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Studies on Diazepines. XVIII.¹⁾ Photochemical Synthesis of 3*H*-1,3-Benzodiazepines from Quinoline *N*-Acylimides

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Irradiation of the 2-methylquinoline *N*-ethoxycarbonylimides (**15a—d**) having an electron-donating substituent in the 6- or 8-position gave the novel 3*H*-1,3-benzodiazepines (**16**), together with the parent quinolines (**13**), whereas substituted quinoline *N*-imides having either an electron-donating or -withdrawing group in other positions gave no benzodiazepines. These substituent effects are discussed. A similar substituent effect was also observed in the photo-induced rearrangement of the isoquinoline *N*-ethoxycarbonylimides (**25**) to the 1*H*-1,3-benzodiazepines (**28**).

Keywords—Photolysis; rearrangement; ring-expansion; quinoline *N*-imides; isoquinoline *N*-imides; 3*H*-1,3-benzodiazepines; 1*H*-1,3-benzodiazepines; substituent effect

Previously, we have reported that 2-unsubstituted quinoline and related fused pyridine *N*-imides (**1a**: X=H) undergo photo-induced rearrangement with ring-expansion to give the corresponding fully unsaturated 1*H*-1,2-benzodiazepines²⁾ and analogous fused 1,2-diazepines (**2**),³⁾ whereas the photolysis of the *N*-acylimides (**1b**: X=CO₂Et, CPh, or Ac) affords only 2-acylaminopyridines (**3**) and no diazepines.⁴⁾ We have also reported⁵⁾ that 2-substituted quinoline-type fused pyridine *N*-acylimides (**4**) condensed with an aromatic five-membered heterocyclic ring such as thiophene, furan, and pyrrole undergo a photo-induced two-step rearrangement to give the corresponding fused 3*H*-1,3-diazepine (**5**), analogous to the cases of 1-substituted isoquinoline⁶⁾ and related fused pyridine *N*-acylimides.⁷⁾ Therefore, the photochemical behavior of 2-substituted quinoline *N*-acylimides was examined. However, irradiation of the 2-methylquinoline *N*-acylimides (**6**) resulted in only N–N fragmentation to give the parent quinoline (**7**) and did not give the 1,3-diazepine (**8**).⁶⁾

Chart 1

On the other hand, we have recently shown^{1,8)} that the thermolysis of monocyclic 1*H*-1,2-diazepines (**9**) having an electron-donating substituent in the 4- or 6-position results in the formation of the 1,3-diazepines (**12**) *via* the intermediates (**10**) and (**11**), whereas both 1,2-diazepines having an electron-withdrawing group in the same position and 3-, 5-, or 7-substituted 1,2-diazepines with either an electron-donating or -withdrawing substituent undergo no such thermal ring-conversion. These results prompted us to examine the photolysis of substituted quinoline *N*-acylimides in more detail, and we now report the formation of novel 3*H*-1,3-benzodiazepines.⁹⁾

Chart 2

Various substituted quinolines (**13a—g**) were aminated with *O*-mesitylenesulfonylhydroxylamine (MSH)¹⁰⁾ to give the corresponding *N*-aminoquinolinium mesitylenesulfonates (**14**) in good yields. Treatment of the salts (**14**) with ethyl chloroformate in ethanol in the presence of potassium carbonate gave the *N*-ethoxycarbonylimides (**15**) in the yields described in the experimental section.

Irradiation of the 2-methylquinoline *N*-imides (**15a—d**) having an electron-donating group (OMe, NMe₂, or Me) in the 6- or 8-position resulted in the formation of the corresponding desired 3*H*-1,3-benzodiazepines (**16a—d**) and the parent quinolines (**13a—d**) in the yields shown in Chart 4. This result is the first reported example of the formation of 3*H*-1,3-benzodiazepines, although 1*H*-1,3-benzodiazepines are already known.⁶⁾

Chart 3

Chart 4

TABLE I. 3*H*-1,3- (16) and 1*H*-1,3-Benzodiazepines (28)

