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

TAKASHI TSUCHIYA,* SATORU OKAJIMA, MICHIKO ENKAKU, and JYOJI KURITA

School of Pharmacy, Hokuriku University, Kanagawa-machi, Kanazawa 920-11, Japan

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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-benzodiazepines[2] and analogous fused 1,2-diazepines (**2**),[3] whereas the photolysis of the *N*-acylimides (**1b**: X=CO_2Et, COPh, or Ac) affords only 2-acylaminopyridines (**3**) and no diazepines.[4] We have also reported[5] 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 isoquinoline[6] 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]

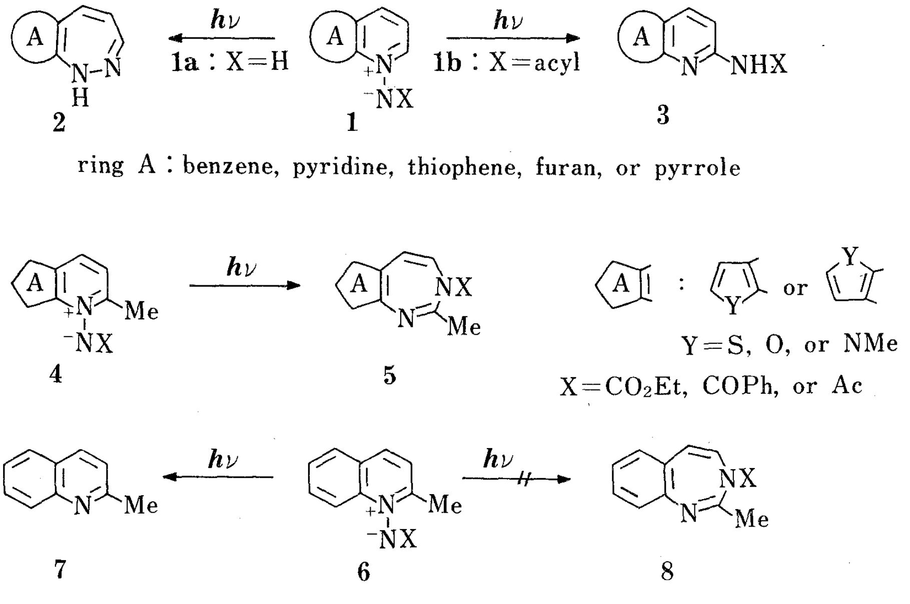
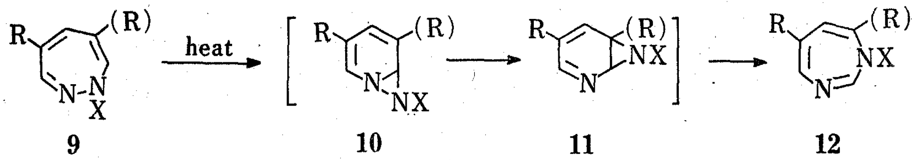


Chart 1

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]

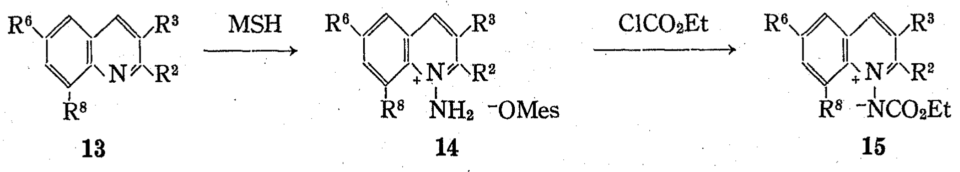


9—**12**: X = CO_2Et, R = Me, OMe, SMe, NMe_2, or Ph

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.

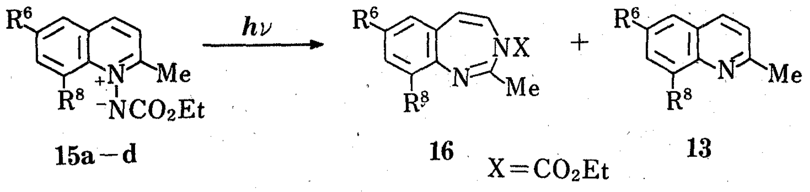
Irradiation of the 2-methylquinoline *N*-imides (**15a**—**d**) having an electron-donating group (OMe, NMe_2, or Me) in the 6- or 8-position resulted in the formation of the corresponding desired 3*H*-1,3-benzodiazepines (**16a**—**d**) and the parent quinolines (**13a**—**d**) in the yields shown in 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]



