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Photochemical Magnetic Field Effects of 4-Methyl-2-quinolinecarbonitrile

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The irradiation of 4-methyl-2-quinolinecarbonitrile **1** in ethanol or cyclohexane resulted in the formation of 2-(1-hydroxyethyl)-4-methylquinoline **2** or 2-cyclohexyl-4-methylquinoline **3** in the yield of *ca.* 48 or 65%. The effects of an external magnetic field upon the photosubstitution reaction were investigated in either the absence or presence of 1,3-pentadiene (triplet quencher). In the case of the photosubstitution reaction (**1**→**2**) in ethanol, the chemical yield of **2** increased quadratically with an increase in the field strength (magnetic field effect due to Δg mechanism) and it also showed a minimum at approximately 1.1T (magnetic field effect due to HFI-J mechanism). The addition of 1,3-pentadiene caused a complete disappearance of the Δg magnetic field effect. Thus, the formation of **2** at a zero field was concluded to occur from the S_1-state *via* the singlet hydrogen-bonded radical pair. In the case of the photosubstitution reaction (**1**→**3**) in cyclohexane, the chemical yield of **3** decreased steeply upon the application of a magnetic field of 40mT (magnetic field effect due to HFI mechanism) and a further increase in the field strength resulted in a quadratic increase in the yield (magnetic field effect due to Δg mechanism). Neither an HFI nor a Δg magnetic field effect was observed in the presence of 1,3-pentadiene. The reaction was thus concluded to proceed from the S_1 and T_1 states *via* the singlet and triplet radical pairs. Reaction mechanisms deduced from the external magnetic field effects were consistent with the results of Stern-Volmer analyses.

Photochemical reactions proceeding *via* a radical-pair intermediate in solution can generally be expected to show an external magnetic field effect which arises from an electronic Zeeman interaction (Δg mechanism), electron-nuclear hyperfine interaction (HFI mechanism), or hyperfine-interaction mechanism including an electron-exchange interaction (HFI-J mechanism) in a radical-pair intermediate (*cf.* Appendix).1) The magnetic field effect due to the HFI-J mechanism is considered to be particularly interesting and important from the viewpoint of mechanistic photochemistry, becuase it is expected when hydrogen- or electron-transfer between a photoexcited molecule and the hydrogen-bonded species occurs to form an appropriate hydrogen-bonded radical pair or radical ion-pair intermediate in a solvent cage.2) In 1976 this type of magnetic field effect was found for the first time by one (N.H.) of the authors in the case of the photochemical isomerization of isoquinoline *N*-oxide in ethanol.2) In order to find a second example of the magnetic field effect due to the HFI-J mechanism, in the present investigation, the photoinduced substitution reaction of 4-methyl-2-quinolinecarbonitrile in ethanol and in cyclohexane were studied in both the absence and presence of a magnetic field.3)

Experimental

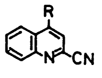
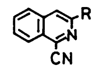
Materials. The 4-methyl-2-quinolinecarbonitrile **1** used as a sample was prepared from 4-methylquinoline *N*-oxide according to a method (Reissert reaction) given in the literature;4) it was then purified by recrystallization from methanol several times; mp 97—98 °C. 1,3-Pentadiene used as a triplet quencher was a Chemical-pure product of Tokyo Kasei Kogyo Co., which was further purified by distillation; bp 42—43.5 °C. The ethanol and cyclohexane used as the photoreaction medium were Reagent-grade products of Wako Pure Chemical Industries; the former was used without further purification, while the latter was purified by silica-gel chromatography.

Isolation and Identification of Photoproducts. 4-Methyl-2-quinolinecarbonitrile **1** (50 mg) dissolved in 50-cm^3 of ethanol (or cyclohexane) in a Pyrex vessel was irradiated with a 100 W high-pressure immersion mercury lamp (Riko Kagaku Sangyo Co.) for 5 h (or 8 h) in an atmosphere of nitrogen at room temperature. After the removal of the solvent under reduced pressure, unreacted **1** and product **2** (or **3**) were separated by means of silica-gel TLC (Merck TLC silica-gel plate $60F_{254}$; layer thickness, 2 mm; the eluent, hexane–diethyl ether (1:2) for the separation of **1** and **2**, and hexane–ethyl acetate (5:1) for the separation of **1** and **3**). The product **2** was 2-(1-hydroxyethyl)-4-methylquinoline, which has been identified previously;5) mp 82—82.5 °C; the yield, *ca.* 48%. The product **3** was a colorless liquid; bp 121 °C/2 mm, mp (the picrate) 182 °C; the yield, *ca.* 65%. It was identified as 2-cyclohexyl-4-methylquinoline by the following analytical data. NMR($CDCl_3$) δ(ppm): 8.2—7.3 (m, 5H, aromatic), 2.70 (s, 3H, $-CH_3$), 2.2—1.1 (m, 11H, $-C_6H_{11}$). MS: 225(M^+). Found (the picrate): C,58.46; H,4.86; N,12.05%. Calcd for $C_{22}H_{22}N_4O_7$ (the picrate): C, 58.15; H, 4.85; N, 12.33%.