Compd. No.	mp ^{a)} (°C)	IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm ⁻¹ (C=O)	UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ)	MS m/e (M ⁺)	Formula	Analysis (%)		
						Calcd (Found)	C	H N
16a	62—64	1700	219 (18000)	260	C ₁₄ H ₁₆ N ₂ O ₃	64.60	6.20	10.76
			256 (14000)			(64.48)	6.22	10.80)
16b	115.5—117	1705	232 (21000)	273	C ₁₅ H ₁₉ N ₃ O ₂	65.91	7.01	15.37
			255 (16000)			(65.68)	7.01	15.40)
16c	110—111.5	1710	215 (17000)	244	C ₁₄ H ₁₆ N ₂ O ₂	68.83	6.60	11.47
			250 (13000)			(68.77)	6.46	11.26)
16d	Oil ^{b)}	1710	247 (20000)	244	C ₁₄ H ₁₆ N ₂ O ₂	68.83	6.60	11.47
						(68.69)	6.62	11.32)
28a	105.5—107	1720	238 (3600)	260	C ₁₄ H ₁₆ N ₂ O ₃	64.60	6.20	10.76
			305 (9000)			(64.48)	6.17	10.77)
28b	Oil ^{b)}	1710	228 (6000)	273	C ₁₅ H ₁₉ N ₃ O ₂	65.91	7.01	15.37
			306 (1700)			(65.82)	6.89	15.36)

a) Recrystallized from isopropyl ether-*n*-hexane. b) Viscous oil.

TABLE II. ¹H-NMR Spectral Data for the 3*H*-1,3-Benzodiazepines (16) and 1*H*-1,3-Benzodiazepines (28)

16a	2.44 (3H, s, 2-Me), 3.78 (3H, s, 7-OMe), 6.13 (1H, d, 5-H), 6.27 (1H, d, 4-H), 6.62 (1H, d, 6-H), 6.82 (1H, dd, 8-H), 7.16 (1H, d, 9-H), $J_{3,4}=7$, $J_{6,8}=3$, $J_{8,9}=9$ Hz, 1.30 and 4.21 (3H, t, and 2H, q, CO ₂ Et).
16b	2.42 (3H, s, 2-Me), 2.92 (6H, s, 7-NMe ₂), 6.12 (1H, d, 5-H), 6.24 (1H, d, 4-H), 6.58 (1H, d, 6-H), 6.66 (1H, dd, 8-H), 7.13 (1H, d, 9-H), $J_{4,5}=7$, $J_{6,8}=3$, $J_{8,9}=9$ Hz, 1.29 and 4.18 (3H, t, and 2H, q, CO ₂ Et).
16c	2.30 (3H, s, 7-Me), 2.44 (3H, s, 2-Me), 6.12 (1H, d, 5-H), 6.24 (1H, d, 4-H), 6.8—7.3 (3H, m, 6-, 8-, and 9-H), $J_{4,5}=7$ Hz, 1.29 and 4.19 (3H, t, and 2H, q, CO ₂ Et)
16d	2.34 (3H, s, 9-Me), 2.46 (3H, s, 2-Me), 6.14 (1H, d, 5-H), 6.27 (1H, d, 4-H), 6.9—7.2 (3H, m, 6-, 7-, and 8-H), $J_{4,5}=7$ Hz, 1.30 and 4.20 (3H, t, and 2H, q, CO ₂ Et)
28a	2.41 (3H, s, 2-Me), 3.90 (3H, s, 6-OMe), 6.8—7.4 (5H, m, Ar-H), 1.26 and 4.25 (3H, t, and 2H, q, CO ₂ Et)
28b	2.38 (3H, s, 2-Me), 2.73 (6H, s, 6-NMe ₂), 6.63 (1H, d, 5-H), 6.8—7.4 (4H, m, Ar-H), $J_{4,5}=9$ Hz, 1.25 and 4.18 (3H, t, and 2H, q, CO ₂ Et)

The physical, analytical, and some spectral data for the 1,3-diazepines (**16**) thus obtained are collected in Table I. The ^1H -nuclear magnetic resonance (^1H -NMR) spectral data are summarized in Table II. These spectral data and the results of the following chemical studies are consistent with the proposed 3*H*-1,3-diazepine structures, ruling out other possible structures such as 1*H*-1,2- and 2*H*-1,2-benzodiazepines.

