Photochemical Reactions of 2-(Dimethylcarbamoyl)quinolines

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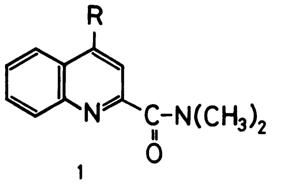
2-(Dimethylcarbamoyl)quinolines are converted into 2-(methylaminoacetyl)quinolines (**2**) and 2-methyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-ones (**3**) by irradiation in a nitrogen atmosphere. The reaction was quite efficient in acetonitrile but inefficient in hydrocarbon solvents and ethanol. The introduction of a chlorine atom to the 4-position of a quinoline nucleus caused an increase of the yield of **3** in company with a decrease of the yield of **2**. On the other hand, irradiation in an oxygen atmosphere afforded 2-(methylcarbamoyl)quinolines as a main product but **2** and **3** were minor products. The results of quenching and sensitization experiments confirmed that the triplet π,π^* state was responsible for the formation of those products. It is suggested that the reaction involves zwitterionic intermediates formed *via* Type II hydrogen abstraction by the ring nitrogen from the *N*-methyl group.

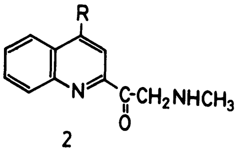
The photochemical behavior of cyano-substituted quinolines and isoquinolines has been a subject of continuing interest in our laboratory since we found that 2-quinolinecarbonitriles undergo the photochemical replacement of the cyano group by a hydroxyalkyl group in an alcoholic solvent.[1] Recently, this reaction was proved to proceed *via* a singlet radical pair formed by hydrogen abstraction by the ring nitrogen from the hydrogen-bonded alcohol.[1e] However, photochemical studies of the quinolines bearing an electron-withdrawing substituent other than the cyano group are few and the photochemical behavior of *N*-alkyl amides substituted on azanaphthalenes is still ambiguous, although α-cleavage of alkyl amides such as the case of *N*-hexylhexanamide is well known.[2] Therefore, we investigated the photochemical reactions of 2-(dimethylcarbamoyl)quinolines (**1**) in several solvents. We discuss the nature of the intermediates involved in this reaction and the reaction pathway.



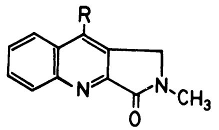
1

1a : R=H
1b : R=CH$_3$
1c : R=Cl

Identification and Chemical Yields of Products. Irradiation of 2-(dimethylcarbamoyl)quinolines **1a**—**c** in a nitrogen atmosphere resulted in the formation of two products, **2** and **3**. The product **2** has the UV spectra of a quinoline type and its IR spectra show weak absorption by NH stretching at 3350 cm^{-1} and CO absorption at 1680 cm^{-1}. On the NMR spectra, the signals due to the methyl and methylene groups were found as doublet lines at 2.85 and 4.62 ppm, respectively. On the basis of these data, in addition to mass spectra and elemental analysis, **2** was determined to be 2-(methylaminoacetyl)quinoline. For the product **3**, the NMR signals due to the methyl and methylene groups were observed as singlet peaks, and it was found that one proton of the aromatic protons disappeared. The mass spectra showed that the molecular weight of **3** was less by two than that of **1**. The presence of the CO group was confirmed by the IR spectra. Hence, **3** was reasonably deduced to be 2-methyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-one.



2



3

2a, 3a : R=H
2b, 3b : R=CH$_3$
2c, 3c : R=Cl

As shown in Table 1, the yield distribution of **2** and **3** in acetonitrile or benzene remarkably changed by introduction of the chloro substituent at the 4-position of a quinoline nucleus, but there was no significant effect by the methyl substituent. That is, the irradiation of **1a** and **1b** produced **2** as a major product and **3** as a minor one, while in the case of **1c** the yield of **2c** decreased extremely and that of **3c** increased. On the other hand, the yields of both products were very low in cyclohexane and ethanol.

