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Reactions of 2-Aminoazulenes with Electron-Deficient Acetylenes

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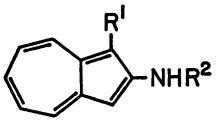
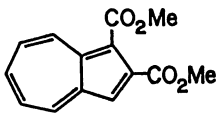
2-Aminoazulene (**1a**) reacted with dimethyl acetylenedicarboxylate (DMAD) to give dimethyl 1,2-azulenedicarboxylate, tetramethyl 2,2′-(2-amino-1,3-azulenediyl)bis[fumarate], and dimethyl 2-(4-methoxycarbonyl-2-oxo-1,2-dihydroazuleno[2,1-*b*]pyridin-10-yl)fumarate. The reaction of ethyl 2-amino-1-azulenecarboxylate (**1b**) with DMAD gave dimethyl 2-(2-amino-3-ethoxycarbonyl-1-azulenyl)fumarate and 10-ethyl 4-methyl 2-oxo-1,2-dihydroazuleno[2,1-*b*]pyridine-4,10-dicarboxylate (**8a**). The treatment of **8a** with phosphoryl chloride gave the 2-chloroazuleno[2,1-*b*]pyridine derivative. Reactions of **1a** and **1b** with methyl propiolate gave corresponding Michael adducts and the azuleno[2,1-*b*]pyridin-3(4*H*)-one derivatives. Reactions of **1a** and **1b** with dibenzoylacetylene gave 4-benzoyl-2-phenylazuleno[2,1-*b*]pyridine derivatives.

Cycloaddition of azaazulenes to acetylenic esters has received attention,[1–6] and it is known that the reactions are strongly influenced by the substituents and/or reaction conditions. In the study of carbocyclic azulene chemistry, it was discovered that azulene reacts with electron-deficient acetylenes or electron-deficient olefines to give Michael-type adducts.[7,8] Later, K. Hafner reported that azulene reacted with reactive acetylenes in aprotic solvent and gave cycloadducts via dipolar intermediates.[9,10] At present, the effects of substituents in these reactions have not been investigated. In order to determine how the substituents on the azulene ring influence the reactions, I investigated the reactions of 2-aminoazulenes with electron-deficient acetylenes. The reactions preferentially gave Michael adducts and azuleno[2,1-*b*]pyridin-2(1*H*)-ones; cycloaddition occurred only rarely.



1a: $R^1 = R^2 = H$
1b: $R^1 = CO_2Et$, $R^2 = H$
1c: $R^1 = CO_2Et$, $R^2 = CHC(CO_2Et)_2$
1d: $R^1 = CO_2Et$, $R^2 = COMe$



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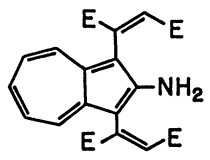

3: E = CO_2Me

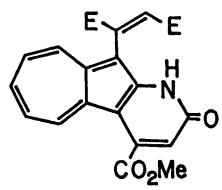

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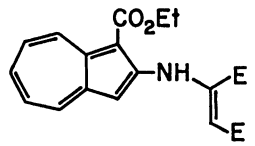
Fig. 1.

The treatment of 2-aminoazulene (**1a**) with dimethyl acetylenedicarboxylate (DMAD) in refluxing *t*-butylbenzene for 1 h gave a complex mixture. From the mixture, three compounds, dimethyl 1,2-azulenedicarboxylate[1,11,12] (**2**), tetramethyl 2,2′-(2-amino-1,3-azulendiyl)bis[fumarate] (**3**), and dimethyl 2-(4-methoxycarbonyl-2-oxo-1,2-dihydroazuleno[2,1-*b*]-pyridin-10-yl)fumarate (**4**) in 0.3, 3, and 15% yields, respectively, were isolated by column chromatography on silica gel. The structures of these compounds were determined on the basis of their spectra, especially ^{1}H NMR spectra, as well as elemental analyses. The yields of **3** and **4** were somewhat increased at room temperature by ultrasonic irradiation, but **2** was not produced. Therefore, I concluded that the formation of **2** required high temperature.