Stern-Volmer Experiments. A determination of the quantum yields (the disappearance of **1** and the formation of **2** or **3**) was performed in a quartz cell (4.5-cm in diameter and 1-cm in length) containing the ethanolic solution (or cyclohexane solution) of **1** (1.62×10^{-3} mol dm^{-3}) and 1,3-pentadiene (0—10.0×10^{-3} mol dm^{-3}) under a nitrogen atmosphere at room temperature. The light source employed was a Ushio Super-high-pressure Mercury Lamp (USH-500D) equipped, for the 313-nm irradiation, with a filter combination of a nickel sulfate solution with Toshiba filters UV-29 and UV-D33S. The light intensity was determined by means of a potassium tris-(oxalato)ferrate (III) actinometer. The amounts of unreacted **1** and product **2** (or **3**) were determined by means of a silica-gel chromatographic separation, using the same eluent as that described before, combined with a spectrophotometric determination.

Magnetic Perturbation Experiments. A 50-cm^3 of ethanolic solution (or cyclohexane solution) containing 4-

TABLE 1. SPECTRAL DATA OF SOME AZAAROMATIC NITRILES[6–8)]

Nitriles		Solvents[a)]	Absorption[b)] λ_{max}/nm (ε_{max})	Fluorescence λ_{max}/nm	Phosphorescence[b)] λ_{max}/nm
	R=H	MCH	330 (2800)	Non	482
		EtOH	331 (2650)	372.5	484
	R=CH$_3$	MCH	330.5 (2600)	Non	483
		EtOH	331 (2300)	365	486
	R=H	MCH	331 (5600)	339 (Very weak)	Non
		EtOH	332 (5600)	365	Non
	R=CH$_3$	MCH	340 (6200)	350 (Very weak)	Non
		EtOH	341 (6100)	370	Non

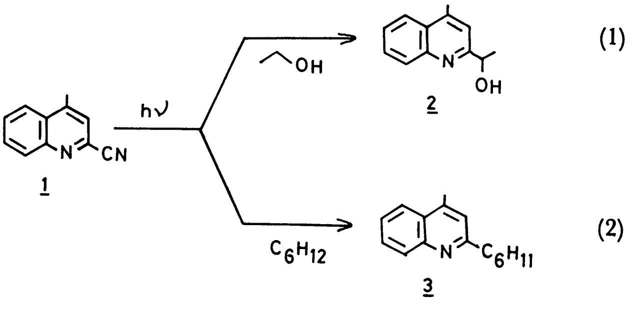
a) MCH: Methylcyclohexane, EtOH: Ethanol. b) The value of the first maximum.

methyl-2-quinolinecarbonitrile **1** (35 mg) and 1,3-pentadiene (0 or 3.0×10^{-1} mol dm^{-3}) in a quartz vessel (44×45×25 mm) was placed in an electromagnet (EEO-1815) supplied by the Maezumi Electric Company and subsequently, irradiated with two 500 W Super-high-pressure Mercury Lamps (USH-500D) equipped with a Toshiba filter UV-31 for 40 min at room temperature while nitrogen was bubbled. The unreacted **1** and product **2** (or **3**) were separated by means of silca-gel TLC in the same manner as that described before and the amounts were determined spectrophotometrically.

Spectroscopic Measurements. UV absorption spectra were taken with a Shimadzu recording spectrophotometer, UV-220. Fluorescence and phosphorescence spectra were determined with a Hitachi recording fluorescence spectrophotometer, MPF-2A. Reagent-grade ethanol (Wako Pure Chemical Industries) and Spectro-grade methylcyclohexane (Dotite Spectrosol) were used as the solvent. NMR spectra were taken in CDCl$_3$ with a Hitachi-Perkin Elmer NMR spectrometer R-20 at 60 MHz, using TMS as the internal standard. Mass spectra were measured with a Hitachi mass spectrometer, RMU-6M.

Results and Discussion

Photochemical Reactions and the Stern-Volmer Analyses. It has been already reported in previous papers[5)] that the irradiation of 2-quinolinecarbonitriles in alcoholic solvents generally results in the replacement of the cyano group at the 2-position of a quinoline nucleus by hydroxyalkyl group. As has been described in the Experimental section, when 4-methyl-2-quinolinecarbonitrile **1** in ethanol was irradiated in an atmosphere of nitrogen, 2-(1-hydroxyethyl)-4-methylquinoline **2** was obtained in a *ca.* 48% yield (Eq. 1). In the case of a cyclohexane solution, there also occurred a similar photosubstitution reaction to give rise to 2-cyclohexyl-4-methylquinoline **3** in a yield of *ca.* 65% (Eq. 2).



In order to characterize the excited states responsible for the photosubstitution reaction of 4-methyl-2-quinolinecarbonitrile **1** in ethanol or cyclohexane, the effects of 1,3-pentadiene upon the quantum yield (Φ_{-1}) of the disappearance of **1** and that (Φ_2 or Φ_3) of the formation of **2** or **3** were examined. The excitation energy of the lowest triplet state of 4-methyl-2-quinolinecarbonitrile was estimated, from the first maximum of the phosphorescence spectrum (Table 1), to be *ca.* 247 kJ mol^{-1}; hence 1,3-pentadiene was used as a triplet quencher for the photochemical reaction of **1**.

