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Photocyclization of Styrylpyrazines

Akihiro Ohta, Kazuko Hasegawa, Katsuyo Amano, Chiharu Mori, Akiko Ohsawa, Kiyotaka Ikeda, and Tokuhiro Watanabe

Tokyo College of Pharmacy[1]

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Irradiation of several 2-(β-arylvinyl)pyrazines at room temperature using a high pressure mercury lamp afforded aza-phenanthrenes in moderate yields. The ring closure of 2-[β-(3-pyridyl)vinyl]pyrazine (IIIb) occurred only at the 4-position of the pyridine ring, whereas 2-[β-(2-naphthyl)vinyl]pyrazine (IIIe) cyclized at the 1-position of the naphthalene ring. 2,5-Distyrylpyrazine (VIa) and 2,5-bis[β-(2-pyridyl)vinyl]pyrazine (VIb) were also irradiated in refluxing benzene to give dibenzo[*a*,*h*]phenazine (XVI) and dipyrido[3,2-*a*:3′,2′-*h*]phenazine (XVII), respectively.

Keywords——2-[β-(pyridyl)vinyl]pyrazines photocyclization; 2-[β-(naphthyl)vinyl]-pyrazines photocyclization; 2,5-bis[β-(aryl)vinyl]pyrazines photocyclization; pyridoquinoxalines; naphthoquinoxalines; polycyclic phenazine derivatives

1,2-Diarylethylene derivatives have long been recognized as useful precursors for the formation of polycyclic aromatic compounds by a photolytic ring closure process.[2] Perkampus and Bluhm obtained benzo[*f*]quinoline by irradiation of 2-styrylpyrazine in cyclohexane, using a 400-W high-pressure mercury lamp.[3] This paper deals with the photocyclization of some other 2-(β-arylvinyl)-pyrazines and 2,5-bis(β-arylvinyl)pyrazines to aza-aromatic compounds.

Preparation of 2-(β-Arylvinyl)pyrazines and 2,5-Bis(β-arylvinyl)pyrazines

In contrast to the work of Perkampus and Bluhm,[3] 2-methylpyrazine 1,4-dioxide[4] (I) was employed as a starting material for the preparation of 2-(β-arylvinyl)pyrazines. Compound I was condensed with pyridine-2-aldehyde, pyridine-3-aldehyde, pyridine-4-aldehyde, 1-naphthaldehyde or 2-naphthaldehyde, in the presence of a small amount of a base, to afford 2-[β-(2-pyridyl)vinyl]pyrazine 1,4-dioxide (IIa), 2-[β-(3-pyridyl)vinyl]pyrazine 1,4-dioxide (IIb), 2-[β-(4-pyridyl)vinyl]pyrazine 1,4-dioxide (IIc), 2-[β-(1-naphthyl)vinyl]pyrazine 1,4-dioxide (IId), and 2-[β-(2-naphthyl)vinyl]pyrazine 1,4-dioxide (IIe), respectively, in good yields. These pyrazine dioxides were deoxygenated by heating with phosphorus trichloride at 100° in a sealed tube to afford the corresponding pyrazines, 2-[β-(2-pyridyl)vinyl]pyrazine (IIIa), 2-[β-(3-pyridyl)vinyl]pyrazine (IIIb), 2-[β-(4-pyridyl)vinyl]pyrazine (IIIc), 2-[β-(1-naphthyl)vinyl]pyrazine (IIId), and 2-[β-(2-naphthyl)vinyl]pyrazine (IIIe), in high yields. These pyrazine derivatives exist in the *trans* configuration. The proton magnetic resonance (PMR) spectra of IIIb—e exhibit an A/B-type quartet (two doublets, $J=16$ Hz), due to the protons of the *trans*-ethylene linkage, in the region between 7.0 and 8.0 ppm. On the other hand, the *trans*-ethylenic protons of IIIa appear as a singlet at 7.75 ppm, due to the anisotropic and electronic properties of the nitrogen-carbon double bonds in the pyridine and pyrazine rings.[5]

1) Location: *1432-1 Horinouchi, Hachioji, Tokyo 192-03, Japan.*
2) A.J. Floyd, S.F. Dyke, and S.E. Ward, *Chem. Rev.*, **76**, 533 (1976).
3) H.H. Perkampus and T. Bluhm, *Tetrahedron*, **28**, 2099 (1972).
4) B. Klein and J. Berkowitz, *J. Am. Chem. Soc.*, **81**, 5160 (1959).
5) F. Coletta, A. Gambaro, and L. Pasimeni, *Gazz. Chim. Ital.*, **103**, 265 (1973).

