

Photoreaction of 4-Substituted Quinoline *N*-Oxide and 2(1*H*)-Quinolinone in Propionic Acid¹⁾

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4-Substituted *cis*-3-ethyl-2-oxo-1,2,3,4-tetrahydro-2-quinoline was formed as a major product, by irradiation of quinoline *N*-oxide and 2(1*H*)-quinolinone substituted with an electron-withdrawing group at the C-4 position in propionic acid. Also, the products were confirmed by direct comparison with synthesized compounds.

Recently, photoalkylation reactions of aza aromatic compounds have been reported by several authors.²⁾ Concerning this reaction, Ide *et al.* have also described the photoalkylation of quinolinecarbonitriles and isoquinolinecarbonitriles in propionic acid.³⁾ The reaction products were found to be ethylated in the aza aromatic rings of quinoline and isoquinoline. Moreover, the position of alkylation was explained well by the reaction indices of nucleophilic or radical superdelocalizability in a simple HMO calculation.³⁾ The present paper is concerned with photoinduced reactions of quinoline *N*-oxide and 2(1*H*)-quinolinone (carbostyryl) having an electron-withdrawing group at the C-4 position in propionic acid.

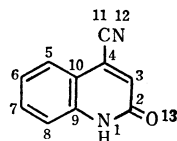
Results and Discussion

It is well known that azanaphthalene *N*-oxide are predominantly transformed into lactams, as a result of ultraviolet irradiation in hydroxylic solvents.^{4,5)} As

TABLE 1. REACTION INDICES FOR 2-OXO-1,2-DIHYDRO-4-QUINOLINECARBONITRILE

No ^{a)}	Superdelocalizability ^{b)}		
	Electrophilic	Nucleophilic	Radical
1	1.570	0.348	0.959
2	0.314	0.711	0.513
3	1.275	1.363	1.319
4	0.705	1.101	0.903
5	0.905	1.004	0.854
6	1.053	0.747	0.900
7	0.844	0.943	0.894
8	1.116	0.810	0.963
9	3.743	0.843	0.793
10	0.959	0.654	0.806
11	0.460	0.996	0.728
12	0.833	1.035	0.934
13	0.987	0.423	0.705

a) Numbered as follows.



b) Calculated according to the method of Fukui.⁶⁾ The following parameters were adopted from the textbook of Pullmann⁷⁾ and were used in the simple HMO calculation. Coulomb integral: $\alpha_N^{\text{CN}} = \alpha + 1.1\beta$, $\alpha_C^{\text{C=O}} = \alpha$, $\alpha_O^{\text{C=O}} = \alpha + 1.2\beta$, $\alpha_N^{\text{CON}} = \alpha + \beta$. Resonance integral: $\beta_{\text{C=N}}^{\text{CN}} = 1.4\beta$, $\beta_{\text{C=N}}^{\text{CON}} = 0.9\beta$, $\beta_{\text{C=O}}^{\text{O}} = 2\beta$.

seen from Table 1, a simple HMO calculation indicates that the C-3 position of the lactam, 2-oxo-1,2-dihydro-4-quinolinecarbonitrile, is the most reactive site in the molecule. Accordingly, irradiation of 4-quinolinecarbonitrile *N*-oxide (**1a**) in propionic acid may give the lactam (**2a**) which then undergoes photoalkylation at the C-3 position. An experimental proof of these assumptions is of interest with respect to the mechanism of the photoalkylation of aza aromatic compounds. Therefore, the present authors carried out the irradiation of **1** and **2** in propionic acid using a high-pressure mercury lamp and a quartz filter.

Both compounds **1** and **2** gave the same products in the yields given in Table 2. The products were determined to be 4-substituted 3-ethyl-2-oxo-1,2,3,4-tetrahydroquinoline on the basis of the spectral data listed in Tables 3 and 4. It is difficult to assign either a *cis* or a *trans* configuration on the basis of the coupling constant between C³-H and C⁴-H. Accordingly, synthesis of the two isomers was attempted accordingly to the scheme shown in Chart 2.

