2,3-Dichloro-1-alkylpyrazinium tetrafluoroborates: the synthesis and reactions with nucleophiles

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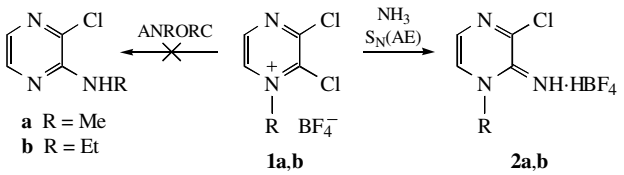
The alkylation of 2,3-dichloropyrazine with the Meerwein reagents $R_3O^+BF_4^-$ (R = Me or Et) afforded 1-alkyl-2,3-dichloropyrazinium tetrafluoroborates, which were transformed into mono- or disubstitution products, while the reaction of these salts with 1,4-N,X-dinucleophiles resulted in fused heterocyclic systems.

The structural modification of pyrazines is of great interest for chemists since their derivatives, including fused pyrazines, are biologically active compounds.[1–4] A common practice to modify the structure of pyrazines is the use of nucleophilic displacement reactions. In particular, nucleophilic substitution for chlorine atoms in 2,3-dichloropyrazine leading to fused pyrazines is well documented.[5,6] The *ortho*-cyclisation based on the diaddition of bifunctional nucleophiles at C-2 and C-3 (C-5 and C-6) carbon atoms in *N*-alkylpyrazinium salts also seems to be a promising synthetic approach to fused pyrazines.[7,8]

By the reactions of 2,3-dichloropyrazine with the Meerwein reagents $R_3O^+BF_4^-$ (R = Me or Et) in CH_2Cl_2 at 20 °C, we first prepared 1-alkyl-2,3-dichloropyrazinium tetrafluoroborates **1a**,**b** (Schemes 1 and 2). Salts **1a**,**b** were expected to be highly reactive towards nucleophiles. Indeed, they are rather sensitive to water; therefore, dry aprotic solvents (for instance, acetonitrile) are required for handling **1a**,**b** to avoid their transformations into the corresponding 1-alkyl-3-chloropyrazin-2-ones. Because of the high reactivity of salts **1a**,**b**, we failed to find an appropriate solvent for their recrystallisation and remove impurities from **1a**, whereas salt **1b** gave satisfactory elemental analysis data.†

We supposed that salts **1a**,**b** exhibit an ambident character in respect to either nucleophilic addition at C-5 (C-6) or displacement reactions at C-2 (C-3) carbons.

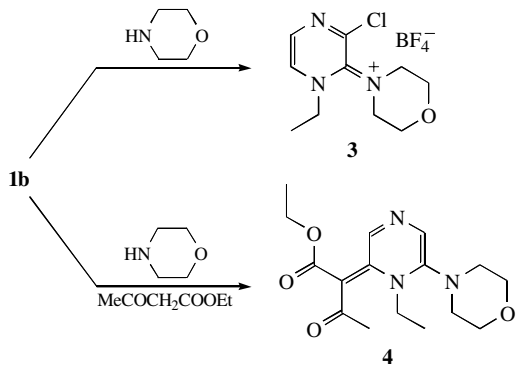
Compounds **1a**,**b** were found to react easily with ammonia in MeCN at 20 °C affording 1-alkyl-3-chloro-2-iminopyrazine hydrotetrafluoroborates **2a**,**b**. Unlike 2-chloropyrazine reacting with ammonia to 2-aminopyrazine exclusively *via* the ANRORC mechanism (the Addition of Nucleophile at C-6–Ring Opening–Ring Closure),[9] in the reactions of **1a**,**b** with ammonia the classical $S_N(AE)^{ipso}$ mechanism takes place, and no ANRORC products were observed (Scheme 1). This is evident from the ^1H and ^{13}C NMR spectra of 1-alkyl-3-chloro-2-iminopyraziniium



