The Photoinduced Substitution Reaction of 2-Quinolinecarbonitrile

Norisuke Hata, Isao Ono, and Seiichi Ogawa

Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University,
Megurisawa-cho, Setagaya-ku, Tokyo

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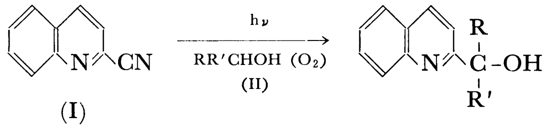
Recently, there has been considerable interest in photochemical alkylations of *N*-heterocyclic compounds.[1,2] However, photochemical hydroxyalkylations have been reported only in the case of quinoline by Stermitz *et al.*[2]; there, ultraviolet irradiations of the quinoline in ethanol solution gave the 2-(1-hydroxyethyl)quinoline in a 20% yield. In the present investigation, the authors found an interesting photochemical substitution reaction of 2-quinolinecarbonitrile in alcoholic solvents, affording 2-(1-hydroxyalkyl)-quinoline.

A solution of 0.8 g of 2-quinolinecarbonitrile in an alcoholic solvent (350 m*l* of ethanol, 1-propanol, or 2-propanol) in a Pyrex vessel was irradiated with a 250-W high-pressure mercury lamp for 18 hr while oxygen was 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). The melting points and the yields of the main products thus obtained are given in Table 1. The UV spectra of these compounds were quite similar to that of quinaldine. The IR spectra of the products in KBr showed a peak at 3300 cm^{-1} (ν_{O-H}) and no absorption at 2230 cm^{-1} characteristic of the C≡N group. In addition to the UV and IR spectra, the structural determinations of the products were made on the basis of the NMR and mass spectra as well as by means of elemental analyses; the results are summarized in Table 1. It was concluded from these results that the quinolinecarbonitrile (I) changed photochemically in alcoholic solvents(II) to give 2-(1-hydroxyalkyl)-quinoline (III) as follows:



(I)

(III)

IIa and IIIa: R=CH_3, R'=H
IIb and IIIb: R=C_2H_5, R'=H
IIc and IIIc: R=CH_3, R'=CH_3

When the irradiation was carried out where nitrogen was bubbled in instead of oxygen, the solution became reddish violet and two main products were separated: one was the product (III), while the other was unidentified. In the presence of piperylene as a triplet quencher,[3] however, no such coloration occurred and only the photoproduct (III) was obtained as a main product. These facts suggest that the lowest triplet state of 2-quinolinecarbonitrile is not responsible for the photochemical conversion (I)→(III).

Further studies are now in progress and will be reported soon.

Table 1. Analytical data for the photoproducts (III)

Solvent (II)	Product (III)	Mp (°C) Yield (%) Mass (M$^+$)	NMR[a]	Elemental analysis Found (%)	Elemental analysis Calcd (%)
Ethanol (IIa)	(IIIa)	79—80 35 173	7.1—8.2 ppm (m, 6H, aromatic) 4.86 ppm (q, *J*=7 Hz, 1H, -C*H*(OH)-CH_3 4.50 ppm (s, 1H, -O*H*, deuterium exchangeable) 1.48 ppm (d, *J*=6.5 Hz, 3H, -CH(OH)-C*H*$_3$)	C 76.22 H 6.44 N 8.07	C 76.30 H 6.36 N 8.09 (for $C_{11}H_{11}NO$)
1-Propanol (IIb)	(IIIb)	68—69 45 187	7.0—8.1 ppm (m, 6H, aromatic) 4.77 ppm (s, 1H, -O*H*, deuterium exchangeable) 4.65 ppm (t, *J*=6 Hz, 1H, -C*H*(OH)-CH_2-CH_3) 1.4—2.1 ppm (m, 2H, -CH(OH)-C*H*$_2$-CH_3) 0.96 ppm (t, *J*=7 Hz, 3H, -CH(OH)-CH_2-C*H*$_3$)	C 76.57 H 6.49 N 7.83	C 77.01 H 6.95 N 7.49 (for $C_{12}H_{13}NO$)
2-Propanol (IIc)	(IIIc)	69—70 40 187	7.2—8.2 ppm (m, 6H, aromatic) 5.10 ppm (s, 1H, -O*H*, deuterium exchangeable) 1.53 ppm (s, 6H, -C(OH)-(C*H*$_3$)$_2$)	C 76.75 H 6.85 N 8.06	C 77.01 H 6.95 N 7.49 (for $C_{12}H_{13}NO$)

a) Measured in CCl_4 solution using TMS as an internal standard.

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[1] M. Ochiai and K. Morita, *Tetrahedron Lett.*, **1967**, 2349; M. Ochiai, E. Mizuta, Y. Asahi, and K. Morita, *Tetrahedron*, **24**, 5861 (1968); 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); F. R. Stermitz, R. P. Seiber, and D. E. Nicodem, *J. Org. Chem.*, **33**, 1136 (1968); E. F. Travecedo and V. I. Stenberg, *Chem. Commun.*, **1970**, 609.

[2] F. R. Stermitz, C. C. Wei, and C. M. O'Donnell, *J. Amer. Chem. Soc.*, **92**, 2745 (1970).

[3] It was estimated, from the first maximum of the phosphorescence spectrum (484 nm) in ethanol at 77°K, that the lowest triplet state of 2-quinolinecarbonitrile has an excitation energy of about 59 kcal·mol^{-1}.