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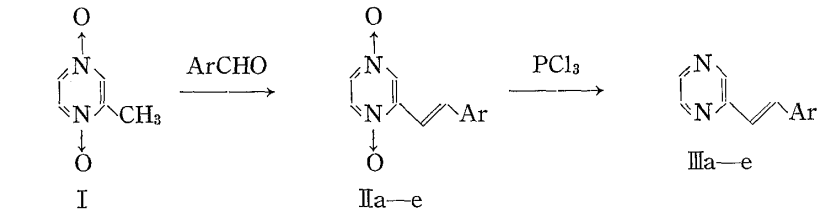
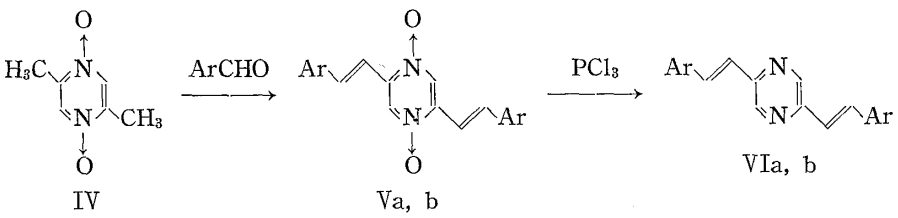


Ar: a; 2-pyridyl, b; 3-pyridyl, c; 4-pyridyl, d; 1-naphthyl, e; 2-naphthyl



Ar: a; phenyl, b; 2-pyridyl

Chart 1

2,5-Distyrylpyrazine (VIa) was prepared by a modification of Koelsch and Gumprecht's method,[6] *i.e.*, by heating 2,5-distyrylpyrazine 1,4-dioxide (Va) with phosphorus trichloride at 100° in a sealed tube. The preparation of 2,5-bis[*β*-(2-pyridyl)vinyl]pyrazine (VIb) was carried out in a similar manner, after condensation of pyridine-2-aldehyde with 2,5-dimethylpyrazine 1,4-dioxide[4] (IV).

Irradiation of 2-(*β*-Arylvinyl)pyrazines and 2,5-Bis(*β*-arylvinyl)pyrazines

The 2-(*β*-arylvinyl)pyrazines (IIIa—e) were dissolved in hexane or benzene and irradiated under an atmosphere of air for several hours, using a 100-W high-pressure mercury lamp, model UM-102 (Ushio Electric Inc., Tokyo), with a quartz cooling jacket. For example, a 0.1% solution of IIIa in hexane was irradiated at room temperature for 5 hr, and the photoproduct was purified by column chromatography on silica gel followed by sublimation to yield pyrido[3,2-*f*]quinoxaline (VII). Irradiation of IIIb—e was carried out under similar conditions to afford cyclized products in 20—30% yields. Cyclization of IIIa, IIIc, and IIId should theoretically give only one compound in each case, and indeed, each product gave a single peak in gas liquid chromatography (GLC). The structures of the photo-products from IIIa, IIIc, and IIId were determined to be VII, pyrido[3,4-*f*]quinoxaline (X), and naphtho[2,1-*f*]quinoxaline (XI), on the basis of the spectral data (UV and MS).

In contrast, the irradiation of IIIb and IIIe should give two photo-products, pyrido[4,3-*f*]-quinoxaline (VIII) and pyrido[2,3-*f*]quinoxaline[7] (IX), and naphtho[1,2-*f*]quinoxaline (XII) and naphtho[2,3-*f*]quinoxaline (XIII), respectively, depending on the direction of cyclization. However, the photo-product from IIIb showed a single peak in GLC. Although the mass spectrum of the product gave a parent ion (*m/e* 181) corresponding to triazaphenanthrene, and its UV spectrum was very similar to those of VII and IX, the melting point and the retention time were not identical with those of IX. On the basis of these data, the photo-product derived from IIIb may be VIII. It is interesting that only one isomer, formed by cyclization to the 4-position of the pyridine ring, is obtained. Photocyclization also occurs mainly at the 4-position of the pyridine ring in the cases of 3-styrylpyridine[8] and phenylazopyridine.[9]

Irradiation of IIIe also gave a sole product as pale yellow crystals. In order to determine the structure of this product, XIII was prepared from 1,2-diaminoanthraquinone (XIV).