Scheme 1

† *2,3-Dichloro-1-ethylpyrazinium tetrafluoroborate* **1b**. Triethyloxonium tetrafluoroborate (1.9 g, 10 mmol) was added to a solution of 2,3-dichloropyrazine (1.4 g, 10 mmol) in 10 ml of CH_2Cl_2. The reaction mixture was stirred for 6 h at 20 °C. The crystals obtained were filtered off, washed with CH_2Cl_2 and dried in air to give 1.6 g (61%) of **1b**, mp 213–214 °C. ^1H NMR (CD_3CN) δ: 9.05 (br. d, 1H, 6-H, *J* 3.5 Hz), 8.83 (d, 1H, 5-H, *J* 3.5 Hz), 4.83 (q, 2H, NCH_2, *J* 6.3 Hz), 1.61 (t, 3H, Me, *J* 6.3 Hz). Found (%): C, 27.22; H, 2.80; N, 10.68. Calc. for $C_6H_7BCl_2F_4N_2$ (%): C, 27.21; H, 2.66; N, 10.58.

Compound **1a** was obtained analogously from 2,3-dichloropyrazine and trimethyloxonium tetrafluoroborate, yield 77%, mp 192–193 °C. ^1H NMR (CD_3CN) δ: 9.00 (br. d, 1H, 6-H, *J* 3.4 Hz), 8.80 (d, 1H, 5-H, *J* 3.4 Hz), 4.41 (s, 3H, NMe). Found (%): C, 23.00; H, 1.98; N, 10.49. Calc. for $C_5H_5BCl_2F_4N_2$ (%): C, 23.94; H, 2.01; N, 11.17.



Scheme 2

hydrotetrafluoroborates **2a**,**b**.‡ In particular, the signal of the NCH_2Me fragment in the ^1H NMR spectrum of **2b** is observed as a quartet at 4.19 ppm, while the methylene protons of the NCH_2Me group in 3-chloro-2-ethylaminopyrazine trifluoroacetate (reference compound) resonate at 3.45 ppm. Thus, the multiplicity of the C-6 resonance signal in the ^{13}C NMR spectrum (double doublet of triplets) with the coupling constants $^1J_{C\text{-}6,H\text{-}6}$ = 192.5 Hz, $^2J_{C\text{-}6,H\text{-}5}$ = 13.5 Hz and $^3J_{C\text{-}6,NCH_2}$ = 4.5 Hz provides unequivocal evidence for the structure of **2b**.

In a similar way the secondary morpholine reacts with 2,3-dichloropyrazinium salt **1b** to form monosubstitution product **3**§ (Scheme 2); only minor quantities of the corresponding disubstitution product were observed in the ^1H NMR spectra of the reaction mixtures. Note that, when the same reaction of **1b** with morpholine was carried out in the presence of an excess of ethyl acetoacetate, *tele*-substitution product **4** was isolated from the complex reaction mixture (Scheme 2).

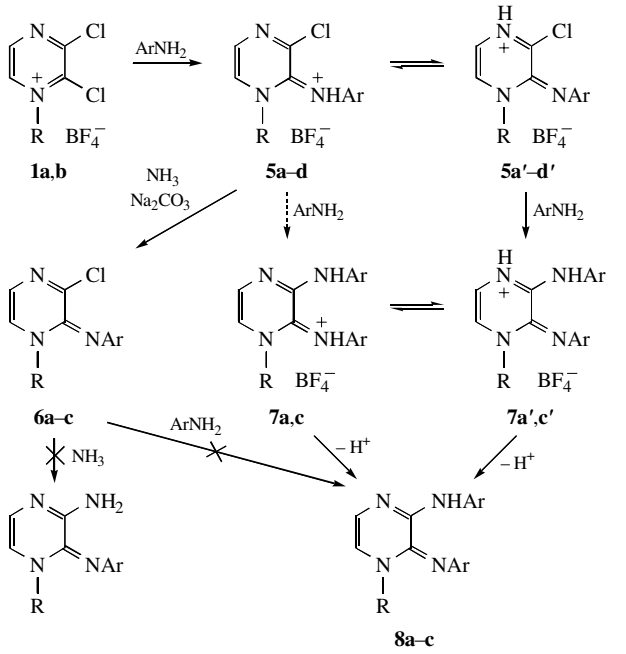
Although the yield of compound **4** was rather small (8%), a nucleophilic attack at the unsubstituted C-6 carbon resulting in the *tele*-substitution of a chloro atom at C-3 is a nice illustration of the ambident character of 1-alkyl-2,3-dichloropyrazinium salts. The structure of **4** was found by two-dimensional NMR. The