Figure 1 shows a plot of $\Phi^{\circ}_{-1}/\Phi_{-1}$ or Φ°_{2}/Φ_2 against the concentration of 1,3-pentadiene ([C$_5$H$_8$]) for the photosubstitution reaction (**1**→**2**) in ethanol (Stern-Volmer plot), where the quantum yield (Φ°_{-1}) of the disappearance of **1** and that (Φ°_{2}) of the formation of **2** at [C$_5$H$_8$]=0 were 0.0825 and 0.0461, respectively. As can be seen from Fig. 1, Φ_2 was independent of the concentration of 1,3-pentadiene, whereas Φ_{-1} decreased with an increase in the concentration of 1,3-pentadiene until it became constant above a concentration of 7.0×10^{-3}mol dm^{-3} 1,3-pentadiene. The results clearly indicate that the photosubstitution reaction (**1**→**2**) proceeds from the S$_1$ state and that some complicating reactions occur from the T$_1$ state.

Figure 2 shows Stern-Volmer plots for a photosubstitution reaction (**1**→**3**) in cyclohexane, where the quantum yield (Φ°_{-1}) of the disappearance of **1** and that (Φ°_{3}) of the formation of **3** at [C$_5$H$_8$]=0 were 0.0374 and 0.0271, respectively. Both quantum yields, Φ_{-1} and Φ_3, decreased with an increase in the concentration of 1,3-pentadiene until no further quenching occurred above a concentration of 1.7×10^{-3} mol dm^{-3} 1,3-pentadiene. This means that, unlike the case of the photosubstitution reaction **1**→**2**, both S$_1$ and T$_1$ states are responsible for the photosubstitution reaction **1**→**3**.

The chemical yield, Y_S or Y_T, of the S$_1$- or T$_1$-born product **3** was estimated from the Stern-Volmer plot (curve (a) in Fig. 2) in the following manner. The chemical yield (Y) of **3** at [C$_5$H$_8$]=0 is given by the sum of Y_S and Y_T (Eq. 3). The chemical yield (Y_S) of the S$_1$-born product **3** is given by Eq. 4, where $(\Phi^{\circ}_{3}/\Phi_3)_0$ and $(\Phi^{\circ}_{3}/\Phi_3)_s$ represent, respectively, Φ°_{3}/Φ_3 at [C$_5$H$_8$]=0 and [C$_5$H$_8$]>1.7×10^{-3} mol dm^{-3}. Y_S and Y_T were thus

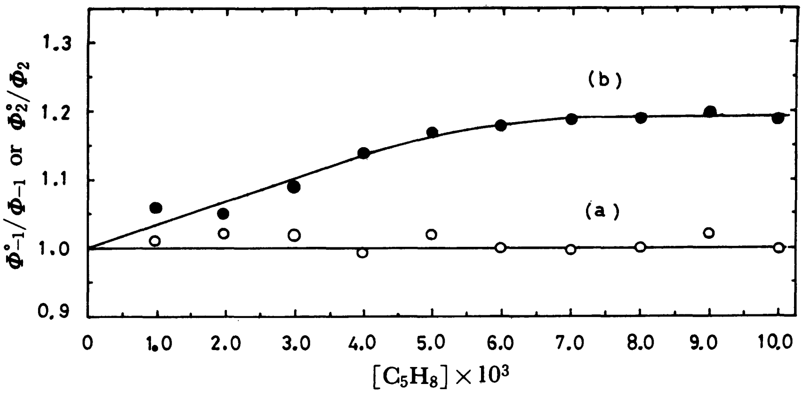


Fig. 1. Triplet quenching of the photosubstitution reaction (**1**→**2**) in ethanol. [**1**]=1.62×10^{-3} mol dm^{-3}. (a) —○—: Φ°_2/Φ_2, (b) —●—: $\Phi^\circ_{-1}/\Phi_{-1}$.

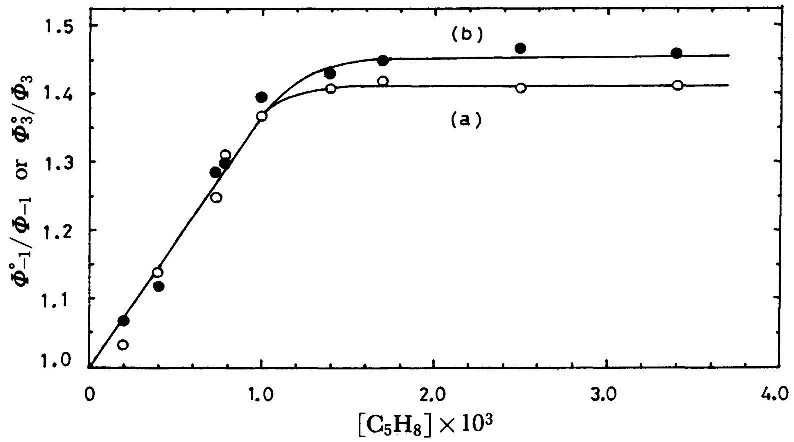


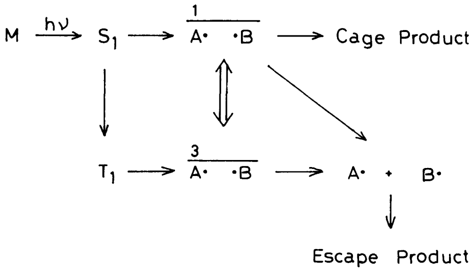
Fig. 2. Triplet quenching of the photosubstitution reaction (**1**→**3**) in cyclohexane. [**1**]=1.62×10^{-3} mol dm^{-3}. (a) —○—: Φ°_3/Φ_3, (b)—●—: $\Phi^\circ_{-1}/\Phi_{-1}$

$$Y = Y_s + Y_T \tag{3}$$

$$Y_s = Y(\Phi^\circ_3/\Phi_3)_0/(\Phi^\circ_3/\Phi_3)_s \tag{4}$$

evaluated by substituting $(\Phi^\circ_3/\Phi_3)_s$=1.41 and Y=65% into Eqs. 3 and 4 to be 46 and 19% respectively.