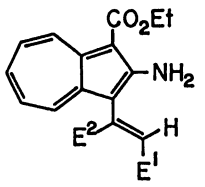
The treatment of ethyl 2-amino-1-azulenecarboxylate (**1b**) with DMAD in benzene at room temperature for 4 d gave dimethyl 2-[(1-ethoxycarbonyl-2-azulenyl)-amino]maleate (**5**) (13% yield), azulenylmaleate derivative **6a** (18% yield), azulenylfumarate derivative **7** (24% yield), and azuleno[2,1-*b*]pyridin-2(1*H*)-one derivative **8a** (35% yield). Ultrasonic irradiation facilitated the reaction which was complete within 6 h, though the yields were slightly low. When the reactions were carried out with heat, **5** was not produced. Refluxing in acetonitrile rather than benzene enhanced the yield of **6a** (61% yield).

To confirm the structure of **8a**, which had the 2-oxo, rather than 4-oxo, form, cyclizations of **6a** and **7** were attempted. Treatment of **6a** with triethylamine in refluxing acetonitrile for 1 h or the contact of **6a** with silica gel for 50 d gave **8a** in 73.5 and 81% yields, respectively. The fumarate **7** did not react under these conditions, but gave **8a** (47% yield) after treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in refluxing xylene for 15 h.

Furthermore, for the purpose of comparison, azuleno[2,1-*b*]pyridin-4(1*H*)-one derivative **9** was synthesized. Treatment of **1b** with diethyl (ethoxy-

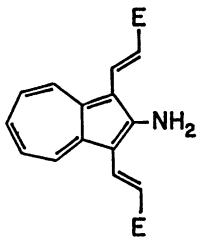


5: E = CO_2Me

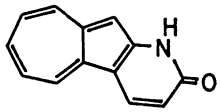


6a: $E^1 = E^2 = CO_2Me$

6b: $E^1 = CO_2Me$, $E^2 = H$



10: E = CO_2Me



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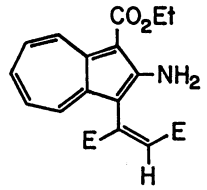
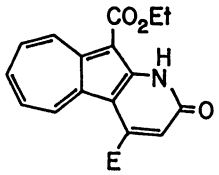


7: E = CO_2Me



8a: E = CO_2Me

8b: E = H

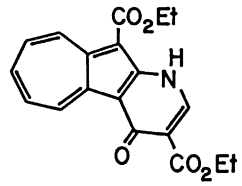


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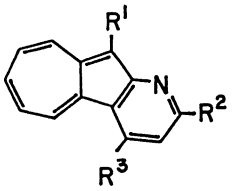
Fig. 2.



12a: $R^1 = H$, $R^2 = Ph$, $R^3 = COPh$

12b: $R^1 = COPhC{=}CHCOPh$, $R^2 = Ph$, $R^3 = COPh$

12c: $R^1 = CO_2Et$, $R^2 = Ph$, $R^3 = COPh$

12d: $R^1 = CO_2Et$, $R^2 = Cl$, $R^3 = CO_2Me$

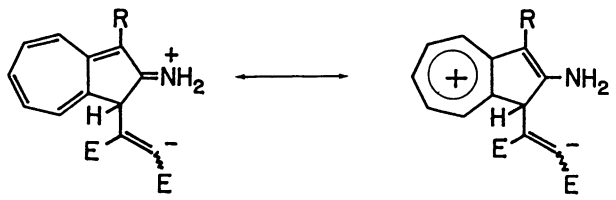
Fig. 3.

methylene)malonate (DEEM) gave diethyl [*N*-(1-ethoxycarbonyl-2-azulenyl)aminomethylene]malonate (**1c**) in a 74% yield. Heating of **1c** in refluxing *t*-butylbenzene for 5 h gave **9** in a 95% yield. In the ^1H NMR spectra, the H-5 proton of **8a** resonated at δ=8.88, whereas the H-5 proton of **9** resonated at δ=10.31. These results supported my conclusion that the structure of **8a** was in the 2-oxo form. The downfield shift of the H-5 proton in **9** may be due to a shielding effect by the carbonyl group at C-4.