6) C.F. Koelsch and W.H. Gumprecht, *J. Org. Chem.*, **23**, 1603 (1958).
7) F.H. Case and J.A. Brennan, *J. Am. Chem. Soc.*, **81**, 6297 (1959).
8) P. Bortolus, G. Cauzzo, U. Mazzucato, and G. Galiazo, *Z. Phys. Chem.*, **63**, 29 (1969) (Frankfurt am Main).
9) J.W. Barton and R.B. Walker, *Tetrahedron Lett.*, **1975**, 569.

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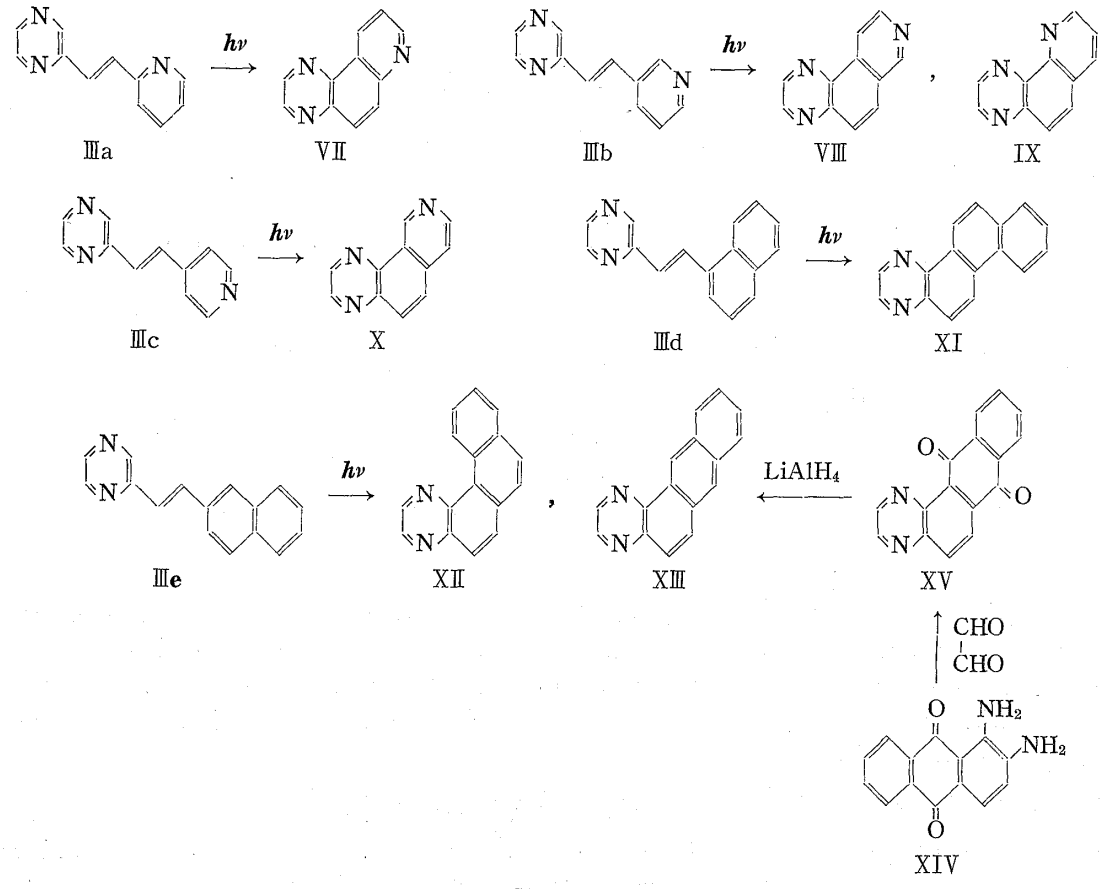

Chart 2

Namely, XIV was condensed with glyoxal to afford naphtho[2,3-*f*]quinoxaline-7,12-dione (XV) as a red-violet compound, which was treated with lithium aluminum hydride in tetrahydrofuran. The analytical and mass spectral data for the pale yellow compound thus obtained were consistent with the structure XIII. The photo-product, derived from IIIe, was shown not to be identical with XIII by comparison of the spectral data. This observation shows conclusively that cyclization of IIIe occurs at the 1-position of the naphthalene ring to give naphtho[1,2-*f*]quinoxaline (XII).

Compound VIa was irradiated in benzene under reflux to give yellow crystals in poor yield. This photo-product was purified by preparative thin-layer chromatography (TLC) on silica gel and shown to be identical with dibenzo[*a*,*h*]phenazine (XVI) prepared by the method of Witt.[10] When irradiation of VIa was carried out at room temperature, or in the presence of iodine, photocyclization failed to occur.

