Photochemical Reactions of 4-Methyl-2-quinolinecarbonitrile with 2,2-Diphenylalkanoic Acids. The Magnetic-Field and Solvent Effects and Reaction Mechanism

Yoko Okumura and Norisuke Hata*
Department of Chemistry, College of Science and Engineering, Aoyama Gakuin University,
Chitosedai, Setagaya-ku, Tokyo 157

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Synopsis. Magnetic-field and solvent effects upon the photochemical reactions of 4-methyl-2-quinolinecarbonitrile with achiral carboxylic acids, such as diphenylacetic acid and 2,2-diphenylpropionic acid, were investigated. Consequently, the photoreactions were concluded to proceed by a radical-pair mechanism.

In previous papers[1,2] the photochemical reaction of 4-methyl-2-quinolinecarbonitrile **1** with optically active (*S*)- or (*R*)-2-phenylpropionic acid **PPCOOH** in benzene (the (S)- or (R)-reaction) has been deduced from studies of magnetic-field and solvent effects to proceed according to an ion-pair or radical-pair mechanism; the (S)-reaction occurs with the formation of an ion-pair intermediate containing the pyramidal 1-phenylethyl anion **PP**$^-$ (the ion-pair mechanism), while the (R)-reaction proceeds along with an intervention of a radical pair containing the planar 1-phenylethyl radical **PP**$^\bullet$ (the radical-pair mechanism). In order to investigate the nature of such chiral-symmetry breaking in a chemical reaction, it may be necessary to learn whether the photochemical reaction involving achiral carboxylic acid proceeds by the ion-pair mechanism or by the radical-pair mechanism. In the present studies, therefore, the photochemical reaction of 4-methyl-2-quinolinecarbonitrile **1** with diphenylacetic acid **DACOOH** or 2,2-diphenylpropionic acid **DPCOOH** in benzene was carried out to examine any magnetic-field and polar-solvent effects.

Experimental

Materials. The 4-methyl-2-quinolinecarbonitrile (**1**) used as a sample was prepared from 4-methylquinoline *N*-oxide by Reissert reaction;[3] mp 97°C (from MeOH). Commercial diphenylacetic acid **DACOOH** and 2,2-diphenylpropionic acid **DPCOOH** (Tokyo Chemical Industries) were purified by recrystallization from benzene. The melting points of **DACOOH** and **DPCOOH** were 147 and 168°C, respectively. The benzene, dichloromethane and acetonitrile were reagent-grade products of Wako Pure Chemical Industries; the first two were used without further purification, while the last was refluxed over P_2O_5 and distilled.

Isolation and identification of Photoproducts. A benzene solution (50 cm^3) of 4-methyl-2-quinolinecarbonitrile (**1**) (100 mg) and **DACOOH** or **DPCOOH** (270 mg) in a Pyrex vessel was irradiated with a 100 W high-pressure immersion mercury lamp (Riko Kagaku Sangyo Co.) for 1.5 h in an atmosphere of nitrogen at room temperature. After removing the solvent under reduced pressure, the residue was neutralized with aqueous sodium carbonate and then extracted with chloroform. The solution was dried with anhydrous sodium sulfate and then concentrated in vacuo. The unreacted **1** and product **2** or **3** were separated by means of silica-gel TLC (Merck silica-gel plate $60F_{254}$; layer thickness, 2 mm; eluent, hexane–ethyl acetate (5 : 1)). The products **2** and **3** were 2-diphenylmethyl-4-methylquinoline and 2-(1,1-diphenylethyl)-4-methylquinoline, respectively. The analytical data of the products were as follows.

Product 2: Mp 110°C (from MeOH). MS *m/z* 309 (M$^+$). ^{1}H NMR ($CDCl_3$, TMS) δ=7.2—8.1 (m, 15H, aromatic), 5.86 (s, 1H, –CH (Ph)$_2$), 2.62 (s, 3H, –CH_3). Found: C, 89.58; H, 6.11; N, 4.34%. Calculated for $C_{23}H_{19}N$: C, 89.28; H, 6.19; N, 4.53%.