Following the synthesizing method for (Z)-2-(2-oxo-3-indolinyldene)propionic acid of Julian *et al.*,⁸⁾ (Z)-2-(2-oxo-3-indolinyldene)butyric acid (**6**) was prepared from oxindole (**5**) and 2-oxobutyric acid. Heating of **6** in hydrochloric acid gave 3-ethyl-2-oxo-1,2-dihydro-4-quinolinecarboxylic acid (**7**) which was identical with the compound obtained by Mulert⁹⁾ from *N*-butylisatin, with respect to the chemical and physical data. Compound (**7**) was catalytically reduced, giving colorless needles. The needles were determined from their infrared spectrum to be *cis*-3-ethyl-2-oxo-1,2,3,4-tetra-

TABLE 2. PHOTOCHEMICAL REACTION YIELDS

Starting compound	Product	Yield ^{a)} (%)	Product	Yield ^{a)} (%)
1a	3a	41 (26)	4a	8
2a	3a	53 (40)	4a	9
1b	3b	28 (8.7)	4b	5
2b	3b	15 (7.0)	4b	8
1c	3c^{b)}	50 (37)	4c^{b)}	12
2c	3c^{b)}	64 (46)	4c^{b)}	15

a) The amount of the product present in the reaction mixture, and determined by gas chromatography. The numbers in parenthesis are the yields for isolated pure products after treatment of the reaction mixtures. The retention times are 35.4 and 40.6 min for **3a** and **4a**, and 140 and 149 min for **3b** and **4b**. b) Obtained from a reaction mixture treated with diazomethane.

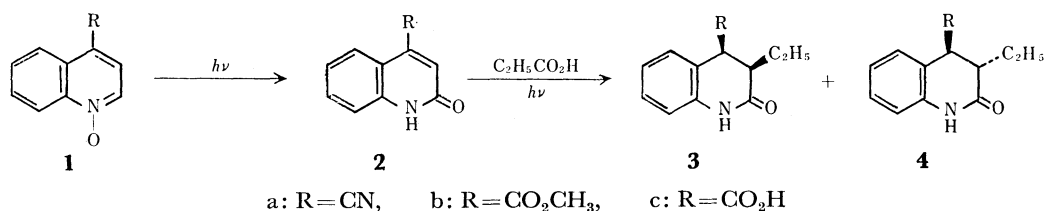


Chart 1.

