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THE PHOTOCHEMISTRY OF 2-QUINOLINECARBONITRILES. III.
THE BENZOPHENONE-SENSITIZED REACTION

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Benzophenone-sensitization of 2-quinolinecarbonitrile (1), 4-methylquinoline-2-carbonitrile (2), or 4-chloroquinoline-2-carbonitrile (3) in ethanol resulted in the formation of triazapentaphene (1a), 2-(hydroxydiphenylmethyl)-4-methylquinoline (2a), or 4,4'-bi-(2,2'-dicyano)quinoline (3a) in a good yield. It appears that 1 → 1a proceeds through the $T_1(\pi,\pi^*)$ state populated by an energy-transfer mechanism, whereas 2 → 2a or 3 → 3a occurs *via* the ketyl radical of benzophenone which exchanges a hydrogen atom with 2 or 3 in the ground state.

As has been described in the previous papers,[1-3] 2-quinolinecarbonitriles underwent a photochemical replacement of the cyano group at the 2-position of a quinoline nucleus by 1-hydroxyethyl group in ethanol. The reaction has been revealed to proceed *via* the $S_1(\pi,\pi^*)$ state through hydrogen-atom abstraction by the ring nitrogen from the hydrogen-bonded ethanol.[3,4] However, such a substitution reaction has been demonstrated not to occur from the lowest triplet state, from which a certain triazapentaphene resulted.[2] In order to elucidate the reactivity of the lowest triplet state, therefore, the present authors carried out the measurements of both the fluorescence and phosphorescence spectra of 2-quinolinecarbonitrile (1), 4-methylquinoline-2-carbonitrile (2), and 4-chloroquinoline-2-carbonitrile (3) and also the photosensitized reaction of these compounds by benzophenone.

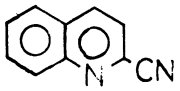
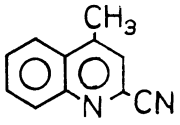
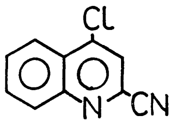
Table 1 lists the fluorescence and phosphorescence data obtained for 1, 2, and 3 in ethanol (EtOH) or methylcyclohexane (MCH).[5] The fluorescence spectra of these compounds were observed around 370 nm in ethanol, but they completely disappeared in methylcyclohexane. As has been reported in the previous paper,[3] such a phenomenon can be interpreted in terms of hydrogen-bonding interaction of quinoline-2-carbonitriles in the $S_1(\pi,\pi^*)$ state with ethanol; that is, the non-fluorescence in methylcyclohexane may result from a mixing of the $S_1(\pi,\pi^*)$ state with a closely lying $^1(n,\pi^*)$ state through the vibronic coupling, and the fluorescence activation in ethanol may be attributable to a great decrease in such a vibronic mixing owing to the formation of hydrogen bond between the ring nitrogen and ethanol. 1, 2 and 3 showed the phosphorescence spectra with some vibrational structures in the region between 480 and 580 nm in both ethanol and methylcyclohexane at 77 K.

Table 1. Fluorescence and Phosphorescence Data of Quinoline-2-carbonitriles

Quinoline-2-carbonitriles	Solvent	Fluorescence	Phosphorescence	
		λ_{max}(nm)	λ_{max}(nm)[a]	τ_p(sec)
1	EtOH	372.5	484	0.95
1	MCH	Non-fluorescent	482	0.95
2	EtOH	365	486	1.20
2	MCH	Non-fluorescent	483	0.95
3	EtOH	375.5	494	0.29
3	MCH	Non-fluorescent	492.5	0.27

a) The value of the first maximum of the phosphorescence spectrum.

Table 2. Photochemical Reactions of Quinoline-2-carbonitriles in Ethanol Containing Benzophenone on 366 nm Irradiation.