‡ *3-Chloro-1-ethylpyrazin-2-iminium tetrafluoroborate* **2b**. Ammonia was added to a solution of 2,3-dichloro-1-ethylpyrazinium tetrafluoroborate **1b** (0.300 g, 1.132 mmol) in 5 ml of MeCN. After stirring at room temperature for 10 min, the precipitated ammonium chloride was filtered off, followed by evaporation of the solvent. The residue was dissolved in MeCN and precipitated with diethyl ether to yield 3-chloro-1-ethylpyrazine-2-iminium tetrafluoroborate **2b**, 0.104 g (37%), mp 162–164 °C. ^1H NMR (CD_3CN) δ: 7.85 and 7.80 (2d, 2×1H, 6-H and 5-H, *J* 4.2 Hz), 6.5–9.0 (br. s, 2H, NH), 4.19 (q, 2H, NCH_2Me, *J* 7.3 Hz), 1.44 (t, 3H, NCH_2Me, *J* 7.3 Hz). ^{13}C NMR ([$^2H_6$]DMSO) δ: 146.64 (m, C-2), 140.31 (dd, C-3, $^3J_{C\text{-}3,H\text{-}5}$ 12.8 Hz, $^3J_{C\text{-}3,NH}$ 1.7 Hz), 130.60 (ddt, C-6, $^1J_{C\text{-}6,H\text{-}6}$ 192.5 Hz, $^2J_{C\text{-}6,H\text{-}5}$ 13.5 Hz, $^3J_{C\text{-}6,NCH_2}$ 4.5 Hz), 128.65 (dd, C-5, $^1J_{C\text{-}5,H\text{-}5}$ 197.9 Hz, $^2J_{C\text{-}5,H\text{-}6}$ 6.3 Hz), 50.21 (tq, NCH_2, ^1J 141.5 Hz, ^2J 4.3 Hz), 12.40 (qt, NCH_2Me, ^1J 129.5 Hz, ^2J 3.7 Hz). Found (%): C, 29.55; H, 3.95; N, 17.07. Calc. for $C_6H_9BClF_4N_3$ (%): C, 29.37; H, 3.70; N, 17.12.

Compound **2a** was obtained analogously from **1a** and ammonia; product **2a** was recrystallised from water. For **2a**: yield 83%, mp 148–149 °C. ^1H NMR (CD_3CN) δ: 7.84 and 7.77 (2d, 1H, 6-H and 5-H, *J* 4.2 Hz), 3.81 (s, 3H, NMe), 9.00–11.00 (br. s, 2H, NH). Found (%): C, 25.60; H, 3.32; N, 17.60. Calc. for $C_5H_7BClF_4N_3$ (%): C, 25.96; H, 3.05; N, 18.15.

signals in the ^{1}H and ^{13}C NMR spectra of **4**¶ were assigned on the basis of ^{1}H–^{13}C correlation spectroscopy, which also enabled us to establish the geometrical configuration of the ylidene substituent at C-2.

In the reactions of **1a**,**b** with arylamines in MeCN at 20 °C substitution of either one (**5a–d**, **6a–c**)†† or two (**7a–c**, **8a–c**)‡‡ chlorine atoms takes place (Scheme 3). In these transformations, proton transfer from the exocyclic amino group to N-4 of the pyrazine ring is an important step since the cationic structures like **5a–d** are undoubtedly more vulnerable for a nucleophilic attack at C-3 than the neutral species. Indeed, non-protonated iminopyrazine **6a–c** is unreactive towards arylamines and ammonia under similar conditions. A plausible way for substitution of the second chlorine atom at C-3 in protonated 2-iminopyrazines **5a–d** is presented in Scheme 3.



