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Photochemical Reactions of Ethoxycarbonyl-Substituted Quinolines

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The photochemical reactions of the quinoline derivatives substituted by an ethoxycarbonyl group at the 2-, 3-, and 4-positions of a quinoline nucleus have been investigated in several alcohols and cyclohexane. Irradiation of ethyl 4-quinolinecarboxylate (**1**) yielded ethyl 2-hydroxyalkyl-4-quinolinecarboxylates (**4a—c**) in alcohols and ethyl 2-cyclohexyl-4-quinolinecarboxylate (**4d**) in cyclohexane in a good yield, respectively. The photochemical reactions of ethyl 3-quinolinecarboxylate (**2**) showed remarkable solvent dependency. Irradiation in methanol and cyclohexane afforded a solvent-additive product, ethyl 4-hydroxymethyl-1,4-dihydro-3-quinolinecarboxylate (**5a**) and ethyl 4-cyclohexyl-1,4-dihydro-3-quinolinecarboxylate (**5b**), while such photoaddition of the solvent did not proceed in ethanol and 2-propanol but instead ethyl 1,4-dihydro-3-quinolinecarboxylate (**6**) and dimeric compounds were formed, both of which were unstable and finally reverted to **2** at room temperature in air. In the case of ethyl 2-quinolinecarboxylate two types of the products, ethyl 4-hydroxyalkyl-1,4-dihydro-2-quinolinecarboxylate (**7**) and ethyl 1,4-dihydro-2-quinolinecarboxylate (**8**) were obtained in ethanol and 2-propanol but the yields of those products were poor. On the basis of triplet quenching experiments, the photochemical reactions of those ethyl quinolinecarboxylates are suggested to occur through hydrogen abstraction from the solvents by the ring nitrogen in the S_1 state.

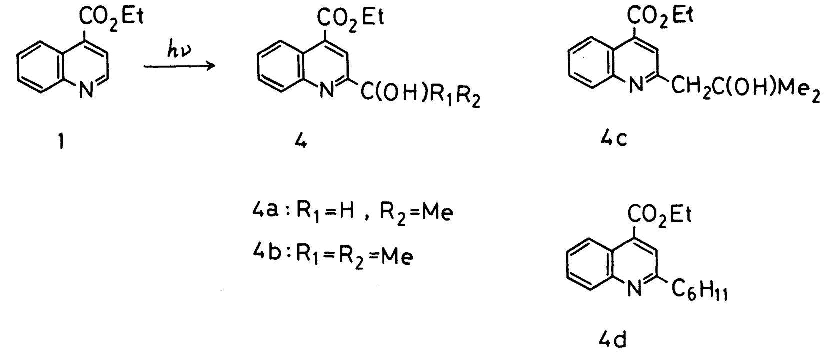
The photochemical reactions of cyano-substituted quinolines have been the subject of a number of investigations.[1] Especially, we have mechanistically investigated in detail the photosubstitution of 2-quinolinecarbonitriles in ethanol and proved that the replacement of a cyano group by a 1-hydroxyethyl one occurred via a hydrogen-bonded radical-pair intermediate formed by hydrogen abstraction by a ring nitrogen from the solvents in the S_1 state.[1b,e] Next, we reported the photochemical reactions of 2-(dimethylcarbamoyl)quinolines, where the ring nitrogen brought about hydrogen abstraction from the dimethylcarbamoyl substituent via the T_1 state to give 2-(methylaminoacetyl)quinolines and cyclized products.[2] In this paper, we report the photochemistry of ethoxycarbonyl quinolines bearing also an electron-withdrawing group such as ethyl 4-quinolinecarboxylate (**1**), ethyl 3-quinolinecarboxylate (**2**), and ethyl 2-quinolinecarboxylate (**3**) in several alcohols and in cyclohexane. Sugimori et al. reported that methyl 2-pyridinecarboxylate underwent methylation at the 5-position in methanol through hydrogen abstraction by the excited carbonyl group from the solvent.[3] In the case of the ethoxycarbonyl quinolines two types of reactions were observed, both of which were initiated by hydrogen abstraction by the ring nitrogen from the solvent. One is a recombination of a radical pair in a solvent cage and another is probably further hydrogen abstraction by a semi-reduced radical from the solvent. We describe the excited state involved in those reactions and reaction mechanism.