Irradiation of VIb in refluxing benzene gave a dark brown product, which was chromatographed on Florisil and then recrystallized from toluene to give yellow prisms, mp 362—

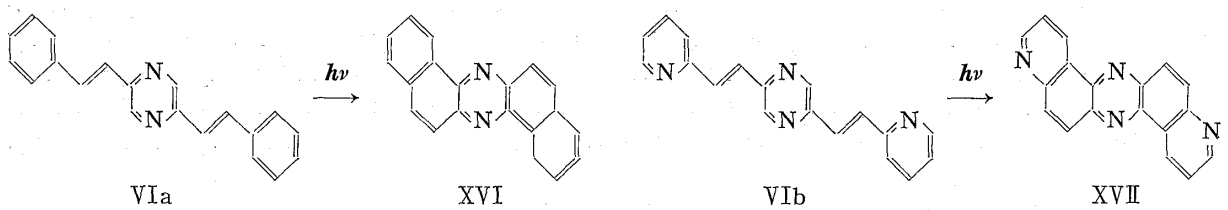

Chart 3

10) D.W. Witt, *Chem. Ber.*, **19**, 2794 (1886).

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364°, undepressed on admixture with a sample of dipyrido[3,2-*a*: 3′,2′-*h*]phenazine prepared by the reported method.[11,12]

From these results, it appears that the photocyclization of *β*-arylvinylpyrazines is available as a synthetic route to polycyclic aza-aromatic compounds. The photocyclization of other complex pyrazinyl polyenes may well provide routes to other interesting compounds.

Experimental

All melting points were recorded on a Yanagimoto micro-melting point apparatus and are uncorrected. Boiling points are also uncorrected. Gas chromatograms were recorded on a Shimadzu GC-4B unit, UV spectra on a Hitachi Model 203 spectrometer, IR spectra on a Shimadzu IR-400 spectrometer, and PMR spectra on a JEOL JNM-PS-100 instrument with tetramethylsilane as an internal standard. Mass spectra were obtained with a Hitachi RMU-7L spectrometer.

(1) **2-[*β*-(2-Pyridyl)vinyl]pyrazine 1,4-Dioxide (IIa)**——A mixture of 2.522 g (20 mmol) of I, 3.213 g (30 mmol) of pyridine-2-aldehyde, and 10 ml of 10% NaOH solution in 40 ml of MeOH was heated at 80° under N_2 for 5 min to give IIa (4.125 g, 96%), which was recrystallized from DMF (dimethylformamide) to give yellow needles, mp 253.5—254°. *Anal.* Calcd. for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.22; N, 19.53. Found: C, 61.18; H, 3.89; N, 19.51. MS *m/e*: 215 (M^+), 199 (M^+-O), 198 (M^+-OH), 183 (M^+-20), 182 (M^+-O-OH). $UV_{max}^{95\%\ EtOH}$ nm (log *ε*), 224 (4.01), 267 (4.13), 315 (4.63), 336 (4.37), 350 (4.22, shoulder).

(2) **2-[*β*-(3-Pyridyl)vinyl]pyrazine 1,4-Dioxide (IIb)**——A mixture of 126 mg (1 mmol) of I, 160.7 mg (1.5 mmol) of pyridine-3-aldehyde, 1 ml of 10% NaOH solution, and 4 ml of MeOH was heated in a sealed tube at 80° for 5 min and worked up as before to afford yellow crystals (90 mg, 45%). Recrystallization from DMF gave yellow needles, mp 276.5—277°. *Anal.* Calcd. for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.22; N, 19.53. Found: C, 61.18; H, 4.25; N, 19.56. MS *m/e*: 215 (M^+), 199 (M^+-O), 188 (M^+-20), 182 (base peak, M^+-O-OH). $UV_{max}^{95\%\ EtOH}$ nm (log *ε*): 272 (3.97), 312 (4.51), 337 (4.23, shoulder).

(3) **2-[*β*-(4-Pyridyl)vinyl]pyrazine 1,4-Dioxide (IIc)**——A mixture of 2.522 g (20 mmol) of I, 3.213 g (30 mmol) of pyridine-4-aldehyde, 5 ml of 10% NaOH solution, and 50 ml of MeOH was heated at 55° for 20 min under N_2 to yield crude IIc (2.580 g, 60%), which was recrystallized from DMF as yellow needles, mp 267—268.5°. *Anal.* Calcd. for $C_{11}H_9N_3O_2$: C, 61.39; H, 4.22; N, 19.53. Found: C, 61.47; H, 4.14; N, 19.81. MS *m/e*: 215 (M^+), 199 (M^+-O), 198 (M^+-OH), 183 (M^+-20), 182 (base peak, M^+-O-OH). $UV_{max}^{95\%\ EtOH}$ nm (log *ε*): 271 (4.26, shoulder), 305 (4.44), 329 (4.37).

