Synthesis of 6-Halo-5-nitroquinoxalines

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The 5-nitro derivatives of 6-haloquinoxalines have been efficiently synthesized by condensation of α-dicarbonyls with 4-bromo- or 4-chloro-3-nitro-1,2-benzenediamines. The novel diamines were readily obtained by reductive cleavage of 5-bromo- and 5-chloro-4-nitro-2,1,3-benzoselenadiazoles. As demonstrated by the synthesis of an imidazo-, a selenadiazolo- and a pyrazinoquinoxaline, the reactive halogen atom *ortho* to the nitro substituent renders the novel quinoxalines versatile intermediates to further heterocycles.

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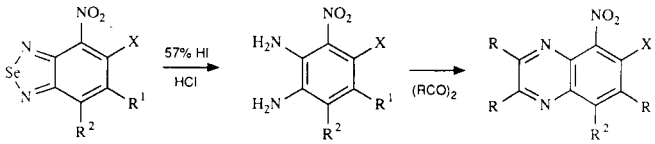
In connection with our studies of mutagenic imidazoquinoxalines [1], a methodology for the synthesis of 6-methylamino-5-nitroquinoxalines *via* 5-methylamino-4-nitro-2,1,3-benzoselenadiazoles has been described [2,3]. We subsequently became interested in ascertaining whether the title 6-halo-5-nitroquinoxalines **3-5** (Scheme 1) could be obtained in a similar fashion, since these compounds are not reported and, moreover, cannot be obtained by nitration of the corresponding 6-bromo- or 6-chloroquinoxalines. Nitration of quinoxaline itself takes place with difficulty, giving low yields of 5-nitroquinoxaline, 5,6-dinitroquinoxaline, 4-nitrobenzotriazole and 6-nitro-2,3-quinoxalinedione, depending on the reaction conditions [4-6]. However, the nitration of quinoxalines is facilitated by introducing an electron-releasing substituent in the homocyclic ring. Thus, 6-methoxy- and 6-aminoquinoxalines have been nitrated in position 5, although in moderate yields due to formation of by-products [7-12]. For instance, 2,7-dimethyl-6-methylaminoquinoxaline also yields the 5,N^6-dinitro product, along with oxidation of the pyrazine methyl groups and considerable formation of tarry products [10]. As to the corresponding 2,3-diphenylquinoxalines, nitration of the phenyl substituents is difficult to avoid [13]. Thus, a procedure affording 6-halo-5-nitroquinoxalines, whose halogen could then be easily replaced by methylamine, methoxide or other nucleophiles, would be highly desirable.

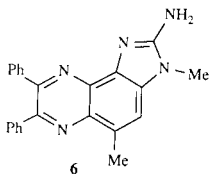
Nitro-substituted 1,2-benzenediamines are important intermediates in the synthesis of nitrogen heterocycles, although their preparation is often difficult and multistage. However, protection of 1,2-benzenediamines by ring closure with selenium dioxide forms 2,1,3-benzoselenadiazoles, which on nitration and subsequent removal of selenium offers a very efficient route to 3-nitro-1,2-benzenediamines [14]. The choice of the reducing agent for the deselenation is of importance. Treament of 4-nitro-2,1,3-benzoselenadiazole with iron in acetic acid does not remove the selenium, but only reduces the nitro group to the amine [15]. Zinc in hydrochloric acid removes selenium and also reduces the nitro substituent to give the hydrochloride of the triamine [16]. However, treatment with 57% hydriodic acid [14] or ammonium sulfide [17] selectively removes selenium without affecting the nitro group.