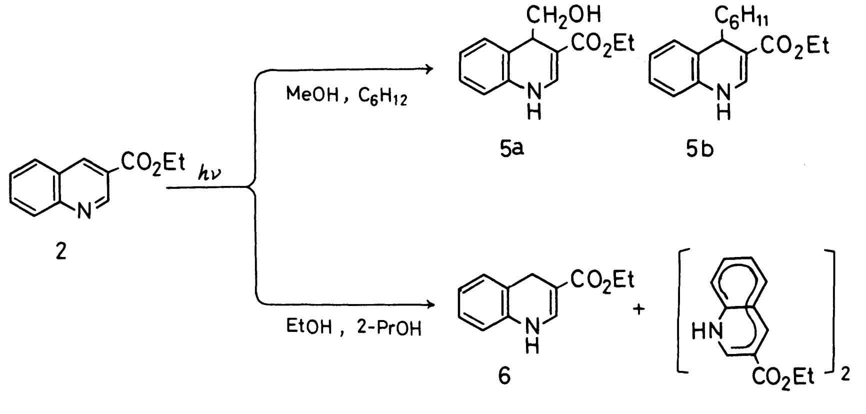
Photochemistry of Ethyl 4-Quinolinecarboxylate (1). Irradiation of **1** in several alcohols and cyclohexane under an oxygen atmosphere gave one major photoproduct **4** in good yield as shown in Table 1. Although we attempted irradiation in nitrogen, the yield of **4** decreased about to 20 percent because of an increase in the amount of decomposition products. The NMR spectra of **4** indicated that the ethoxycarbonyl substituent at the 4-position of a quinoline remained and the proton at the 2-position was replaced by a corresponding hydroxyalkyl group derived from the alcohol used as a solvent or a cyclohexyl group when irradiation was carried out in cyclohexane. From the data of MS, IR, or elemental analysis, **4** was assigned to be ethyl 2-hydroxyalkyl-4-quinolinecarboxylate (**4a—c**) or ethyl 2-cyclohexyl-4-quinolinecarboxylate (**4d**), respectively.

Photochemistry of Ethyl 3-Quinolinecarboxylate (2). Irradiation of **2** was carried out in nitrogen atmosphere, because no reaction occurred in oxygen. Any photoproduct obtained in each solvent (MeOH, EtOH, 2-PrOH, or cyclohexane) has a UV spectrum showing its maximum at a wavelength longer than

Table 1. Photochemical Reactions of **1** in Several Solvents

Solvent	Irradiation time/h	Atm	Conversion %		Product yield %
Ethanol	4	O_2	80	**4a**	67
	2.5	N_2	84	**4a**	22
2-Propanol	4	O_2	74	**4b**	50
	2.5	N_2	56	**4b**	21
t-Butyl alcohol	7	O_2	68	**4c**	45
Cyclohexane	4	O_2	64	**4d**	56





320 nm which remarkably shifts from that of **2** (UV-(MeOH)λ_{max} 286 nm). The types of those products were, however, different depending on the nature of the solvent used. That is, irradiation in methanol and cyclohexane gave the solvent addition products, ethyl 4-hydroxymethyl-1,4-dihydro-3-quinolinecarboxylate (**5a**) and ethyl 4-cyclohexyl-1,4-dihydro-3-quinolinecarboxylate (**5b**) as only one major product, respectively. The structures were determined on the basis of NMR, IR, and MS spectra. NMR proved that the addition of the solvent occurred at the 4-position but not the 2-position. IR showed absorption by NH stretching at about 3340 cm^{-1} and a strong peak due to a CO group at 1650 cm^{-1}. On the other hand, irradiation in both ethanol and 2-propanol did not afford any solvent addition product, but instead lead to two unstable products which finally reverted to the starting material **2**. Both were especially labile in solution, for example, if the solutions after irradiation were allowed to stand 12 h at room temperature in dark, their UV spectra completely reverted to that of **2**. Therefore, the reaction solvent was evaporated under 30 °C immediately after irradiation, and the residue was subjected to separation on plate layer chromatography at 10 °C. As a result, two colorless solid products of mass 203 and 404 were isolated. Although both were unstable at room temperature, especially, the latter more rapidly changed to **2**, they were stable in a sealed tube, indicating that their lability was due to oxygen. The IR spectrum of the former showed absorption by NH stretching at 3340 cm^{-1} and a strong peak due to a CO group at 1640 cm^{-1}. In the NMR spectra taken in CDCl$_3$ using TMS as a standard, a broad peak at δ 6.00 due to the NH and a singlet line at δ 3.76 due to two

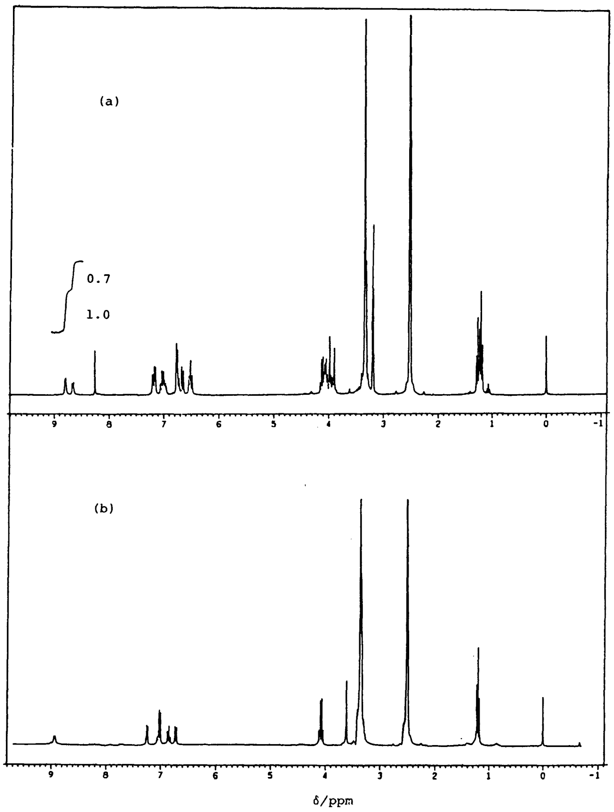


Fig. 1. 270 MHz ^{1}H NMR spectra of (a) dimeric compound and (b) **6** measured in DMSO-d_6 using TMS as a standard.