a R = Me, Ar = Ph
b R = Et, Ar = Ph
c R = Et, Ar = 4-MeOC$_6$H$_4$
d R = Me, Ar = 4-MeOC$_6$H$_4$

Scheme 3

The reactions of **1a**,**b** with 1,4-N,X-dinucleophiles, such as *ortho*-phenylenediamine and *ortho*-aminophenol, in MeCN at 20 °C result in the formation of N-alkyl derivatives of diazaphenazine and diazaphenoxazine in good yields (Scheme 4).§§ Contrary to that, 6,7-difluoro substituted 1-ethylquinoxalinium salts were found to react with bifunctional nucleophiles to give fused quinoxalines through the diaddition reaction at C-2 and C-3 carbons of the pyrazine ring instead of the replacement of two fluorine atoms.[10]

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§ *3-Chloro-1-ethyl-2-(morpholin-4-yl)pyrazinium tetrafluoroborate* **3**. Morpholine (0.260 ml, 3 mmol) was added dropwise to a solution of 2,3-dichloro-1-ethylpyrazinium tetrafluoroborate **1b** (0.396 g, 1.5 mmol) in 5 ml of MeCN. After stirring at room temperature for 10 min, the precipitated morpholine hydrochloride was filtered off, MeCN was evaporated, and the residue was recrystallised from propan-2-ol to yield 3-chloro-1-ethyl-2-(morpholin-4-yl)pyrazinium tetrafluoroborate **3**, 0.258 g (55%), mp 124–125 °C. ^{1}H NMR ([^{2}H$_6$]DMSO) δ: 8.72 and 8.63 (2d, 2×1H, 5-H and 6-H, J 3.9 Hz), 4.46 (q, 2H, NCH_2Me, J 7.2 Hz), 3.82 (t, 4H, CH_2OCH_2, J 4.8 Hz), 3.54 (t, 4H, CH_2NCH_2, J 4.8 Hz), 1.52 (t, 3H, Me, J 7.2 Hz). Found (%): C, 37.93; H, 4.69; N, 13.28. Calc. for $C_{10}H_{15}BClF_4N_3O$ (%): C, 38.07; H, 4.79, N, 13.32.

¶ *Ethyl 2-[1-Ethyl-6-(morpholin-4-yl)-1*H*-pyrazin-2-ylidene]-3-oxobutyrate* **4**. Morpholine (0.104 ml, 1.2 mmol) was added to a solution of ethyl acetoacetate (0.50 ml, 4 mmol) and 2,3-dichloro-1-ethylpyrazinium tetrafluoroborate **1b** (0.106 g, 0.4 mmol) in 5 ml of MeCN. After stirring at room temperature for 10 min, the precipitated morpholine hydrochloride was filtered off, and the solvent was evaporated to dryness. The residue was separated by column chromatography on silica gel first with acetone and then with methanol to collect an orange fraction. Methanol was evaporated, and the product was recrystallised from *n*-octane. Yield 0.010 g (8%), mp 130–132 °C. ^{1}H NMR ($CDCl_3$) δ: 8.74 (s, 1H, H-3), 7.74 (s, 1H, H-5), 4.38 (q, 2H, NCH_2, J 7.0 Hz), 4.21 (q, 2H, OCH_2, J 7.1 Hz), 3.87 (t, 4H, CH_2OCH_2, J 4.6 Hz), 3.22 (t, 4H, CH_2NCH_2, J 4.6 Hz), 2.47 (s, 3H, CO*Me*), 1.3–1.2 (m, 6H, 2Me). ^{13}C NMR ($CDCl_3$) δ: 190.28 (q, Me*C*O, ^2J 5.9 Hz), 167.78 (t, *C*OOCH$_2$, ^3J 3.1 Hz), 154.52 (m, C-2, $^2J_{C\text{-}2,H\text{-}3}$ 12.6 Hz, $^3J_{C\text{-}2,NCH_2}$ 3.6 Hz), 150.25 (dd, C-3, $^1J_{C\text{-}3,H\text{-}3}$ 199.6 Hz, $^3J_{C\text{-}3,H\text{-}5}$ 10.0 Hz), 149.19 (m, C-6, $^2J_{C\text{-}6,H\text{-}5}$ 7.7 Hz), 127.59 (m, C-5, $^1J_{C\text{-}5,H\text{-}5}$ 188.9 Hz, $^3J_{C\text{-}5,H\text{-}3}$ 12.7 Hz), 98.61 [s, (MeCO)(COOEt)*C*=], 66.16 (m, CH_2OCH_2, ^1J 138.2 Hz), 59.11 (m, OCH_2Me, ^1J 146.5 Hz, ^2J 4.4 Hz), 52.78 (t, NCH_2Me, ^1J 146.1 Hz), 51.32 [t, N$(CH_2)_2$, ^1J 138.4 Hz], 29.83 (q, CO*Me*, ^1J 127.8 Hz), 14.99 (qt, ^1J 128.9 Hz, ^2J 3.6 Hz) and 14.58 (qt, ^1J 126.6 Hz, ^2J 2.5 Hz) (OCH_2*Me* and NCH_2*Me*). Found (%): C, 59.76; H, 7.56; N, 13.00. Calc. for $C_{16}H_{23}N_3O_4$ (%): C, 59.80; H, 7.21; N, 13.01.