Chart 5

Treatment of the diazepine (**16a**) with hydrochloric acid in methanol at room temperature gave the ring-opened product (**17**) in 63% yield, and this was further converted into 1-acetyl-5-methoxyindole (**18**) in 45% yield by heating in methanol containing hydrochloric acid.

These results are analogous to those observed for fused 3*H*-1,3-diazepines⁷⁾ and 1*H*-1,3-benzodiazepines.⁶⁾

Next, the 2-unsubstituted 6-methoxyquinoline *N*-imide (**15e**) was irradiated to afford the ring-opened product (**20**) in 6% yield, together with the 2-aminoquinoline (**19**: 71%) and 6-methoxyquinoline (**13e**: 3%). The product (**20**) may be derived from the initially formed 1,3-diazepine (**16e**) by hydrolysis during isolation, analogous to the ring-opening of **16a** to **17**. In contrast, irradiation of the 2-methylquinoline *N*-imides (**15f, g**) having an electron-donating group in the 3-position resulted in only N–N fragmentation to give the parent quinolines (**13f, g**) and did not give rearrangement products.

Chart 6

In addition, quinoline *N*-acylimides having an electron-withdrawing substituent in the 6- or 8-position such as 6-chloro-, 6-acetyl-, 6-nitro-, and 8-chloro-quinoline *N*-ethoxycarbonylimide gave the parent quinolines, but no diazepines, on irradiation. Similarly, quinolines with an electron-donating group in other positions such as 5- and 7-methoxyquinoline *N*-ethoxycarbonylimide also gave no diazepines. These results clearly indicate that the presence of an electron-donating substituent in either the 6- or 8-position is essential for this ring conversion of quinolines into 1,3-benzodiazepines.

The formation of the 1,3-diazepines (**16**) from quinolines (**15**) may involve the diaziridine intermediates (**21**), which then rearrange to the aziridines (**23**) followed by ring expansion to **16**. The electron-donating groups may assist both the cleavage of the N–N bond in the

Chart 7

diaziridine (**21**) and the cyclization of the resulting dipolar intermediate (**22**) to give **23** as shown in Chart 7. Although electron-donating substituents at C-3 in the pyridine ring showed no such assistance as in the case of **15f, g**, this substituent effect is analogous to that observed for the thermal ring conversion of monocyclic 1,2-diazepines into 1,3-diazepines.⁸⁾ The formation of **5** from **4** can also be explained by this substituent effects, as shown in the structure (**24**).

Finally, a similar substituent effect was also observed in the photo-induced rearrangement of the isoquinoline *N*-imides (**25**) into the 1*H*-1,3-benzodiazepines (**28**), as shown in the structure (**26**). Irradiation of the isoquinoline *N*-imides (**25a, b**) having an electron-donating group in the 5-position gave the 1*H*-1,3-benzodiazepines (**28a, b**) in 35–40% yields. These yields are about two times higher than that of **28c** (15–20%).⁶⁾

Chart 8

Experimental

Melting points were measured on a Yamato MP-21 apparatus and are uncorrected. Infrared (IR) spectra were determined with a JASCO IRA-2 spectrometer and mass spectra (MS) were recorded on a JEOL D-100 instrument. Proton nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-MH100 spectrometer in CDCl₃ using tetramethylsilane as an internal standard unless otherwise stated; spectral assignments were confirmed by spin-decoupling experiments and, in the case of NH protons, by exchange with D₂O. Microanalyses were performed in the Microanalytical Laboratory of this school by Mrs. R. Igarashi. Photolyses were carried out under a nitrogen atmosphere in an immersion apparatus equipped with a 400 W high-pressure Hg lamp and a Pyrex filter, which was cooled internally with running water.