Table 2. Photochemical Reactions of **2** in Several Solvents in N_2

Solvent	Irradiation time/h	Conversion	Yield of product/%		
		%	**5**	**6**	Dimer
Methanol	5	76	69	—	—
Cyclohexane	5	67	55	—	—
Ethanol	15	72	—	53	33
2-Propanol	10	77	—	24	59
	15	82	—	50	38

protons at the 4-position of the quinoline were observed. Thus, it was determined to be ethyl 1,4-dihydro-3-quinolinecarboxylate (**6**). The treatment of this product with $FeCl_3$ caused quantitative conversion to **2**, giving further proof for this structure. The latter product, which is insoluble in alcohols and chloroform, seems to have the structure akin to the dimeric compound of **6**, considering that its molecular weight was 404 and the IR spectrum was similar to that of **6**. Although the NMR spectrum (in DMSO-d_6) was complicated as shown in Fig. 1a, it seems similar to that of **6** in DMSO (Fig. 1b). Two broad peaks observed at δ 8.65 and 8.79 were confirmed to be due to the protons on the ring nitrogen by decoupling the protons at the 2-position which appeared as two doublets at δ 7.15 and 7.19, respectively. The relative intensity of the signals at δ 8.65 and 8.79 was 0.7 : 1, indicating that this consisted of a mixture of two dimers (0.7 : 1 ratio). The multiplet around δ 1.35 may show the overlap of two triplet signals arising from the methyl groups. A number of peaks around δ 3.9—4.15 corresponding to those of methylene protons are complicated by overlap by the signals of some impurities. At present, the assignment of these dimers was unsuccessful. Separation and purification could not be achieved. On irradiation in *t*-butyl alcohol an unidentified oily product of mass 275 was obtained, but formation of **6** and the dimers was not observed. Table 2 shows the product yields.

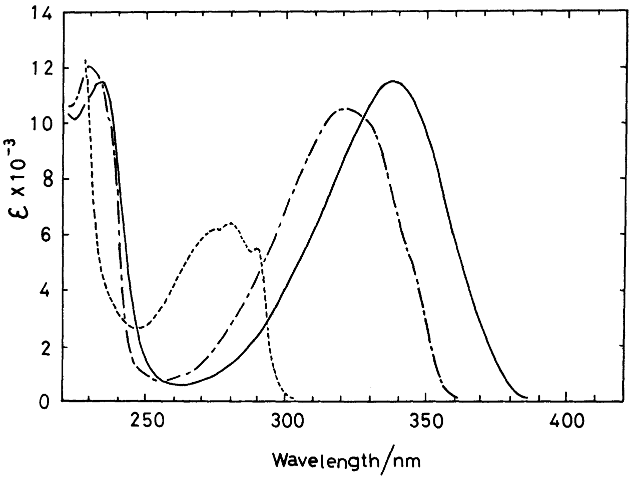
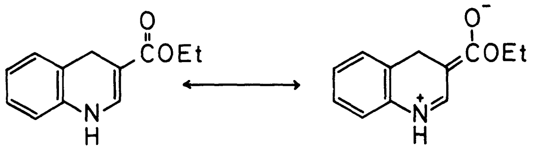


Fig. 2. UV spectra of **6** and **8** in methanol or cyclohexane. (——) **6** in methanol, (–·–·–) **6** in cyclohexane, and (----) **8** in methanol.

It is noteworthy that the UV spectra of the photoproducts arising from the ethyl 3-quinolinecarboxylate shifted to much longer wavelength than that expected from their structures. Figure 2 displayed the absorption spectra of **6** in methanol and cyclohexane together with that of ethyl 1,4-dihydro-2-quinolinecarboxylate (**8**) in methanol. Such a large bathochromic shift can be explained by a resonance contribution from a zwitterion structure. It is supported by the fact that the UV spectrum of **6** shifted to shorter wavelength in cyclohexane. That the IR absorption of the CO group appeared at a considerably lower frequency of 1650 cm^{-1} also supports the possibility of a contribution from an ionic structure.

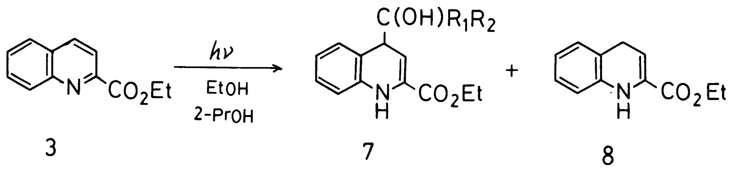


Photochemistry of Ethyl 2-Quinolinecarboxylate (3). The irradiation of **3** in nitrogen lead to two low yield products ethyl 4-hydroxyalkyl-1,4-dihydro-2-quinolinecarboxylate (**7**) and ethyl 1,4-dihydro-2-quinolinecarboxylate (**8**) in ethanol and 2-propanol (Table 3), but the major product in *t*-butyl alcohol or cyclohexane was an intractable tar. The structures of **7** and **8** were determined in a similar manner with to **5** and **6**. The experiments in an atmosphere of oxygen were discontinued, because the reaction in oxygen was hard to achieve.