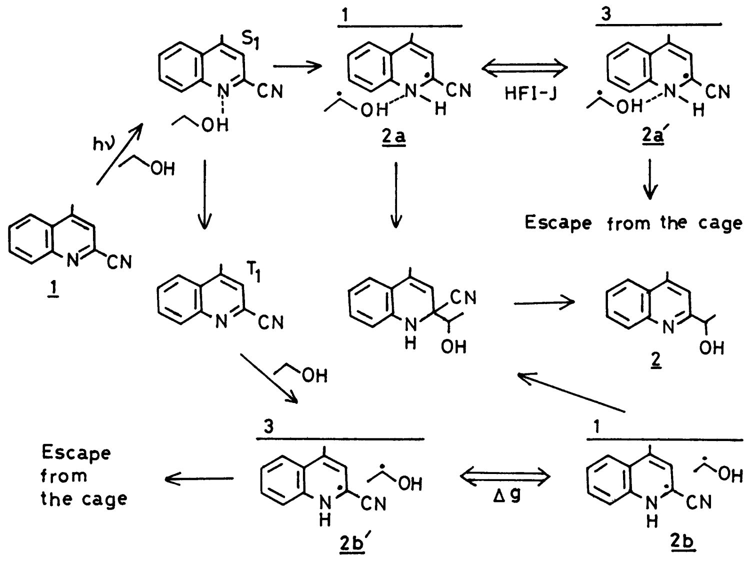
Magnetic Field Effects. In the case where the photochemical reactions in solution proceed *via* a radical-pair intermediate (as is shown in Scheme 1), the chemical yield of the cage product or escape product shows a magnetic field dependence provided that the rate of the intersystem crossing of a radical pair is influenced by an external magnetic field.[1] As will be briefly described in Appendix, such a field dependence of chemical yield has been currently classified into six patterns (Figs. 5 and 6), depending on whether the product is a cage- or escape-product and an S_1- or T_1-born product and also whether the magnetic perturbation is due to Δg, HFI, or HFI-J mechanism. Consequently, an examination of the field dependence of chemical yield is supposed to furnish quite significant information regarding photochemical reaction mechanism.[6]



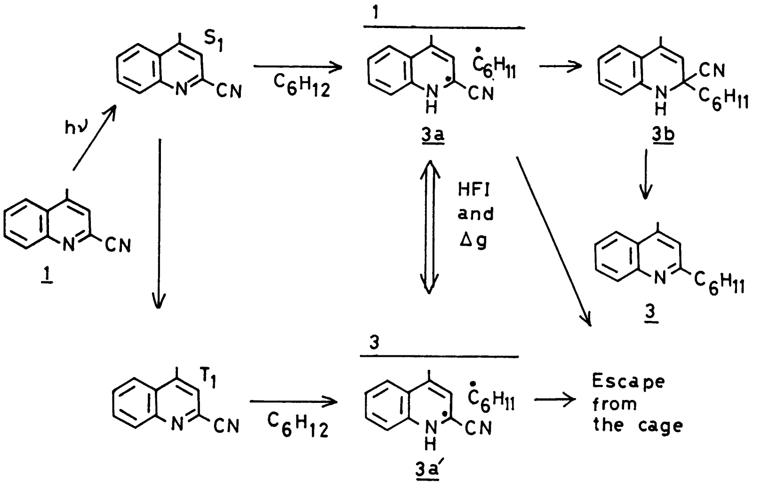
Scheme 1.