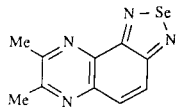
Scheme 1



	a	b	c	d	e
X	Cl	Cl	Cl	Br	Me
R^1	H	Me	H	Me	Cl
R^2	H	H	Me	Me	H

To avoid nucleophilic displacement of the halogen in the 2,1,3-benzoselenadiazoles **1**, we used hydriodic acid as reducing agent. The prescribed [14] amount of hydriodic acid was decreased considerably by the use of hydrochloric acid as the solvent. Reductive cleavage of the readily available selenadiazoles **1** gave the novel 4-bromo- and 4-chloro-3-nitro-1,2-benzenediamines **2**, which on condensation with the α-dicarbonyls glyoxal, biacetyl and benzil yielded 15 novel bromo- and chloro-5-nitroquinoxalines **3-5** (Scheme 1). The halogen atom *ortho* to the nitro group makes the title quinoxalines versatile molecules, capable of entering into further chemistry. For example, treatment of **5c** with methylamine followed by reduction to the corresponding diamine and ring closure with cyanogen bromide yielded the imidazoquinoxaline **6**, a potential mutagen on account of the 2-amino-3-methylimidazole moiety of the molecule [18,19]. When quinoxaline **4a** was allowed to react with ammonia, reduced to the corresponding diamine and cyclized with selenium dioxide, the new 7,8-dimethyl[1,2,5]selenadiazolo[3,4-*f*]quinoxaline (**7**) was obtained. Further, reaction of **5b** with ammonia, reduction to the diamino compound and condensation with benzil afforded 5-methyl-2,3,8,9-tetraphenylpyrazino[2,3-*f*]quinoxaline (**8**), also obtainable from **5c**.


6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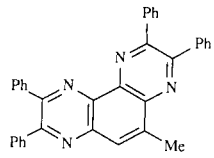
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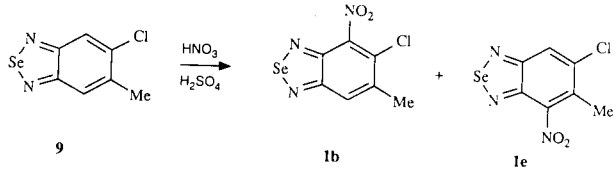
Nitration of 5-chloro-6-methyl-2,1,3-benzoselenadiazole (**9**) gave a mixture of **1b** and **1e** (Scheme 2) in a 3:1 ratio, respectively. Treatment of the mixture with hydriodic acid afforded the diamines **2b** and **2e** which were separated from each other by flash liquid chromatography. Treatment of **2e** with glyoxal, biacetyl and benzil afforded the respective novel quinoxalines **3e**, **4e** and **5e**. In **3e-5e**, the nitro group is *meta*- rather than *ortho*-related to the halogen atom. Hence, **3e-5e** do not belong to the title compounds, but they were nevertheless included in Scheme 1.

Scheme 2


9 1b 1e

EXPERIMENTAL

Melting points (uncorrected) marked (M) were taken by means of a Mettler FP5, all other on a Mettler FP62 apparatus. The ^{1}H nmr spectra were obtained with a Varian VXR-400 spectrometer at 400 MHz and 20°, and referenced to the solvent [δ (chloroform) 7.26 or δ (DMSO) 2.49]. Electron impact mass spectra (70 eV, direct insertion) were obtained with a Finnigan 4021 instrument with an ion source temperature of 250°. Ions containing isotopes other than ^{79}Br, ^{35}Cl or ^{80}Se are not listed. Flash liquid chromatography (fc) was performed on silica gel (230-400 mesh ASTM, Merck). All reactions and purifications were monitored by tlc (uv detection) on aluminium sheets coated with silica 60 F_{254} (Merck).

General Procedure for the Preparation of 4-Halo-3-nitro-1,2-benzenediamines **2**.

The selenadiazoles **1** were prepared as described for **1c** [3]. Experimental details and physical data will be published elsewhere [20]. To a suspension of **1** (4 mmoles) in concentrated hydrochloric acid (10 ml), 57% hydriodic acid (3 ml) was added dropwise at room temperature with vigorous stirring. The reaction was complete after *ca.* 2 hours (tlc solvent: dichloromethane-ethyl acetate, 1:1 v/v). A 5% aqueous sodium hydrogen sulfite solution (20 ml) was added to the dark-red reaction mixture. This was then warmed to *ca.* 80°, filtered hot and cooled to 4°. The needle-like salt of the diamine was collected and washed with 1 *M* hydrochloric acid. The diamine was crystallized from ethanol - concentrated ammonia (4:1 v/v).