Triplet Quenching Experiment. In order to identify the reactive excited state of the photochemical reactions of those ethoxycarbonyl quinolines the triplet quenching experiment was carried out for **1** and **2**. The experiment for **3** was excluded because of too low yield of the products. From the phosphorescence spectra measured in ethanol and methylcyclohexane at 77 K the triplet excitation energy (E_T) of **1** was estimated to be 244.1 kJ mol^{-1} in both solutions. E_T for **2** were

Table 3. Photochemical Reactions of **3** in Nitrogen Atmosphere

Solvent	Conversion/%	**7**	**8**
		%	
Ethanol	86	31	9
2-Propanol	65	6	17



7a : $R_1 = H$, $R_2 = Me$
7b : $R_1 = R_2 = Me$

Table 4. Quantum Yields of Photochemical Reactions of **1** in 2-Propanol and Cyclohexane

Solvent	Atmosphere	Quencher/dm³ mol⁻¹	Φ_d	Φ_f
2-Propanol	N_2	0	0.064	0.017
	N_2	5.0×10^{-4}	0.071	0.012
	N_2	1.0×10^{-3}	0.056	0.014
	N_2	1.0×10^{-2}	0.067	0.013
	N_2	1.0×10^{-1}	0.054	0.011
	N_2[a]	0	0.063	<0.004
	O_2	0	0.051	0.024
Cyclohexane	N_2	0	0.048	0.016
	N_2	1.0×10^{-1}	0.042	0.016

a) Nitrogen gas was passed through an aqueous basic solution of pyrogallol.

259.4 kJ mol⁻¹ in ethanol and 258.1 kJ mol⁻¹ in methylcyclohexane, respectively. As a triplet quencher 1,3-cyclohexadiene (E_T=219 kJ mol⁻¹) could be used for **1** and 1,3-pentadiene (E_T=240.6 kJ mol⁻¹) for **2**. The relatively long phosphorescence lifetimes of 0.9 s for **1** and 0.46 s for **2** in ethanol indicated that the lowest triplet excited states were of π,π^* configuration. The lifetimes could not be estimated in methylcyclohexane because of the very weak phosphorescence intensity. The fluorescence was observed in ethanol for both quinolines but was not clear in methylcyclohexane, suggesting that the singlet n,π^* and π,π^* states lies closely to each other as in the case of 2-quinolinecarbonitrile.[1b]

Table 4 shows the quantum yields of the disappearance of **1** (Φ_d) and the formation of **4** (Φ_f) on irradiation in 2-propanol or cyclohexane under various conditions. Both the quantum yields Φ_d and Φ_f were independent of the concentration of 1,3-cyclohexadiene, indicating that the S_1 state was responsible for the reaction of **1**. It is noted that Φ_f under an oxygen atmosphere was greater than the value in nitrogen. This means that oxygen plays an important part in the formation of **4b**. In practice, Φ_f was only less than 0.004 in the 2-propanol purged by nitrogen gas from which oxygen was removed more completely through a potassium hydroxide solution of pyrogallol. The quantum yields for the photochemical reaction of **2** were carried out in methanol and cyclohexane using 1,3-pentadiene as a triplet quencher. As shown in Fig. 3, the triplet quencher had no influence on the reaction. We could not take the measurement of the quantum yields in ethanol and 2-propanol because **6** and the dimers obtained in those solution easily changed to the starting material **2** during the isolation procedure.

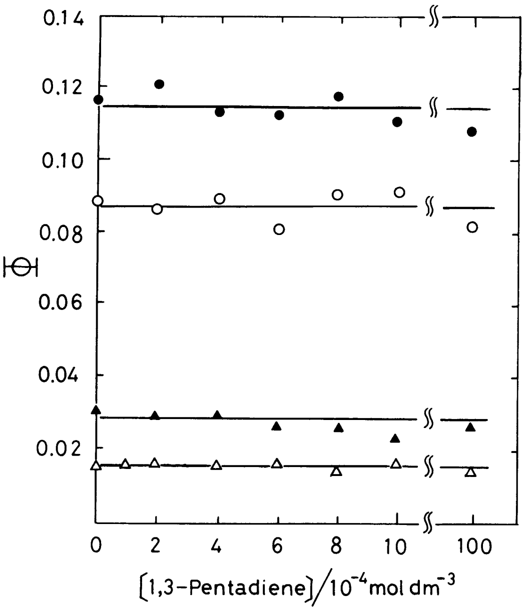
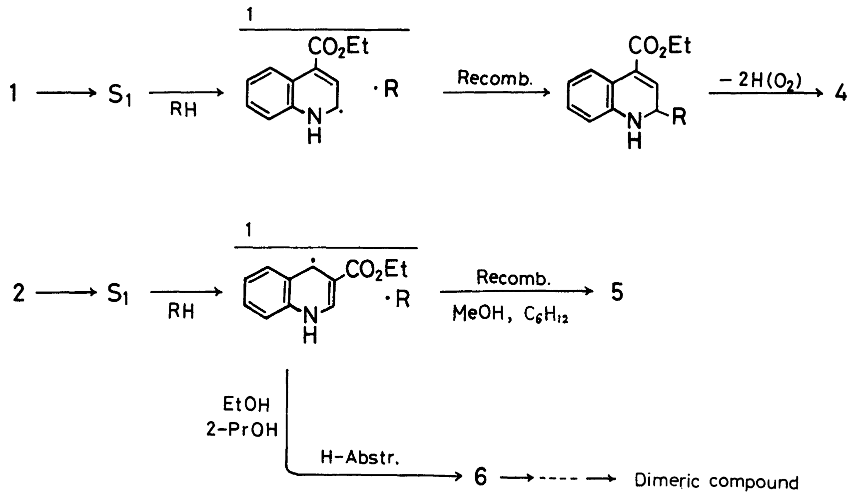