a: R^2=Me, R^6=OMe, R^3=R^8=H
b: R^2=Me, R^6=NMe_2, R^3=R^8=H
c: R^2=R^6=Me, R^3=R^8=H
d: R^2=R^8=Me, R^3=R^6=H

e: R^6=OMe, R^2=R^3=R^8=H
f: R^2=R^3=Me, R^6=R^8=H
g: R^2=Me, R^3=OMe, R^6=R^8=H

Chart 3



	R^6	R^8	Yields	
a	OMe	H	48%	15%
b	NMe_2	H	26%	32%
c	Me	H	8%	50%
d	H	Me	10%	22%

Chart 4

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

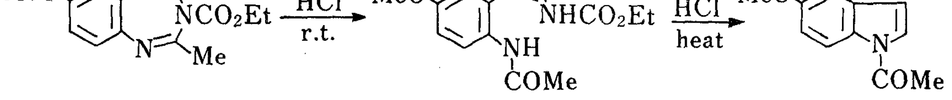
Compd. No.	mp[a] (°C)	IR $\nu_{max}^{CHCl_3}$ cm^{-1} (C=O)	UV λ_{max}^{EtOH} nm (ε)	MS m/e (M$^+$)	Formula	Analysis (%) Calcd (Found) C	H	N
16a	62—64	1700	219 (18000) 256 (14000)	260	$C_{14}H_{16}N_2O_3$	64.60 (64.48	6.20 6.22	10.76 10.80)
16b	115.5—117	1705	232 (21000) 255 (16000)	273	$C_{15}H_{19}N_3O_2$	65.91 (65.68	7.01 7.01	15.37 15.40)
16c	110—111.5	1710	215 (17000) 250 (13000)	244	$C_{14}H_{16}N_2O_2$	68.83 (68.77	6.60 6.46	11.47 11.26)
16d	Oil[b]	1710	247 (20000)	244	$C_{14}H_{16}N_2O_2$	68.83 (68.69	6.60 6.62	11.47 11.32)
28a	105.5—107	1720	238 (3600) 305 (9000)	260	$C_{14}H_{16}N_2O_3$	64.60 (64.48	6.20 6.17	10.76 10.77)
28b	Oil[b]	1710	228 (6000) 306 (1700)	273	$C_{15}H_{19}N_3O_2$	65.91 (65.82	7.01 6.89	15.37 15.36)

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

Table II. ^{1}H-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_2Et).
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_2Et).
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_2Et)
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_2Et)
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_2Et)
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_2Et)

The physical, analytical, and some spectral data for the 1,3-diazepines (**16**) thus obtained are collected in Table I. The ^{1}H-nuclear magnetic resonance (^{1}H-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.



16a **17** **18**

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-diazepines[7] 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.