Irradiation of **1** under an oxygen atmosphere gave 2-(methylcarbamoyl)quinolines (**4**) as a major product, and **2** and **3** as the minor products (Table 2). Identification of **4** was made by comparison with an authentic sample prepared according to the literature.[3] The

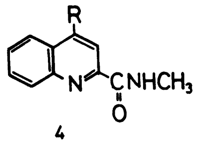
Table 1. Photochemical reactions of 2-(dimethylcarbamoyl)quinolines **1** under a nitrogen atmosphere

Amide	Solvent	Conversion %	Yield of product / % **2**	**3**
1a	Acetonitrile	70	44	5
	Benzene	65	32	3
	Cyclohexane	34	15	—
	Ethanol	76	10	—
1b	Acetonitrile	64	46	2
	Benzene	68	39	2
	Cyclohexane	41	16	—
	Ethanol	79	18	—
1c	Acetonitrile	70	4	25
	Benzene	65	3	26
	Cyclohexane	37	Trace	5
	Ethanol	67	Trace	Trace

Table 2. Photochemical reactions of **1** in an oxygen atmosphere

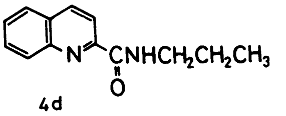
Amide	Solvent	Conversion	Yield of product / %		
		%	**2**	**3**	**4**
1a	Acetonitrile	65	11	3	31
	Acetonitrile[a)]	50	14	2	24+14(**4d**)
	Benzene	60	8	1	10
1b	Acetonitrile	56	5	Trace	38
1c	Acetonitrile	41	—	—	30

a) **1a** was irradiated in acetonitrile solution containing 20% (v/v) propylamine.



4

4a: R=H
4b: R=CH_3
4c: R=Cl



4d

Table 3. Phosphorescence data of **1** in ethanol and methylcyclohexane (MCH)

Amide	Solvent	λ_{max}/nm	E_T/kJ mol^{-1}	τ_p/s
1a	Ethanol	472	253	1.56
	MCH	473	253	1.12
1b	Ethanol	470	254	1.60
	MCH	470	254	1.35
1c	Ethanol	480	249	0.28
	MCH	480	249	0.25

Table 4. Benzophenone sensitization of **1**

Amide	Solvent	Recovered	Product yield / %		
		Benzophenone / %	**2**	**3**	**4**
1a	Acetonitrile	93	70	11	—
	Acetonitrile[a)]	71	25	3	18
	Benzene	94	57	9	—
1b	Acetonitrile	97	61	6	—
	Benzene	94	54	5	—
1c	Acetonitrile	98	6	46	—
	Benzene	99	5	33	—

a) Irradiation was carried out in an oxygen atmosphere for 40 h.

Table 5. Quantum yields of photochemical reactions of **1a** and **1c**

Solvent	Φ_d(**1a**)	Φ_f(**2a**)	Φ_d(**1c**)	Φ_f(**3c**)
Acetonitrile	0.016	0.010	0.011	0.0036
Benzene	0.0087	0.0047	0.010	0.0025
Cyclohexane	0.0058	0.0018	0.0072	0.0003
Ethanol	0.011	0.0024	0.013	0.0004

irradiation of acetonitrile solution of **1a** containing propylamine produced **4a** and 2-(propylcarbamoyl)-quinoline **4d** in 24 and 14% yields, respectively.