Fig. 3. Effect of triplet quencher on quantum yields of photochemical reactions of **2**. [**2**]=0.002 mol dm⁻³. —○—: Formation of **5a**, —●—: disappearance of **2** in methanol, —△—: formation of **5b**, —▲—: disappearance of **2** in cyclohexane.

Reaction Mechanism. The photochemistry of **1** could be explained in terms of the mechanism as shown in Scheme 1. Hydrogen abstraction from the solvent by the ring nitrogen in the S_1 state forms a radical pair which combines to give 1,2-dihydroquinoline derivatives expected as a precursor of **4**. Its conversion to **4** may be caused by oxidation but not via disproportionation, considering that Φ_f of **4b** become extremely low in the nitrogen gas including almost no oxygen (Table 4). Although we tried to isolate the precursor from the reaction mixture obtained on irradiation in nitrogen, the attempt failed because of its



Scheme 1.

lability. Such 1,2-dihydroquinolines are known to be unstable.[4] The initial step of the photochemical reaction of **2** may also be hydrogen abstraction by the ring nitrogen from the solvent in the S_1 state. Considering that this reaction was not affected by 1,3-pentadiene in both high polar methanol and less polar cyclohexane, the photochemical reaction of **2** in ethanol and 2-propanol leading to the formation of **6** is thought to occur also in the S_1 state. Apparently, the solvent dependency of the photoproducts of **2** could be ascribed to the hydrogen-donating efficiency of the solvent used. The reaction mechanism is summarized in Scheme 1. In methanol or cyclohexane the formed radical pair recombines as the case of **1** to give **5**, while in ethanol or 2-propanol being a good hydrogen-donor solvent the semi-reduced radical of **2** may carry out further hydrogen abstraction from the solvent to afford **6** before undertaking recombination. The formation of the dimer types would be expected as follows, considering the results that the yields of **6** and the dimers varied remarkably depending on irradiation time as shown in Table 2, and also that the latter products were not formed in methanol, cyclohexane and *t*-butyl alcohol; **6** (QH_2) excited by light absorption donates a hydrogen atom to **2** (Q) to generate two semi-reduced radicals (2·QH), whose recombination yields the dimeric compounds Q_2H_2.

$$QH_2 \xrightarrow{h\nu} QH_2^*$$

$$QH_2^* + Q \longrightarrow 2\cdot QH$$

$$2\cdot QH \longrightarrow Q_2H_2$$

We tried the irradiation of QH_2 in the ethanol solution in the presence of Q under a nitrogen atmosphere with 366 nm light which could be absorbed only by the former. As a result, QH_2 disappeared rapidly, but the product found in the reaction solution after irradiation was only Q. Perhaps, the formed Q_2H_2 is thought to have reverted to Q by reabsorbing 366 nm light. Actually, the irradiation of Q_2H_2 by 366 nm light in the absence of Q induced its rapid conversion to Q, although the mechanism of the conversion was now ambiguous. Anyway, the photochemical reaction of **2** in ethanol or 2-propanol may shuttle between the starting material **2** and the products.

The photochemical reaction of **3** may be thought to be essentially similar to that of **2**. The simultaneous formation of **7** and **8** shows that the recombination of the radical pair and the hydrogen abstraction by the semi-reduced radical of **3** from the solvent occurs competitively.

Experimental

The NMR spectra were measured on a JEOL GX-270 with TMS as an internal standard. The mass spectra were obtained by a Hitachi RMU-6M, a JEOL JMS-DX303, or a Shimadzu GCMS-9020DF machines. The IR spectra were taken on a JASCO-302. For the measurement of fluorescence and phosphorescence spectra a Hitachi MPF-2A was used, and UV spectra were recorded with a Shimadzu UV-220.