As mentioned before, the Stern-Volmer plots (Fig. 1) of the photoinduced substitution reaction (**1**→**2**) in ethanol revealed the S_1 state to be responsible for this reaction. Previously,[7,8] it had also been demonstrated from the solvent dependence of the absortpion and fluorescence spectra of 2-quinolinecarbonitriles (*cf.* Table 1) that a hydrogen-bonding interaction between the ring nitrogen and an ethanol does exist in the S_1 state, although there is no appreciable interaction in the S_0 state.[9] Furthermore, the photoreaction has been reasonably assumed to proceed *via* the S_1 state through hydrogen abstraction by the ring nitrogen from the hydrogen-bonded ethanol.[7] Hence, as is shown in Scheme 2, it seems quite reasonable to assume that the S_1-born singlet hydrogen-bonded radical pair **2a** is formed as a transient intermediate of this reaction. If this assumption is valid, the magnetic field effect due to the HFI-J mechanism (curve (3) in Fig. 5) may be expected for the photosubstitution reaction **1**→**2**, just as the case of the photoisomerization of isoquinoline *N*-oxide in ethanol;[2] it is because the radical centers in the radical pair **2a** are in close proximity as a result of hydrogen-bonding interaction between the two radicals (consequently, the electron-exchange interaction is much greater than the electron-nuclear hyperfine energy). On the other hand, the photosubstitution reaction (**1**→**3**) in cyclohexane was demonstrated from Stern-Volmer plots (Fig. 2) to occur from both the S_1 and T_1 states. Therefore, as is shown in Scheme 3, if the reaction proceeds *via* the S_1-born singlet and T_1-born triplet radical pairs, **3a** and **3a′**, as the reactive intermediate, then it may be subject to a magnetic field effect due to Δ*g* or HFI mechanism (curve (1) or (2) in Fig. 5 and curve (1′) or (2′) in Fig. 6), because either the radical pair **3a** or **3a′** is not a hydrogen-bonding pair of radicals in close proximity and therefore the electron-exchange interaction is disregarded. For these reasons, the effects of an external magnetic field on the photoinduced substitution reactions of 4-methyl-2-quinolinecarbonitrile **1** in ethanol and in cyclohexane were investigated in either the absence or presence of 1,3-pentadiene (triplet quencher).

First we will describe the magnetic field effect upon the photosubstitution reaction (**1**→**2**) in ethanol. Figure 3 shows the results when the chemical yield of **2** is plotted as a function of the field strength in the absence and presence of 1,3-pentadiene, where the conversion remained almost constant (20—22%). In the absence of 1,3-pentadiene, as is shown by curve (a) in Fig. 3, the chemical yield of **2** was *ca.* 48% at the zero field, but it increased quadratically with an increase in the field strength to be *ca.*58% at about 1.5 T (the



Scheme 2.



Scheme 3.

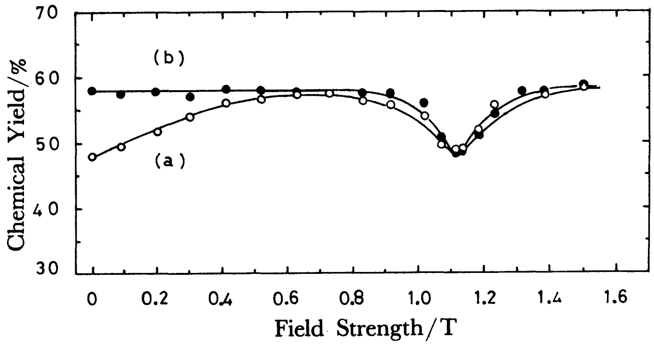


Fig. 3. External magnetic field effect upon the photosubstitution reaction (**1**→**2**) in ethanol. Chemical yield of **2** *vs.* magnetic field strength. [**1**]=4.01×10^{-3} mol dm^{-3}.
(a) —○—: [C_5H_8]=0, (b) —●—: [C_5H_8]=3.0×10^{-1} mol dm^{-3}.

magnetic field effect due to Δg mechanism); this is the same pattern as for the field dependence of the chemical yield of the S_1-born escape product or the T_1-born cage product (curve (1′) in Fig. 6). The chemical yield of **2** also showed a minimum (*ca.* 49%) at approximately 1.1 T (the magnetic field effect due to HFI-J mechanism); this is the same pattern as for the field dependence of the chemical yield of the S_1-born cage product or the T_1-born escape product (curve (3) in Fig. 5). The Δg magnetic field effect, as is shown by curve (b) in Fig. 3, disappeared completely upon the addition of 1,3-pentadiene, although the magnetic field effect due to the HFI-J mechanism was still observed. Thus, the chemical yield of **2** was *ca.* 58% at a magnetic field below 0.8 T, but it decreased steeply with an increase in the field strength to become *ca.* 48% at about 1.1 T. A further increase in the magnetic field resulted in a steep increase in the chemical yield until it became approximately constant (*ca.* 58%). The results explicitly indicate that the Δg or the HFI-J magnetic field effect observed in a photochemical reaction can be assigned to the field dependence of the chemical yield of the T_1- or S_1-born cage product.

Such an examination of the magnetic field effects leads to the conclusion that a photosubstitution reaction of 4-methyl-2-quinolinecarbonitrile **1** in ethanol (Eq. 1) proceeds according to the mechanism shown in Scheme 2. Thus, the photoexcitation of **1** into the S_1 state results in the formation of a hydrogen bond between the ring nitrogen and an ethanol. This is followed by hydrogen abstraction by the ring nitrogen from the hydrogen-bonded ethanol, which gives rise to the singlet hydrogen-bonded radical pair **2a** that is responsible for the formation of **2** (S_1-born cage product). The S_1-born singlet hydrogen-bonded radical pair **2a** undergoes a magnetic perturbation due to the HFI-J mechanism. As a result, the chemical yield of the S_1-born cage product **2** comes to show a minimum at approximately 1.1 T. In addition, an observation of the magnetic field effect due to the Δg mechanism (which disappears upon the addition of 1,3-pentadiene) indicates, unambiguously, that in the T_1 state there also occurs hydrogen abstraction by the ring nitrogen from an ethanol to yield the triplet radical pair **2b′**. The T_1-born triplet radical pair **2b′**, because of its triplet character, undergoes a diffusive separation into the solvent bulk to cause some complicating radical reactions. It should also be noted that a magnetic field effect due to the HFI mechanism, ascribed to the T_1-born triplet radical pair **2b′** (curve (2′) in Fig. 6), was not observed in this reaction system. This implies that, unless a magnetic field is applied to this system, the triplet radical pair **2b′** does not undergo an intersystem crossing to the singlet radical pair **2b** responsible for the formation of **2** (T_1-born cage product). This agrees well with the conclusion from Stern-Volmer analyses (Fig. 1) that the photosubstitution reaction **1**→**2** proceeds from the S_1 state, while some complicating reactions occur from the T_1 state.