Product 3: Mp 130°C (from MeOH). MS *m/z* 323 (M$^+$). ^{1}H NMR ($CDCl_3$, TMS) δ=7.1—8.1 (m, 15H, aromatic), 2.56 (s, 3H, –CH_3), 2.32 (s, 3H, –$C(Ph)_2CH_3$). Found: C, 89.09; H, 6.55;N, 4.34%. Calculated for $C_{24}H_{21}N$: C, 89.16; H, 6.50; N, 4.33%. The ^{1}H NMR spectra were taken with a JEOL NMR spectrometer (JNM-GX-270). The mass spectra were obtained with a JEOL mass spectrometer (JMS-HX 100M).

Quantitative Experiments. A 50-cm^3 portion of a benzene solution containing 50 mg of **1** and 270 mg of **DACOOH** or **DPCOOH** in a quartz vessel (44×45×25 mm^3) was irradiated with a 500 W Ushio super-high-pressure Mercury Lamp (USH-500D) equipped with a Toshiba filter UV-31 for 40 min at room temperature, while nitrogen was bubbled in, in the absence or presence of a magnetic field. The amounts of the unreacted **1** and product **2** or **3** were determined by means of HPLC (JASCO Gulliver series) to evaluate the chemical yield of the product (the conversion, 35—40%). Photoreactions at zero field were also undertaken in polar solvents, such as dichloromethane and acetonitrile. The experiments were repeated five times for each point of Figs. 1 and 2 to obtain the average chemical yield and the standard error.

Results and Discussion

The irradiation of a benzene solution of 4-methyl-2-quinolinecarbonitrile (**1**) and diphenylacetic acid **DACOOH** or 2, 2-diphenylpropionic acid **DPCOOH** resulted in the formation of **2** or **3** in a ca. 68 or 77% yield; hereafter, the photoreaction involving **DACOOH** or **DPCOOH** is referred to as the DA- or DP-reaction (Scheme 1).

As is well-known, a photoreaction proceeding via a radical-pair intermediate in solution generally shows some magnetic field effect, while a reaction occurring along with the intervention of an ion pair does not.[4]

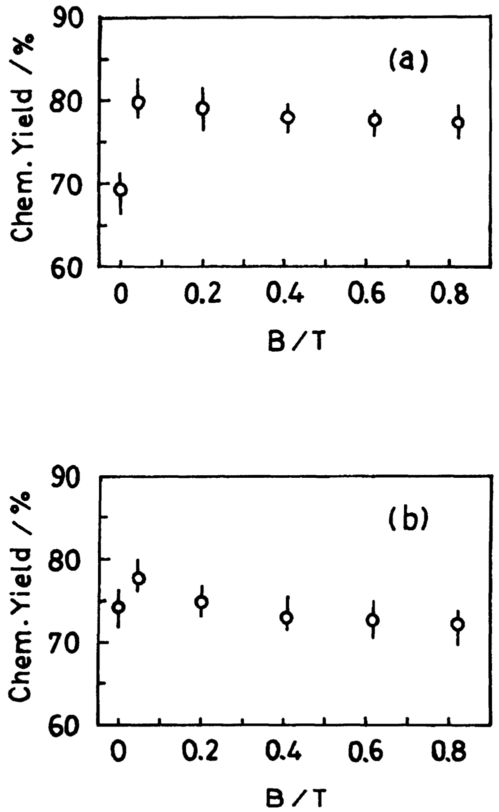
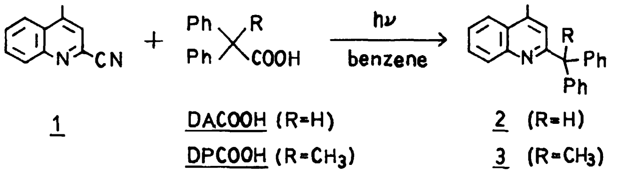


Fig. 1. Chemical yield of product versus the magnetic-field strength. (a) DA-reaction (product **2**). (b) DP-reaction (product **3**).