Materials—2,6-Dimethylquinoline (**13c**) was obtained from Tokyo Kasei Kogyo Co., Japan. 6-Methoxy-2-methyl- (**13a**),¹¹⁾ 6-dimethylamino-2-methyl- (**13b**),¹¹⁾ 2,8-dimethyl- (**13d**),¹²⁾ 6-methoxy- (**13e**),¹³⁾ 2,3-dimethyl- (**13f**),¹⁴⁾ and 3-methoxy-2-methyl-quinoline (**13g**)¹⁴⁾ were prepared according to the reported procedures. 5-Methoxy-1-methyl-¹⁵⁾ and 5-dimethylamino-1-methyl-isoquinoline¹⁶⁾ were also prepared by the reported methods.

***N*-Aminoquinolinium Mesitylenesulfonates (**14a–g**)**—General Procedure: A solution of *O*-mesitylene-sulfonylhydroxylamine (1.1 mol eq) in CH₂Cl₂ (100–150 ml) was added dropwise to a solution of a quinoline (**13**; ca. 0.05 mol) in CH₂Cl₂ (30–50 ml) with stirring in an ice bath. The reaction mixture was stirred for an additional 1 h at room temperature. After addition of ether (300–400 ml) to the mixture, the resulting crystalline precipitate was collected by filtration and recrystallized from methanol-isopropyl ether to give the corresponding salt (**14**).

14a: 82% yield, mp 216–218°C. *Anal.* Calcd for C₂₀H₂₄N₂O₄S: C, 61.83; H, 6.23; N, 7.21. Found: C, 61.81; H, 6.26; N, 7.20.

14b: 88% yield, mp 223–225°C. *Anal.* Calcd for C₂₁H₂₇N₃O₃S: C, 62.82; H, 6.78; N, 10.47. Found: C, 62.66; H, 6.83; N, 10.21.

14c: 96% yield, mp 214.5–216°C. *Anal.* Calcd for C₂₀H₂₄N₂O₃S: C, 64.49; H, 6.49; N, 7.52. Found: C, 64.25; H, 6.44; N, 7.47.

14d: 98% yield, mp 153–155°C. *Anal.* Calcd for C₂₀H₂₄N₂O₃S: C, 64.49; H, 6.49; N, 7.52. Found: C, 64.36; H, 6.47; N, 7.44.

14e: 89% yield, mp 164–166°C (lit.²⁾ mp 163–165°C). *Anal.* Calcd for C₁₉H₂₂N₂O₄S: C, 60.94; H, 5.92; N, 7.48. Found: C, 60.96; H, 5.84; N, 7.36.

14f: 98% yield, mp 118–120°C. *Anal.* Calcd for C₂₀H₂₄N₂O₃S: C, 64.49; H, 6.49; N, 7.52. Found: C, 64.28; H, 6.48; N, 7.44.

14g: 80% yield, mp 207—209°C. *Anal.* Calcd for $C_{20}H_{24}N_2O_4S$: C, 61.83; H, 6.23; N, 7.21. Found: C, 61.95; H, 6.24; N, 7.17.

Quinoline *N*-Ethoxycarbonylimides (15a—g)—General Procedure: Solid potassium carbonate (*ca.* 2.5 mol eq) and ethyl chloroformate (1.5—2.0 mol eq) were added to a solution of a salt (**14**: *ca.* 0.05 mol) in ethanol (100—200 ml) with stirring. The mixture was stirred for an additional 7—8 h at room temperature and the resulting inorganic precipitate was filtered off. The filtrate was concentrated *in vacuo* and the residue was extracted with CH_2Cl_2 . The extract was dried over $MgSO_4$ and evaporated to dryness *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2 –acetone as an eluent to give the corresponding imide (**15**), which was recrystallized from benzene–ethyl acetate.