TABLE 3. PHYSICAL PROPERTIES OF THE COMPOUNDS

Compound	mp (°C)	IR ($\nu_{\text{max}}^{\text{KBr}}$, cm ⁻¹)	MS (m/e , %)
3a	187—188	2280(ν_{CN} , carbonitrile), 1681($\nu_{\text{C=O}}$, lactam)	200(85, M ⁺), 172(67, M ⁺ -(CH ₂ =CH ₂)), 171(96, M ⁺ -(CH ₂ =CH ₂ , H)), 146(100, M ⁺ -(CH ₂ =CH ₂ , CN)), 145(20, M ⁺ -(CH ₂ =CH ₂ , HCN))
3b	166—167	1737($\nu_{\text{C=O}}$, ester), 1690($\nu_{\text{C=O}}$, lactam)	233(77, M ⁺), 174(99, M ⁺ -(CH ₂ =CH ₂ , OCH ₃)), 146(100, M ⁺ -(CH ₂ =CH ₂ , CO ₂ CH ₃))
3c	221—222	1720($\nu_{\text{C=O}}$, acid), 1662($\nu_{\text{C=O}}$, lactam)	219(63, M ⁺), 191(58, M ⁺ -(CH ₂ =CH ₂)), 174(99, M ⁺ -(OH, CH ₂ =CH ₂)), 146(100, M ⁺ -(CH ₂ =CH ₂ , CO ₂ H))
4a	194—195	2300(ν_{CN} , carbonitrile), 1685($\nu_{\text{C=O}}$, lactam)	200(78, M ⁺), 172(72, M ⁺ -(CH ₂ =CH ₂)), 171(100, M ⁺ -C ₂ H ₅), 146(70, M ⁺ -(CH ₂ =CH ₂ , CN))
4b	121—122	1726($\nu_{\text{C=O}}$, ester), 1674($\nu_{\text{C=O}}$, lactam)	233(54, M ⁺), 174(100, M ⁺ -(CO ₂ CH ₃)), 146(91, M ⁺ -(CO ₂ -CH ₃ , CH ₂ =CH ₂)), 132(68, M ⁺ -(CO ₂ CH ₃ , CH ₂ =CH ₂ , CH ₂))
4c	127—128	1720($\nu_{\text{C=O}}$, acid), 1670($\nu_{\text{C=O}}$, lactam)	219(50, M ⁺), 174(100, M ⁺ -(CO ₂ H)), 146(71, M ⁺ -(CO ₂ H, CH ₂ =CH ₂)), 132(65, M ⁺ -(CO ₂ H, CH ₂ =CH ₂ , CH ₂))
6	203—204	1756($\nu_{\text{C=O}}$, lactam(5 membered)), 1720($\nu_{\text{C=O}}$, acid), 1644($\nu_{\text{C=C}}$, exo)	217(48, M ⁺), 199(61, M ⁺ -H ₂ O), 171(100, M ⁺ -(C=O, H ₂ O)), 143(61, M ⁺ -(C, C ₂ H ₅ , CO ₂ H))
8	246—247	1700(amide I), 1680($\nu_{\text{C=O}}$, lactam)	218(50, M ⁺), 174(100, M ⁺ -(CONH ₂)), 146(78, M ⁺ -(CONH ₂ , CH ₂ =CH ₂)), 132(67, M ⁺ -(CONH ₂ , CH ₂ =CH ₂ , CH ₂))
10	205—206	1700(amide I), 1670($\nu_{\text{C=O}}$, lactam)	218(51, M ⁺), 174(100, M ⁺ -(CONH ₂)), 146(80, M ⁺ -(CONH ₂ , CH ₂ =CH ₂)), 132(85, M ⁺ -(CONH ₂ , CH ₂ =CH ₂ , CH ₂))

TABLE 4. NMR DATA OF PHOTOLYSATES AND RELATED COMPOUNDS
(from internal TMS, δ value (ppm))^{a)}

Compound	-CH ₂ CH ₃ (3H)	-CH-CH ₂ -CH ₃ (2H)	-CH-CH-CH ₂ - (1H)	-CH-CH (1H)	Others
3a^{b)}	1.10 (t, $J=7$ Hz)	1.6—2.5 (m)	2.7—3.0 (m)	4.6 (d, $J=6$ Hz)	7.0—7.5(4H, m, Ar-H), 9.5(1H, bs, N-H)
3b^{b)}	1.10 (t, $J=7$ Hz)	1.7—2.5 (m)	2.6—3.0 (m)	4.10 (d, $J=6$ Hz)	6.9—7.5(4H, m, Ar-H), 9.25(1H, bs, N-H), 3.65(3H, s, CO ₂ CH ₃)
3c	1.21 (t, $J=7$ Hz)	1.8—2.1 (m)	2.6—2.9 (m)	4.28 (d, $J=5$ Hz)	
4a	1.11 (t, $J=7$ Hz)	1.91 (d × q, $J=7$ and 7 Hz)	3.00 (d × t, $J=8$ and 7 Hz)	4.59 (d, $J=8$ Hz)	
4b	1.02 (t, $J=7$ Hz)	1.67 (d × q, $J=7$ and 7 Hz)	3.11 (d × t, $J=4$ and 7 Hz)	4.02 (d, $J=4$ Hz)	3.56(3H, s, CO ₂ CH ₃)
4c^{b)}	1.08 (t, $J=7$ Hz)	1.69 (d × q, $J=7$ and 7 Hz)	3.28 (d × t, $J=3$ and 7 Hz)	4.08 (d, $J=3$ Hz)	
8	1.21 (t, $J=8$ Hz)	1.8—2.4 (m)	2.6—2.9 (m)	4.32 (d, $J=6$ Hz)	
10	1.14 (t, $J=7$ Hz)	1.82 (d × q, $J=7$ and 7 Hz)	3.45 (d × t, $J=4$ and 7 Hz)	4.23 (d, $J=4$ Hz)	
6	1.36(3H, t, $J=7$ Hz, -CH ₂ CH ₃),	2.94(2H, q, $J=7$ Hz, -CH ₂ CH ₃),			6.9—7.7(4H, m, Ar-H)

a) Measured in pyridine, except for b). S, di t, q, m, and bs stand for singlet, doublet, triplet, quartet, multiplet, and broad singlet, respectively. b) Measured in acetone-*d*₆.