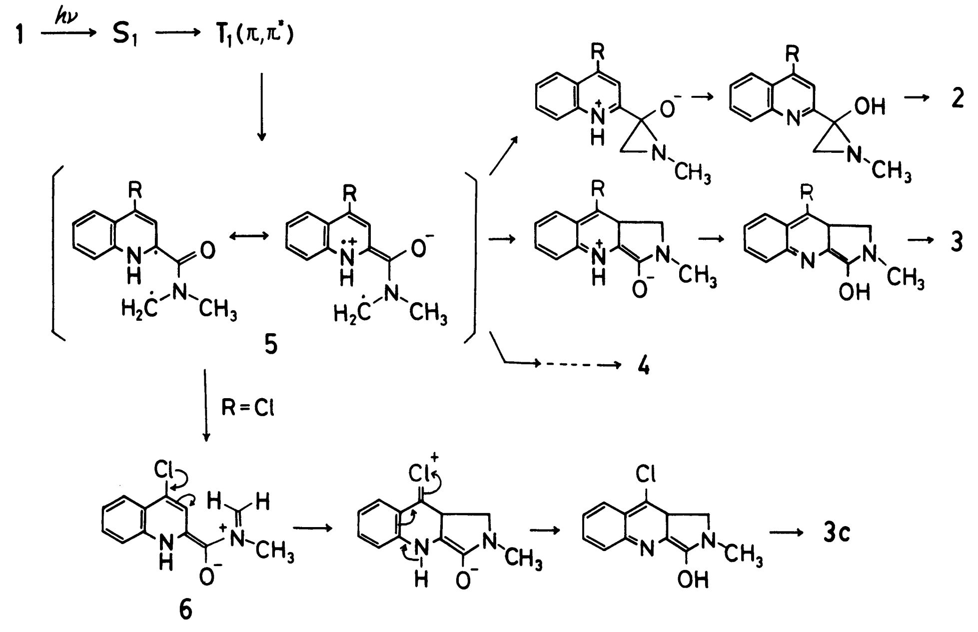
Emission and Absorption Spectra of 1. The phosphorescence spectra of **1** could be measured in methylcyclohexane and ethanol at 77 K (Table 3), although no fluorescence was observed in either solution. From the first maxima of the spectra, the triplet excitation energy (E_T) was determined to be about 250 kJ mol^{-1}, which is higher than that of 1,3-cyclohexadiene (E_T=219 kJ mol^{-1}) and lower than that of benzophenone (E_T=289 kJ mol^{-1}). This long phosphorescence lifetime, over 1 s, indicates that the T_1 state of **1** can be assigned to $^3\pi,\pi^*$ type. The UV spectra of **1** was similar to that of quinoline, but not to that of 2-quinolinecarbonitrile, suggesting that the carbamoyl substituent conjugates with a quinoline nucleus to only a small extent. This implies that the excitation energy of **1** may be localized in a quinoline moiety, namely the $T_1(\pi,\pi^*)$ is the excited state of the quinoline nucleus.

Triplet Sensitization. A solution of **1** in deaerated acetonitrile or benzene containing benzophenone was irradiated with 366 nm light for 20 h. As a result, **2** and **3** were obtained in a product distribution similar to that in the case of the direct photolysis (Table 4). On the other hand, benzophenone sinsitization of **1a** in acetonitrile in the presence of oxygen gave **4a** in a 18% yield besides 25% of **2a** and a small amount of **3a**. This fact suggests that the triplet state is responsible for the formation of **4** as well as for **2** and **3**, and that the reaction to **4** involves an oxidation process.

Quantum Yields and Triplet Quenching. The quantum yields of both the disappearance (Φ_d) and the formation (Φ_f) for the photochemical reactions of **1a** and **1c** were determined under a nitrogen atmosphere; the results are given in Table 5. The quantum yields for the formation of **2a** and **3c** were larger in acetonitrile than in benzene, and became very low in cyclohexane and ethanol. The measurements for the minor products **3a** and **2c** were not attempted in this experiment, because those yields were too low to be precisely evaluated.

Next, the quantum yields in the presence of 1,3-cyclohexadiene were determined in deaerated acetonitrile. The Stern-Volmer plots are shown in Fig. 1. The linear relation of the plots for the quantum yields of **2a** and **3c** indicates that both products were formed through the $T_1(\pi,\pi^*)$ state. The quenching constants were estimated from the slopes to be 1.6×10^4 dm^3 mol^{-1} for **2a** and 1.0×10^4 dm^3 mol^{-1} for **3c**. The quenching constants for the quantum yields of disappearance evaluated from the linear portion of the plots were 1.2×10^4 dm^3 mol^{-1} for **1a** and 0.7×10^4 dm^3 mol^{-1} for **1c**. No large difference between the constants for formation quantum yield and for disappearance quantum yield indicates that, even if any reaction proceeds *via* the excited singlet state, it may be quite inefficient.

