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Does a Magnetic Field Induce Optical Activity in Photochemical Reaction of 4-Methyl-2-quinolinecarbonitrile with Optically Active (*S*)-(+)-2-Phenylpropionic Acid ?

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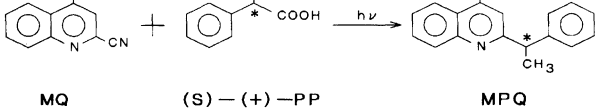
Synopsis. The effect of a magnetic field on optical activity of a product was reinvestigated in photochemical reaction of 4-methyl-2-quinolinecarbonitrile with optically active (*S*)-(+)-2-phenylpropionic acid. The spectroscopic data show that the product, 4-methyl-2-(1-phenylethyl)quinoline, becomes racemic both in the presence and absence of a magnetic field (45 mT), indicating no induction of the optical activity by the magnetic field.

Recently, Hata presented stimulating investigation that the optical activity of a photoproduct, 4-methyl-2-(1-phenylethyl)quinoline (MPQ), had been induced by a magnetic field (45 mT) in photochemical reaction of 4-methyl-2-quinolinecarbonitrile (MQ) with optically active (*S*)-(+)-2-phenylpropionic acid (PP) (Scheme 1).[1] Although it is usually believed that reactions of optically inactive substances with optically active reagents yield racemic compounds, he reported that MPQ had become optically active only when reacted in the presence of a magnetic field (45 mT): $[\alpha]_D^{23}$ of MPQ is −2.5° (*c* 2.36, $CHCl_3$)[1] and that its enantiomeric excess determined by ^1H NMR had been 17%.[1c] This novel magnetic field effect, if it is correct, can not be explained by conventional theories of magnetic field effects.[2]

The purpose of this paper is to reinvestigate whether optical activity of MPQ is induced by a magnetic field in the photoreaction of MQ and PP, using the same spectroscopic methods of specific rotation and ^1H NMR as reported. In order to examine the reported magnetic field effect, it is indispensable to follow experimental procedures reported in the literature as precisely as possible. However, its description is very brief. For example, the conversion of MQ in the case of optical activity experiments was not written in the literature. Therefore, we have obtained detailed information about experimental procedures from Hata, and special care has been taken to follow the procedures suggested by Hata in the present study.

Experimental

Materials. 4-Methyl-2-quinolinecarbonitrile (MQ) was synthesized and purified according to methods described in the literature.[1,3] (*S*)-(+)-2-Phenylpropionic acid (Nacalai) (PP) was used as received. Reagent-grade benzene (Wako) and $CHCl_3$ (Nacalai) were used as solvents for photolysis and the succeeding treatments. A chiral NMR shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato] europium(III) derivative (Aldrich) (Eu(hfc)$_3$), was treated over P_2O_5 in vacuo for 6 h before use.



Scheme 1.

Photolysis. Starting materials of 72 mg MQ (1.2×10^{-2} mol dm^{-3}) and 360 mg PP (6.7×10^{-2} mol dm^{-3}) were dissolved in 36 ml benzene. The sample solution transferred into a quartz vessel (36 ml volume) was placed between pole pieces of a conventional electromagnet. After deoxygenating by N_2 gas (15 min), the solution was irradiated with a 500 W super-high-pressure Hg lamp (Ushio, USH-500D) equipped with a UV cut-off filter (Toshiba, UV-31) at room temperature in the presence (45 mT) and absence (<0.6 mT) of a magnetic field. The deoxygenation by N_2 gas was continued throughout irradiation. The 25% conversion of MQ was consequently performed after 1.5 h irradiation.[4] The solvent was evaporated from the reaction mixture under reduced pressure at 33 °C, and then unreacted PP was removed by alkalinizing the residue with aqueous Na_2CO_3. The extract by $CHCl_3$ from the residue was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The product, 4-methyl-2-(1-phenylethyl)quinoline (MPQ), was isolated purely by thin layer chromatography on silica gel (Merck, silica gel plate $60F_{254}$) with hexane–ethyl acetate (5 : 1), followed by column chromatography on silica gel (Wako, C-300) with $CHCl_3$. The total amount (ca. 300 mg) of the product was obtained by repeating the preceding procedure more than 10 times, and was purified by recrystallization from spectro-grade methanol (Nacalai) to give white crystals of MPQ: Mp 88—89 °C; ^1H NMR ($CDCl_3$) $\delta=1.78$ (3H, d, $J=7.3$ Hz), 2.59 (3H, s), 4.44 (1H, q, $J=7.2$ Hz), 7.02 (1H, s), 7.20 (1H, t, $J=7.3$ Hz), 7.29 (2H, t, $J=7.6$ Hz), 7.35 (2H, d, $J=7.8$ Hz), 7.50 (1H, t, $J=7.8$ Hz), 7.68 (1H, t, $J=7.8$ Hz), 7.91 (1H, d, $J=8.3$ Hz), 8.10 (1H, d, $J=8.3$ Hz).

