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# THE EFFECT OF EXTERNAL MAGNETIC FIELD ON THE PHOTOINDUCED SUBSTITUTION REACTION OF 1-ISOQUINOLINECARBONITRILE

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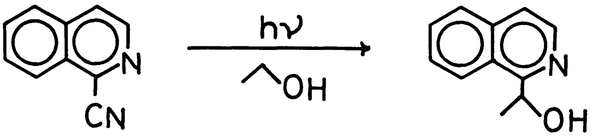
The photosubstitution reaction of 1-isoquinolinecarbonitrile in ethanol was found to be subject to a magnetic field effect due to the $\Delta g$ mechanism. The result suggests that the reaction proceeds predominantly via the formation of triplet radical pair subsequent to hydrogen abstraction by the triplet nitrile from the solvent, although it does not exclude the singlet reaction pathway.

As a part of our studies on the photochemical magnetic field effect of aza-aromatic compounds,1) we now report the photoinduced substitution reaction of 1-isoquinolinecarbonitrile in the presence of a magnetic field.

We have reported previously that irradiation of 2-quinolinecarbonitrile in ethanol resulted in a replacement of the cyano group at the 2-position of a quinoline nucleus by 1-hydroxyethyl group.2) The reaction has been elucidated to proceed via the $S_1(\pi,\pi^*)$ state through hydrogen abstraction by the ring nitrogen from ethanol.3,4) In the present investigation, 1-isoquinolinecarbonitrile 1 in ethanol was also found to undergo similar substitution reaction to give 1-(1-hydroxyethyl)isoquinoline 2 in ca.60% yield.5) This reaction is assumed to be initiated by hydrogen abstraction from the solvent by the nitrogen atom of an isoquinoline nucleus (Scheme 1), just as in the case of 2-quinolinecarbonitrile.3) If this mechanism is correct, magnetic field effect may be expected in this reaction since the radicals are formed in a pair of definite multiplicity in the solvent cage.6) Therefore, irradiation of 1 in ethanol was carried out in the absence and in the presence of magnetic field (0-17 kG) to determine the chemical yield of 2 as a function of the field strength and furthermore, we discussed the primary photochemical process.



1 2

A 50 ml of ethanol solution containing 30 mg of 1 in a quartz vessel was placed in an electromagnet and was illuminated with a 500W Ushio high-pressure mercury lamp (USH-500D) equipped with a Toshiba filter UV-31 for 3h in nitrogen atmosphere. The unreacted nitrile 1 and product 2 were separated by means of a thin layer