Reactions of **1a** and **1b** with methyl propiolate (MP) gave results similar to the reactions with DMAD. Thus, the treatment of **1a** with MP in refluxing *t*-butylbenzene in the presence of Pd–C gave **10** (7% yield) and **11** (16% yield). The treatment of **1b** with MP in refluxing *t*-butylbenzene in the presence of Pd–C gave **6b** (16%) and **8b** (14.5%). The *trans*-configurations of the vinylic protons of **10** and **6b** were confirmed by their ^1H NMR spectra, in which pertinent vicinal coupling constants (both J=15.9 Hz) were observed. Compound **6b** produced **8b** (11% yield) when reacted with DBU in refluxing xylene for 4 d.

When **1a** was treated with dibenzoylacetylene (DBA) in benzene with ultrasonic irradiation in the presence of Pd–C, azuleno[2,1-*b*]pyridine derivatives[13] **12a** (28.5% yield) and **12b** (53% yield) were obtained. Reaction of **1b** with DBA under similar conditions gave **12c** in a 63% yield.

All the results showed that the Michael adducts were obtained in greater yields than the cycloadducts in the reactions of 2-aminoazulenes with electron-deficient acetylenes. The resonance form **A** of the intermediates may facilitate the prototropy of the dipolar intermediates leading to the preferential formation of the Michael adducts. I believe that the amino substituent may enhance the reactivity of the C-1 position of **1a** (and the C-3 position of **1b**) allowing the reaction of **1a** (or **1b**) to occur under milder conditions than those used for azulene.[9] The presence of an electron-withdrawing group on the amino group, such as an acetylamino group, should supress the reaction. Indeed, ethyl 2-acetylaminoazulene-1-carboxylate (**1d**) reacted very lit-



A B

Fig. 4.

tle with DMAD even under refluxing tetralin; over 95% of the starting material was recovered after 70 h.

Chlorination of **6a** with phosphoryl chloride gave the azuleno[2,1-*b*]pyridine derivative **12d** in a 54% yield. In its ^{1}H NMR spectrum, the H-10 proton resonated at δ=9.31, and this again supported the 2-oxo form of 8a. A large divergence of the vicinal spin-spin coupling constants in the seven-membered ring protons of **12d**, $\Delta J=J_{8,9}-J_{5,6}$=1.8 Hz, was observed. This indicated a bond alternation in the azulene ring, reflecting the large aromaticity of the pyridine ring.[14,15]

Experimental

Melting points were uncorrected. ^{1}H NMR spectra (250 MHz) were taken on a Hitachi R-250H spectrometer using $CDCl_3$ as a solvent (TMS as an internal standard) unless otherwise stated. IR spectra were recorded for Nujol mulls with a Hitachi 270-50 infrared spectrophotometer. Column chromatography was performed on Kieselgel 60.

Reaction of 1a with DMAD. a) A mixture of **1a**[16] (0.500 g) and DMAD (1.50 g) in dry *t*-butylbenzene (20 ml) was refluxed for 1 h. The solvent was then evaporated, and cromatography of the residue with benzene gave **2**[1,11,12] (0.003 g, 0.3% yield). Elution with benzene–chloroform (1 : 1) gave **3** (0.041 g, 23% yield) and **4** (0.249 g, 15% yield), successively.

3: Red prisms (from hexane–dichloromethane); mp 155—157 °C; ^{1}H NMR δ=3.82 (6H, s), 3.89 (6H, s), 5.91 (2H, brs), 6.11 (2H, s), 7.20—7.60 (3H, m), and 8.09 (2H, dm, *J*=9.8 Hz); IR 3452, 3340 (NH), 1730, and 1710 cm^{-1} (C=O). Found: C, 61.73; H, 4.94; N, 3.19%. Calcd for $C_{22}H_{21}NO_8$: C, 61.82; H, 4.95; N, 3.28%.