As a general rule (*cf.* Appendix), a magnetic field effect due to the Δg or the HFI mechanism should be expected when the two components of a field-sensitive radical pair in a solvent cage is sufficiently far apart that the electron-exchange interaction can be neglected. On the other hand, a magnetic field effect due to the HFI-J mechanism should be expected when the two component radicals are in close proximity as a result of a hydrogen-bonding interaction (the electron-exchange interaction can not be disregarded). Thus, it may be considered that the S_1-born singlet radical pair **2a** which undergoes a magnetic perturbation due to HFI-J mechanism is a hydrogen-bonding pair, whereas the T_1-born triplet radical pair **2b′** which is subject to a magnetic perturbation due to the Δg mechanism is a nonhydrogen-bonding pair. This in turn leads to the conclusion that hydrogen-bonding interaction between the ring nitrogen and an ethanol does exist in the S_1 state, but that it is negligibly small in the T_1 state. This agrees well with the previously obtained conclusion from solvent-effect studies on the fluorescence and phosphorescence spectra of 2-quinolinecarbonitriles (*cf.* Table 1).[9]

Next, we describe the effect of an external magnetic field on a photosubstitution reaction (**1**→**3**) in cyclohexane. Figure 4 shows the results when the chemical yield of **3** is plotted against the field strength in either the absence or presence of 1,3-pentadiene. In either case the conversion was almost independent of the field strength (19—21%). In the absence of 1,3-pentadiene, as can be seen from curve (a) in Fig. 4, the chemical yield of **3** was *ca.* 65% at a zero field. However, it steeply decreased upon the application of a magnetic field of 40 mT to be *ca.* 54% (the magnetic field effect due to HFI mechanism). This is the same pattern as that for the field dependence of the chemical yield of the S_1-born escape product or the T_1-born cage product (curve (2′) in Fig. 6). A further increase in the field strength resulted in a quadratic increase in the chemical yield (the

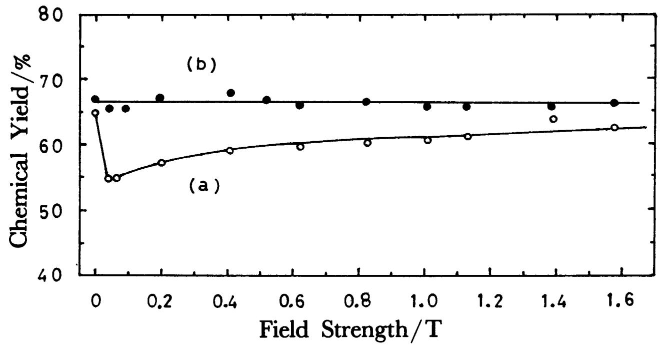


Fig. 4. External magnetic field effect upon the photosubstitution reaction ($1 \rightarrow 3$) in cyclohexane. Chemical yield of **3** *vs.* magnetic field strength. $[1]=4.01 \times 10^{-3}$ mol dm^{-3}.
(a) —○—: $[C_5H_8]=0$, (b) —●—: $[C_5H_8]=3.0 \times 10^{-3}$ mol dm^{-3}.

magnetic field effect due to Δg mechanism). This is the same pattern as the field dependence of chemical yield of the S_1-born escape product or the T_1-born cage product (curve (1′) in Fig. 6). The addition of 1,3-pentadiene, however, caused a complete disappearance of these magnetic field effects; as a result, the chemical yield of **3** became independent of the field strength to show *ca.* 67%. This means that both the HFI and Δg magnetic field effects observed in this reaction can be assigned to the field dependence of chemical yield of the T_1-born cage product. Also, the fact that the product **3** was obtained in a high yield (*ca.* 67%), even in the presence of 1,3-pentadiene, suggests strongly that the photosubstitution reaction proceeds from the S_1 state as well as the T_1 state. This is consistent with a conclusion from Stern-Volmer analyses (Fig. 2).

The external magnetic field effects described above lead to the conclusion that the photosubstitution reaction of 4-methyl-2-quinolinecarbonitrile **1** in cyclohexane (Eq. 2) proceeds according to the mechanism shown in Scheme 3. Thus, the photochemical reaction is initiated by a hydrogen abstraction from cyclohexane by the ring nitrogen, which occurs from both the S_1 and T_1 states, to yield the S_1-born singlet radical pair **3a** and T_1-born triplet radical pair **3a′** as transient intermediates. The S_1-born singlet radical pair **3a** undergoes mostly efficient cage recombination to generate the product **3** (S_1-born cage product). On the other hand, the T_1-born triplet radical pair **3a′** undergoes partly hyperfine-induced intersystem crossing to the singlet radical pair **3a** responsible for the formation of **3** (T_1-born cage product) and partly diffusive separation into the solvent bulk.