Measurements. Specific rotations $[\alpha]_D^{23}$ of MPQ were determined with a digital polarimeter (Horiba, SEPA-300) in freshly opened, spectro-grade $CHCl_3$ (Nacalai). Its ac-

Table 1. $[\alpha]_D^{23}$ of MPQ (*c* 2.37, $CHCl_3$) Formed in the Presence (45 mT) and Absence (<0.6 mT) of a Magnetic Field

	45 mT	<0.6 mT
This work	−0.09±0.03°	−0.26±0.04°
Hata's work[a)]	−2.5°	0°

a) Refs. 1a and 1b.

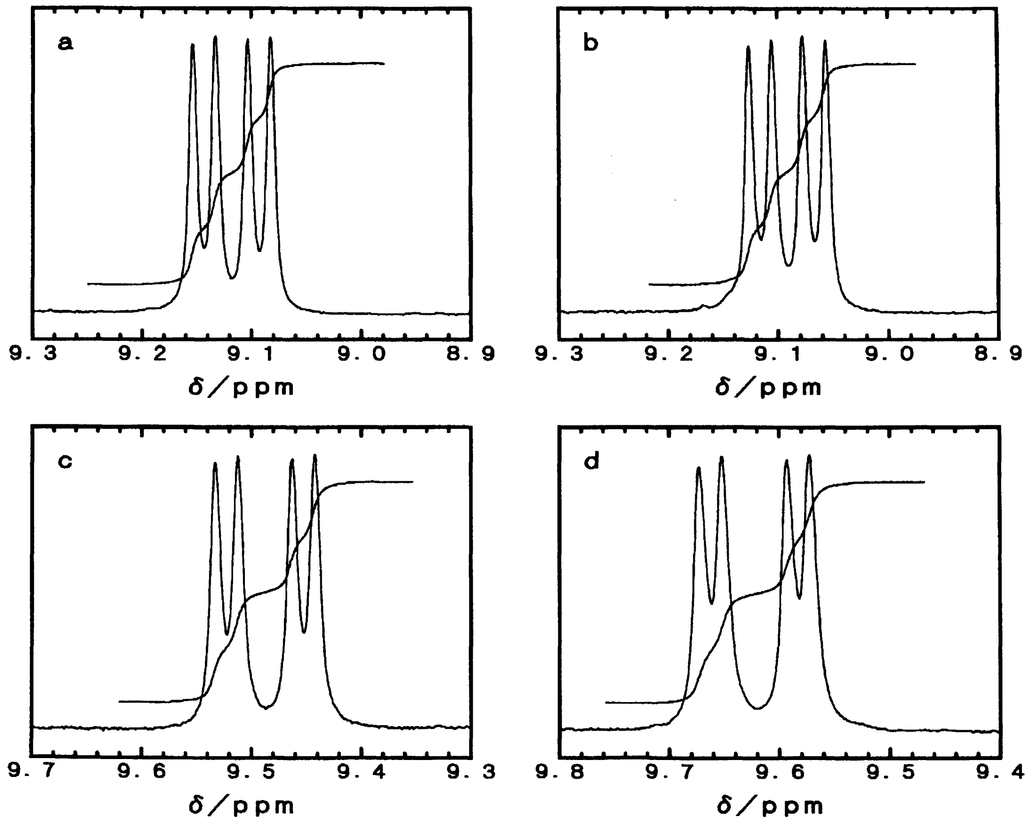


Fig. 1. ^{1}H NMR spectra and their integration curves at 8-position of a quinoline ring of MPQ obtained in the presence (45 mT) and absence (<0.6 mT) of a magnetic field. The conditions are the following: (a) 45 mT, Eu(hfc)$_3$=0.6 molar amount; (b) <0.6 mT, Eu(hfc)$_3$=0.6 molar amount; (c) 45 mT, Eu(hfc)$_3$=1.1 molar amount; (d) <0.6 mT, Eu(hfc)$_3$=1.1 molar amount.