hydro-4-quinolinecarboxylic acid (**3c**) with bands at 1720 (ν C=O, acid) and 1662 cm⁻¹ (ν C=O, lactam), and by the *cis*-addition mechanism for catalytic hydrogenation. Compound (**6**) was catalytically reduced, giving an oily product which was presumed to have the

structure of **9** shown in Chart 2. The crude oily product was refluxed in hydrochloric acid yielding colorless prisms, mp 127 °C. The prisms were determined to be *trans*-3-ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxylic acid (**4c**), since the physical properties of

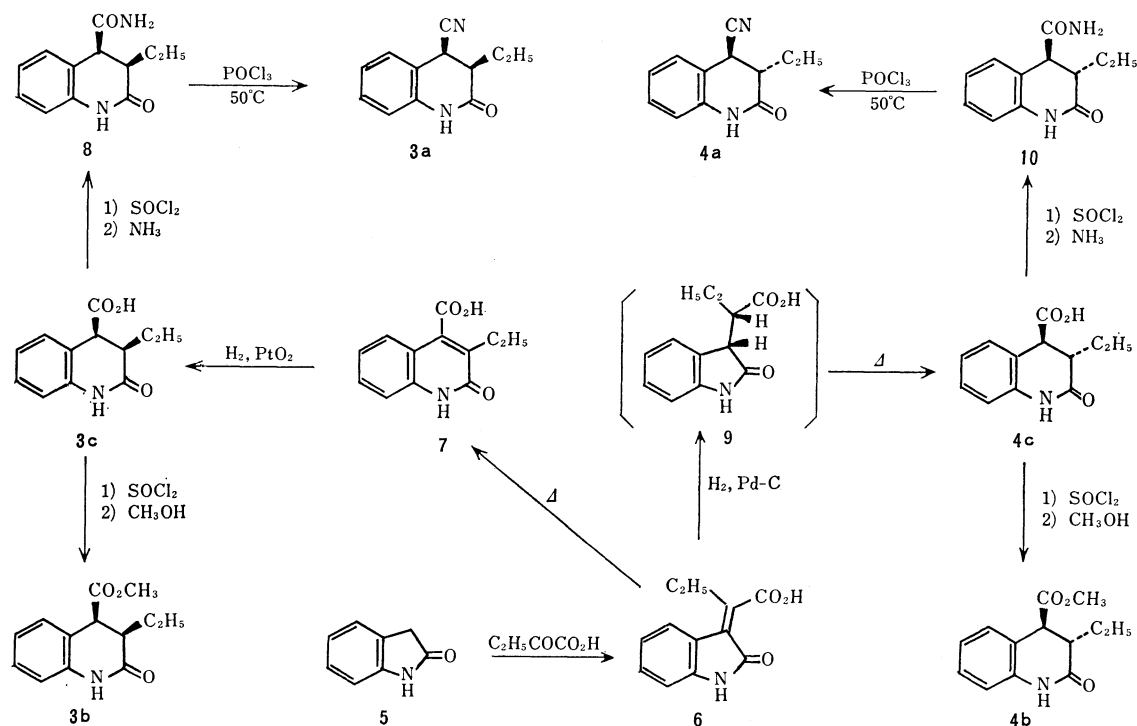


Chart 2.

4c were similar but not identical to those of **3c**. *cis*-(**3a**) and *trans*-3-ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinoline-carbonitrile (**4a**) were synthesized from **3c** and **4c** *via cis*-(**8**) and *trans*-3-ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxamide (**10**), respectively. The main product isolated from the mixture of the photoreactions of **1** and **2** coincided with compound **3**, the *cis* isomer obtained above. However, a small amount of the *trans* isomer, although difficult to isolate, was detected in the mixture by means of gas chromatography, as indicated in Table 2.

