cuprous cyanide. I. Nakayama, *Yakugaku Zasshi*, **71**, 1391 (1951).

6) The UV absorption and the IR spectra were, respectively, determined with a Hitachi recording spectrophotometer EPS-3T and a JASCO infrared spectrophotometer IR-G.

7) The NMR spectra were measured with a Hitachi-Perkin Elmer NMR spectrometer R-20 at 60 MHz.

8) The mass spectra were obtained with a Hitachi RMU-6L or a JEOL JMS-OlSG-2 mass spectrometer.

9) However, such a remarkable difference between 2- and 4-quinolinecarbonitriles in the hydrogen abstraction reaction is also inferred to be due partly to the electronic effect of a cyano group.