4: Red needles (from hexane–dichloromethane); mp 199—200 °C; ^{1}H NMR δ=3.86 (3H, s), 3.92 (3H, s), 4.09 (3H, s), 6.22 (1H, s), 6.77 (1H, s), 7.52 (2H, t, *J*=9.8 Hz), 7.73 (1H, t, *J*=9.8 Hz), 8.57 (1H, d, *J*=9.8 Hz), 8.77 (1H, d, *J*=9.8 Hz), and 10.28 (1H, brs); IR 3092 (NH), 1738, 1728, 1720, and 1648 cm^{-1} (C=O). Found: C, 63.47; H, 4.46; N, 3.26%. Calcd for $C_{21}H_{17}NO_7$: C, 63.79; H, 4.34; N, 3.54%.

b) A mixture of **1a** (0.500 g), DMAD (1.50 g), and 5% Pd–C (0.500 g) in *t*-butylbenzene (30 ml) was refluxed for 1 h. The solvent was then evaporated, and chromatography of the residue with benzene gave **2** (0.005 g, 0.6% yield). Elution with benzene–chloroform (1 : 1) gave **3** (0.103 g, 7% yield) and **4** (0.212 g, 15% yield), successively.

c) A mixture of **1a** (0.500 g), DMAD (1.50 g), and 5% Pd–C (0.500 g) in dry benzene (50 ml) was ultrasonically irradiated for 1 h. The solvent was then evaporated, and chromatography of the residue with benzene–chloroform (1 : 1) gave **3** (0.144 g, 9% yield) and **4** (0.356 g, 26% yield).

Reaction of 1b with DMAD. a) A mixture of **1b**[16] (0.215 g) and DMAD (0.430 g) in dry benzene (50 ml) was set for 4 d at room temperature. The solvent was then evaporated, and the residue was chromatographed. Elution with benzene gave **5** (0.045 g, 13% yield) and **6a** (0.064 g, 18% yield), successively. Elution with benzene–chloroform (1 : 1) gave **7** (0.085 g, 24% yield). Elution with chloroform gave **8a** (0.115 g, 35% yield).

5: Red needles (from hexane); mp 116—117; ^{1}H NMR δ=1.51 (3H, t, *J*=7.0 Hz), 3.80 (3H, s), 3.86 (3H, s), 5.62 (1H, s), 6.47 (1H, s), 7.36—7.60 (3H, m), 8.04 (1H, d, *J*=9.8 Hz), 9.22 (1H, d, *J*=10.4 Hz), and 11.78 (1H, s); IR 3248 (NH), 1735, 1696, and 1668 cm^{-1} (C=O). Found: C, 64.19; H, 5.38; N, 4.06%. Calcd for $C_{19}H_{19}NO_6$: C, 63.86; H, 5.36; N, 3.92%.

6a: Orange needles (from hexane); mp 96—97 °C; ^{1}H NMR δ=1.46 (3H, t, *J*=7.3 Hz), 3.82 (3H, s), 3.88 (3H, s), 4.44 (2H, q, *J*=7.3 Hz), 6.14 (1H, s), 6.90 (2H, brd), 7.28—7.46 (3H, m), 8.08—8.15 (1H, m), and 9.00 (1H, d, *J*=9.8 Hz); IR 3480, 3324 (NH), 1738, 1714, and 1662 cm^{-1} (C=O). Found: C, 63.45; H, 5.26; N, 3.86%. Calcd for $C_{19}H_{19}NO_6$: C, 63.86; H, 5.36; N, 3.92%.

7: Red needles (from hexane); mp 123—124 °C; ^{1}H NMR δ=1.47 (3H, t, *J*=7.3 Hz), 3.55 (3H, s) , 3.76 (3H, s), 4.45 (2H, q, *J*=7.3 Hz), 5.6—6.5 (2H, br), 7.23 (1H, t, *J*=9.2 Hz), 7.30 (1H, t, *J*=9.2 Hz), 7.39 (1H, t, *J*=9.2 Hz), 7.53 (1H, d, *J*=9.2 Hz), and 8.99 (1H, d, *J*=9.2 Hz); IR 3440, 3332 (NH), 1714, and 1668 cm^{-1} (C=O). Found: C, 63.71; H, 5.43; N, 3.91%. Calcd for $C_{19}H_{19}NO_6$: C, 63.86; H, 5.36; N, 3.92%.