The fact that the *cis* isomer was obtained as a major product indicates that the *trans*-addition of ethyl and hydrogen groups occurs at the C-3 double bond of 2(1*H*)-quinolinone. This also indicates that the alkylated position in the present alkylation reaction is easily explained by the reaction indices in the simple HMO calculation. These results are important to an understanding of the mechanism of photoalkylation of aza aromatic compounds.

Experimental

All melting points were determined using a YANACO micromelting point apparatus and are uncorrected. Infrared spectra were recorded on a JASCO IR-S infrared spectrometer. Ultraviolet spectra were determined with a Hitachi 124 spectrophotometer. Nuclear magnetic resonance spectra were measured with a JEOL JNM-100H spectrometer at 100 MHz using TMS as an internal standard. Mass spectra were obtained with a JEOL JMS-01SG-2 mass spectrometer, using a direct inlet and an electron energy of 75 eV.

Irradiation was carried out using a high-pressure mercury arc (USHIO UM-102) surrounded by a quartz water jacket at 30 °C.

The yield of the reaction products was determined by

analysis on a SHIMADZU GC-5A gas chromatograph using a column (3 mm \times 2 m) packed with OV-225 (1.5%) on Chromosorb-W (DMSC-A/W). The oven temperature was 186 °C for **3a** and **4a**, and 155 °C for **3b** and **4b**. The flow rate of the carrier gas (N₂) was 60 ml/min.

Materials. 2-Oxo-1,2-dihydro-4-quinolinecarboxylic acid, 2-oxo-1,2-dihydro-4-quinolinecarbonitrile, methyl 2-oxo-1,2-dihydro-4-quinolinecarboxylate and 4-quinolinecarbonitrile *N*-oxide were prepared according to the methods of Jacobs *et al.*,¹⁰⁾ Daeniker *et al.*,¹¹⁾ Mayer,¹²⁾ and Daeniker,¹¹⁾ respectively.

4-Substituted quinoline *N*-oxide were synthesized by the method of Ochiai.¹⁴⁾

Methyl 4-Quinolincarboxylate N-Oxide (1b). Colorless needles (from methanol), mp 149–150 °C. IR(KBr): 1701 (ν C=O), 1250 (ν N–O) cm^{-1} . Found: C, 70.72; H, 4.81; N, 7.36%. Calcd for $\text{C}_{11}\text{H}_9\text{NO}_2$: C, 70.58; H, 4.86; N, 7.48%.

4-Quinolinecarboxylic Acid N-Oxide (Ic). Colorless prisms (from acetic acid), mp 256 °C (dec). IR (KBr): 2400—2900 (b, ν OH), 1714 (ν C=O), 1170 (ν N-O) cm^{-1} . Found: 63.53; H, 3.65; N, 7.49%. Calcd for $\text{C}_{10}\text{H}_7\text{NO}_3$: C, 63.49; H, 3.37; N, 7.41%.

(Z)-2-(2-Oxo-3-indolinylidene)butyric Acid (**6**). Metallic sodium (2.1 g) was added to absolute ethanol (70 ml). To this solution was added a solution of oxindol (**5**, 3.9 g) in absolute ethanol (30 ml) with stirring and then a solution of 2-oxobutyric acid (3.0 g) in absolute ethanol (30 ml). The mixture was refluxed for 3 h with stirring. The solid formed upon cooling was collected by filtration and dissolved in water (50 ml). The solution was acidified with 2M-hydrochloric acid. The resulting solid was dried and recrystallized from ethyl acetate to give yellow prisms, mp 203–204 °C, in 3.7 g (58.1%) yield. UV ($\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ)): 346(1600), 293 (7200), 258 (31300), 252(28000). Found: C, 66.52; H, 5.12; N, 6.43%. Calcd for $\text{C}_{12}\text{H}_{11}\text{NO}_3$: C, 66.35; H, 5.11; N, 6.45%.