(4) **2-[*β*-(1-Naphthyl)vinyl]pyrazine 1,4-Dioxide (IId)**——A mixture of 1.261 g (10 mmol) of I, 3.124 g, (20 mmol) of 1-naphthaldehyde, and NaOMe (prepared from 0.230 g (10 mg atom) of Na and 25 ml of dehyd. MeOH) was heated at 90° for 15 min in a sealed tube. The yellow crystals were purified by recrystallization from DMF to furnish yellow prisms (1.53 g, 58%), mp 274—275°. *Anal.* Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.52; H, 4.43; N, 10.49. MS *m/e*: 264 (M^+), 247 (M^+-OH), 231 (base peak, M^+-O-OH). $UV_{max}^{95\%\ EtOH}$ nm (log *ε*): 222 (4.77), 253 (4.22), 279 (4.13), 322 (4.44).

(5) **2-[*β*-(2-Naphthyl)vinyl]pyrazine 1,4-Dioxide (IIe)**——A mixture of 1.260 g (10 mmol) of I, 2.340 g (15 mmol) of 2-naphthaldehyde, and NaOMe (prepared from 0.230 g (10 mg atom) of Na and 25 ml of dehyd. MeOH) was treated as described in (4). The yellow precipitate was collected by filtration and recrystallized from DMF to give 2.520 g (95%) of IIe as yellow leaflets, mp 258°. *Anal.* Calcd. for $C_{16}H_{12}N_2O_2$: C, 72.72; H, 4.58; N, 10.60. Found: C, 72.73; H, 4.56; N, 10.78. MS *m/e*: 264 (M^+), 248 (M^+-O), 247 (M^+-OH), 231 (base peak, M^+-O-OH). $UV_{max}^{95\%\ EtOH}$ nm (log *ε*): 219 (4.59), 269 (4.33), 280 (4.35, shoulder), 291 (4.39), 321 (4.64), 350 (4.42, shoulder).

(6) **2,5-Bis[*β*-(2-pyridyl)vinyl]pyrazine 1,4-Dioxide (Vb)**——A mixture of 2.803 g (20 mmol) of IV, 4.494 g (42 mmol) of pyridine-2-aldehyde, and NaOMe (prepared from 1.00 g (43.5 mg atom) of Na and 50 ml of dehyd. MeOH) was heated in a sealed tube at 110° for 1 hr. The brownish yellow precipitate was collected by filtration, washed with H_2O and MeOH, and recrystallized from AcOH to furnish yellow prisms (3.740 g, 59%), mp 240° (darkening). *Anal.* Calcd. for $C_{18}H_{14}N_4O_2$: C, 67.91; H, 4.43; N, 17.60. Found: C, 67.90; H, 4.32; N, 17.75. MS *m/e*: 318 (M^+), 302 (M^+-O), 286 (M^+-2O). $UV_{max}^{95\%\ EtOH}$ nm (log *ε*): 315 (4.41, shoulder), 329 (4.58).

(7) **2-[*β*-(2-Pyridyl)vinyl]pyrazine (IIIa)**——A mixture of 108 mg (0.5 mmol) of IIa and 3 ml of PCl_3 was heated in a sealed tube at 100° for 30 min, poured into ice-water, and made alkaline by adding solid K_2CO_3. Crude IIIa (86 mg 47%) was collected by filtration as brownish-yellow crystals, then decolorized by chromatography on 5 g of alumina, eluting with benzene and $CHCl_3$, and recrystallized from cyclohexane to give colorless scales, mp 108—109°. *Anal.* Calcd. for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.46; H, 5.24; N, 22.46. MS *m/e*: 183 (M^+), 182 (M^+-H), 155 ($M^+-H-HCN$), 129 (base peak, M^+-2HCN). $UV_{max}^{95\%\ EtOH}$ nm (log *ε*): 260 (4.14), 321 (4.35). PMR ($CDCl_3$) *δ* ppm: 7.75 (2H, s).

11) C. Knueppel, *Ann. Chem.*, **310**, 75 (1900).
12) F.H.A. Rummens and A.C. Bellaart, *Tetrahedron*, **23**, 2755 (1967).