8a: Red needles (from hexane–dichloromethane); mp 175—176 °C; ^{1}H NMR δ=1.53 (3H, t, *J*=7.0 Hz), 4.10 (3H, s), 4.56 (2H, q, *J*=7.0 Hz), 6.79 (1H, d, *J*=2.4 Hz), 7.68 (1H, dd, *J*=10.2 and 9.8 Hz), 7.76 (1H, dd, *J*=10.4 and 9.8 Hz), 7.87 (1H, dd, *J*=10.2 and 9.8 Hz), 8.88 (1H, d, *J*=9.8 Hz), 9.64 (1H, d, *J*=10.4 Hz), and 10.84 (1H, brd, *J*=2.4 Hz); IR 3388 (NH), 1734, 1696, and 1668 cm^{-1} (C=O). Found: C, 66.17; H, 4.84; N, 4.19%. Calcd for $C_{18}H_{15}NO_5$: C, 66.46; H, 4.65; N, 4.31%.

b) A mixture of **1b** (0.430 g), DMAD (0.860 g), and 5% Pd–C (0.500 g) in dry benzene (100 ml) was ultrasonically irradiated for 3 h at room temperature. The solvent was then evaporated, and chromatography of the residue as above gave **5** (0.067 g, 9% yield), **6a** (0.117 g, 16% yield), **7** (0.113 g, 16% yield), and **8a** (0.116 g, 18% yield).

c) A mixture of **1b** (0.430 g) and DMAD (0.86 g) in *t*-butylbenzene (30 ml) was refluxed for 3 h. The solvent was then evaporated, and chromatography of the residue as above gave **6a** (0.187 g, 26% yield), **7** (0.070 g, 9% yield), and **8a** (0.133 g, 20.5% yield).

d) A mixture of **1b** (0.500 g), DMAD (0.99 g), and 5% Pd–C (0.500 g) in *t*-butylbenzene (30 ml) was refluxed for 2 h. The residue was then evaporated, and chromatography of the residue as above gave **6a** (0.164 g, 20% yield), **7** (0.143 g, 17% yield), and **8a** (0.148 g, 20% yield).

e) A mixture of **1b** (0.580 g) and DMAD (1.15 g) in acetonitrile (50 ml) was refluxed for 6 h. The solvent was then evaporated, and chromatography of the residue as above gave **6a** (0.587 g, 61% yield), **7** (0.117 g, 12% yield), and **8a** (0.102 g, 12% yield).

Reaction of 7 with Triethylamine. A solution of **7** (0.13 g) and triethylamine (0.5 ml) in acetonitrile (10 ml) was refluxed for 1 h. The solvent was then evaporated, and the residue was chromatographed with benzene to give **8a** (0.087 g, 73.5% yield).

Cyclization of 7 on Silica Gel. A mixture of **7** (0.045 g) and silica gel (5.0 g) in chloroform (20 ml) was allowed to stand at room temperature for 50 d. The mixture was then filtered and residual silica gel was washed with chloroform. Evaporation of the combined filtrates gave **8a** (0.033 g, 81% yield).

Reaction of 6a with DBU. A mixture of **6a** (0.160 g) and DBU (0.3 ml) in dry xylene (50 ml) was refluxed for 15 h. The solvent was then evaporated, and chromatography of the residue with benzene gave **8a** (0.068 g, 47% yield).

Reaction of 1b with DEEM. A mixture of **1b** (0.250 g) and DEEM (0.750 g) in ethanol (50 ml) was refluxed for 64 h.

The solvent was then evaporated, and chromatography of the residue with benzene gave **1c** (0.424 g, 95% yield), which was recrystallized from hexane–dichloromethane to give red needles, mp 118—119 °C; ^{1}H NMR δ=1.37 (3H, t, J=7.3 Hz), 1.40 (3H, t, J=7.0 Hz), 1.52 (3H, t, J=7.0 Hz), 4.30 (2H, q, J=7.3 Hz), 4.40 (2H, q, J=7.0 Hz), 4.58 (2H, q, J=7.0 Hz), 7.12 (1H, s), 7.42 (1H, d, J=9.8 Hz), 7.52 (1H, dd, J=9.8 and 9.2 Hz), 7.60 (1H, t, J=9.8 Hz), 8.21 (1H, d, J=9.8 Hz), 8.65 (1H, d, J=14.0 Hz), 9.31 (1H, d, J=9.2 Hz), and 12.59 (1H, brd, J=14.0 Hz); IR 3260 (NH), 1698, 1680, and 1660 cm^{-1} (C=O). Found: C, 65.42; H, 6.06; N, 3.55%. Calcd for $C_{21}H_{23}NO_6$: C, 65.44; H, 6.01; N, 3.63%.