Reaction Mechanism. The primary step of the reaction of **1** may be γ-hydrogen abstraction by the ring nitrogen in the $T_1(\pi,\pi^*)$ state. Considering that the product formation is more effective in acetonitrile than in the hydrocarbon solvents, the reaction is expected to proceed *via* an ionic intermediate. Such a solvent effect and the chloro substituent effect on the reaction may be explained in terms of the mechanism involving zwitterionic intermediates, as shown in Scheme 1.



Scheme 1.

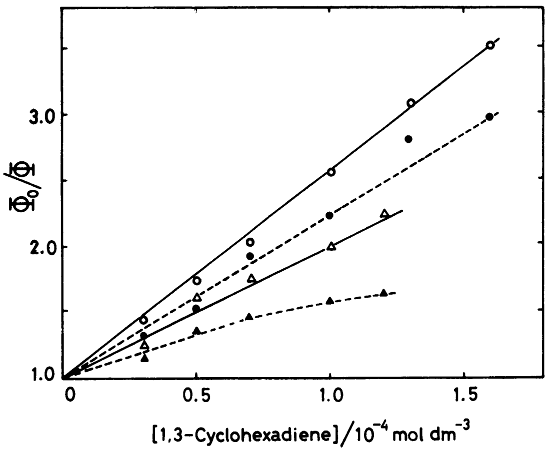
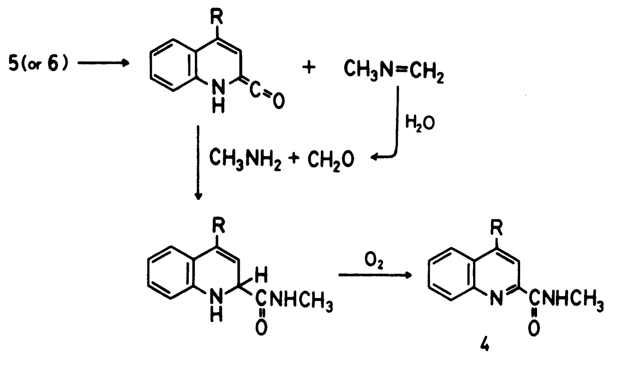


Fig. 1. Stern-Volmer plots for 1,3-cyclohexadiene quenching of the photochemical reactions of **1a** and **1c** in acetonitrile.

—○—: Formation of **2a**, ···●···: disappearance of **1a**, —△—: formation of **3c**, ···▲···: disappearance of **1c**.

The intermediate **5** formed by the γ-hydrogen abstraction is in a resonance form of diradical and zwitterionic structures. The products **2** and **3** may be formed not *via* diradical structure but *via* zwitterionic one, because the contribution of the latter structure increases in a polar solvent, acetonitrile. The prominent increase of the yield of **3c** could be rationallized by assuming that the reaction **1c**→**3c** proceeds through a zwitterion **6**; the mesomery effect of the chlorine atom promotes the electron density on the carbon atom at the 3-position of a quinoline nucleus, which would be favorable for the cyclization of **6** followed by the formation of **3c**. Aoyama *et al.* have clarified that Type II cyclization of α-oxoamides occurs *via* zwitterion intermediates analoguous to the type of **6** and that the zwitterions were stabilized in protic solvents.[4a)] This explains the result that the yield of **3c** is larger in acetonitrile. The lower yields of the products **2** and **3** in ethanol may be attributed to the formation of a hydrogen bond between the ring nitrogen and the solvent. Such hydrogen-bonding is expected to suppress intramolecular hydrogen abstraction by the excited ring nitrogen. Previously, we have reported that 2-quinolinecarbonitriles undergo photochemical substitution derived from hydrogen abstraction by the ring nitrogen from the solvent alcohol.[1)] However, we could not find the corresponding reaction in the case of **1**.

