Photosubstitution Reactions of 4-Methyl-2-quinolinecarbonitrile with Arylalkanoic Acids. No Evidence for the External Magnetic Field Effects or Chiral Symmetry Breaking

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No appreciable magnetic field effects were observed on the relative quantum yield for photochemical reactions of 4-methyl-2-quinolinecarbonitrile with (*R*)-(−)-2-phenylpropionic, diphenylacetic, and 2,2-diphenylpropionic acids in benzene. Observed results were reasonably explained in terms of kinetic parameters which are dependent on and independent of an external magnetic field. (*S*)-(+)- and (*R*)-(−)-*α*-methoxyphenylacetic acids exhibit equivalent reactivity toward the excited state of 4-methyl-2-quinolinecarbonitrile in acetonitrile. No unusual phenomena were observed under well controlled conditions with sufficient repetitions.

Photochemical alkylation of heteroaromatic compounds has been known for a various combination of heterocycles and carboxylic acids.[1—5] In the case of quinoline and its derivatives, the alkylation takes place at 2, 4, and both positions. Since the same orientation is observed for thermal alkylation of quinolines by radical species,[6,7] the photochemical alkylation may involve alkyl radicals formed by decarboxylation of the carboxylic acids. This type of photoreactions can be characterized as photo-induced alkylation and photodecarboxylation. Photochemical reduction of acridine has been studied by CIDNP method and the singlet radical pair has been assumed as a precursor.[3] Recently Hata proposed two independent reaction pathways for photochemistry of 4-methyl-2-quinolinecarbonitrile (MQCN) with (*S*)-(+)- or (*R*)-(−)-2-phenylpropionic acid,[8] namely, suggested that the (*R*)-type acid and the (*S*)-type acids exhibit inequivalent reactivity toward the excited state of 4-methyl-2-quinolinecarbonitrile. In addition, he has reported magnetic field effects (MFE) on the reaction yields for photoproduct obtained after photolysis of the reactant quinoline with the (*R*)-type acid in benzene. Although this work is of some significance in connection with the magnetic field effects on asymmetric synthesis of biological molecules, the author has attributed the appearance of optical activity to some unidentified type of chiral symmetry breaking. In a previous paper,[9] we have investigated the photosubstitution and found no appreciable field effects on the end product formation. The purpose of the present paper is to report the magnetic field effects on the photoreaction yields of MQCN for a variety of arylalkanoic acids and to show that the (*S*)- and (*R*)-type acids exhibit equivalent reactivity toward the excited state of 4-methyl-2-quinolinecarbonitrile. It should be noted that recently Tanimoto and co-workers attempted to reproduce the results reported by Hata, but in vain.[10] No evidence for the chiral symmetry breaking has been revealed from a recent CIDNP study by Azumi and his collaborators.[11]

Experimental

General. Electronic absorption spectra were measured on a Hitachi U-3200 spectrophotometer. An electromagnet (Tokin SEE-9G) were used. The magnetic field strength was monitored with a Denshi-jiki Kogyo GM-1220 gaussmeter, and the residual field was less than 0.08 mT. Optical rotations were determined on a Horiba digital polarimeter SEPA-300.

Material. 4-Methyl-2-quinolinecarbonitrile was prepared and purified according to methods described in the literature.[8,12] (*R*)-(−)-phenylpropionic acid of guaranteed reagent grade was supplied by Nacalai Tesque. The specific rotation of the (*R*)-type acid was $[\alpha]_D=-72.2$ (solvent chloroform, *c* 1.0). (*S*)-(+)- and (*R*)-(−)-*α*-methoxyphenylacetic acids were obtained from Aldrich. The specific rotations (solvent water, *c* 1.0) were determined to be $[\alpha]_D=+157.1$ for the *S*-type acid and $[\alpha]_D=-158.7$ for the *R*-type acid. Benzene and acetonitrile for high-performance liquid chromatography (HPLC) were used as solvents for photochemical reactions and chromatographic analysis. Chloroform and tetrahydrofuran of spectroscopy grade were used for the optical rotation measurement and for the HPLC analysis, respectively. One of the photoproduct, 4-methyl-2-(1-phenylethyl)quinoline, is a gift from Drs. Y. Fujiwara and Y. Tanimoto, and has been characterized in the literature.[8,10]

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This end product was identified by comparing its HPLC retention time with that of the authentic sample. Other photoproducts were identified by means of LC-UV method (vide infra). All photoproducts derived from MQCN exhibit absorption spectra which can be well simulated by superposition of those of 2,4-dimethylquinoline and appropriately substituted benzenes.