†† *3-Chloro-1-methylpyrazin-2-[(4-methoxyphenyl)iminium] tetrafluoroborate* **5d**. A solution of *para*-anizidine (0.098 g, 0.8 mmol) in 1.5 ml of MeCN was added to a solution of 2,3-dichloro-1-methylpyrazinium tetrafluoroborate **1a** (0.100 g, 0.4 mmol) in 1.5 ml of MeCN. The precipitate of *para*-anizidine hydrochloride obtained after stirring for 0.5 h was filtered off, the solvent was evaporated, and the residue was recrystallised from water to yield 1-methyl-3-chloropyrazine-2-(4-methoxyphenylimine) tetrafluoroborate, 0.116 g (86%), mp 129–130 °C. ^{1}H NMR ([^{2}H$_6$]DMSO) δ: 8.32 and 8.03 (2d, 2×1H, 5-H and 6-H, J 4.1 Hz), 7.10 (m, 4H, Ar), 3.84 and 3.81 (2s, 2×3H, NMe and OMe), 9–11 (br. s, 1H, NH). Found (%): C, 42.78; H, 3.71; N, 12.45. Calc. for $C_{12}H_{13}BClF_4N_3O$ (%): C, 42.72; H, 3.58; N, 12.45.

Compound **5c** was obtained analogously, yield 86%, mp 102 °C. ^{1}H NMR ([^{2}H$_6$]DMSO) δ: 8.32 and 8.0 (2d, 2×1H, 5-H and 6-H, J 4.0 Hz), 7.3–6.9 (m, 4H, Ar), 4.3 (q, 2H, NCH_2), 1.3 (t, 3H, Me). Found (%): C, 44.46; H, 4.36; N, 11.94. Calc. for $C_{13}H_{15}BClF_4N_3O$ (%): C, 44.42; H, 4.30; N, 11.95.

3-Chloro-1-methylpyrazin-2-phenylimine **6a**. A solution of aniline (0.018 g, 0.2 mmol) in 1.5 ml of MeCN was added to a solution of 2,3-dichloro-1-methylpyrazinium tetrafluoroborate **1a** (0.050 g, 0.2 mmol) in 1.5 ml of MeCN. The precipitate of aniline hydrochloride obtained after stirring for 0.5 h was filtered off, the solvent was evaporated, and the residue was recrystallised from aqueous 60% MeOH to yield 1-methyl-3-chloropyrazine-2-phenylimine **6a**, 0.017 g (39%), mp 106 °C. ^{1}H NMR ($CDCl_3$) δ: 7.1–6.7 (m, 7H, Ar, 5-H, 6-H), 3.42 (s, 3H, NMe). Found (%): C, 59.95; H, 4.39; N, 19.18. Calc. for $C_{11}H_{10}ClN_3$ (%): C, 60.14; H, 4.59; N, 19.13.