As can be seen from Fig. 4, a magnetic field effect which could be ascribed to the S_1-born singlet radical pair **3a** was not observed at all, although the formation of the product **3** undoubtedly occurs from the S_1 state, probably, *via* the intermediate **3a**. This may be interpreted as follows. As is shown in Scheme 3, the S_1-born singlet radical pair **3a** undergoes mainly the following two processes; one of them is a cage recombination (**3a**$\rightarrow$**3b**) or diffusive separation of the component radicals, while the other is a magneto-sensitive intersystem crossing (**3a**$\rightarrow$**3a′**) which occurs with a rate of the order of 10^7—10^8 s^{-1} *via* electron-nuclear hyperfine interaction. Therefore, if the cage recombination takes place in competition with the intersystem crossing, the singlet radical pair **3a** is supposed to be subject to a magnetic perturbation due to the Δg or HFI mechanism. However, the fact that such a magnetic field effect as shown in curve (1) or (2) in Fig. 5 is not observed at all implies that the cage recombination is much faster than an intersystem crossing. A similar interpretation has been made regarding the photochemical magnetic field effect of 1-isoquinolinecarbonitriles in ethanol.[6)]

The chemical yield, Y_S or Y_T, of the S_1-born or T_1-born cage product **3** was estimated from data regarding the magnetic field effects in the absence of 1,3-pentadiene (curve (a) in Fig. 4) in the following way. The chemical yield (Y°) of **3** at a zero field is equal to the sum of Y_S and Y_T (Eq. 5). The chemical yield (Y^H) of **3** at a magnetic field of 40 mT is given by Eq. 6, where the chemical yield of the T_1-born cage product **3** at a magnetic field of 40 mT is assumed to be $(1/3)Y_T$ because the number of effective working channels for the hyperfine-induced intersystem crossing of a radical pair reduces by the application of a magnetic field from three ($T_{0,\pm} \leftrightarrow S$) to one ($T_0 \leftrightarrow S$). Thus, Y_S and Y_T were evaluated by substituting $Y^\circ=65\%$ and $Y^H=54\%$ into

$$Y^\circ = Y_S + Y_T \tag{5}$$

$$Y^H = Y_S + (1/3)Y_T \tag{6}$$

Eqs. 5 and 6 to be 48.5 and 16.5% respectively. These values approximately agree with those ($Y_S=46\%$ and $Y_T=19\%$) obtained by Stern-Volmer analyses (Fig. 2).

Conclusion

The second example of a magnetic field effect due to the HFI-J mechanism (ascribed to the S_1-born singlet radical pair) was found for the case of a photoinduced substitution reaction of 4-methyl-2-quinolinecarbonitrile in ethanol (Eq. 1). This reaction also showed the magnetic field effect due to the Δg mechanism which can be ascribed to the T_1-born triplet radical pair. In the case of a photosubstitution reaction in cyclohexane (Eq. 2), the formation of a T_1-born triplet radical pair intermediate was concluded by the observation of magnetic field effects due to the HFI and Δg mechanisms. However, a magnetic field effect which could be ascribed to an S_1-born singlet radical pair was not observed. From the experimental results, the photosubstitution reaction of 4-methyl-2-quinolinecarbonitrile in ethanol or cyclohexane was unambiguously determined to proceed according to the mechanism shown in Scheme 2 or 3. This is consistent with the results of Stern-Volmer analyses. The present studies explicitly demonstrate that magnetic-perturbation experiments are quite useful for the mechanistic elucidation of photochemical reactions in solutions.

Appendix

Magnetic Field Dependence of the Chemical Yield of Photoproduct. Scheme 1 shows the case of a compound M in a solution absorbing light and, thus, being excited into S_1 and T_1 states. It thus forms singlet and triplet radical-pair intermediates. The S_1-born singlet radical pair, because of its singlet character, mostly undergoes recombination or disproportionation within a solvent cage to give rise to the S_1-born cage product. On the other hand, the T_1-born triplet radical pair, because of its triplet character, undergoes a diffusive separation into a solvent bulk to give the T_1-born escape product. Also, the intersystem crossing of the radical-pair intermediates results in the formation of the S_1-born escape product or T_1-born cage product. If such an intersystem crossing is subject to a magnetic perturbation, the chemical yield of the cage- or escape-product comes to show a magnetic-field dependence (external magnetic field effect upon photochmical reactions in solution).[1]

If the exchange interaction between the unpaired electrons in a radical pair is neglected, the singlet (S) and triplet ($T_{0,\pm}$) levels being degenerate, the rate of the intersystem crossing may be affected by an external magnetic field in the following ways. (1) Electronic Zeeman interaction (Δg mechanism); the external magnetic field causes the intersystem crossing ($S\leftrightarrow T_0$) of a radical pair by virtue of the different g-values of the component radicals. (2) Electron-nuclear hyperfine interaction (HFI mechanism); the external magnetic field causes the number of effective working channels for the hyperfine-induced intersystem crossing of a radical pair to reduce from three ($S\leftrightarrow T_{0,\pm}$) to one ($S\leftrightarrow T_0$).