Materials. The solvents used in the irradiation experiments were reagent grade obtained from Wako Pure Chemical Industry. Methanol, ethanol, and *t*-butyl alcohol were used without purification but 2-propanol and cyclohexane were purified by distillation and silica-gel chromatography, respectively. 1,3-Cyclohexadiene and 1,3-pentadiene (Tokyo Kasei Kogyo) were used after distillation. Ethoxycarbonyl quinolines **1**, **2**, and **3** were synthesized by adding trimethylamine and ethanol to the chloroform solution including the corresponding quinolinecarboxylic acids treated with $SOCl_2$.[5] Those carboxylic acids were obtained from the basic hydrolysis of quinolinecarbonitriles. 2-Quinolinecarbonitrile of those was synthesized by a Reisert reaction of quinoline *N*-oxide,[6] but 3-and 4-quinolinecarbonitriles were prepared by heating the corresponding bromoquinoline with copper (I) cyanide.[7] 3-Bromoquinoline was reagent grade from Tokyo Kasei Kogyo and 4-bromoquinoline was synthesized by treatment with phosphorus trichloride of 4-bromoquinoline *N*-oxide obtained by refluxing 4-nitroquinoline *N*-oxide in hydrobromic acid.[8]

Ethyl 4-Quinolinecarboxylate (1). Colorless liquid, bp 120 °C/1 mmHg (1 mmHg=133.32 Pa); IR (neat) 3050, 2990, 2910, 1725 (CO), 1585, 1250, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.49 (3H, t, J=7.25 Hz, $CH_2C\underline{H}_3$), 4.53 (2H, q, J=7.25 Hz, $C\underline{H}_2CH_3$), 7.63—7.81 (2H, m, H-6 and 7), 7.90 (1H, d, J=4.43 Hz, H-3), 8.18 (1H, d, J=8.46 Hz), 8.77 (1H, d, J=8.46 Hz), 9.02 (1H, d, J=4.43 Hz, H-2); MS m/z 201 (M^+).

Ethyl 3-Quinolinecarboxylate (2). Mp 68 °C (from hexane-ethanol); IR (KBr) 3050, 2990, 2930, 1710 (CO), 1570, 1240, 1130 cm^{-1}; ^{1}H NMR($CDCl_3$) δ=1.47 (3H, t, J=7.25 Hz, $CH_2C\underline{H}_3$), 4.49 (2H, q, J=7.25 Hz, $C\underline{H}_2CH_3$), 7.63—7.81 (2H, m, H-6 and 7), 7.94 (1H, d, J=8.24 Hz), 8.17 (1H, d, J=8.25 Hz), 8.85 (1H, s, H-4), 9.46 (1H, s, H-2); MS m/z 201 (M^+).

Ethyl 2-Quinolinecarboxylate (3). Colorless liquid, bp 140 °C/1 mmHg; IR (KBr) 3050, 2980, 2930, 1705 (CO), 1590, 1245, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.50 (3H, t, J=7.25 Hz, $CH_2C\underline{H}_3$), 4.57 (2H, q, J=7.25 Hz, $C\underline{H}_2CH_3$), 7.64—7.79 (2H, m, H-6 and 7), 7.88 (1H, d, J=8.25 Hz), 8.19, 8.30 (2H, AB, q, J=8.58 Hz, H-3 and 4), 8.32 (1H, d, J=8.24 Hz); MS m/z 201 (M^+).

Photochemical Reactions of 1 and 3. 1 or 3 (100 mg) dissolved in 70 cm^3 of alcohol (EtOH, 2-propanol, or *t*-BuOH) or cyclohexane was irradiated in a Pyrex vessel with a 100 W high pressure immersion mercury lamp (Riko Kagaku Sangyo Co.) under nitrogen or oxygen. After the evaporation of the reaction solvent, the residue was developed on thin-layer chromatography of Kieselgel (PF_{254}, Merck) with a mixture of chloroform and diethyl ether to isolate the starting material and the products.

Photochemical Reaction of 2. A solution of 2 (50 mg) in 70 cm^3 of alcohol or cyclohexane was irradiated in nitrogen with the same setup. The isolation of the reaction mixture on irradiation in methanol and cyclohexane was carried out by a method similar to the former two cases. However, the photoproducts 6 and dimeric compounds in ethanol and 2-propanol were labile, the latter especially was easily decomposed to the starting material 2. Therefore, the evaporation of the reaction solvent was done below 30 °C and the development on thin-layerchromatography was undertaken at 10 °C, using chloroform and ethanol (20 : 1 V/V). Still, the dimeric compounds are thought partly to have reverted to 2 during the isolation procedure.

Ethyl 2-(1-Hydroxyethyl)-4-quinolinecarboxylate (4a). Colorless liquid (it gradually decomposed at room temperature); IR (neat) 3400 (OH), 3070, 2990, 2940, 1715 (CO), 1600, 1510, 1240, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.51 (3H, t, J=7.25 Hz, $CH_2C\underline{H}_3$), 1.64 (3H, d, J=6.43 Hz, CH (OH)$C\underline{H}_3$), 4.55 (2H, q, J=7.25 Hz, $C\underline{H}_2CH_3$), 4.75 (1H, s, OH), 5.12 (1H, q, J=6.43 Hz, $C\underline{H}(OH)CH_3$), 7.67—7.80 (2H, m, H-6 and 7), 7.88 (1H, s, H-3), 8.16 (1H, d, J=8.91 Hz), 8.75 (1H, d, J=8.91 Hz); Found: m/z 245.1049. Calcd for $C_{14}H_{15}NO_3$: M, 245.1052.