15a: 61% yield, mp 147—148°C. IR (KBr) cm^{-1} : 1620 (C=O). NMR δ : 2.80 (3H, s, 2-Me), 3.88 (3H, s, OMe), 7.07 (1H, d, 5-H), 7.3—7.6 (2H, m, 3- and 7-H), 8.05 (1H, d, 4-H), 8.58 (1H, d, 8-H), $J_{3,4}=9$, $J_{5,7}=3$, $J_{7,8}=9$ Hz, 1.39 and 4.23 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.75; H, 6.16; N, 10.55.

15b: 20% yield, mp 88—89°C. IR (KBr) cm^{-1} : 1610 (C=O). NMR δ : 2.69 (3H, s, 2-Me), 2.92 (6H, s, N-Me₂), 6.59 (1H, d, 5-H), 7.18 (1H, d, 3-H), 7.22 (1H, dd, 7-H), 7.82 (1H, d, 4-H), 8.29 (1H, d, 8-H), $J_{3,4}=9$, $J_{5,7}=3$, $J_{7,8}=9$ Hz, 1.39 and 4.23 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{15}H_{18}N_3O_2$: C, 65.91; H, 7.01; N, 15.37. Found: C, 65.65; H, 7.06; N, 15.28.

15c: 56% yield, mp 143.5—145°C. IR (KBr) cm^{-1} : 1640 (C=O). NMR δ : 2.51 (3H, s, 6-Me), 2.83 (3H, s, 2-Me), 7.34 (1H, d, 3-H), 7.5—7.7 (2H, m, 5- and 7-H), 8.10 (1H, d, 4-H), 8.46 (1H, d, 8-H), $J_{3,4}=9$, $J_{5,7}=3$, $J_{7,8}=9$ Hz, 1.42 and 4.21 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.70; H, 6.60; N, 11.38.

15d: 18% yield, oil. IR ($CHCl_3$) cm^{-1} : 1620 (C=O). NMR δ : 2.81 (3H, s, 2-Me), 3.11 (3H, s, 8-Me), 7.2—7.8 (4H, m, 3-, 5-, 6-, and 7-H), 8.16 (1H, d, 4-H), $J_{3,4}=9$ Hz, 1.36 and 4.21 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.61; H, 6.68; N, 11.21.

15e: 81% yield, mp 123—125°C. IR (KBr) cm^{-1} : 1615 (C=O). NMR δ : 3.92 (3H, s, OMe), 7.21 (1H, d, 5-H), 7.3—7.6 (2H, m, 3- and 6-H), 8.19 (1H, d, 4-H), 8.67 (1H, d, 8-H), 7.97 (1H, d, 2-H), $J_{2,3}=6$, $J_{3,4}=9$, $J_{5,7}=3$, $J_{7,8}=9$ Hz, 1.37 and 4.23 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{13}H_{14}N_2O_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.41; H, 5.67; N, 11.30.

15f: 71% yield, mp 124—125.5°C. IR (KBr) cm^{-1} : 1610 (C=O). NMR δ : 2.50 (3H, s, 3-Me), 2.87 (3H, s, 2-Me), 7.5—8.0 (3H, m, 5-, 6-, and 7-H), 8.24 (1H, s, 4-H), 8.64 (1H, d, 8-H), $J_{7,8}=9$ Hz, 1.43 and 4.37 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.57; H, 6.50; N, 11.69.

15g: 72% yield, mp 177—178°C. IR (KBr) cm^{-1} : 1605 (C=O). NMR δ : 2.78 (3H, s, 2-Me), 3.90 (3H, s, OMe), 7.3—7.7 (4H, m, 4-, 5-, 6-, and 7-H), 8.44 (1H, d, 8-H), $J_{7,8}=9$ Hz, 1.38 and 4.22 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.49; H, 6.07; N, 10.75.

Photolysis of the Imides (15a—d)—General Procedure: A solution of an imide (**15**: 1—2 g) in benzene (300 ml) was irradiated; the photolysis was followed in terms of the disappearance of the spot of the starting imide on thin-layer chromatography, and was complete in 1—4 h. After removal of the solvent *in vacuo*, the residue was chromatographed on alumina using ether–*n*-hexane (1: 10) as an eluent to give the parent quinoline (**13**) and the 1,3-benzodiazepine (**16**) successively. The yields of the products are shown in Chart 4. Physical, analytical, and spectral data of the 1,3-diazepines (**16a—d**) are collected in Tables I and II.