Photolysis. Three types of quartz cell were used in the photolysis experiment. A quartz cuvette ($10\times10\times45$ mm^3) was used for a small-scale photolysis, while in a large-scale photolysis used were cylindrical cells with 30 mm diameter and 50 mm optical pathlength and 40 mm diameter and 40 mm optical pathlength. Sample solutions for the small-scale photolysis were deaerated by several freeze-pump-thaw cycles and then sealed under vacuum before irradiation. The sample solution in a quartz cell was irradiated with UV light from an Ushio 500 W xenon short arc lamp (UXL 500D) or an Ushio 500 W mercury lamp (super-high-pressure USH-500D) filtered through Toshiba UV-31 filter. The light intensity was monitored by a photosensor. The accumulation of output signal from the sensor for a constant period indicated that the light intensity fluctuation was less than 0.8%.[13] The quartz cell containing the sample solution was placed between the pole pieces of the electromagnet during photolysis at room temperature.

Chromatographic Analysis and Evaluation of Experimental Errors. Reaction mixtures were analyzed on a Waters Model 510 HPLC equipped with a liquid chromatography spectrophotometer (Waters Model 481 or Shimadzu SPD-10A). Normal- and reversed-phase columns were used for the HPLC analysis of photochemical reaction mixtures obtained in benzene and acetonitrile, respectively. A 10 µl portion of the sample solution before irradiation or the photolyzed solution was withdrawn by a micro-syringe and then injected into the column. The integrated intensity (I^X) was determined from the chromatogram recorded after photolysis in the presence and the absence, respectively, of an external magnetic field (X=45 or 0 mT). Average values for the integrated area of peaks due to the starting species and to the photoproduct (I^X, X=0 or H) were obtained from six to eight separate chromatograms for each set of measurements, and a ratio $R=I^H/I^0$ was calculated. This ratio will be referred to as an MFE parameter. Averages of the R values determined from repeated measurements were listed in Tables 2 and 3 together with the number of measurements. The ratio is considered to be relative quantum yield (Φ^H/Φ^0) for the reaction product. A ratio defined as $R=I^R/I^S$ was also evaluated from the peak intensity determined for solutions containing the (R)- and (S)-type acids in a manner similar to that described for the MFE experiment except the fact that the experiments were performed in the zero field. The uncertainty quoted in Tables 1, 2, 3, and 4 represents the square root of the unbiased variance, $\{ns^2/(n-1)\}^{1/2}$, where s^2 is the sample variance and n is the number of measurements.[14] This quantity is frequently called the standard deviation. Photoproducts were identified on the basis of LC-UV absorption spectra obtained by combination of the HPLC apparatus and a spectromultichannel photodetector for liquid chromatography (Otsuka Electronics MCPD-3600). By means of LC-UV absorption spectroscopy, it was confirmed that each chromatographic peak corresponds to a single species under the analytical conditions employed in the present study.

Individual Photolysis and Analysis. Photoreaction of MQCN with α-Methoxyphenylacetic acid: The concentrations of reactants were as follows: [α-methoxyphenylacetic acid]=6.02×10^{-2} M and [4-methyl-2-quinolinecarbonitrile]=5.94×10^{-3} M (1 M=1 mol dm^{-3}). Excitation source: Xe arc 500 W (small-scale photolysis) and Hg arc 500 W (large-scale photolysis). Analysis was made by the use of reversed-phase column (Cica–Merck, Hibar, LiChrosorb RP-18 [7 µm]) with a flow rate of 1 cm^3 min^{-1}. The eluting solvent was mixture of acetonitrile and distilled water with the volume ratio of 90 : 10. Photoreaction of MQCN with diphenylacetic and 2,2-diphenylpropionic acids: Excitation source for the small-scale photolysis: Xe arc (500 W) with a Toshiba UV-31 filter. The concentrations of reactants were as follows: [diphenylacetic acid]=2.55×10^{-2} M, [2,2-diphenylpropionic acid]=2.38×10^{-2} M, and [4-methyl-2-quinolinecarbonitrile]=5.95×10^{-3} M. Analysis was made by the use of a normal-phase column (Cica–Merck, Hibar, LiChrosorb Si-60 [10 µm]) with a flow rate of 1 cm^3 min^{-1}. The eluting solvent was a mixture of benzene and tetrahydrofuran with the volume ratio of 200 : 1. Photoreaction of MQCN with 2-Phenylpropionic acid: The concentrations of reactants were as follows: [(R)-(−)-2-phenylpropionic acid]=6.67×10^{-2} M