Ethyl 2-(1-Hydroxy-1-methylethyl)-4-quinolinecarboxylate (4b). Mp 72 °C (from hexane); IR (KBr) 3250 (OH), 3050, 2980, 2920, 1720 (CO), 1590, 1505, 1240, 1140 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.50 (3H, t, J=7.10 Hz, $CH_2C\underline{H}_3$), 1.65 (6H, d, J=5.28 Hz, $(CH_3)_2$), 4.54 (2H, q, J=7.10 Hz, $C\underline{H}_2CH_3$), 5.53 (1H, s, OH), 7.64—7.77 (2H, m, H-6 and 7), 7.95 (1H, s, H-3), 8.14 (2H, d, J=8.57 Hz), 8.70 (1H, d, J=8.24 Hz); MS m/z 259 (M^+); Found: C, 69.41; H, 6.60; N, 5.35%. Calcd for $C_{15}H_{17}NO_3$: C, 69.49; H, 6.61; N, 5.40%.

Ethyl 2-(2-Hydroxy-2-methylpropyl)-4-quinolinecarboxylate (4c). Colorless liquid, picrate 172 °C (decomp); IR (neat) 3380 (OH), 3050, 2990, 2920, 1720 (CO), 1590, 1510, 1240, 1145 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.31 (6H, s, $C(OH)(C\underline{H}_3)_2$), 1.48 (3H, t, J=7.23 Hz, $CH_2C\underline{H}_3$), 3.16 (2H, s, $C(OH)C\underline{H}_2$), 4.52 (2H, q, J=7.23 Hz, $C\underline{H}_2CH_3$), 5.71 (1H, s, OH), 7.73—7.79 (3H, m, H-3, 6, and 7), 8.09 (1H, d, J=8.14 Hz), 8.70 (1H, d, J=8.58 Hz); MS m/z 273 (M^+); Found (for picrate): C, 52.51; H, 4.37; N, 11.10%. Calcd for $C_{22}H_{22}N_4O_{10}$: C, 52.59; H, 4.41; N, 11.15%.

Ethyl 2-Cyclohexyl-4-quinolinecarboxylate (4d). Colorless liquid, picrate 156—158 °C; IR (neat) 3070, 2990, 2930, 1720 (CO), 1595, 1240, 1150 cm^{-1}; ^{1}H NMR δ=1.37—2.07 (10H, m, cyclohexyl), 1.49 (3H, t, J=7.09 Hz, $CH_2C\underline{H}_3$), 2.96 (1H, tt, J=11.9 , 3.5 Hz, H′-1), 4.52 (2H, q, J=7.09 Hz, $C\underline{H}_2CH_3$), 7.54—7.75 (2H, m, H-6 and 7), 7.81 (1H, s, H-3), 8.10 (1H, d, J=8.57 Hz), 8.66 (1H, d, J=8.57 Hz); MS m/z 283 (M^+); Found (for picrate): C, 56.20; H, 4.72; N, 10.87%. Calcd for $C_{24}H_{24}N_4O_9$: C, 56.25; H, 4.72; N, 10.93%.

Ethyl 4-Hydroxymethyl-1,4-dihydro-3-quinolinecarboxylate (5a). Unstable colorless liquid (it easily released H_2O); UV (CH_3OH) λ_{max} 330 nm (ε 11600); IR (neat) 3400 (br, OH and NH), 3110, 2960, 2930, 1680 (CO), 1585, 1490, 1235, 1190 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.30 (3H, t, J=7.25 Hz, $CH_2C\underline{H}_3$), 3.67 (2H, d, J=5.28 Hz, $C\underline{H}_2OH$), 4.10 (1H, t, J=5.28 Hz, H-4), 4.25 (2H, q, J=7.25 Hz, $C\underline{H}_2CH_3$), 6.32 (1H, s, NH), 6.71—7.21 (4H, m, ArH), 7.55 (1H, d, J=6.72 Hz, H-2); MS m/z 233 (M^+); Found after loss of $H_2O(M^+-18)$: m/z 215.0931. Calcd for $C_{13}H_{11}NO_2$: M, 215.0946.