Cyclization of 1c. A solution of **1c** (0.210 g) in *t*-butylbenzene (15 ml) was refluxed for 5 d. The solvent was then evaporated, and chromatography of the residue with ethyl acetate gave **9** (0.176 g, 95% yield), which was recrystallized from hexane–dichloromethane to give orange needles, mp 185—187 °C; ^{1}H NMR δ=1.44 (3H, t, J=7.0 Hz), 1.52 (3H, t, J=7.0 Hz), 4.43 (2H, q, J=7.0 Hz), 4.55 (2H, q, J=7.0 Hz), 7.83 (1H, t, J=9.8 Hz), 7.88 (1H, dd, J=9.8 and 9.2 Hz), 7.96 (1H, t, J=9.8 Hz), 8.61 (1H, s), 9.50 (1H, d, J=9.8 Hz), 10.31 (1H, d, J=9.2 Hz), and 10.95 (1H, brs); IR 3320 (NH), 1724, 1690, and 1644 cm^{-1} (C=O). Found: C, 67.17; H, 4.99; N, 4.23%. Calcd for $C_{19}H_{17}NO_5$: C, 67.25; H, 5.05; N, 4.13%.

Reaction of 1a with MP. A mixture of **1a** (0.500 g), MP (0.880 g), and 5% Pd–C (0.500 g) in dry *t*-butylbenzene (30 ml) was refluxed for 1 h. The solvent was then evaporated, and the residue was purified by silica-gel column chromatography with benzene–chloroform (1 : 1) to give **10** (0.075 g, 7% yield). Elution with chloroform gave **11** (0.068 g, 16% yield).

10: Red-brown prisms (from hexane–dichloromethane); mp 188—190 °C; ^{1}H NMR δ=3.85 (6H, s), 5.38 (2H, brs), 6.25 (2H, d, J=15.9 Hz), 7.30—7.50 (3H, m), 8.19 (2H, d J=10.4 Hz), and 8.26 (2H, d, J=15.9 Hz); IR 3384, 3250 (NH), 1710, 1690, and 1652 cm^{-1} (C=O). Found: C, 69.16; H, 5.39; N, 4.64%. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.51; N, 4.50%.

11: Red needles (from hexane–dichloromethane); mp 280 °C (decomp); ^{1}H NMR δ (DMSO-d_6)=6.31 (1H, d, J=9.8 Hz), 7.06 (1H, s), 7.37 (1H, t, J=9.8 Hz), 7.45 (1H, dd, J=9.8 and 9.2 Hz), 7.64 (1H, t, J=9.8 Hz), 8.36 (1H, d J=9.8 Hz), 8.47 (1H, d, J=9.8 Hz), 8.62 (1H, d, J=9.2 Hz), and 12.12 (1H, brs); IR 3200 (NH) and 1642 cm^{-1} (C=O). Found: C, 79.65; H, 4.78; N, 7.18%. Calcd for $C_{13}H_9NO$: C, 79.98; H, 4.64; N, 7.17%.

Reaction of 1b with MP. A mixture of **1b** (0.500 g), MP (0.590 g), and 5% Pd–C (0.500 g) in dry *t*-butylbenzene (30 ml) was refluxed for 2 h. The solvent was then evaporated, and the residue was purified by silica-gel column chromatography with benzene to give **1b** (0.117 g, 23% yield) and **6b** (0.112 g, 16% yield), successively. Elution with chloroform gave **8b** (0.135 g, 14.5% yield).

6b: Red needles (from hexane); mp 107—108 °C; ^{1}H NMR δ=1.49 (3H, t, J=7.0 Hz), 3.84 (3H, s), 4.48 (2H, q, J=7.0 Hz), 6.22 (2H, d, J=15.9 Hz), 6.5—7.0 (2H, br), 7.35—7.58 (3H, m), 8.21 (1H, dm, J=10.4 Hz), 8.23 (1H, d, J=15.9 Hz), and 9.02 (1H, d, J=9.8 Hz); IR 3500, 3348 (NH), 1720, and 1672 cm^{-1} (C=O). Found: C, 68.50; H, 5.68; N, 4.80%. Calcd for $C_{17}H_{17}NO_4$: C, 68.21; H, 5.73; N, 4.68%.