4-Chloro-3-nitro-1,2-benzenediamine (**2a**).

This compound was obtained as red needles, yield 70%, mp 127.5-129.5° (M); ^{1}H nmr (deuteriochloroform): δ 3.5 and 4.6 (2 br s, 2 H each, 1- and 2-NH_2), 6.74 and 6.75 (ABq, 1 H each, J = 8.3 Hz, 5- and 6-H); ms: m/z (% relative intensity) 187 (M^+, 100), 170 (31), 169 (35), 141 (27), 140 (27), 114 (40), 105 (57).

Anal. Calcd. for $C_6H_6ClN_3O_2$: C, 38.42; H, 3.22; N, 22.40. Found: C, 38.30; H, 3.00; N, 22.50.

4-Chloro-5-methyl-3-nitro-1,2-benzenediamine (**2b**).

This compound was separated from **2e** (fc solvent: petroleum ether-ethyl acetate, 5:3 v/v) and obtained as red needles after recrystallization, yield 47%, mp 131-132° (M); ^{1}H nmr (deuteriochloroform): δ 2.27 (d, 3 H, J = 0.5 Hz, 5-Me), 3.5 and 4.2 (2 br s, 2 H each, 1- and 2-NH_2), 6.70 (q, 1 H, J = 0.5 Hz, 6-H); ms: m/z (% relative intensity) 201 (M^+, 100), 184 (30), 183 (21), 155 (30), 154 (36), 128 (32), 119 (60).

Anal. Calcd. for $C_7H_8ClN_3O_2$: C, 41.70; H, 3.99; N, 20.84. Found: C, 41.60; H, 3.60; N, 20.75.

4-Chloro-6-methyl-3-nitro-1,2-benzenediamine (**2c**).

This compound was obtained as red needles, yield 75%, mp 168-171° (M); ^{1}H nmr (deuteriochloroform): δ 2.21 (d, 3 H, J = 0.4 Hz, 6-Me), 3.4 and 4.7 (2 br s, 2 H each, 1- and 2-NH_2), 6.71 (q, 1 H, J = 0.4 Hz, 5-H); ms: m/z (% relative intensity) 201 (M^+, 100), 184 (34), 183 (42), 155 (30), 154 (39), 139 (12), 128 (22), 119 (38).

Anal. Calcd. for $C_7H_8ClN_3O_2$: C, 41.70; H, 3.99; N, 20.84. Found: C, 40.80; H, 3.90; N, 20.40.

4-Bromo-5,6-dimethyl-3-nitro-1,2-benzenediamine (**2d**).

This compound was obtained as red needles, yield 85%, mp 158-161° (M); ^{1}H nmr (deuteriochloroform): δ 2.21 and 2.39 (2 s, 3 H each, 5- and 6-Me), 3.6 and 4.0 (2 br s, 2 H each, 1- and 2-NH_2); ms: m/z (% relative intensity) 259 (M^+, 86), 242 (24), 241 (22), 213 (31), 212 (29), 186 (16), 133 (100).

Anal. Calcd. for $C_8H_{10}BrN_3O_2$: C, 36.94; H, 3.88; N, 16.16. Found: C, 36.40; H, 3.90; N, 16.00.

5-Chloro-4-methyl-3-nitro-1,2-benzenediamine (**2e**).

This compound was obtained as red needles after separation from **2b** and recrystallization, yield 23%, mp 119-120° (M); ^{1}H nmr (deuteriochloroform): δ 2.33 (s, 3 H, 4-Me), 3.4 and 4.5 (2 br s, 2 H each, 1- and 2-NH_2), 6.87 (s, 1 H, 6-H); ms: m/z (% relative intensity) 201 (M^+, 100), 184 (59), 155 (19), 154 (28), 139 (36), 128 (30), 119 (34).