3-Ethyl-2-oxo-1,2-dihydro-4-quinolinecarboxylic Acid (7).
A suspension of **6** (2.2 g) in hydrochloric acid (6%, 200 ml) was refluxed for 20 h and the mixture was concentrated under

reduced pressure. The residue was recrystallized from 50% ethanol to give colorless needles (1.1 g, 50%), mp 308—310 °C (lit.⁹ 289 °C). IR (KBr): 1705 (ν C=O, acid), 1655 (ν C=O, lactam) cm^{-1} . MS (m/e (%)): 217 (M^+ , 98), 172 ($M^+ - \text{COOH}$, 100).

cis-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxylic Acid (**3c**).

(a) *By Photochemical Reaction Involving 1c*: A solution of **1c** (1.0 g) in propionic acid (500 ml) was irradiated for 3 h. The mixture was concentrated to dryness *in vacuo*. The residue was shaken in a sodium hydrogencarbonate solution (2%, 20 ml). The aqueous solution was washed three times with ethyl acetate, acidified with concentrated hydrochloric acid, and extracted with ethyl acetate (20 ml \times 3). The combined extract was washed with a saturated sodium chloride solution, dried over sodium sulfate, and evaporated. The syrupy residue was purified through a silica gel column (120 g, 3 \times 40 cm) with a mixed solvent of dichloromethane-methanol (9:1, v/v). The purified **3c** was recrystallized twice from water to afford colorless needles (0.43 g, 37%), mp 221—222 °C. Found: C, 65.93; H, 5.82; N, 6.41%. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3$: C, 65.74; H, 5.98; N, 6.31%.

(b) *By Photochemical Reaction Involving 2c*: Photolysis of **2c** (0.5 g) in propionic acid (400 ml) was performed in a manner similar to that described in (a), and **3c** was obtained (0.27 g, 46%).

(c) *By Catalytic Reduction of 3-Ethyl-2-oxo-1,2-dihydro-4-quinolinecarboxylic Acid (7) in the Presence of Platinum Oxide*: A mixture of **7** (217 mg), methanol (40 ml) and platinum oxide (0.1 g) prepared according to the method of Bruce¹³ was shaken in an atmosphere of hydrogen for 4 h. The mixture was filtered and the filtrate was concentrated to dryness. The residue was taken up with methanol and subjected to chromatography on a preparative silicagel thin layer with dichloromethane-methanol (4:1, v/v). The product was recrystallized from water. Mp 211—212 °C. Yield 156 mg (71%).

trans-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxylic Acid (**4c**). (*Z*)-2-(2-Oxo-3-indolinylidene)butyric acid (2.17 g) and palladium on charcoal (10%, 0.5 g) were stirred in ethanol (30 ml) in a hydrogen atmosphere at room temperature and normal pressure. After 30 min, the catalyst was removed by filtration, and then the filtrate was evaporated. The residue was distilled at 0.08 Torr to give 2.17 g of colorless oils, bp 210 °C (bath temp). The oily product was refluxed in hydrochloric acid (6%, 200 ml) for 20 h. The reaction mixture was concentrated to dryness. The residue was recrystallized from water to give colorless prisms (1.56 g, 71.2%), mp 127 °C. Found: C, 60.88; H, 6.45; N, 5.97%. Calcd for $\text{C}_{12}\text{H}_{13}\text{NO}_3 \cdot \text{H}_2\text{O}$: C, 60.75; H, 6.37; N, 5.90%.

cis-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxamide (**8**).

3c (380 mg) was refluxed in thionyl chloride (5 ml) for 3 h. The reaction mixture was concentrated to dryness and the residue was suspended in absolute ether. Through this suspension, dry ammonia gas was passed with stirring. The precipitate was collected, washed with and recrystallized from ethanol to give colorless needles (212 mg, 56%), mp 246—247 °C. Found: C, 66.17; H, 6.58; N, 12.81%. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$: C, 66.04; H, 6.47; N, 12.83%.

trans-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxamide (**10**).