The formation of **4** is explained by assuming the decomposition of **5** to ketenes and imines. The decomposition is possible from both diradical and zwitterionic structures, and also from the zwitterion **6**. It is well known that such ketenes and imines are responsible for the formation of *N*-monosubstituted amides in the presence of moisture. For example, the photochemical reaction of *N*,*N*-diisopropylmethacrylamide was reported to give *N*-isopropylbutyramide *via* the dimethylketene and the corresponding imine.[4b)] The photochemical formation of 2-(propylcarbaboyl)quinoline **4d** from **1a** in the presence of propylamine supports the reaction mechanism. The fact that **4** was formed only in the presence of oxygen indicates that it may be necessary for the oxidation of dihydroquinolines to **4**.



4-Acylpyrimidines were suggested to undergo γ-hydrogen abstraction by the ring nitrogen and Type II elimination by the carbonyl group in each n,π* triplet state situated close together.[5] The carbamoyl group of **1** is easily deduced to possess the ^{3}CT state on the analogy of the fact that a formamid has an excited intramolecular charge transfer state.[6] If the ^{3}CT state lies close to the $T_1(\pi,\pi^*)$ state, the hydrogen abstraction by the carbonyl group from the *N*-methyl group may occur by way of an electron transfer mechanism well known for the photoreduction of amino ketones[7] and give a 1,3-biradical, which could also account for the formation of **2** and **3**. However, such a hydrogen transfer through the five-membered transition state is ineffective and there are few reports.[8] Therefore, hydrogen abstraction by the ring nitrogen is thought to be a more reasonable mechanism for the reaction of **1**.

Experimental

The NMR spectra were determined in $CDCl_3$ on a Hitachi-Perkin Elmer R-20, using TMS as an internal standard. The mass spectra were measured by a Hitachi RMU-6M or a Hitachi M-80 A double focus mass spectrometer. The IR spectra were taken on a JASCO A-302 and UV spectra were measured on a Shimadzu UV-220. The phosphorescence spectra were recorded with a Hitachi MPF-2A.

Materials. All solvents used in the irradiation experiment were reagent grade from Wako Pure Chemical Industry. Acetonitrile was refluxed in the presence of phosphorus pentaoxide for 10 h and distilled. Cyclohexane was used after purification by silica gel chromatography. Ethanol and benzene were used without further purification. 1,3-Cyclohexadiene and benzophenone from Tokyo Kasei Kogyo Co. were purified by distillation or recrystallization from ethanol, respectively. 2-(Dimethylcarbamoyl)quinoline **1a**—**c** were prepared by treating the corresponding 2-quinolinecarboxylic acids with $SOCl_2$ and dimethylamine.[3] The carboxylic acids were obtained from the basic hydrolysis of 2-quinolinecarbonitriles[9] synthesized by Reisert reaction of quinoline, 4-methylquinoline, and 4-chloroquinoline *N*-oxides which were prepared by the methods given in the literature.[10] **1a** and **1b** were purified by alumina chromatography, using a mixture of chloroform and diethyl ether as an eluent, and **1c** was recrystallized from a mixture of hexane and ethanol.

2-(Dimethylcarbamoyl)quinoline (1a). Colorless liquid; NMR δ=3.15 (3H, s, CH_3), 3.21 (3H, s, CH_3), 7.40—8.34 (6H, m, ArH); MS *m/e* 200 (M^+); IR (neat) 3050, 2910, 1670 (CO) cm^{-1}.

2-(Dimethylcarbamoyl)-4-methylquinoline (1b). Colorless liquid; NMR δ=2.62 (3H, s, CH_3 on ring), 3.15 (3H, s, *N*-CH_3), 3.18 (3H, s, *N*-CH_3), 7.34—8.24 (5H, m, ArH); MS *m/e* 214 (M^+); IR (neat) 3050, 2940, 1650 (CO) cm^{-1}.