Anal. Calcd. for $C_7H_8ClN_3O_2$: C, 41.70; H, 3.99; N, 20.84. Found: C, 40.90; H, 3.91; N, 20.70.

General Procedure for the Preparation of Quinoxalines **3** by Condensation of Benzenediamines **2** with Glyoxal.

A threefold excess of 30% aqueous glyoxal was added to a saturated ethanolic solution of the diamine. The mixture was boiled for *ca.* 1 hour (tlc solvent: dichloromethane-ethyl acetate, 16:1 v/v), diluted with water, allowed to cool and extracted with chloroform. Pure quinoxalines were obtained by evaporation of the extract and crystallization (70% ethanol) of the residue.

6-Chloro-5-nitroquinoxaline (**3a**).

This compound was obtained as yellowish needles, yield 87%, mp 134.5-135.5°; ^{1}H nmr (deuteriochloroform): δ 7.86 and 8.24 (ABq, 1 H, each, J = 9.1 Hz, 7- and 8-H), 8.96 and 8.98 (ABq, 1 H each, J = 1.8 Hz, 2- and 3-H); ms: m/z (% relative intensity)

209 (M^+, 100), 179 (33), 163 (70), 151 (81), 136 (24), 127 (47).

Anal. Calcd. for $C_8H_4ClN_3O_2$: C, 45.85; H, 1.92; N, 20.05. Found: C, 45.90; H, 1.80; N, 20.30.

6-Chloro-7-methyl-5-nitroquinoxaline (**3b**).

This compound was obtained as pale yellow needles, yield 85%, mp 132.5-133.5°; ^1H nmr (deuteriochloroform): δ 2.70 (d, 3 H, J = 0.9 Hz, 7-Me), 8.14 (q, 1 H, J = 0.9 Hz, 8-H), 8.89 and 8.93 (ABq, 1 H each, J = 1.8 Hz, 2- and 3-H); ms: m/z (% relative intensity) 223 (M^+, 62), 193 (33), 177 (29), 165 (58), 150 (7), 142 (100).

Anal. Calcd. for $C_9H_6ClN_3O_2$: C, 48.34; H, 2.70; N, 18.79. Found: C, 48.40; H, 2.60; N, 18.92.

6-Chloro-8-methyl-5-nitroquinoxaline (**3c**).

This compound was obtained as pale yellow needles, yield 85%, mp 119.5-120.5°; ^1H nmr (deuteriochloroform): δ 2.85 (d, 3 H, J = 0.8 Hz, 8-Me), 7.69 (q, 1 H, J = 0.8 Hz, 7-H), 8.94 and 8.96 (ABq, 1 H each, J = 1.8 Hz, 2- and 3-H); ms: m/z (% relative intensity) 223 (M^+, 100), 193 (60), 177 (24), 165 (12), 150 (11), 142 (71).

Anal. Calcd. for $C_9H_6ClN_3O_2$: C, 48.34; H, 2.70; N, 18.79. Found: C, 48.65; H, 2.70; N, 18.65.

6-Bromo-7,8-dimethyl-5-nitroquinoxaline (**3d**).

This compound was obtained as yellowish needles, yield 74%, mp 151.5-152.5°; ^1H nmr (deuteriochloroform): δ 2.72 and 2.89 (2 s, 3 H each, 7- and 8-Me), 8.86 and 8.95 (ABq, 1 H each, J = 1.7 Hz, 2- and 3-H); ms: m/z (% relative intensity) 281 (M^+, 59), 251 (21), 235 (17), 223 (3), 156 (81), 155 (100).

Anal. Calcd. for $C_{10}H_8BrN_3O_2$: C, 42.58; H, 2.86; N, 14.90. Found: C, 43.00; H, 2.85; N, 14.90.

7-Chloro-6-methyl-5-nitroquinoxaline (**3e**).