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(8) **2-[β-(3-Pyridyl)vinyl]pyrazine (IIIb)**——A mixture of 1.076 g (5 mmol) of IIb and 20 ml of PCl_3 was treated as described above to afford 89 mg (98%) of pale yellow crystals, which were decolorized by chromatography on alumina (5 g) using a mixture of benzene and $CHCl_3$, then recrystallized from hexane to furnish colorless needles, mp 95—96.5°. *Anal.* Calcd. for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.16; H, 5.06; N, 23.01. MS *m/e*: 183 (M^+), 182 (base peak, M^+-H), 156 (M^+-HCN), 155 ($M^+-H-HCN$). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 267 (4.08), 319 (4.20). PMR ($CDCl_3$) δ ppm: 7.20 (1H, d, $J=16.5$ Hz), 7.76 (1H, d, $J=16.5$ Hz).

(9) **2-[β-(4-Pyridyl)vinyl]pyrazine (IIIc)**——Crude yellowish IIIc (1.766 g, 96%), prepared from 2.152 g (10 mmol) of IIc by treatment with 40 ml of PCl_3, was decolorized by chromatography (alumina, 9 g) using a mixture of benzene and $CHCl_3$, and then recrystallized from cyclohexane to give colorless needles, mp 102.5—103°. *Anal.* Calcd. for $C_{11}H_9N_3$: C, 72.11; H, 4.95; N, 22.94. Found: C, 72.54; H, 5.33; N, 23.11. MS *m/e*: 183 (M^+), 182 (base peak, M^+-H), 155 ($M^+-H-HCN$). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 270 (4.34), 315 (4.52). PMR ($CDCl_3$) δ ppm: 7.12 (1H, d, $J=16.0$ Hz), 7.76 (1H, d, $J=16.0$ Hz).

(10) **2-[β-(1-Naphthyl)vinyl]pyrazine (IIId)**——A mixture of 0.956 g (4 mmol) of IId and 16 ml of PCl_3 was heated in a sealed tube at 100° for 1 hr. The reaction mixture was treated with ice-water, made alkaline by adding powdered K_2CO_3, and extracted with ether. Usual work-up of the ether extract gave a pale yellow solid, which was recrystallized from MeOH–H_2O to furnish 600 mg (65%) of IIId as colorless prisms, mp 61°. *Anal.* Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.56; H, 5.26; N, 12.08. MS *m/e*: 232 (M^+), 231 (M^+-H), 204 ($M^+-H-HCN$). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 222 (4.68), 286 (4.01). PMR ($CDCl_3$) δ ppm: 7.16 (1H, d, $J=16.0$ Hz), 7.56 (1H, d, $J=16.0$ Hz).

(11) **2-[β-(2-Naphthyl)vinyl]pyrazine (IIIe)**——A mixture of 792 mg (3 mmol) of IIe and 12 ml of PCl_3 was heated in a sealed tube at 100° for 2.5 hr and worked up as before to give pale yellow crystals, which were recrystallized from MeOH to give 320 mg (60%) of IIIe as pale yellow leaflets, mp 135—136°. *Anal.* Calcd. for $C_{16}H_{12}N_2$: C, 82.73; H, 5.21; N, 12.06. Found: C, 82.40; H, 5.04; N, 11.96. MS *m/e*: 232 (M^+), 231 (M^+-H), 204 ($M^+-H-HCN$). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 220 (4.53), 252 (4.26, shoulder), 265 (4.30, shoulder), 272 (4.31), 305 (4.20, shoulder), 332 (4.27). PMR ($CDCl_3$) δ ppm: 7.34 (1H, d, $J=16.5$ Hz), 7.96 (1H, d, $J=16.5$ Hz).

(12) **2,5-Distyrylpyrazine (VIa)**——A mixture of 1.00 g (3.2 mmol) of Va and 20 ml of PCl_3 was heated under reflux for 1 hr and then worked up as described in (7) to give brown crystals, which were recrystallized from benzene to furnish yellow prisms (731 mg, 81%), mp 221—222° (lit.[6] mp 218—219°).