2-(Dimethylcarbamoyl)-4-chloroquinoline (1c). Mp 64—65 °C; NMR δ=3.21 (6H, s, $(CH_3)_2$), 7.32—8.33 (5H, m, ArH); MS *m/e* 236/234 (M^+); IR (KBr) 3050, 2950, 1650 (CO) cm^{-1}.

General Procedure of Direct Irradiation of **1**. **1a**—**c** (200 mg) dissolved in 70 cm^3 of acetonitrile, benzene, cyclohexane, or ethanol were irradiated in a Pyrex vessel with a 100 W high pressure immersion mercury lamp (Riko Kagaku Sangyo Co.) in a nitrogen or oxygen atmosphere for 20 h. After the evaporation of the solvent, the residue was chromatographed on silica gel (Wakogel C-300). Elution with a mixture of chloroform and diethyl ether separated **2**, **3**, and **4**. Liquid products were purified on thin-layer chromatography of Kieselgel (PF_{254}, Merck) by being developed with the same eluent.

2-(Methylaminoacetyl)quinoline (2a). Colorless liquid; NMR δ=2.85 (3H, d, *J*=6.0 Hz, $NHC\underline{H}_3$), 4.62 (2H, d, *J*=9.1 Hz, $C\underline{H}_2NH$), 7.00—8.41 (7H, m, ArH and NH); MS *m/e* 200 (M^+); IR (neat) 3400 (broad), 3350 (NH), 3070, 2950, 1680 (CO) cm^{-1}. Found: C, 69.83; H, 6.14; N, 13.06%. Calcd for $C_{12}H_{12}N_2O$ 1/3 H_2O: C, 69.90; H, 6.15; N, 13.59%.

2-(Methylaminoacetyl)-4-methylquinoline (2b). Mp 80—81 °C (from hexane–ethanol); NMR δ=2.69 (3H, s, CH_3 on ring), 2.93 (3H, d, *J*=6.2 Hz, $NHC\underline{H}_3$), 4.72 (2H, d, *J*=9.1 Hz, $C\underline{H}_2NH$), 7.09—8.40 (6H, m, ArH and NH); MS *m/e* 214 (M^+); IR (KBr) 3330 (NH), 3050, 2940, 1675 (CO) cm^{-1}. Found: C, 72.77; H, 6.59; N, 13.09%. Calcd for $C_{13}H_{14}N_2O$: C, 72.90; H, 6.54; H, 13.08%.

2-(Methylaminoacetyl)-4-chloroquinoline (2c). Colorless liquid; NMR δ=2.99 (3H, d, *J*=7.0 Hz, $NHC\underline{H}_3$), 4.75 (2H, d, *J*=8.9 Hz, $C\underline{H}_2NH$), 7.33—8.45 (6H, m, ArH and NH); MS *m/e* 236/234 (M^+); $C_{12}H_{11}N_2OCl$ was determined with a Hitachi M-80 A double focus mass spectrometer; IR (neat) 3350 (NH), 3080, 2940, 1680 (CO) cm^{-1}.

*2-Methyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-one (3a).* Mp 198 °C (from ethanol); NMR δ=3.22 (3H, s, CH_3), 4.48 (2H, s, CH_2), 7.18—8.50 (5H, m, ArH), MS *m/e* 198 (M^+); IR (KBr) 3050, 2940, 1680 (CO) cm^{-1}. Found: C, 72.11; H, 5.02; N, 13.97%. Calcd for $C_{12}H_{10}N_2O$: C, 72.73; H, 5.05; N, 14.14%.