Scheme 1.

Thus, it is quite useful for a mechanistic elucidation of a photochemical reaciton in solution to examine whether or not the chemical yield of the product is influenced by an external magnetic field.[5] For this reason, a DA- or DP-reaction in benzene was carried out in the absence or presence of a magnetic field to obtain information concerning the mechanism. Figure 1 shows a plot of the chemical yield against the field strength. In the case of the DA-reaction (Fig. 1a), the chemical yield of **2** was 68.8±2.3% at zero field, but it steeply increased upon the application of a magnetic field of 45 mT to be 79.4±2.6%; the magnetic-field effect was due to the HFI mechanism. A further increase in the field strength resulted in a slight decrease in the chemical yield (77.0±2.0% at 0.82 T); the magnetic-field effect was due to the Δg mechanism. In the case of the DP-reaction (Fig. 1b), also, the magnetic field effects due to the HFI and Δg mechanisms were observed, though they were not very large; the chemical yield of **3** was 74.3±2.2% at zero field, 77.7±2.2% at 45 mT and 72.3±2.3% at 0.82 T.

Observation of the magnetic-field effects clearly indicates that both the DA- and DP-reactions, just as the (R)-reaction,[2] proceed according to a radical-pair mechanism, as shown in Scheme 2.[6] Field-sensitive species may be considered to be a radical pair comprising the quinolinium radical and **DA$^\bullet$** (or **DP$^\bullet$**), but not the precursor pair (quinolinium radical and the hydrogen-bonded **DACOO$^\bullet$** (or **DPCOO$^\bullet$**)). If the precursor pair is subject to a magnetic perturbation the magnetic-field effect due to the HFI-J mechanism is supposed to be observed, because in such a hydrogen-bonding pair the electron-exchange interaction is much greater than the electron-nuclear hyperfine energy.[2]

Next, in order to obtain further evidence concerning the radical-pair mechanism, a DA- or DP-reaction at zero field was carried out in polar solvents, such as dichloromethane (dielectric constant, 9.1) and acetoni-

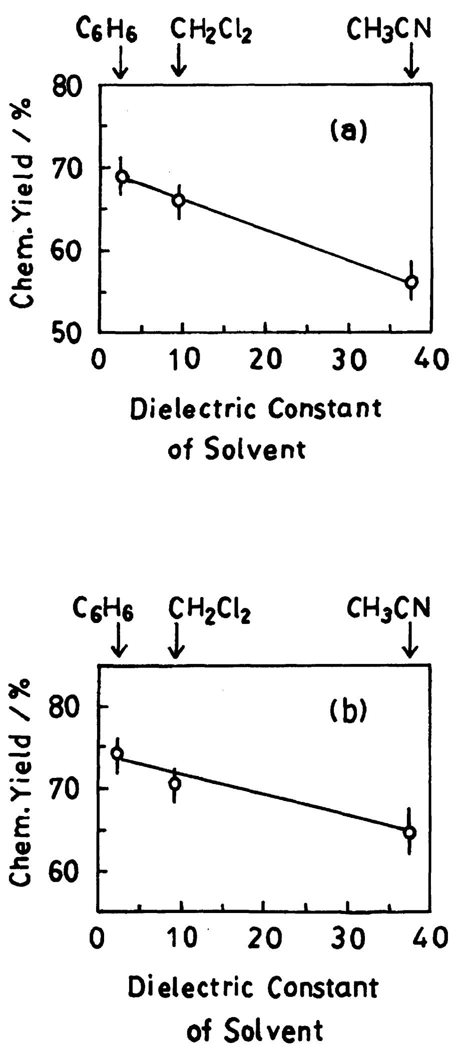
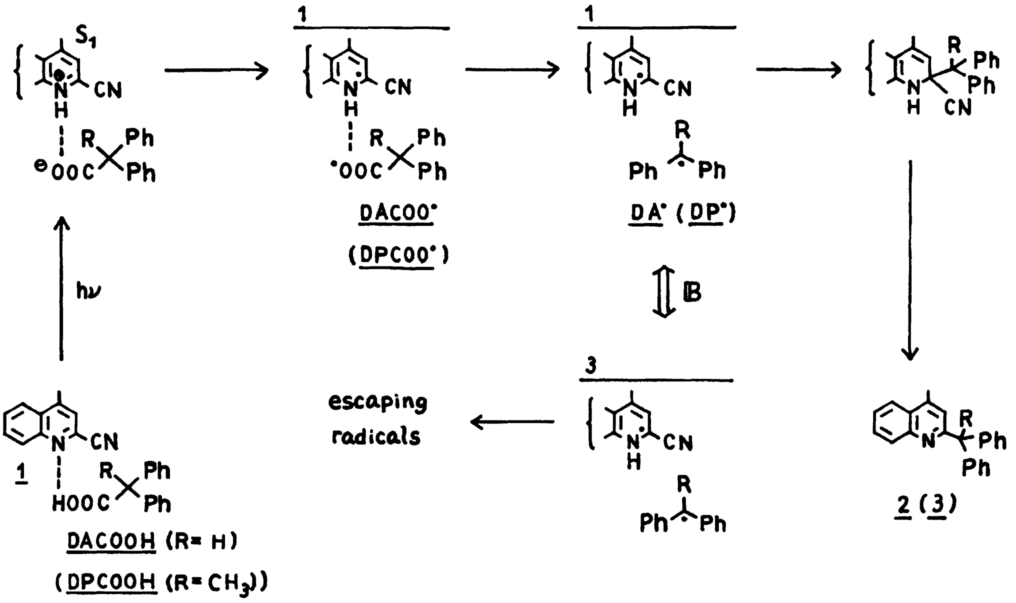