Treatment of the Diazepine (16a) with Hydrochloric Acid—A mixture of **16a** (100 mg), methanol (5 ml), and 10% HCl (0.5 ml) was stirred for 2 h at room temperature. The reaction mixture was diluted with CH_2Cl_2 (100 ml) and successively washed with satd. $NaHCO_3$ and satd. NaCl, then dried over $MgSO_4$, and evaporated to dryness *in vacuo*. The resulting solid residue was recrystallized from ethyl acetate–benzene to give the ring-opened product (**17**): 63% yield, mp 190—191°C, colorless needles. IR (KBr) cm^{-1} : 3300 (NH), 1665 and 1675 (C=O). MS m/e : 278 (M^+). NMR δ : 2.31 (3H, s, COMe), 3.78 (3H, s, OMe), 5.54 (1H, d, $J=9$ Hz, $-CH=CH-NH-$), 6.06 (1H, d, $J=9$ Hz, $-CH=CH-NH-$), 6.1 (1H, br, NH), 6.6—6.9 (2H, m, 3- and 5-H), 6.8 (1H, br, NH), 8.01 (1H, d, 6-H), $J_{5,6}=9$ Hz. *Anal.* Calcd for $C_{14}H_{18}N_2O_4$: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.37; H, 6.43; N, 9.99.

Treatment of 17 with Hydrochloric Acid—A mixture of **17** (50 mg), methanol (5 ml), and 10% HCl (0.5 ml) was heated at *ca.* 50°C for 2 h. After cooling, the reaction mixture was diluted with CH_2Cl_2 (50 ml) and successively washed with satd. $NaHCO_3$ and satd. NaCl, then dried, and concentrated *in vacuo*. The residue was chromatographed on silica gel using *n*-hexane–ether (5: 1) as an eluent to give 1-acetyl-5-methoxyindole (**18**): 45% yield, mp 83—84°C, colorless prisms (from *n*-hexane–isopropyl ether). IR (KBr) cm^{-1} : 1695 (C=O). MS m/e : 189 (M^+). NMR δ : 2.63 (3H, s, COMe), 3.89 (3H, s, OMe), 6.60 (1H, d, 3-H), 7.01 (1H, dd, 6-H), 7.05 (1H, d, 4-H), 7.42 (1H, d, 2-H), 8.36 (1H, d, 7-H), $J_{2,3}=4$, $J_{4,6}=2$, $J_{6,7}=9$ Hz. *Anal.* Calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.82; H, 5.76; N, 7.25.

Photolysis of the Imide (15e)—A solution of **15e** (1 g) in benzene (300 ml) was irradiated for 2 h. After removal of the solvent *in vacuo*, the residue was chromatographed on alumina. Elution with *n*-hexane–ether (10: 1) gave 2-ethoxycarbonylamino-6-methoxyquinoline (**19**: 710 mg, 71% yield) and the parent 6-methoxyquinoline (**13e**: 30 mg, 3% yield) successively. Further elution with ether–methanol (20: 1) afforded the ring-opened product (**20**: 60 mg, 6% yield).

19: mp 109.5–111°C, colorless prisms (from ethyl acetate). IR (KBr) cm^{-1} : 3200 (NH), 1730 (C=O). MS m/e : 246 (M^+). NMR δ : 3.88 (3H, s, OMe), 1.21 and 4.20 (3H, t, and 2H, q, CO_2Et), 7.00 (1H, d, 5-H), 7.25 (1H, dd, 7-H), 7.79 (1H, d, 8-H), 7.99 (1H, d, 3- or 4-H), 8.16 (1H, d, 3- or 4-H), 9.19 (1H, br, NH), $J_{3,4}=9$, $J_{5,7}=3$, $J_{7,8}=9$ Hz. Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_3$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.35; H, 5.74; N, 11.29.