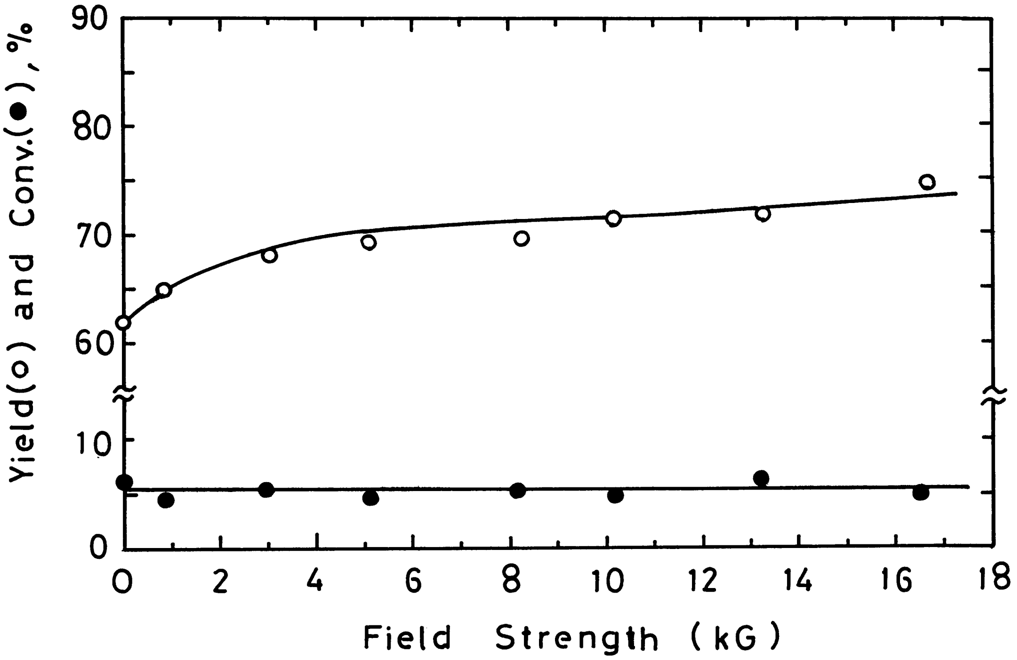
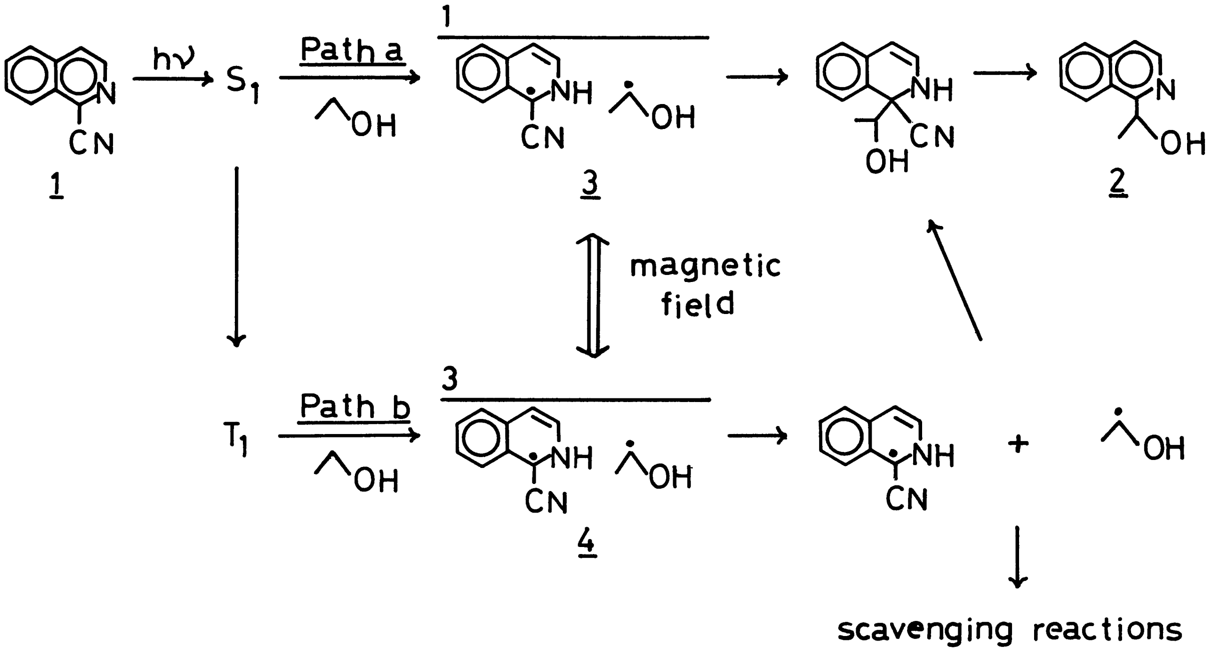


Fig.1 Chemical yield (○) of product 2 and conversion (●) as a function of field strength.

Scheme 1



chromatography (Merck TLC silicagel plate 60 $F_{254}$, layer thickness 2 mm) and the amounts were determined spectrophotometrically. Figure 1 shows the results when the chemical yield of 2 and the conversion were plotted against the magnetic field strength. As can be seen from the figure, the yield was ca.62% at zero field (earth's magnetic field), but it increased quadratically with the field strength to become ca.72% at approximately 16 kG, while the conversion remained almost unchanged.

The results indicate clearly the participation of a radical pair intermediate in this reaction. The intermediate, as shown in Scheme 1, results most likely from hydrogen abstraction by the ring nitrogen from ethanol. If such a hydrogen abstraction occurs from the $S_1$ state, the singlet radical pair 3 is formed in the solvent cage and undergoes efficient cage recombination reaction to generate the product 2 (Path a). On the other hand, if the $T_1$ state is responsible for hydrogen abstraction the radical pair intermediate 4 thus formed is in a triplet spin state so that it undergoes diffusive separation (Path b); the two radicals diffused into the solvent bulk will recombine as a result of a random encounter to give rise to 2 and also react with the solvent molecule (scavenging reactions). In the two pathways the former is apparently much more efficient route to the product 2 than the latter.