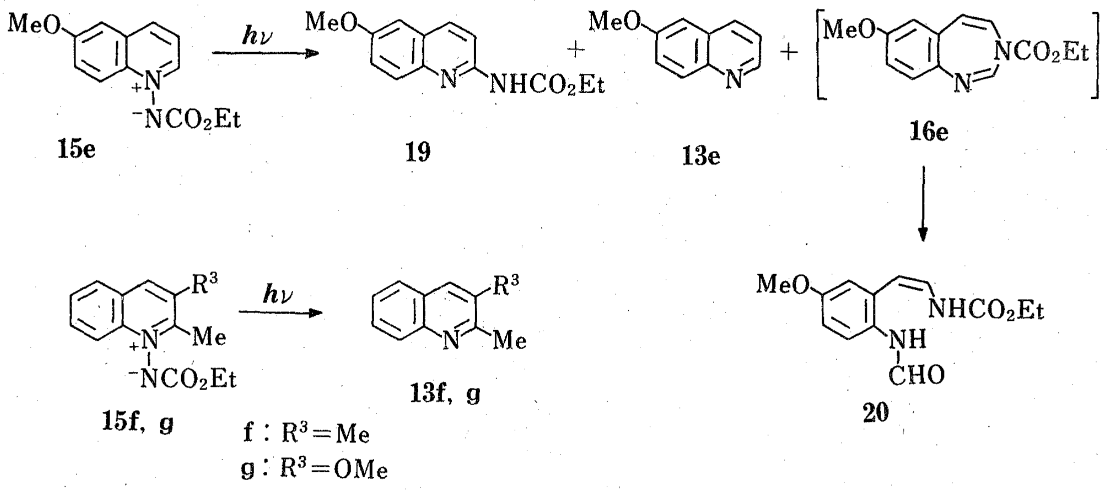


Chart 6

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

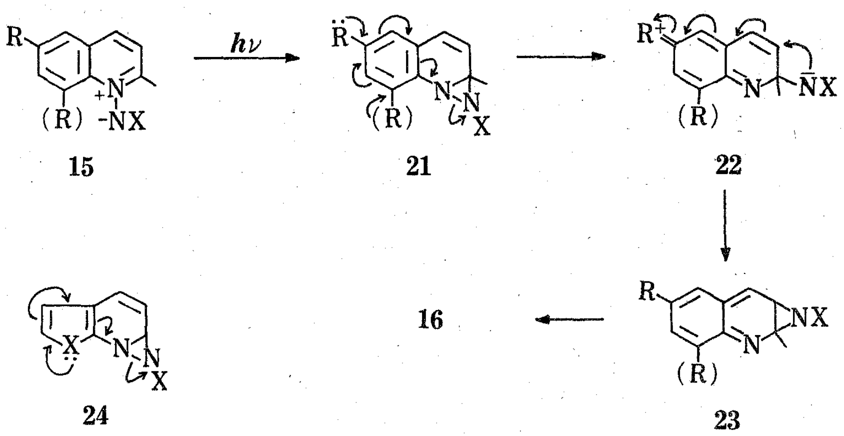
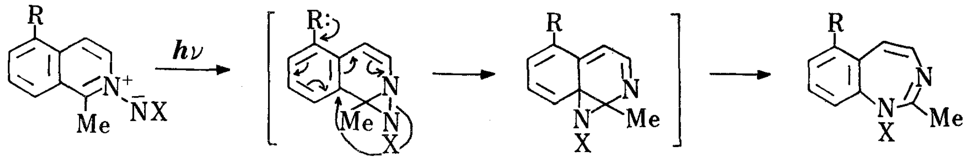


Chart 7

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]



25 X = CO_2Et **26** **27** **28**

a: R = OMe
b: R = NMe_2
c: R = H

28a: 40%
28b: 35—40%
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 $CDCl_3$ 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 D_2O. 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-isoquinoline[16] were also prepared by the reported methods.

***N*-Aminoquinolinium Mesitylenesulfonates (14a—g)**——General Procedure: A solution of *O*-mesitylenesulfonylhydroxylamine (1.1 mol eq) in CH_2Cl_2 (100—150 ml) was added dropwise to a solution of a quinoline (**13**: *ca.* 0.05 mol) in CH_2Cl_2 (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 $C_{20}H_{24}N_2O_4S$: 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 $C_{21}H_{27}N_3O_3S$: 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 $C_{20}H_{24}N_2O_3S$: 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 $C_{20}H_{24}N_2O_3S$: 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 $C_{19}H_{22}N_2O_4S$: 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 $C_{20}H_{24}N_2O_3S$: 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, $N{-}Me_2$), 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 $C_{15}H_{19}N_3O_2$: 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, $-C\underline{H}=CH-NH-$), 6.06 (1H, d, $J=9$ Hz, $-CH=C\underline{H}-NH-$), 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 $C_{13}H_{14}N_2O_3$: 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, -C$\underline{H}$=CH-NH-), 6.4—7.4 (5H, m, 3-, 5-, and 2N-H, and -CH=C$\underline{H}$-NH-), 8.02 (1H, d, 6-H), 8.29 (1H, s, CHO), $J_{5,6}=9$ Hz. *Anal.* Calcd for $C_{13}H_{16}N_2O_4$: 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 $C_{20}H_{24}N_2O_4S$: C, 61.84; H, 6.23; N, 7.21. Found: C, 61.64; H, 6.18; N, 7.09. 5-NMe_2 compound: 70% yield, mp 130—131.5°C. *Anal.* Calcd for $C_{21}H_{27}N_3O_3S$: 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 $C_{14}H_{16}N_2O_3$: C, 64.60; H, 6.20; N, 10.76. Found: C, 64.41; H, 6.04; N, 10.49.

25b (5-NMe_2): 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-NMe_2), 3.05 (3H, s, 1-Me_2), 7.3—8.3 (5H, m, Ar–H), 1.56 and 4.20 (3H, t, and 2H, q, CO_2Et). *Anal.* Calcd for $C_{15}H_{19}N_3O_2$: 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.

References and Notes

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