Table 1. HPLC Analysis of the Photochemical Reaction Mixture Obtained for (R)-(−)- and (S)-(+)-α-Methoxyphenylacetic Acids and 4-Methyl-2-quinolinecarbonitrile in Acetonitrile[a)]

Intensity ratio of the peak due to the residual starting quinoline derivative ($R=I^R/I^S$)			
Photolysis	$R\pm\delta R$	Conversion	Number of measurements
Small-scale	0.98±0.02	16.9±1.0%	3
Large-scale	1.01±0.04	25.9±1.1%	3
Intensity ratio of the peak due to the end product ($R=I^R/I^S$)			
Photolysis	$R\pm\delta R$	Conversion	Number of measurements
Small-scale	0.99±0.01	16.9±1.0%	3
Large-scale	1.04±0.05	25.9±1.1%	3

a) The integrated peak intensity, I^R or I^S was measured by monitoring absorbance at 315 nm, where I^R and I^S are average peak areas observed for the photoreaction of the quinolinecarbonitrile with the (R)- and (S)-type acids, respectively.

Table 2. HPLC Analysis of the Photochemical Reaction Mixture Obtained for Diphenylacetic and 2,2-Diphenylpropionic Acids and 4-Methyl-2-quinolinecarbonitrile in Benzene[a]

Intensity ratio of the peak due to the residual starting quinoline derivative ($R=I^H/I^0$)			
Acid	$R\pm\delta R$	Conversion	Number of measurements
Diphenylacetic	1.00±0.02	7.9±1.5%	8
Diphenylpropionic	1.01±0.03	7.4±1.9%	8
Intensity ratio of the peak due to the end product ($R=I^H/I^0$)			
Acid	$R\pm\delta R$	Conversion	Number of measurements
Diphenylacetic	1.00±0.01	7.9±1.5%	8
Diphenylpropionic	0.99±0.01	7.4±1.9%	8

a) The integrated peak intensity, I^X, was measured by monitoring absorbance at 315 nm, where X=45 or 0 mT. The residual starting quinoline was determined in comparison with the amount of the quinoline dissolved in the solution before irradiation.

Table 3. HPLC Analysis of the Photochemical Reaction Mixture Obtained for (*R*)-(−)-2-Phenylpropionic Acid and 4-Methyl-2-quinolinecarbonitrile in Benzene

Intensity ratio of the peak due to the residual reactant quinoline ($R=I^H/I^0$)			
Photolysis	$R\pm\delta R$	Conversion	Number of measurements
Small-scale	1.00±0.01	7—20%	7[a]
Large-scale	1.00±0.02	20—40%	24[b]
Intensity ratio of the peak due to the product quinoline ($R=I^H/I^0$)			
Photolysis	$R\pm\delta R$	Conversion	Number of measurements
Small-scale	1.00±0.01	7—20%	7[a]
Large-scale	1.00±0.06	20—40%	24[b]

The residual starting quinoline was determined in comparison with the amount of the quinoline dissolved in the solution before irradiation. a) An average value for the data given in Ref. 9. b) Excitation source for the large-scale photolysis: Hg arc (500 W) with a Toshiba UV-31 filter.