8b: Red-violet needles (from hexane–dichloromethane); mp 209—210 °C; ^{1}H NMR δ=1.53 (3H, t, J=7.0 Hz), 4.56 (2H, q, J=7.0 Hz), 6.57 (1H, d, J=9.2 Hz), 7.65—7.90 (3H, m), 8.23 (1H, d, J=9.8 Hz), 8.59 (1H, d, J=9.2 Hz), 9.60 (1H, d, J=10.4 Hz), and 10.44 (1H, brs); IR 3392 (NH), 1682, and 1660 cm^{-1} (C=O). Found: C, 71.83; H, 4.97; N, 5.18%. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24%.

Reaction of 6b with DBU. A solution of **6b** (0.110 g) and DBU (0.1 ml) in dry xylene (20 ml) was refluxed for 4 d. The residue was then evaporated, and chromatography of the residue with chloroform gave **6b** (0.057 g, 52% yield) and **8b** (0.011 g, 11% yield), successively.

Reaction of 1a with DBA. A mixture of **1a** (0.500 g), DBA (2.454 g), and 5% Pd–C (0.500 g) in dry benzene (50 ml) was ultrasonically irradiated for 3 h. The solvent was then evaporated, and chromatography of the residue with benzene gave **12a** (0.358 g, 28.5% yield), and **12b** (1.092 g, 53% yield).

12a: Blue-green needles (from hexane–dichloromethane); mp 182—183 °C; ^{1}H NMR δ=6.92 (1H, dd, J=11.0 and 8.6 Hz), 7.01 (1H, dd, J=11.0 and 8.5 Hz), 7.25 (1H, dd, J=11.0 and 8.5 Hz), 7.42—7.68 (6H, m), 7.65 (1H, s), 7.70 (1H, s), 7.96 (2H, dd, J=7.9 and 1.8 Hz), 8.06 (1H, d, J=8.6 Hz), 8.14 (1H, d, J=11.0 Hz), and 8.19 (2H, dd, J=7.9 and 1.2 Hz); IR 1668 (C=O), 714, and 700 cm^{-1} (phenyl). Found: C, 87.21; H, 4.91; N, 3.96%. Calcd for $C_{26}H_{17}NO$: C, 86.88; H, 4.77; N, 3.90%.

12b: Yellow-brown prisms (from hexane–dichloromethane); mp 184—186 °C; ^{1}H NMR δ=7.06 (1H, dd, J=11.0 and 8.6 Hz), 7.19 (1H, dd, J=11.0 and 8.6 Hz), 7.30—7.55 (11H, m), 7.57 (1H, brd, J=6.7 Hz), 7.66 (1H, brd, J=6.7 Hz), 7.79 (1H, s), 7.95 (4H, dd, J=7.9 and 1.2 Hz), 8.07 (2H, dd, J=7.3 and 1.2 Hz), 8.18 (1H, d, J=8.6 Hz), 8.26 (2H, dd, J=7.9 and 1.2 Hz), 8.42 (1H, s), and 8.70 (1H, d, J=11.0 Hz); IR 1668, 1634 (C=O), 714, and 688 cm^{-1} (phenyl). Found: C, 85.01; H, 4.70; N, 2.42%. Calcd for $C_{42}H_{27}NO_3$: C, 84.97; H, 4.58; N, 2.36%.

Reaction of 1b with DBA. A mixture of **1b** (0.160 g), DBA (0.350 g), and 5% Pd–C (0.200 g) in dry benzene (50 ml) was urtrasonically irradiated for 4 h. The solvent was then evaporated, and chromatography of the residue with benzene–chloroform (1 : 1) gave **12c** (0.166 g, 63% yield).