Quinoline-2-carbonitriles	a) Irradiation Time (hr) b) Conversion (%) c) Benzophenone, Recov. (%) d) Yield of Pinacol (%)	Products (Yield, %) and Their Analytical Data
 1	a) 1 b) 71 c) 95 d) 0	1a (45)[6]
 2	a) 4 b) 100 c) 0 d) 50	2a (71) mp 166∼167°C, M^+ 325, ir 3265 cm^{-1} (ν_{O-H}), nmr(δ,$CDCl_3$) 7.03∼8.20 (m, 15H, aromatic), 2.62 (s, 3H, -CH_3), 4.85 (s, 1H, -OH, deuterium exchangeable), Anal. Found (C, 84.75; H, 5.94; N, 4.25) Calc for $C_{23}H_{19}NO$ (C, 84.92; H, 5.85; N, 4.31)
 3	a) 2 b) 46 c) 96 d) 0	3a (62) mp 322∼324°C, M^+ 306, ir 2250 cm^{-1} ($\nu_{C\equiv N}$), nmr(δ,$CDCl_3$) 7.36∼8.69 (m, aromatic), Anal. Found (C, 78.70; H, 3.45; N, 17.85) Calc for $C_{20}H_{10}N_4$ (C, 78.43; H, 3.27; N, 18.30)

As seen from Table 1, both the maximum wavelength (λ_{max}) and phosphorescence lifetime (τ_p) were not affected significantly by changing the solvent from methylcyclohexane to ethanol, indicating that hydrogen bond between the ring nitrogen and ethanol does not exist in the lowest triplet state (T_1). In addition, it is evident from the value of τ_p that the T_1 state, as well as the S_1 state, is of a π,π^* nature.

From the value of the triplet excitation energy of 1, 2, or 3 (E_T = 58∿59 kcal.mol^{-1}) estimated from the first maximum of the phosphorescence spectrum, the benzophenone (E_T = 69 kcal.mol^{-1}) is expected to be usuable as a triplet sensitizer for these compounds. Therefore, the irradiation (366 nm) of three quinoline-2-carbonitriles was carried out in ethanol containing benzophenone. The general procedure of the photolytic experiment was as follows. A 50 ml of ethanol solution containing 100 mg of 1, 2, or 3 and 100 mg of benzophenone in a quartz cylindrical vessel (3.5 cm in length and 4.5 cm in diameter) was illuminated with a 250W high-pressure mercury lamp (USH-250D) equipped with a Toshiba filter UV-35 for 1 to 4 hr while nitrogen 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 dichloromethane and n-hexane (4 : 1) to afford the products. Experimental results are shown in Table 2.

When a solution of 2-quinolinecarbonitrile (1) in ethanol containing benzophenone was irradiated with 366 nm light being absorbed only by benzophenone, the solution became reddish-violet, just as the case of the direct excitation of 1 by 313 nm light in deaerated ethanol.$^{2)}$ Consequently, triazapentaphene (1a)$^{6)}$ was obtained as a main product in a 45% yield, but 2-(hydroxyethyl)quinoline was not detected. As well as the case of the direct photoexcitation (cf. Ref.2), the reaction 1 → 1a is assumed to be initiated by the reduction of the cyano group in the $T_1(\pi,\pi^*)$ state populated by an energy-transfer mechanism. Then, it can be probably said that the $T_1(\pi,\pi^*)$ state of 2-quinolinecarbonitrile is responsible for hydrogen-atom abstraction by the cyano group, whereas the $S_1(\pi,\pi^*)$ state is involved in hydrogen-atom abstraction by the ring nitrogen. Such a great difference in the reactivity between the $S_1(\pi,\pi^*)$ and $T_1(\pi,\pi^*)$ states may be closely related to the fact that hydrogen bond between the ring nitrogen and ethanol exists in the S_1 state, but not in the T_1 state.