Table 4. Chemical Yields of Photosubstitution of MQCN with (*R*)-(−)-2-Phenylpropionic Acid in Benzene

$Y(0)$[a]	$Y(\mathrm{H})$[b]	
83.4±5.7%	84.2±5.8%	This work
81.2±2.1%	89.3±2.3%	Ref. 8

a) The yield in the zero-magnetic field. b) The yield in the presence of 45 mT. The quoted uncertainty represents the standard deviation evaluated from 13 separate measurements of $Y(0)$ and $Y(\mathrm{H})$. $Y(X)$ is determined in the following manner: $Y(X)=\mathrm{PQ}(X)/[\mathrm{RQ_i}-\mathrm{RQ_f}(X)]$ where $\mathrm{PQ}(X)$ refers to the amount of product quinoline, and $\mathrm{RQ_i}$ and $\mathrm{RQ_f}(X)$ denote the initial and residual amounts of reactant quinoline in the presence of X mT. These amounts were determined by means of HPLC.

and [4-methyl-2-quinolinecarbonitrile]$=5.95\times10^{-3}$ M. Analytical conditions were essentially the same as those described for photolysis of MQCN with diphenylacetic and 2,2-diphenylpropionic acids.

Our procedures for detecting MFE on product yields are reproducible, because the reaction mixture obtained on photolysis is immediately analyzed by means of HPLC without any chemical treatment. The experimental procedures in the present study are summarized as follows:

(1) The dissolved oxygen was removed under vacuum for the small-scale photolysis. Nitrogen bubbling was employed in the large-scale photolysis.

(2) The UV-irradiation was stopped at conversions (2—20%) with respect to the starting quinoline for the small-scale photolysis, while higher conversion (20—40%) conditions were employed in the large-scale photolysis.

(3) Conditions for photolysis and analysis were kept as constant as possible throughout the experiment.

Results

The results given in Table 1 shows that equivalent photochemical reactivity is observed for acetonitrile solutions of the quinolinecarbonitrile and the (*R*)- and (*S*)-type α-methoxyphenylacetic acids in the zero field. The disappearance of the starting species and the formation of the end product are equal irrespective of the photolysis condition.

No appreciable difference was observed on the product yield for the photoreaction between diphenylacetic and diphenylpropionic acids and 4-methyl-2-quinolinecarbonitrile in the absence and the presence of 45 mT. It can be concluded that the magnitude of MFE is smaller than 2% from the data shown in Table 2.

Figures 1 and 2 illustrate histograms of R values observed for the photosubstitution of MQCN with (R)-(−)-2-phenylpropionic acid. The most frequently observed values are in the range of 1.00±0.01 in both figures. Table 3 shows that the magnitude of MFE on photoreaction of MQCN is less than 1% in photolysis with low conversions. Table 4 lists the chemical yields determined in the presence and absence of 45 mT.

The present findings are summarized as follows: the photosubstitution reaction yield does not depend on the applied magnetic field strength (45 mT), the excitation light source, photolysis scale, degasing, or nitrogen bubbling. The results obtained in our study are completely in variance with those reported by Hata.[8,15,16] The reasons for this are not clear at the present stage of investigation. Some speculations were already given in the previous paper.[9]

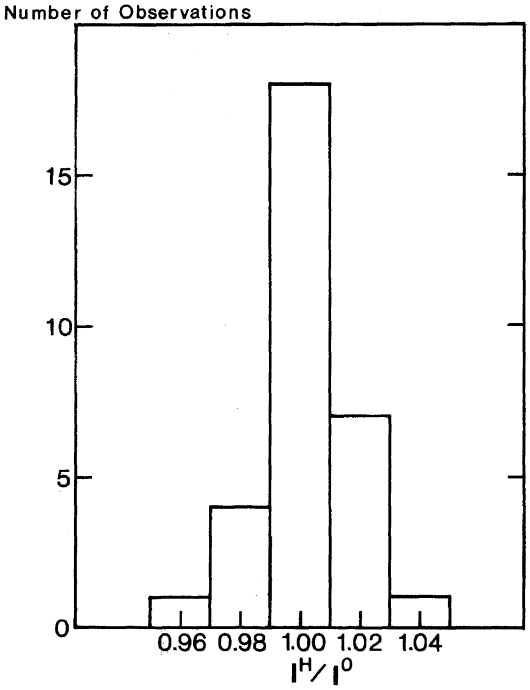

Fig. 1. Histogram for the reactant disappearance of photosubstitution of MQCN with (R)-(−)-2-phenylpropionic acid in benzene. Small- and large-scale photolysis data are combined. Total 31 observations were plotted.