This compound was obtained as off-white needles, yield 79%, mp 155.5-156.5°; ^1H nmr (deuteriochloroform): δ 2.59 (s, 3 H, 6-Me), 8.31 (s, 1 H, 8-H), 8.90 and 8.93 (ABq, 1 H each, J = 1.8 Hz, 2- and 3-H); ms: m/z (% relative intensity) 223 (M^+, 70), 207 (6), 206 (56), 193 (13), 177 (46), 165 (13), 150 (7), 142 (100).

Anal. Calcd. for $C_9H_6ClN_3O_2$: C, 48.34; H, 2.70; N, 18.79. Found: C, 48.20; H, 2.40; N, 18.90.

General Procedure for the Preparation of Quinoxalines **4** by Condensation of Benzenediamines **2** with Biacetyl.

An equimolar amount of biacetyl was added to a warm (60°) saturated ethanolic solution of the diamine. The mixture was kept at 60° for 20 minutes (tlc solvent: dichloromethane-ethyl acetate, 16:1 v/v), diluted with water and allowed to cool to room temperature. The crystalline product was collected and recrystallized (ethanol).

6-Chloro-2,3-dimethyl-5-nitroquinoxaline (**4a**).

This compound was obtained as yellowish needles, yield 84%, mp 162.5-163.5°; ^1H nmr (deuteriochloroform): δ 2.75 and 2.76 (2 s, 3 H each, 2- and 3-Me), 7.71 and 8.05 (ABq, 1 H each, J = 9.0 Hz, 7- and 8-H); ms: m/z (% relative intensity) 237 (M^+, 81), 207 (14), 191 (23), 179 (10), 165 (100), 156 (15).

Anal. Calcd. for $C_{10}H_8ClN_3O_2$: C, 50.54; H, 3.39; N, 17.68. Found: C, 50.65; H, 3.20; N, 17.85.

6-Chloro-2,3,7-trimethyl-5-nitroquinoxaline (**4b**).

This compound was obtained as off-white needles, yield 84%, mp 141.5-142.5°; ^1H nmr (deuteriochloroform): δ 2.63 (d, 3 H, J = 0.9 Hz, 7-Me), 2.72 and 2.73 (2 s, 3 H each, 2- and 3-Me), 7.96 (q, 1 H, J = 0.9 Hz, 8-H); ms: m/z (% relative intensity) 251 (M^+, 54), 221 (14), 205 (18), 193 (13), 179 (44), 170 (6), 43 (100).

Anal. Calcd. for $C_{11}H_{10}ClN_3O_2$: C, 52.50; H, 4.00; N, 16.69. Found: C, 52.75; H, 3.90; N, 17.05.

6-Chloro-2,3,8-trimethyl-5-nitroquinoxaline (**4c**).

This compound was obtained as yellowish needles, yield 61%, mp 156.5-157.5°; ^1H nmr (deuteriochloroform): δ 2.73 and 2.75 (2 s, 3 H each, 2- and 3-Me), 2.78 (d, 3 H, J = 0.9 Hz, 8-Me), 7.54 (q, 1 H, J = 0.9 Hz, 7-H); ms: m/z (% relative intensity) 251 (M^+, 93), 221 (36), 205 (8), 193 (4), 179 (30), 170 (9), 169 (11), 43 (100).

Anal. Calcd. for $C_{11}H_{10}ClN_3O_2$: C, 52.50; H, 4.00; N, 16.69. Found; C, 52.10; H, 3.65; N, 16.70.

6-Bromo-2,3,7,8-tetramethyl-5-nitroquinoxaline (**4d**).

This compound was obtained as yellowish needles, yield 85%, mp 178-179°; ^1H nmr (deuteriochloroform): δ 2.65 and 2.83 (2 s, 3 H each, 7- and 8-Me), 2.71 and 2.73 (2 s , 3 H each, 2- and 3-Me); ms: m/z (% relative intensity) 309 (M^+, 100) 279 (19), 263 (29), 251 (4), 237 (9), 183 (33).