*2,9-Dimethyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-one (3b).* Mp 178 °C (from ethanol); NMR δ=3.12 (3H, s, CH_3 on ring), 3.25 (3H, s, *N*-CH_3), 4.47 (2H, s, CH_2), 7.20—8.34 (4H, m, ArH); MS *m/e* 212 (M^+); $C_{13}H_{12}N_2O$ was determined with a Hitachi M-80 A double focus mass spectrometer; IR (KBr) 3080, 2930, 1680 (CO) cm^{-1}.

*9-Chloro-2-methyl-1*H*-pyrrolo[3,4-*b*]quinolin-3(2*H*)-one (3c).* Mp 166 °C (from ethanol); NMR δ=3.26 (3H, s, CH_3), 4.46 (2H, s, CH_2), 7.34—8.48 (4H, m, ArH); MS *m/e* 234/232 (M^+); IR (KBr) 3050, 2910, 1690 (CO) cm^{-1}. Found: C, 61.62; H, 3.93; N, 11.91%. Calcd for $C_{12}H_9N_2OCl$: C, 61.94; H, 3.87; N, 12.04%.

The structures of **4a**—**d** were determined by the comparison with the authentic sample synthesized according to the same method as that used for the preparation of **1**.[3]

2-(Methylcarbamoyl)quinoline (4a). Mp 118 °C (from ethanol); NMR δ=3.12 (3H, d, *J*=5.1 Hz, $NHC\underline{H}_3$), 7.41—8.31 (7H, m, ArH and NH); MS *m/e* 186 (M^+); IR (KBr) 3350 (NH), 3080, 2960, 1660 cm^{-1}.

2-(Methylcarbamoyl)-4-methylquinoline (4b). Mp 109 °C (from ethanol); NMR δ=2.76 (3H, s, CH_3 on ring), 3.18 (3H, d, *J*=5.4 Hz, $NHC\underline{H}_3$), 7.40—8.35 (6H, m, ArH and NH); MS *m/e* 200 (M^+); IR (KBr) 3330 (NH), 3090, 2940, 1660 (CO) cm^{-1}.

2-(Methylcarbamoyl)-4-chloroquinoline (4c). Mp 140 °C (from ethanol); NMR δ=3.11 (3H, d, *J*=5.5 Hz, $NHC\underline{H}_3$), 7.37—8.42 (6H, m, ArH and NH); MS *m/e* 222/220 (M^+); IR (KBr) 3350 (NH), 3080, 2950, 1660 (CO) cm^{-1}.

2-(Propylcarbamoyl)quinoline (4d). Colorless liquid; NMR δ=0.978 (3H, t, *J*=6.6 Hz, $CH_2C\underline{H}_3$), 1.34—2.04 (2H, m, $CH_2C\underline{H}_2CH_3$), 3.49 (2H, q, *J*=7.6 Hz, $NHC\underline{H}_2CH_2$), 7.44—8.43 (7H, m, ArH and NH); MS *m/e* 214 (M^+); IR (neat) 3380 (NH), 3050, 2950, 1670 (CO) cm^{-1}.

Triplet Sensitization. Acetonitrile or benzene solution (110 cm^3) containing **1** (0.05 g) and benzophenone (0.1 g) was irradiated for 20 h with 366 nm light through a UV-35 Toshiba filter from a 500 W high pressure mercury lamp (USH-500D, Ushio Electric Inc.). The products were isolated by thin-layer chromatography of Kieselgel (PF_{254}, Merck), using a mixture of chloroform and diethyl ether.

Quantum Yield Determination. A deaerated solution containing 3×10^{-4} mol dm^{-3} **1a** or **1c** was irradiated at 313 nm in a quartz cylindrical cell (5-cm in diameter and 1-cm in length), using a USH-500D lamp as a light source. The 313-nm line was isolated by a combination of a $NiSO_4$ solution with UV-29 and UVD-33S filters. The light intensity was determined by means of a potassium trioxalatoferrate(III) actinometer. The amount of the products (**2a** and **3c**) and consumed starting materials (**1a** and **1c**) were determined spectrometrically after the separation by a silica-gel column (chloroform was used as an eluent). Conversions ranged from 10 to 20%.

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