Ethyl 4-Cyclohexyl-1,4-dihydro-3-quinolinecarboxylate (5b). Mp 149—150 °C (from hexane-ethanol); UV (CH_3OH) λ_{max} 327 nm (ε 11500); IR (KBr) 3290 (NH), 3100, 3030, 2990, 2920, 1650 (CO), 1635, 1585, 1490, 1238, 1160 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.60—1.60 (11H, m, cyclohexyl), 1.30 (3H, t, J=7.26 Hz, $CH_2C\underline{H}_3$), 3.82 (1H, d, J=4.19 Hz, H-4), 4.15—4.25 (2H, m, $C\underline{H}_2CH_3$), 6.15 (1H, s, NH), 6.68—7.14 (4H, m, ArH), 7.55 (1H, d, J=5.94 Hz, H-2); MS m/z 285 (M^+); Found: C, 75.72; H, 8.13; N, 4.82%. Calcd for $C_{18}H_{23}NO_2$: C, 75.76; H, 8.12; N, 4.91%

Ethyl 1,4-Dihydro-3-quinolinecarboxylate (6). Mp 139 °C (it changed gradually to 2 at room temperature); UV (CH_3OH) λ_{max} 338 nm (ε 11500); IR (KBr) 3280 (NH), 3100, 2980, 2930, 1640 (CO), 1590, 1495, 1250, 1120 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.29 (3H, t, J=7.04 Hz, $CH_2C\underline{H}_3$), 3.76 (2H, s, H-4), 4.20 (2H, q, J=7.04 Hz, $C\underline{H}_2CH_3$), 6.00 (1H, s, NH), 6.57—7.04 (4H, m, ArH), 7.32 (1H, d, J=5.61 Hz, H-2); Found: m/z 203.0931. Calcd for $C_{13}H_{13}NO_2$: M, 203.0947.

Dimeric Compound. From inspection of the NMR spectrum of Fig. 1a it consisted of two dimers (1 : 0.7 ratio) which melted ranging from 176 to 182 °C, and finally to reverted to 2. UV (CH_3OH) λ_{max} 336 nm; IR (KBr) 3300 (NH), 3100, 3040, 2990, 2910, 1660 (CO), 1630, 1590, 1495, 1240, 1120 cm^{-1}; MS m/z 404 (M^+).

Ethyl 4-(1-Hydroxyethyl)-1,4-dihydro-2-quinolinecarboxylate (7a). Mp 88.5 °C (from hexane-benzene); IR (KBr) 3450 (NH), 3220 (OH), 3050, 2970, 2920, 1708 (CO), 1620, 1450, 1225, 1165 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23 (3H, t, J=7.20 Hz, $CH_2C\underline{H}_3$), 1.55 (3H, d, J=6.92 Hz, $CH(OH)C\underline{H}_3$), 3.80 (1H, s, H-4), 4.16 (2H, q, J=7.20 Hz, $C\underline{H}_2CH_3$), 5.20 (1H, q, J=6.92 Hz, $C\underline{H}(OH)CH_3$), 7.11—7.80 (5H, m, ArH and H-3), 8.79 (1H, s, NH); MS m/z 247 (M^+); Found: C, 67.87; H, 6.89; N, 5.66%. Calcd for $C_{14}H_{17}NO_3$: C, 67.99; H, 6.93, N, 5.66%.

Ethyl 4-(1-Hydroxy-1-methylethyl)-1,4-dihydro-2-quinolinecarboxylate (7b). Colorless liquid, bp 130 °C/1 mmHg; IR (neat) 3500 (br, NH and OH), 3070, 2990, 2940, 1730 (CO), 1610, 1495, 1250, 1160 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=1.24 (3H, t, J=7.10 Hz, $\mathrm{CH_2C\underline{H}_3}$), 1.29 (6H, d, J=6.26 Hz, $\mathrm{(CH_3)_2}$), 3.71 (1H, s, H-4), 4.13 (2H, q, J=7.10 Hz, $\mathrm{C\underline{H}_2CH_3}$), 7.07—7.56 (5H, m, ArH and H-3), 8.45 (1H, s, NH); Found: m/z 261.1330. Calcd for $\mathrm{C_{15}H_{19}NO_3}$: M, 261.1365.

Ethyl 1,4-Dihydro-2-quinolinecarboxylate (8). Colorless liquid, bp 130 °C/1 mmHg; IR (neat) 3500 (NH), 3070, 2990, 2940, 1730 (CO), 1610, 1495, 1250, 1160 cm^{-1}; ^{1}H NMR($\mathrm{CDCl_3}$) δ=1.26 (3H, q, J=7.12 Hz, $\mathrm{CH_2C\underline{H}_3}$), 3.80 (2H, s, H-4), 4.17 (2H, q, J=7.12 Hz, $\mathrm{C\underline{H}_2CH_3}$), 7.11—7.25 (3H, m, H-3, 6, and 7), 7.36 (1H, d, J=8.24 Hz), 7.63 (1H, d, J=7.19 Hz), 8.10 (1H, s, NH); Found: m/z 203.0948. Calcd for $\mathrm{C_{12}H_{13}NO_2}$: M, 203.0947.

Quantum yields were determined by irradiating a sample solution (2×10^{-3} mol dm^{-3}) in a quartz cylindrical cell (5-cm in diameter and 1-cm in length) with 313 nm-light from a USH-500D lamp. The 313-nm line was isolated by a combination of a $\mathrm{NiSO_4}$ solution with a UV-31 filter. The light intensity was determined by means of a potassium trioxalatoferrate(III) actinometer. The amounts of the products and consumed starting material **1** and **2** were spectrometrically measured after the separation on a silica-gel chromatograph using the mixture of chloroform and diethyl ether.

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