(13) **2,5-Bis[β-(2-pyridyl)vinyl]pyrazine (VIb)**——A mixture of 500 mg (1.57 mmol) of Vb and 5 ml of PCl_3 was heated in a sealed tube at 100° for 1 hr and worked up as described in (7) to afford a yellow powder (440 mg), which was chromatographed on Florisil (43 g), eluting with a mixture of $CHCl_3$ and MeOH (98: 2), to give 262 mg (58%) of yellow crystals. Recrystallization from DMF furnished yellow scales, mp 275—277°. *Anal.* Calcd. for $C_{18}H_{14}N_4$: C, 75.50; H, 4.93; N, 19.57. Found: C, 75.65; H, 4.64; N, 19.84. MS *m/e*: 286 (M^+), 259 (M^+-HCN), 205 ($M^+-C_5H_4N$), 129 (base peak, $M^+-H-2C_5H_4N$). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 223 (3.88, shoulder), 280 (3.89, shoulder), 299 (3.99), 310 (3.99).

(14) **Pyrido[3,2-*f*]quinoxaline (VII)**——Irradiation of 50 mg of IIIa in 50 ml of hexane gave 22 mg of yellow crystals, which were purified by chromatography on silica gel (Wakogel C-200, 2 g), eluting with a mixture of benzene and $CHCl_3$, to furnish 11 mg (22%) of pale yellow prisms. A sample for analysis was sublimed at 100—120°/2 torr and recrystallized from cyclohexane to give colorless prisms, mp 125—126°. *Anal.* Calcd. for $C_{11}H_7N_3$: C, 72.91; H, 3.89; N, 23.19. Found: C, 72.79; H, 3.58; N, 22.93. MS *m/e*: 181 (M^+), 154 (M^+-HCN), 107 (base peak, M^+-2HCN). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 222 (4.62), 276 (4.48), 329 (3.43), 344 (3.41).

(15) **Pyrido[4,3-*f*]quinoxaline (VIII)**——After irradiation of 50 mg of IIIb in 50 ml of hexane for 4 hr, the product was worked up as before to afford 20 mg of crystals, which were recrystallized from cyclohexane to furnish pale yellow needles (13 mg, 26%), mp 136—139°. Before purification, the product was subjected to GLC; column, 1.5% SE-30 on Chromosorb W, 1.5 m×3 mm; column temp. 155°; N_2 flow rate, 50 ml/min. *Anal.* Calcd. for $C_{11}H_7N_3$: C, 72.91; H, 3.89; N, 23.19. Found: C, 72.75; H, 3.89; N, 23.50. MS *m/e*: 181 (base peak, M^+), 154 (M^+-HCN), 127 (M^+-2HCN), 100 (M^+-3HCN). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 220 (4.66, shoulder), 224 (4.70), 270 (4.30), 343 (3.30), 358 (3.25).

(16) **Pyrido[3,4-*f*]quinoxaline (X)**——Irradiation of 50 mg of IIIc in 50 ml of hexane for 3 hr and work-up as described in (11) gave 22 mg of a yellow solid, which was chromatographed on silica gel (Wakogel C-200, 2 g), eluting with a mixture of $CHCl_3$ and AcOEt, to give 16 mg (32%) of pale yellow crystals. Sublimation at 100—120°/2 torr and recrystallization from cyclohexane furnished pale yellow prisms, mp 174—175°. *Anal.* Calcd. for $C_{11}H_7N_3$: C, 72.91; H, 3.89; N, 23.19. Found: C, 73.04; H, 3.81; N, 22.95. MS *m/e*: 181 (base peak, M^+), 180 (M^+-H), 154 (M^+-HCN), 127 (M^+-2HCN). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 228 (4.60), 260 (4.14), 281 (3.86, shoulder), 320 (3.70, shoulder), 336 (3.92), 352 (3.89).

(17) **Naphtho[2,1-*f*]quinoxaline (XI)**——A solution of 200 mg of IIId in 150 ml of benzene was irradiated for 9 hr and then evaporated to dryness *in vacuo*. The brown residue was chromatographed on silica gel (Wakogel C-200, 50 g), eluting with benzene, to give 285 mg (71%) of XI as pale brown leaflets, which were recrystallized from MeOH to give pale brown leaflets, mp 171°. *Anal.* Calcd. for $C_{16}H_{10}N_2$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.26; H, 4.10; N, 11.97. MS *m/e*: 230 (M^+), 203 (M^+-HCN), 176 (M^+-2HCN).

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$UV_{max}^{95\%\ EtOH}$ nm (log ε): 215 (4.43), 255 (4.60), 273 (4.42), 281 (4.33, shoulder), 301 (4.35), 337 (3.68, shoulder), 353 (3.67).