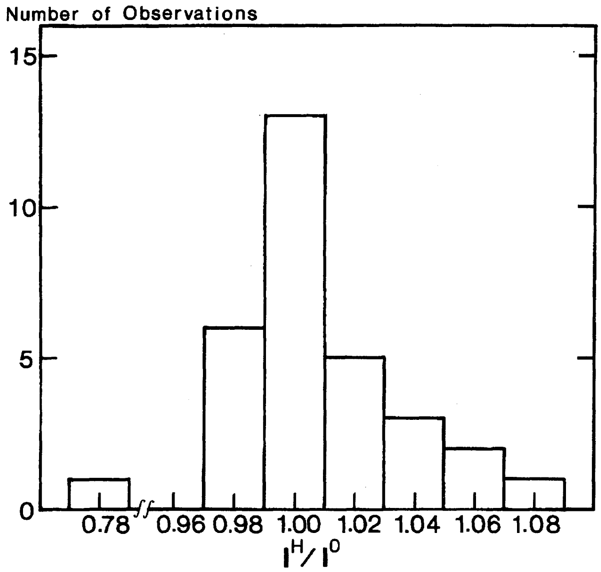

Fig. 2. Histogram for the product formation of photosubstitution of MQCN with (R)-(−)-2-phenylpropionic acid in benzene. The combined data are given.

Discussion

In general MFE on the yields of end products derived from the singlet precursor can be explained in terms of kinetic parameters which are magnetic-field-dependent and -independent. The intersystem crossing rate induced by hyperfine coupling mechanism is evaluated by

$$k_{\mathrm{isc}}^{(\mathrm{hfc})} = 2\pi g\mu B_{\mathrm{av}}/h, \tag{1}$$

where μ is Bohr magneton, and B_{av} is the effective hyperfine in the radical pair, which can be expressed as the weighted average of the hyperfine interaction, B_i between the nuclear spin I_{k} and the unpaired electron in each component radical,[17]

$$B_{\mathrm{av}} = (B_1^2 + B_2^2)/(B_1 + B_2), \tag{2}$$

$$B_i = \left\{ \sum_k a_{ik}^2 I_k (I_k + 1) \right\}^{1/2}. \tag{3}$$

The values of B_i for 2-cyano-4-methyl-1,4-dihydroquinolin-4-yl (CMQ), 1-phenylethyl (PE), and diphenylmethyl (DPM) radicals are calculated by the use of isotropic hfc constant for the k-th nucleus, a_{ik}, in the literature.[18—20] In the case of CMQ radical no hfc constants have been reported and the hfc values are estimated from those observed for radicals with similar structures. The hfc constants given in Figs. 3 and 4 are used for evaluation of B_i values. Numerical results were given Table 5.

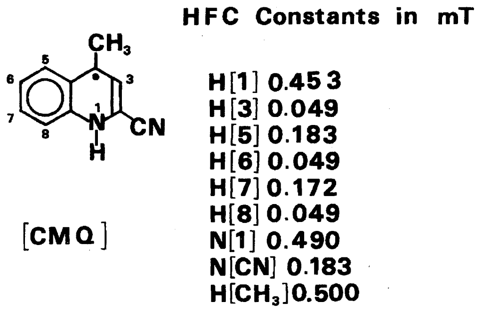

Fig. 3. Hyperfine coupling constants for CMQ radical.

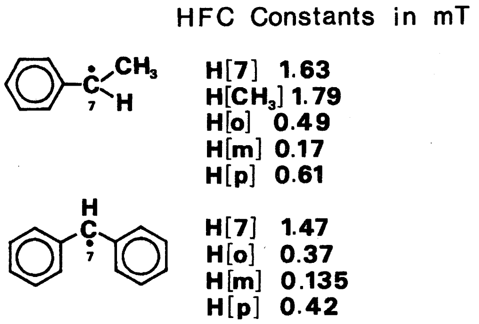

Fig. 4. Hyperfine coupling constants for PE and DPM radicals.