20: mp 106–107.5°C, colorless prisms (from *n*-hexane–benzene). IR (KBr) cm^{-1} : 3280 (NH), 1660 and 1700 (C=O). MS m/e : 264 (M^+). NMR δ : 1.26 and 4.15 (3H, t, and 2H, q, CO_2Et), 3.79 (3H, s, OMe), 5.44 (1H, d, $J=9$ Hz, $-\text{CH}=\text{CH}-\text{NH}-$), 6.4–7.4 (5H, m, 3-, 5-, and 2N-H, and $-\text{CH}=\text{CH}-\text{NH}-$), 8.02 (1H, d, 6-H), 8.29 (1H, s, CHO), $J_{5,6}=9$ Hz. Anal. Calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{O}_4$: C, 59.08; H, 6.10; N, 10.60. Found: C, 59.10; H, 6.10; N, 10.58.

Photolysis of the Imides (15f, g)—A solution of an imide (15f or g: 1–2 g) in benzene (300 ml) was irradiated and then worked up as described for 15a–d to give only the parent quinoline (13f or g) in 50–60% yields.

Isoquinoline *N*-Ethoxycarbonylimides (25a, b)—A solution of MSH (1.1 mol eq) in CH_2Cl_2 (100 ml) was added dropwise to a solution of 5-methoxy-1-methyl- or 1-methyl-5-dimethylamino-isoquinoline (1.5–2.0 g) in CH_2Cl_2 (10 ml) with stirring in an ice bath. The reaction mixture was stirred for an additional 1 h at room temperature. After addition of ether (200–300 ml) to the mixture, the resulting precipitate was collected by filtration and recrystallized from ethanol–ethyl acetate to give the corresponding *N*-aminoisoquinolinium mesitylene sulfonate [5-OMe compound: 98% yield, mp 156–158°C. Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$: C, 61.84; H, 6.23; N, 7.21. Found: C, 61.64; H, 6.18; N, 7.09. 5-NMe₂ compound: 70% yield, mp 130–131.5°C. Anal. Calcd for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_3\text{S}$: C, 62.82; H, 6.78; N, 10.47. Found: C, 62.69; H, 6.81; N, 10.44].

Solid potassium carbonate (1.5 mol eq) and ethyl chloroformate (1.1 mol eq) were added to a solution of the salt (2–3 g) thus obtained in ethanol (50 ml) with stirring, and the reaction mixture was worked up as described for 15 to give the corresponding imide (25).

25a (5-OMe): 25% yield, mp 142.5–144°C, yellow prisms (from benzene–isopropyl ether). IR (KBr) cm^{-1} : 1610 (C=O). NMR δ : 3.09 (3H, s, 1-Me), 4.08 (3H, s, 5-OMe), 7.2–8.5 (5H, m, Ar-H), 1.39 and 4.28 (3H, t, and 2H, q, CO_2Et). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.41; H, 6.04; N, 10.49.

25b (5-NMe₂): 80% yield, mp 123–124.5°C, yellow prisms (from benzene). IR (KBr) cm^{-1} : 1620 (C=O). NMR δ : 2.85 (6H, s, 5-NMe₂), 3.05 (3H, s, 1-Me), 7.3–8.3 (5H, m, Ar-H), 1.56 and 4.20 (3H, t, and 2H, q, CO_2Et). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_2$: C, 65.91; H, 7.01; N, 15.37. Found: C, 65.81; H, 7.03; N, 15.38.

Photolysis of the Imides (25a, b)—A solution of an imide (25: 0.4–0.5 g) in benzene (300 ml) was irradiated for 30 min and then concentrated *in vacuo*. The residue was chromatographed on silica gel using CH_2Cl_2 –*n*-hexane (2:1) as an eluent to give the corresponding 1*H*-1,3-benzodiazepine (28) and parent isoquinoline (15–25% yields). The yields of 28 are shown in Chart 8. The physical, analytical, and some spectral data for 28a, b are also collected in Tables I and II.

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