(**18**) **Naphtho[1,2-*f*]quinoxaline (XII)**——A solution of 200 mg of IIIe in 150 ml of benzene was irradiated for 9 hr and worked up as before. The brown crystalline product was chromatographed on silica gel (Wakogel C-200, 50 g), eluting with benzene, to give pale yellow crystals, which were recrystallized from MeOH to furnish pale yellow needles, mp 145°. *Anal.* Calcd. for $C_{16}H_{10}N_2$: C, 83.45; H, 4.38; N, 12.17. Found: C, 83.42; H, 4.25; N, 12.44. MS *m/e*: 230 (M^+), 229 (M^+-H), 202 ($M^+-H-HCN$), 176 (M^+-2HCN). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 232 (4.60), 237 (4.56, shoulder), 247 (4.52), 284 (4.36), 299 (4.37), 345 (3.63), 360 (3.74), 380 (3.78).

(**19**) **Naphtho[2,3-*f*]quinoxaline-7,12-dione (XV)**——A solution of 4.76 g (20 mmol) of XIV and 5.80 g (40 mmol) of 40% glyoxal in 50 ml of MeOH was heated under reflux for 10 hr. The solvent was removed by distillation *in vacuo*, and the residue was dissolved in $CHCl_3$. The $CHCl_3$ solution was chromatographed on silica gel (Wakogel, C-200, 120 g) and the resulting red crystals (1.78 g) were recrystallized from 1,2-dichloroethane to give 0.646 g (12%) of XV as red-violet needles, mp 241—242°. *Anal.* Calcd. for $C_{16}H_8N_2O_2$: C, 73.84; H, 3.10; N, 10.76. Found: C, 73.75; H, 3.13; N, 10.63. MS *m/e*: 260 (M^+), 233 (M^+-HCN), 204 (M^+-2CO), 178 ($M^+-CN-2CO$), 150 ($M^+-2HCN-2CO$). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 245 (4.59), 255 (4.55), 260 (4.55, shoulder), 280 (4.22, shoulder), 290 (4.14, shoulder), 342 (3.95). IR (KBr) cm^{-1}: 1670 (C=O).

(**20**) **Naphtho[2,3-*f*]quinoxaline (XIII)**——A mixture of 260 mg (1 mmol) of XV and 1 g (26 mmol) of $LiAlH_4$ in 100 ml of dry THF was refluxed for 6 hr and worked up as usual. The brown solid product (216 mg) was chromatographed on silica gel (Wakogel C-200, 10 g), eluting with hexane containing an increasing amount of benzene, to give 75 mg (33%) of XIII as pale yellow crystals, which were recrystallized from MeOH to furnish pale yellow leaflets, mp 132—134°. *Anal.* Calcd. for $C_{16}H_{10}N_2$: C, 83.46; H, 4.38; N, 12.17. Found: C, 83.39; H, 4.11; N, 12.34. MS *m/e*: 230 (M^+), 229 (M^+-H), 202 ($M^+-H-HCN$), 176 (M^+-2HCN). $UV_{max}^{95\%\ EtOH}$ nm (log ε): 222 (4.38), 247 (4.70, shoulder), 254 (4.72), 276 (4.13, shoulder), 308 (4.33, shoulder), 318 (4.36), 339 (3.94), 358 (3.86).

(**21**) **Dibenzo[*a*,*h*]phenazine (XVI)**——After irradiation of 50 mg of VIa in 25 ml of benzene under reflux for 17 hr, the solvent was evaporated off and the browish-yellow residue was subjected to preparative TLC/silica gel (1.5 mm thick). Elution with benzene gave 2.8 mg (5.7%) of yellow crystals, which were recrystallized from toluene to furnish XVI as yellow scales, mp 289—290°, undepressed on admixture with an authentic sample,[10] mp 289—290°. The two samples had identical IR spectra and were identical by GLC analysis (1.5% OV-I on Chromosorb W, 1.5 m × 3 mm; column temp. 260°; N_2 flow rate, 40 ml/min).

(**22**) **Dipyrido[3,2-*a*: 3′,2′-*h*]phenazine (XVII)**——After irradiation of 210 mg of VIb in 105 ml of benzene under reflux for 20 hr, the solvent was evaporated off *in vacuo*. The resulting brown solid was dissolved in $CHCl_3$ and washed with dil. HCl. Removal of the $CHCl_3$ gave crude XVII (12.8 mg, 6.2%), which was chromatographed on Florisil (2 g), eluting with a mixture of $CHCl_3$ and MeOH (97: 3), then recrystallized from toluene to furnish yellow needles, mp 362—364°, undepressed on admixture with an authentic sample,[11] mp 363—365°. The two samples were also shown to be identical by IR spectroscopy and GLC (as for XVI).

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