Anal. Calcd. for $C_{12}H_{12}BrN_3O_2$: C, 46.47; H, 3.90; N, 13.55. Found: C, 46.25; H, 3.55; N, 13.50.

7-Chloro-2,3,6-trimethyl-5-nitroquinoxaline (**4e**).

This compound was obtained as off-white needles, yield 90%, mp 158.5-159.5°; ^1H nmr (deuteriochloroform): δ 2.53 (s, 3 H, 6-Me), 2.72 and 2.74 (2 s, 3 H each, 2- and 3-Me), 8.13 (s, 1 H, 8-H); ms: m/z (% relative intensity) 251 (M^+, 94), 234 (100), 221 (15), 205 (53), 193 (14), 179 (27), 170 (32).

Anal. Calcd. for $C_{11}H_{10}ClN_3O_2$: C, 52.50; H, 4.00; N, 16.70. Found: C, 52.00; H, 3.85; N, 16.70.

General Procedure for the Preparation of Quinoxalines **5** by Condensation of Benzenediamines **2** with Benzil.

A hot solution of benzil (0.5 mmole) in acetic acid (10 ml) was added to a warm saturated ethanolic solution of the diamine (0.5 mmole). The mixture was kept at 100° for 30 minutes (tlc solvent: dichloromethane-ethyl acetate, 20:1 v/v) and cooled to room temperature. The product precipitated after addition of water (3 ml). It was collected and crystallized (acetic acid).

6-Chloro-5-nitro-2,3-diphenylquinoxaline (**5a**).

This compound was obtained as light yellow crystals, yield 78%, mp 192.5-193.5°; ^1H nmr (deuteriochloroform): δ 7.30-7.55 (m, 10 H, 2- and 3-Ph), 7.80 and 8.23 (ABq, 1 H each, J = 9.0 Hz, 7- and 8-H); ms: m/z (% relative intenstity) 361 (M^+, 26), 314 (18), 279 (4), 105 (100), 77 (29).

Anal. Calcd. for $C_{20}H_{12}ClN_3O_2$: C, 66.40; H, 3.34; N, 11.61. Found: C, 66.40; H, 3.40; N, 11.70.

6-Chloro-7-methyl-5-nitro-2,3-diphenylquinoxaline (**5b**).

This compound was obtained as light yellow crystals, yield 80%, mp 181.5-183.0°; ^1H nmr (deuteriochloroform): δ 2.69 (d, 3 H, J = 1.0 Hz, 7-Me), 7.30-7.55 (m, 10 H, 2- and 3-Ph), 8.15 (q, 1 H, J = 1.0 Hz, 8-H); ms: m/z (% relative intensity) 375 (M^+, 24), 328 (15), 293 (3), 105 (100), 77 (25).

Anal. Calcd. for $C_{21}H_{14}ClN_3O_2$: C, 67.12; H, 3.75; N, 11.18. Found: C, 67.20; H, 3.40; N, 11.20.

6-Chloro-8-methy-5-nitro-2,3-diphenylquinoxaline (**5c**).

This compound was obtained as light yellow crystals, yield 75%, mp 171-172°; ^{1}H nmr (deuteriochloroform): δ 2.87 (d, 3 H, J = 1.0 Hz, 8-Me), 7.30-7.60 (m, 10 H, 2- and 3-Ph), 7.63 (q, 1 H, J = 1.0 Hz, 7-H); ms: m/z (% relative intensity) 375 (M^+, 21), 328 (12), 293 (2), 105 (100), 77 (25).

Anal. Calcd. for $C_{21}H_{14}ClN_3O_2$: C, 67.12; H, 3.75; N, 11.18. Found: C, 66.80; H, 3.80; N, 11.20.

6-Bromo-7,8-dimethyl-5-nitro-2,3-diphenylquinoxaline (**5d**).