12c: Brown-violet needles (from hexane); mp 176—177 °C; ^{1}H NMR δ=1.66 (3H, t, J=7.0 Hz), 4.65 (2H, q, J=7.0 Hz), 7.26 (1H, dd, J=9.8 and 8.5 Hz), 7.40—7.70 (8H, m), 7.80 (1H, s), 7.92 (2H, dd, J=7.3 and 1.2 Hz), 8.36 (2H, dd, J=7.9 and 1.5 Hz), 8.41 (1H, d, J=8.6 Hz), and 9.66 (1H, d, J=9.8 Hz); IR 1680, 1666 (C=O), 714, and 700 cm^{-1} (phenyl). Found: C, 80.70; H, 4.98; N, 3.11%. Calcd for $C_{29}H_{21}NO_3$: C, 80.71; H, 4.91; N, 3.26%.

Chlorination of 8a. A mixture of **8a** (0.100 g), phosphoryl chloride (10 ml), and a drop of pyridine was refluxed for 1 h. The mixture was poured into ice-water, neutralized with sodium hydrogen carbonate, and extracted with chloroform. The extract was dried (Na_2SO_4) and the solvent was evaporated. Chromatography of the residue with benzene gave **12d** (0.057 g, 54% yield), which was recrystallized from hexane–dichloromethane to give violet needles, mp 150—151 °C; ^{1}H NMR δ=1.55 (3H, t, J=7.0 Hz), 4.13 (3H, s), 4.59 (2H, q, J=7.0 Hz), 7.58 (1H, dd, J=10.4 and 9.2 Hz), 7.62 (1H, dd, J=11.0 and 7.9 Hz), 7.68 (1H, s), 7.80 (1H, dd, J=10.4 and 7.9 Hz), 9.31 (1H, d, J=9.2 Hz), and 9.64 (1H, d, J=11.0 Hz); IR 1728 and 1686 cm^{-1} (C=O). Found: C, 63.04; H, 4.26; N, 4.15%. Calcd for $C_{18}H_{14}ClNO_4$: C, 62.89; H, 4.10; N, 4.08%.

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References

1) N. Abe and T. Takehiro, *Bull. Chem. Soc. Jpn.*, **61**, 1225 (1988), and references cited therein.
2) N. Abe and K. Yatabe, *Bull. Chem. Soc. Jpn.*, **64**, 1704 (1991).
3) T. Nishiwaki and N. Abe, *Heterocycles*, **15**, 547 (1981).
4) O. Meth-Cohn, C. Moore, and P. H. van Rooyen, *J. Chem. Soc., Perkin Trans. 1*, **1985**, 1793.
5) K. Hafner, *Lect. Heterocycl. Chem.*, **3**, 33 (1976).
6) K. Hafner and J. Haring, *Erdoel Kohle, Erdgas, Petrochem.*, **32**, 136 (1979).
7) W. Treibs, *Naturwissenschaften*, **47**, 156 (1960); *ibid.*, **52**, 452 (1965); *Chimia*, **24**, 440 (1970).
8) K. Hafner and K. L. Moritz, *Ann. Chem.*, **650**, 92 (1961).
9) K. Hafner, H. Diehl, and U. Süss, *Angew. Chem., Int. Ed. Engl.*, **15**, 104 (1976).
10) K. Hafner, H. J. Lindner, and W. Ude, *Angew. Chem., Int. Ed. Engl.*, **18**, 161 (1979); *ibid.*, **18**, 162 (1979).
11) W. von E. Doering and D. W. Wiely, *Tetrahedron*, **11**, 183 (1960).
12) I. Kawamoto, Y. Sugimura, N. Soma, and Y. Kishida, *Chem. Lett.*, **1972**, 931.
13) An azuleno[2,1-*b*]pyridine system was synthesized. T. Nozoe, K. Takase, T. Nakazawa, S. Sugita, and M. Saito, *Bull. Chem. Soc. Jpn.*, **47**, 1750 (1974); T. Nozoe and K. Kikuchi, *Bull. Chem. Soc. Jpn.*, **36**, 633 (1963).
14) D. J. Bertelli and P. Crewa, *Tetrahedron*, **26**, 4717 (1970).
15) T. Morita, T. Nakadate, and K. Takase, *Heterocycles*, **15**, 835 (1980).
16) T. Nozoe, S. Seto, S. Matsumura, and Y. Murase, *Bull. Chem. Soc. Jpn.*, **35**, 1179 (1962).