On the other hand, when the unpaired electrons in a radical pair is in close proximity as a result of a hydrogen-bonding interaction between the two component radicals, the electron-exchange interaction may be greater than the electron-nuclear hyperfine energy; the singlet (S) and triplet ($T_{0,\pm}$) levels of the pair are nondegenerate, having an energy gap of $2|J|$, where J denotes the electron-exchange integral. In this case, the intersystem crossing $S\leftrightarrow T_+$ or $S\leftrightarrow T_-$ may be induced by an electron-nuclear hyperfine interaction mechanism at the magnetic field in which the S level is in resonance with the T_+ or T_- level (HFI-J mechanism).

Figure 5 shows the field dependence of chemical yield of the S_1-born cage product (CP-S_1) or the T_1-born escape product (EP-T_1). In Fig. 6 the field dependence of chemical yield of the S_1-born escape product (EP-S_1) or T_1-born cage product (CP-T_1) is also shown. In the case of a magnetic field effect due to the Δg mechanism, the chemical yields of CP-S_1 and EP-T_1 (or EP-S_1 and CP-T_1) decrease (or increase) quadratically with an increase in the field strength (curve (1) in Fig.5 or curve (1′) in Fig. 6). In the case of a magnetic field effect due to the HFI mechanism, the chemical yields of CP-S_1 and EP-T_1 (or EP-S_1 and CP-T_1) increase (or decrease) steeply at a very low field (curve (2) in Fig. 5 or curve (2′) in Fig. 6). Also, in the case of a magnetic field effect due to the HFI-J mechanism, the chemical yields of CP-S_1 and EP-T_1 (or EP-S_1 and CP-T_1) show a minimum (or a maximum) at a particualr magnetic field (curve (3) in Fig.5 or curve (3′) in Fig. 6).

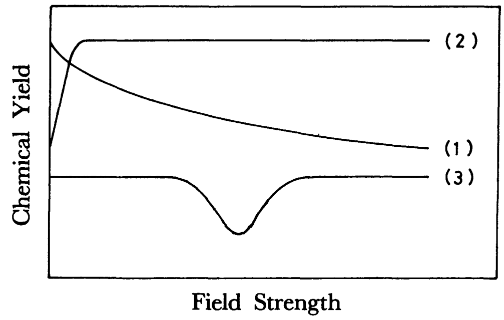


Fig. 5. Magnetic field dependence of the chemical yield of S_1-born cage product (CP-S_1) and T_1-born escape product (EP-T_1).
(1): Δg mechanism, (2): HFI mechanism, (3): HFI-J mechanism.

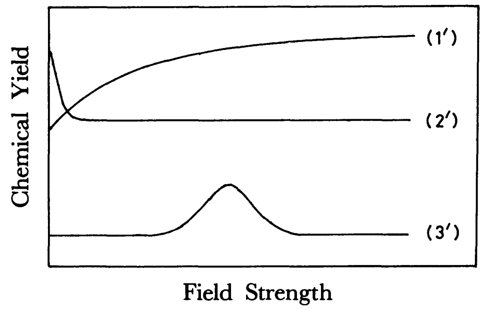


Fig. 6. Magnetic field dependence of the chemical yield of S_1-born escape product (EP-S_1) and T_1-born cage product (CP-T_1).
(1′): Δg mechanism, (2′): HFI mechanism, (3′): HFI-J mechanism.

References

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6) N. Hata, *Nippon Kagaku Kaishi*, **1984**, 1759. It has been reported that examination of the magnetic-field and heavy-atom effects on the photosubstitution reaction of 1-isoquinolinecarbonitrile or photochemical substitution and decyanation reactions of 3-methyl-1-isoquinolinecarbonitrile in ethanol were quite useful for the mechanistic elucidation of the reactions. From the experimental results, the photosubstitution reaction was revealed to proceed *via* the S_1 and/or T_1 states through hydrogen abstraction by the ring

nitrogen from ethanol, whereas the photodecyanation reaction was concluded to occur from the S_1 state through hydrogen abstraction by the ring nitrogen from the methyl group at the 3-position of an isoquinoline nucleus.

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9) In previous papers,[6-8] hydrogen-bonding interaction of the ring nitrogen of some azaaromatic nitriles in the S_0, S_1, or T_1 state with an ethanol has been discussed on the basis of the solvent effect of absorption and emission spectra (*cf.* Table 1). The absorption spectrum, both the spectral shape and maximum wavelength (the extinction coefficient), was essentially unchanged in either methylcyclohexane (MCH) or ethanol (EtOH). This means that there is no appreciable hydrogen-bonding interaction between the ring nitrogen and an ethanol in the S_0 state. On the other hand, the fluorescence spectrum showed a remarkable dependence on the solvent. The non-fluorescence (or very weak fluorescence) in MCH was interpreted in terms of a mixing of the S_1 (π,π^*) state with a closely lying $^1n, \pi^*$ state through the vibronic coupling, and the fluorescence activation in ethanol was attributable to a great decrease in such a vibronic mixing owing to the formation of hydrogen bond between the ring nitrogen and an ethanol in the S_1 state. The phosphorescence spectrum, which was observed only in the case of 2-quinolinecarbonitriles, was not affected significantly by changing the solvent from MCH to EtOH, indicating that hydrogen-bonding interaction of the ring nitrogen with an ethanol is negligibly small in the T_1 state as well as in the S_0 state.