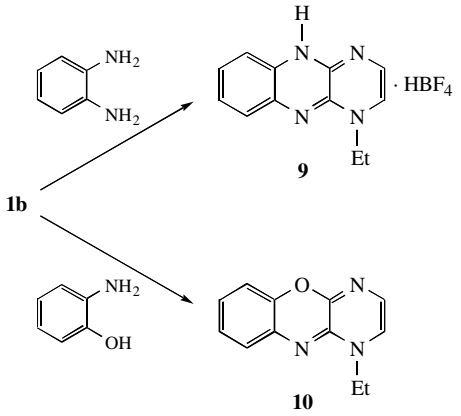
Compounds **6b**,**c** were prepared analogously. For **6b**: yield 75%, mp 64 °C. ^{1}H NMR ($CDCl_3$) δ: 7.10–6.7 (m, 7H, Ar, 5-H, 6-H), 3.91 (q, 2H, NCH_2, J 7.1 Hz), 1.362 (t, 3H, Me, J 7.1 Hz). Found (%): C, 61.43; H, 5.19; N, 17.77. Calc. for $C_{12}H_{12}ClN_3$ (%): C, 61.67; H, 5.18; N, 17.98.

For **6c**: yield 94%, mp 109 °C. ^{1}H NMR ($CDCl_3$) δ: 7.1–6.7 (m, 6H, Ar, 5-H, 6-H), 3.91 (q, 2H, NCH_2Me, J 7.1 Hz), 3.78 (s, 3H, OMe) 1.34 (t, 3H, NCH_2*Me*, J 7.1 Hz). Found (%): C, 58.93; H, 5.62; N, 15.93. Calc. for $C_{13}H_{14}ClN_3O$ (%): C, 59.21; H, 5.35; N, 15.93.

‡‡ *1-Ethyl-3-phenylaminopyrazin-2-phenylimine* **8b**. A solution of aniline (0.5 ml) in 3 ml of MeCN was added dropwise to a solution of 2,3-dichloro-1-ethylpyrazinium tetrafluoroborate **1b** (0.265 g, 1 mmol) in 4 ml of MeCN, and the reaction mixture was stirred for 0.5 h. The precipitate of aniline hydrochloride was filtered off, and the solvent was evaporated. The residue was recrystallised from water, washed with an aqueous Na_2CO_3 solution, and dried in air to give 0.266 g (91%) of 1-ethyl-3-phenylpyrazine-2-phenyliminium **8b**, mp 118–119 °C. ^{1}H NMR ($CDCl_3$) δ: 8.70 (s, 1H, NH), 7.7–6.3 (m, 12H, Ar, 5-H and 6-H), 3.69 (q, 2H, NCH_2Me, J 7.2 Hz), 1.11 (t, 3H, NCH_2*Me*, J 7.2 Hz). Found (%): C, 74.41; H, 6.17; N, 19.46. Calc. for $C_{18}H_{18}N_4$ (%): C, 74.46; H, 6.25; N, 19.30.

Compounds **8a**,**c** were obtained analogously. For **8a**: yield 83.6%, mp 122–123 °C. ^{1}H NMR ($CDCl_3$) δ: 8.90 (br. s, 1H, NH), 7.70–6.80 (m, 10H, Ar), 6.61 and 6.17 (2d, 2×1H, 5-H and 6-H, J 4.8 Hz), 3.06 (s, 3H, NMe). Found (%): C, 73.72; H, 6.24; N, 20.12. Calc. for $C_{17}H_{16}N_4$ (%): C, 73.89; H, 5.84; N, 20.27.

For **8c**: yield 73%, mp 126–127 °C. ^{1}H NMR ([^{2}H$_6$]DMSO) δ: 8.79 (s, 1H, NH), 7.70–6.30 (m, 10H, Ar, 5-H and 6-H), 3.75 (s, 3H, OMe), 3.74 (s, 3H, OMe), 3.52 (q, 2H, NCH_2Me, J 7.1 Hz), 1.11 (t, 3H, NCH_2Me, J 7.1 Hz). Found (%): C, 68.63; H, 6.39; N, 15.63. Calc. for $C_{20}H_{22}N_4O_2$ (%): C, 68.55; H, 6.33; N, 15.99.