Table 5. Internal Magnetic Field Strength and Intersystem Crossing Rate Induced by Hyperfine Coupling

B_1/mT	B_2/mT	B_{av}/mT	$k_{\mathrm{isc}}(\mathrm{hfc})/\mathrm{s}^{-1}$
(CMQ)	(PE)		
1.15	3.14	2.61	4.54×10^8
(CMQ)	(DPM)		
1.15	1.37	1.27	2.23×10^8

CMQ: 2-cyano-4-methyl-1,4-dihydroquinolin-4-yl radical, PE: 1-phenylethyl radical, DPM: diphenylmethyl radical.

The magnetic field effects on the cage product formation is given by

$$Y(\mathrm{H})/Y(0)=\{k_{\mathrm{sum}}+k_{\mathrm{isc}}(0)\}/\{k_{\mathrm{sum}}+k_{\mathrm{isc}}(H)\}, \quad (4)$$

where k_{sum} means the sum of rate constants for radical pair recombination (k_{rec}), in-cage disproportionation (k_{dis}), and escape from a solvent cage (k_{esc}).[17] It is reasonably assumed that k_{sum} is independent of applied magnetic field strength, while $k_{\mathrm{isc}}(\mathrm{H})=k_{\mathrm{isc}}(0)/3$ in the high field region. The ratio of $k_{\mathrm{sum}}/k_{\mathrm{isc}}(0)=6.33$ is evaluated from the reported MFE on the yield of 4-methyl-2-(1-phenylethyl)quinoline, $Y(\mathrm{H})/Y(0)=89.3/81.2=1.10$.[8] By introducing the numerical value for $k_{\mathrm{isc}}=4.54\times10^8$ s^{-1}, k_{sum} is estimated to be 2.88×10^9 s^{-1}. A value of this order of magnitude is small by a factor of 10^{-1} in comparison with the value generally accepted for cage process in fluid solutions.[21] In the case of photosubstitution by diphenylacetic acid,[15] large MFE were observed, namely, $Y(\mathrm{H})/Y(0)=1.15$. In the same manner, k_{sum} is estimated to be 9.2×10^8 s^{-1} for the radical pair consisting of DPM and CMQ. If the magnitude of MFE reported by Hata is correct, the escape process from the solvent cage and in-cage recombination are unusually slow.

It is also possible to estimate the magnitude of MFE on the basis of kinetic parameters experimentally determined for similar radical pair reactions. The following values have been typically observed for radical pair recombination, in-cage disproportionation, and escape from a solvent cage:[22] $k_{\mathrm{rec}}=10^9$—10^{10} s^{-1}, $k_{\mathrm{dis}}=10^8$—10^9 s^{-1}, and $k_{\mathrm{esc}}=10^9$—10^{10} s^{-1}. On the other hand, it has been empirically known that Eq. 1 gives an overestimation. A value of $k_{\mathrm{isc}}(0)=4.4\times10^6$ s^{-1} has been reported by Tanimoto and co-workers for the pair consisting of 1,4-dihydroquinolin-4-yl and xanthenyl radicals.[23] Since the radical pair studied by Tanimoto et al. is closely related to that consisting of CMQ and DPM, it can be easily concluded that almost no MFE are expected for the end product yield from the radical pair composed of CMQ and DPM in the singlet state.

It is quite probable that the radical pair ISC is very slow in comparison with the radical pair recombination or escape from the solvent cage. It should be noted that the escape process of the singlet pair from the solvent cage has not been explicitly considered in the reaction scheme proposed by Hata.[8]

Hata has reported inequivalent reactivity for some optically active carboxylic acids toward MQCN in the zero magnetic field.[8,16] Although this was referred to as "polar-solvent effect", any reasonable explanation has not been described for the mechanism of this phenomenon. It is highly desirable to explain the mechanism that an external magnetic field can induce inequivalent reactivity of the two isomeric acids. Barron has discussed the possibility of absolute asymmetric synthesis by introducing the concept of "true" and "false" chirality.[24] The discussion developed by Barron is based upon the theoretical treatment by de Gennes.[25] According to Barron, a uniform static magnetic field parallel to the propagation direction of a light beam of arbitrary polarization constitutes a truly chiral influence and is a candidate for inducing asymmetric synthesis. It is to be noted that no reliable absolute synthesis has been so far reported for photochemical reactions.

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