On the other hand, the photosensitized reaction of 2 and 3 by benzophenone was entirely different from that of 1. In the case of 4-methylquinoline-2-carbonitrile (2), a replacement of the cyano group by hydroxydiphenylmethyl group occured to give rise to 2-(hydroxydiphenylmethyl)-4-methylquinoline (2a) in a 71% yield. However, there was observed neither the formation of triazapentaphene nor the substitution of the cyano group by 1-hydroxyethyl group. These suggest that the reaction 2 → 2a takes place *via* the ketyl radical of benzophenone which exchanges a hydrogen atom with 2 in the ground state (Scheme 1), just as the case of acridine reduction by benzophenone.$^{7)}$

In the case of 4-chloroquinoline-2-carbonitrile (3), neither the formation of triazapentaphene nor the substitution of the cyano group by 1-hydroxyethyl or hydroxydiphenylmethyl group occured, but 4,4'-bi-(2,2'-dicyano)quinoline (3a) was produced in a 62% yield with the recovery of benzophenone. The results also appear to be accounted for by assuming as an initial step of this reaction hydrogen abstraction by the ring nitrogen of 3 in the ground state from the ketyl radical of benzophenone (Scheme 2).

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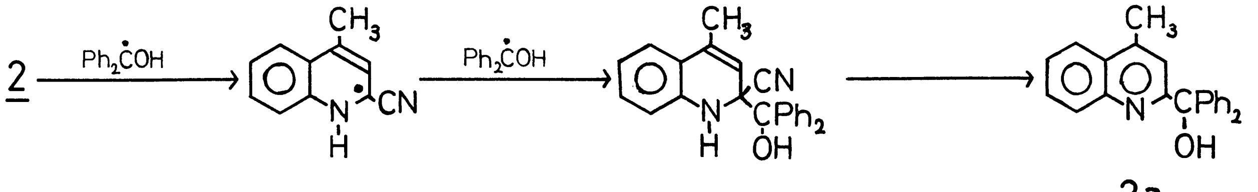
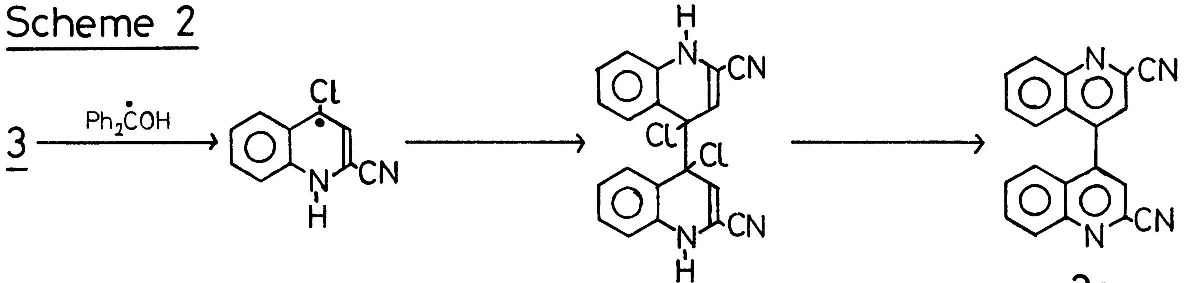
Scheme 1



2a

Scheme 2



3a

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1) N.Hata, I.Ono, and S.Ogawa, Bull.Chem.Soc.Japan, 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) N.Hata, I.Ono, and H.Suzuki, ibid., 47, 2609 (1974).
5) The fluorescence spectra were taken with a Hitachi fluorescence spectrophotometer MPF-2A. The phosphorescence spectra were measured with an Aminco-Bowman fluorescence spectrophotometer with a phosphorescence accessory attached.
6) The product 1a was concluded, from the UV and IR spectra as well as the melting point (214∿215°C (decomp)), to be identical with the triazapentaphen (6,8,14- or 5,6,8-triazapentaphene) resulted from the direct excitation of 1 in deaerated ethanol.[2)]
7) E.V.Donckt and G.Porter, J.Chem.Phys., 46, 1173 (1967).

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