This compound was obtained as light yellow crystals, yield 76%, mp 205.5-207.5°; ^{1}H nmr (deuteriochloroform): δ 2.71 and 2.92 (2 s, 3 H each, 7- and 8-Me), 7.30-7.60 (m, 10 H, 2- and 3-Ph); ms: m/z (% relative intensity) 433 (M^+, 14), 388 (4), 307 (11), 105 (100), 77 (24).

Anal. Calcd. for $C_{22}H_{16}BrN_3O_2$: C, 60.84; H, 3.71; N, 9.68. Found: C, 60.80; H, 3.68; N, 9.50.

7-Chloro-6-methyl-5-nitro-2,3-diphenylquinoxaline (**5e**).

This compound was obtained as light yellow crystals, yield 85%, mp 201-202°; ^{1}H nmr (deuteriochloroform): δ 2.59 (s, 3 H, 6-Me), 7.30-7.50 (m, 10 H, 2- and 3-Ph), 8.31 (s, 1 H, 8-H); ms: m/z (% relative intensity) 375 (M^+, 18), 358 (6), 328 (13), 105 (100), 77 (26).

Anal Calcd. for $C_{21}H_{14}ClN_3O_2$: C, 67.12; H, 3.75; N, 11.18. Found: C, 66.90; H, 3.40; N, 11.10.

2-Amino-3,5-dimethyl-7,8-diphenyl-1*H*-imidazo[4,5-*f*]quinoxaline (**6**).

Quinoxaline **5c** was treated with methylamine, reduced and cyclized with cyanogen bromide as previously [9] to give **6** in 72% overall yield, mp >300°; ^{1}H nmr (DMSO-d_6): δ 2.79 (s, 3 H, 5-Me), 3.66 (s, 3 H, 3-Me), 6.5 (br s, 2 H, NH_2), 7.3-7.5 (m, 10 H, 7- and 8-Ph), 7.75 (s, 1 H, 4-H); ms: m/z (% relative intensity) 365 (M^+, 100), 350 (3), 182 (13), 159 (35), 77 (11).

Anal. Calcd. for $C_{23}H_{19}N_5$: C, 75.59; H, 5.24; N, 19.16. Found: C, 76.00; H, 5.20; N, 19.00.

7,8-Dimethyl[1,2,5]selenadiazolo[3,4-*f*]quinoxaline (**7**).

Quinoxaline **4a** was treated with concentrated ammonia in a pressure bomb (110°, 3 hours) reduced with Raney nickel and hydrogen gas in ethanol and then cyclized with selenium dioxide as previously [3] to give **7** in 65% overall yield, mp 208-209°; ^{1}H nmr (deuteriochloroform): δ 2.78 and 2.86 (2 s, 3 H, 7- and 8-Me), 7.92 and 7.93 (ABq, 1 H, each, J = 9.7 Hz, 4- and 5-H); ms: m/z (% relative intensity) 264 (M^+, 100), 249 (5), 223 (24), 183 (92), 143 (30).

Anal. Calcd. for $C_{10}H_8N_4Se$: C, 45.64; H, 3.06; N, 21.29. Found; C, 45.60; H, 2.65; N, 21.25.

5-Methyl-2,3,8,9-tetraphenylpyrazino[2,3-*f*]quinoxaline (**8**).

Quinoxaline **5b** was treated with concentrated ammonia in a pressure bomb (110°, 3 hours) reduced with hydrogen and Raney nickel in ethanol as previously [9] and then treated with benzil to give **8** in 60% overall yield, mp 235.5-236.5°; ^{1}H nmr (deuteriochloroform): δ 2.99 (d, 3 H, J = 1.2 Hz, 5-Me), 7.30-7.40 and 7.60-7.80 (2 m, 20 H, 2-, 3-, 8- and 9-Ph), 8.21 (q, 1 H, J = 1.2 Hz, 6-H); ms: m/z (% relative intensity) 500 (M^+, 56), 397 (7), 279 (9), 250 (100), 242 (11).

Anal. Calcd. for $C_{35}H_{24}N_4$: C, 83.98; H, 4.83; N, 11.19. Found: C, 84.10; H, 4.70; N, 11.15.

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