4c (474 mg) was allowed to react in a manner similar to that described for the preparation of **8** to give 240 mg (55%) of colorless flakes, mp 205 °C. Found: C, 66.12; H, 6.51; N, 12.86%. Calcd for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2$: C, 66.04; H, 6.47; N, 12.83%.

cis-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarbonitrile (**3a**)

(a) *By Photochemical Reaction Involving 1a*: A solution of **1a** (5 g) in propionic acid (500 ml) was irradiated for 28 h. The

mixture was concentrated and the residue was taken up with ethyl acetate. The ethyl acetate layer was successively washed with 2M-hydrochloric acid, an aqueous 2M-ammonia solution and a saturated sodium chloride solution, dried over sodium sulfate, and evaporated. The residue was recrystallized from methanol and then from ethanol to give colorless needles (1.5 g, 26%), mp 191—192 °C. Found: C, 72.09; H, 6.12; N, 14.10%. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}$: C, 71.98; H, 6.04; N, 13.99%.

(b) *By Photochemical Reaction Involving 2a*: A solution of **2a** (1.5 g) in propionic acid (500 ml) was irradiated for 20 h. The mixture was treated in a manner similar to that for (a), giving 0.7 g (40%) of **3a**, mp 191—192 °C.

(c) *By Synthesis*: A mixture of **8** (108 mg) and phosphoryl chloride (3 ml) was stirred at 50 °C for 2.5 h. The mixture was concentrated under reduced pressure (5 Torr). The residue was taken up with ethyl acetate. The ethyl acetate solution was washed sodium hydrogen carbonate and saturated sodium chloride solutions, dried over sodium sulfate and evaporated. The residue was recrystallized twice from ethanol to give colorless needles (50 mg, 50%), mp 192—193 °C.

trans-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarbonitrile (**4a**).

A mixture of **10** (109 mg) and phosphoryl chloride (5 ml) was treated in a manner similar to that for (c) to give colorless prisms (53 mg, 53%), mp 194—195 °C. Found: C, 72.13; H, 5.93; N, 14.04%. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_2\text{O}$: C, 71.98; H, 6.04; N, 13.99%.

Methyl cis-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxylate (**3b**).

(a) *By Photochemical Reaction Involving Methyl 4-Quinolinecarboxylate N-Oxide*: A solution of **1b** (5.0 g) in propionic acid (500 ml) was irradiated for 22 h. The mixture was concentrated under reduced pressure. The residue was fractionally distilled *in vacuo*. The distillate having a boiling point from 190 to 200 °C at 0.02 Torr was collected and crystallized by the addition of a mixture of hexane and ethyl acetate (1:1, v/v). The crystals were recrystallized from ethanol to give colorless needles (0.5 g, 8.7%), mp 166—167 °C. Found: C, 67.02; H, 6.53; N, 5.94%. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$: C, 66.94; H, 6.84; N, 6.00%.

(b) *By photochemical Reaction Involving 2b*: A solution of **2b** (0.50 g) in propionic acid (100 ml) was irradiated for 4 h. The mixture was concentrated to dryness under reduced pressure. The residue was taken up with ethyl acetate (100 ml). The ethyl acetate solution was washed with sodium hydrogencarbonate (5%) and saturated sodium chloride solutions, dried over sodium sulfate, and evaporated. The residue was treated with methanol (20 ml) and filtered. The filtrate was concentrated. The syrupy residue was purified on a column (1 \times 30 cm) of silica gel (30 g) with a mixed solvent of benzene and ethyl acetate (9:1, v/v). The resultant crystals were recrystallized twice from ethanol to give colorless needles (0.04 g, 7.0%).

(c) *By Esterification of 3c*: A mixture of **3c** (119 mg) in thionyl chloride (5 ml) was refluxed for 2 h. After evaporation of the excess thionyl chloride, the residue was refluxed in absolute methanol (10 ml) for 1 h. The mixture was concentrated under reduced pressure. The residue was recrystallized from ethanol to give colorless needles (85 mg, 67.1%), mp 165—166 °C.

Methyl trans-3-Ethyl-2-oxo-1,2,3,4-tetrahydro-4-quinolinecarboxylate (**4b**).

A mixture of **4c** (226 mg) in thionyl chloride (3 ml) was refluxed for 2 h. A procedure was carried out similar to that described of the preparation of **3b**. The crops were recrystallized from diisopropyl ether to give colorless prisms (107 mg, 42%), mp 121—122 °C. Found: C, 66.98; H, 6.51; N, 5.91%. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_3$: C, 66.94;

H, 6.48; N, 6.00%.

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