Scheme 4

References

1 G. B. Barlin, in *The Chemistry of Heterocyclic Compounds*, eds. A. Wessberger and E. C. Taylor, Wiley Interscience, New York, 1982, vol. 41.

2 G. W. H. Cheesman and R. F. Cookson, in *The Chemistry of Heterocyclic Compounds*, eds. A. Wessberger and E. C. Taylor, Wiley Interscience, New York, 1979, vol. 35.

3 W. Kaim, *Angew. Chem*., 1983, **95**, 201.

4 J. A. Maga, *Food Rev. Int*., 1992, **8** (4), 479.

5 V. N. Charushin, M. G. Ponizovsky and O. N. Chupakhin, *Khim. Geterotsikl. Soedin*., 1985, 1011 [*Chem. Heterocycl. Compd*. (*Engl. Transl*.), 1985, **21**, 839].

6 C. O. Okafor, *J. Heterocycl. Chem*., 1981, **18**, 405.

7 V. N. Charushin, O. N. Chupakhin and H. C. van der Plas, *Adv. Heterocycl. Chem*., 1988, **43**, 301.

8 O. N. Chupakhin, V. N. Charushin and A. I. Chernyshev, *Prog. NMR Spectroscopy*, 1988, **20** (2), 95.

9 P. J. Lont, H. C. van der Plas and A. J. Verbeek, *Recl. Trav. Chim. Pays-Bas*, 1972, **91**, 949.

10 V. N. Charushin, G. A. Mokrushina, G. M. Petrova, G. G. Alexandrov and O. N. Chupakhin, *Mendeleev Commun*., 1998, 133.

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§§ *9-Ethyl-6,9-diazaphendiazine tetrafluoroborate* **9**. A solution of **1b** (0.265 g, 1.0 mmol) in 2 ml of MeCN was added to a solution of *ortho*-phenylenediamine (0.216 g, 2 mmol) in 1 ml of MeCN. After 0.5 h, the precipitate of *ortho*-phenylenediamine hydrochloride was filtered off, and the solvent was evaporated. The residue was recrystallised from isopropanol. Yellow crystals were filtered off and dried in air to give 9-ethyl-6,9-diazaphendiazine tetrafluoroborate **9**, 0.092 g (31%), mp 225 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 6.90–6.70 (m, 4H, Ar), 6.42 and 6.31 (2d, 2×1H, 6-H and 5-H, *J* 5.2 Hz), 3.67 (q, 2H, NC*H*$_2$Me, *J* 7.2 Hz), 1.30 (t, 3H, NCH$_2$*Me*, *J* 7.2 Hz). Found (%): C, 47.96; H, 4.39; N, 18.46. Calc. for $C_{12}H_{13}BF_4N_4$ (%): C, 48.03; H, 4.37; N, 18.67.

9-Ethyl-6,9-diazaphenoxazine **10**. A solution of *ortho*-aminophenol (0.218 g, 2 mmol) in 2 ml of MeCN was added to a solution of 2,3-dichloro-1-ethylpyrazinium tetrafluoroborate **1b** (0.530 g, 2 mmol) in 1 ml of MeCN. The solvent was evaporated, the residue was recrystallised from aqueous Na_2CO_3. The crystals were filtered off and dried in air to give 9-ethyl-6,9-diazaphenoxazine **10**, 0.376 g (88%), mp 108 °C. ^{1}H NMR ($CDCl_3$) δ: 6.74 (m, 4H, Ar), 6.22 and 6.13 (2d, 2×1H, 6-H and 5-H, *J* 4.7 Hz), 3.67 (q, 2H, NC*H*$_2$Me, *J* 7.1 Hz), 1.30 (t, 3H, NCH$_2$*Me*, *J* 7.1 Hz). Found (%): C, 67.35; H, 5.19; N, 19.44. Calc. for $C_{12}H_{11}N_3O$ (%): C, 67.59; H, 5.20; N, 19.71.