As will be described below, the observed magnetic field effect (Fig.1) provides important information concerning a pathway (Path a or b) of the photosubstitution reaction. In general, the following mechanisms are accepted for the effect of an external magnetic field on the rate of the singlet-triplet transition of a radical pair in a solvent cage, where the exchange interaction in the pair is disregarded.<sup>6)</sup> First, the external magnetic field results in a reduction of the number of effective working channels for the hyperfine induced singlet-triplet transition of the radical pair (HFI mechanism). Second, the external magnetic field causes the singlet-triplet transition of a radical pair by virtue of the different g-values of the component radicals ($\Delta g$ mechanism). The basic difference between these two mechanisms can be observed in weak magnetic field which is comparable to the local field due to hyperfine couplings (cf. Ref. 6b and 6c). It may be judged from this criterion that the observed magnetic field dependence of the chemical yield of 2 (Fig.1) is not due to the HFI mechanism but due to the $\Delta g$ mechanism; the $\Delta g$ interaction causes a transition from the triplet to singlet in radical pair at a rate which increases with the strength of applied magnetic field. This leads to the conclusion that, although the singlet reaction pathway (Path a) is not excluded, the photosusbtitution reaction of 1-isoquinolinecarbonitrile proceeds predominantly via the formation of triplet radical pair 4 (Path b).

It has been reported in previous papers that, in the case of 2-quinolinecarbonitrile, hydrogen abstraction by the ring nitrogen from ethanol did not occur from the $T_1$ state which was assigned to a $\pi,\pi^*$ from the phosphorescence data.3) In the present study, the phosphorescence from 1-isoquinolinecarbonitrile was not detected at all in either methylcyclohexane or ethanol at 77 K, suggesting that the $T_1$ state of 1-isoquinolinecarbonitrile different from that of 2-quinolinecarbonitrile is most probably an $n,\pi^*$ state from which hydrogen abstraction by the ring nitrogen is considered feasible; this is consistent with the conclusion from the photochemical magnetic field effect described above.

In summary, magnetic field effect was found for the photosubstitution reaction of 1-isoquinolinecarbonitrile in ethanol. The results were qualitatively interpreted in terms of the reaction mechanism represented in Scheme 1. Such a study of photochemical magnetic field effect seems to be important and useful for the elucidation of the primary photochemical process and reaction pathway. Further studies are in progress.

## References and Notes

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2) N.Hata, I.Ono and S.Ogawa, Bull.Chem.Soc.Jpn., 44, 2286 (1971); N.Hata, I.Ono, S.Matono and H.Hirose, Bull.Chem.Soc.Jpn., 46, 942 (1973).
3) N.Hata and T.Saito, Bull.Chem.Soc.Jpn., 47, 942 (1974); N.Hata and R.Ohtsuka, Chem.Lett., 1975, 1107.
4) Although the $S_1$ state of 2-quinolinecarbonitrile is of a $\pi,\pi^*$ nature, hydrogen abstraction by the ring nitrogen from ethanol occurs from this state because of its mixing with a closely lying $^1n,\pi^*$ state through the vibronic coupling.[3)]
5) Analytical data of the product 2 were as follows: mp 163° (picrate); ir 3400 $cm^{-1}$ ($\nu_{O-H}$); $M^+$ 173; nmr($\delta$,$CDCl_3$) 8.30-7.50 (m, 6H, aromatic), 5.64 (q, J=7 Hz, 1H, $-C\underline{H}(CH_3)OH$), 1.62 (d, J=6.5 Hz, 3H, $-CH(C\underline{H}_3)OH$); elem. anal. found C 50.72, H 3.50, N 13.90, calc C 50.30, H 3.50, N 13.89 for $C_{17}H_{14}N_4O_8$(picrate).
6) As to discussions of magnetic field effect on chemical reactions in solution, see, for example,
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