Fig. 2. Chemical yields of the product of the DA- and DP-reactions in benzene, dichloromethane, or acetonitrile. (a) DA-reaction (product **2**). (b) DP-reaction (product **3**).



Scheme 2.

trile (37.5), as well as in non-polar benzene (2.3). If the photochemical reaction proceeds via radical-pair inermediates, in analogy with the (R)-reaction, the chemical yield of product is supposed to linearly decrease with an increase in the dielectric constant of the solvent (cf. Fig. 3 in Ref. 2). On the other hand, the photoreaction, provided that it occurs with the formation of an ion-pair intermediate, is supposed to be affected by a slight increase in the dielectric constant of the solvent, similarly to the (S)-reaction, so that the chemical yield quadratically decreases by changing the solvent from C_6H_6 to CH_2Cl_2, and then CH_3CN (cf. Fig. 3 in Ref. 2).

Figures 2a and 2b show the chemical yields of products **2** and **3**, respectively, when the reaction was carried out in C_6H_6, CH_2Cl_2, or CH_3CN. As can be seen from the figures, both the DA- and DP-reactions showed the same pattern of solvent dependence as did the (R)-reaction. The results strongly support the conclusion drawn from the magnetic-perturbation experiments: The photoreactions proceed by the radical-pair mechanism.

In conclusion, the photochemical reactions of 4-methyl-2-quinolinecarbonitrile **1** with achiral carboxylic acids, such as **DACOOH** and **DPCOOH**, were revealed by an examination of the magnetic-field and solvent effects to proceed by the radical-pair mechanism, but not proceed by the ion-pair mechanism, clearly indicating that the achiral carboxylic acids show a chemical behavior that is similar to (*R*)-**PPCOOH**, rather than (*S*)-**PPCOOH**. This may serve as a clue to elucidate the reason why the (*S*)- and (*R*)-forms of the 2-phenylpropionate ion $\mathbf{PPCOO^-}$ differ in their chemical reactivities toward the hydrogen-bonded excited quinolinium ion (the chiral-symmetry breaking).[1,2]

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5) See, for example, Ref. 2 and the following literature: N. Hata and H. Nishida, *Bull. Chem. Soc. Jpn.*, **58**, 3423 (1985).
6) The photorections might proceed partly according to the ion-pair mechanism, but the magnetic perturbation experiment tells us nothing about it.