Table 2. Enantiomeric Excess (e.e.) Obtained from ^{1}H Integration of MPQ Formed in the Presence (45 mT) and Absence (<0.6 mT) of a Magnetic Field

	Eu(hfc)$_3$ molar amount	45 mT	<0.6 mT
This work	0.6	1.4±0.06%	2.2±0.09%
	1.1	0.0±0.004%	0.4±0.02%
Hata's work[a]	1.1	17%	0.2%

a) Ref. 1c.

curacy was checked by measuring $[\alpha]_{\mathrm{D}}^{23}=+65.4\pm0.01°$ of a standard solution of sucrose (c 26.0, H_2O). ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer (JEOL, EX-400) in $CDCl_3$ at 25 °C, using TMS as internal standard. The relative quantum yield (enantiomeric excess) of the product was evaluated by means of ^{1}H integration of the enantiomers' signals separated with Eu(hfc)$_3$.

Results and Discussion

The photolysis was carried out as accurately as possible to follow Hata's procedure as described in the experimental section. The product, MPQ, was identified both chromatographically and spectroscopically. After careful purification of MPQ, spectroscopic measurements of specific rotation and ^{1}H NMR were performed to check the optical activity induced by a magnetic field (45 mT).

Table 1 shows specific rotation, $[\alpha]_{\mathrm{D}}^{23}$, of MPQ ($c$ 2.37, $CHCl_3$) obtained in the presence (45 mT) and absence (<0.6 mT) of a magnetic field. The data of $[\alpha]_{\mathrm{D}}^{23}$ at 45 mT and <0.6 mT were $-0.09\pm0.03°$ and $-0.26\pm0.04°$, respectively. Since both of them were nearly equal to zero irrespective of a magnetic field, it is considered that there is no difference between their values in experimental error. On the other hand, Hata has reported the $[\alpha]_{\mathrm{D}}^{23}$ of MPQ at 45 mT is $-2.5°$ (c 2.36, $CHCl_3$).[1] Therefore, the data indicate that MPQ generated in the presence of a magnetic field is a racemic compound different from the case of Hata, and deny possibility of induction of optical activity by a magnetic field (45 mT).

In order to confirm the conclusion derived from the results for the specific rotation, direct observation of each enantiomer was attempted by using ^{1}H NMR spectroscopy as reported.$^{1c)}$ In this experiment, the chiral shift reagent, Eu(hfc)$_3$ was used. It commonly affords respective enantiomers different NMR chemical shifts by forming an Eu(hfc)$_3$–(*S*)-(or (*R*)-)MPQ diastereoisomer. Figure 1 illustrates ^{1}H NMR spectra and their integration curves at 8-position of an MPQ quinoline ring in the presence of 0.6 and 1.1 molar amount of Eu(hfc)$_3$. The signals shifted from the original position (δ=8.10 ppm) (see Experimental section) to δ=9—9.6 in the presence of the shift reagent. All of the spectra show quartets. They are respectively divided into two parts at the central valley and interpreted by superimposition of a spectrum of each enantiomer, which shows a doublet (J=8 Hz) spectrum owing to magnetic shielding by a proton at 7-position of the quinoline ring. For example, a couple of signals at δ=9.082 and 9.103 and a couple of signals at δ=9.133 and 9.155 in Fig. 1a are attributable to enantiomers. Since two doublets are separated better than Hata's NMR spectra,$^{1c)}$ it is possible to estimate an enantiomeric excess (e.e.) accurately by integrating each doublet signal, as depicted in Fig. 1. The results are summarized in Table 2. Hata has shown ^{1}H NMR spectra and described ^{1}H integration ratio of one enantiomer to another one is 0.714 in the case of MPQ obtained at 45 mT. He has obtained that e.e. is 17% from it. In our case, however, the data of e.e. were almost zero in all cases in accord with the result of the specific rotation. These results mean that enantiomers of MPQ are generated completely equivalently. Therefore, the fact undoubtedly reveals that this photoreaction originally yields equivalent enantiomers in the presence and absence of a magnetic field (45 mT), in contrast to the results by Hata.

In conclusion, no magnetic-field-induced optical activity of MPQ in this photoreaction was observed in spectroscopic measurements of its specific rotation and ^{1}H NMR. At present stage, we have no reasonable explanation for the discrepancy between this result and the reported ones.$^{1)}$

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4) The conversion of MQ used in the optical activity measurement was not appeared in Ref. 1. According to the private information from Hata, it was ca. 40%. He also suggested that the photolysis should be carried out at 25% conversion of MQ in order to improve its purification procedure without reducing optical activity.