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Mendeleev Commun., 2011, **21**, 48–49
Mendeleev Communications

N-Fluoro derivatives of nitrated pyrazole-containing fused heterocycles

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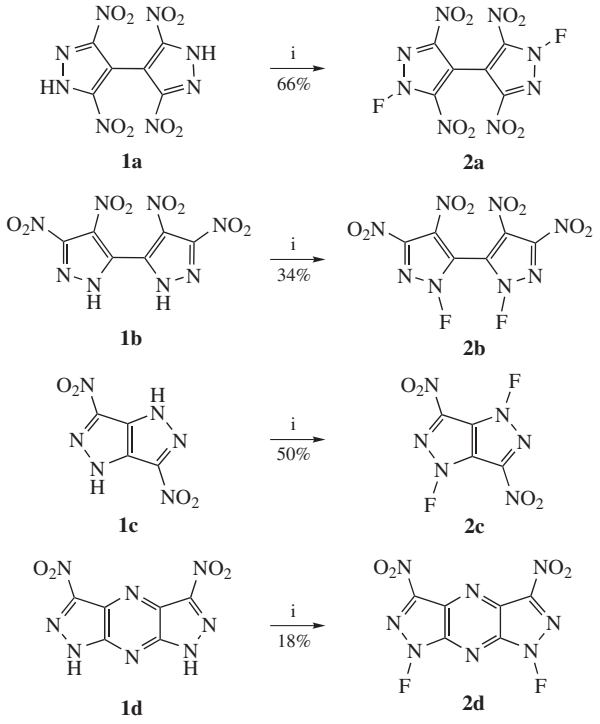
DOI: 10.1016/j.mencom.2011.01.020

N-Fluorination of Na-salts of polynitrated bipyrazoles and pyrazole-based fused heterocycles with fluorine–nitrogen mixture (10% F_2) at –60 to –70 °C in MeOH in the presence of NaF occurs regiospecifically at the nitrogen atom most distant from nitro groups.

Earlier we reported the synthesis of fully C-nitrated N-unsubstituted bipyrazoles **1a,b**,[1] pyrazolopyrazole **1c**[2] and dipyrazolopyrazine **1d**.[3]

This work aiming the N-fluorination of compounds **1a–d** is a continuation of our earlier studies[2–6] on functionalization of nitropyrazoles exploiting the reactivity of endocyclic NH group. According to quantum chemistry calculations,[7] *N*-fluoropyrazoles should be of interest as energetic materials. They also can be the promising electrophilic fluorinating reagents like *N*-fluoro-4,5-dinitroimidazole.[8] The synthetic approaches to *N*-fluoroazoles are scarce; the most efficient of them include direct fluorination of N anions of azoles with diluted F_2 or with $CsOSO_2F$ (CEFOX).[9]

We have found that interaction of Na-salts of compounds **1a–d** with excess of CEFOX in MeOH or MeCN at –30 to +20 °C did not lead to the desired N-fluoro derivatives even in small quantity. During these reactions the CEFOX was fully consumed and the reaction mixture grew acidic, presumably, due to interaction of CEFOX with solvent. As a result, nitropyrazolate anion transforms into unreactive H-form.



1a **2a** **1b** **2b** **1c** **2c** **1d** **2d**

Scheme 1 *Reagents and conditions*: NaOH/NaF, then F_2 (10%)/N_2, –60 to –70 °C, 2 h.

Fluorination of Na-salts of **1a–d** with 10% F_2/N_2 led to *N*-fluoropolynitrobipyrazoles **2a–d** (Scheme 1).† To minimize the side processes, including the acidifying of the reaction mixture, the fluorination should be performed by passing the 10% F_2/N_2 mixture through the MeOH solution of the reactant at –60 to –70 °C in the presence of NaF serving as the scavenger of the HF formed.

The structures of all products were established based on ^{13}C (TMS), ^{14}N ($MeNO_2$), ^{19}F ($CFCl_3$) NMR and IR spectra. The composition was confirmed by elemental analysis data. In all cases the reactions proceed regiospecifically, *e.g.*, the fluorination of substrates **1b–d** occurs only at the nitrogen atom most distant from the nitro group.

† *Synthesis of* N-*fluoropyrazoles* **2a–d** *(general procedure)*. Sodium fluoride (20 mmol) and the appropriate nitropyrazole **1a–d** (1 mmol) were added to a solution of NaOH (2.2 mmol) in MeOH (30 ml). After stirring for 20 min, the reaction mixture was cooled down (–60 to –70 °C) and then the mixture of F_2 (10 %) in N_2 was slowly (2 h) passed through the suspension of Na-salt of pyrazole. Then temperature was raised up, the solvent was removed *in vacuo*, the residue was extracted with hot 1,2-dichloroethane. The organic layer was dried with $MgSO_4$, and the solvent was removed *in vacuo*. The residue was crystallized from $CHCl_3$ in case of **2a** or chromatographed on silica (eluent $CHCl_3$) in case of **2b–d**.

*1,1′-Difluoro-3,3′,5,5′-tetranitro-1*H,*1′*H-*4,4′-bipyrazole* **2a**: yield 66%, mp 180 °C, $T_{decomp.}$ 190 °C. ^{19}F NMR ($CDCl_3$) δ: 20.92 (N–F). ^{13}C NMR (acetone-d_6) δ: 141.83 (C^3), 134.84 (d, C^5, ^2J 7.6 Hz), 100.72 (dd, C^4, ^3J 13.0 Hz, ^4J 1.4 Hz). ^{14}N NMR (acetone-d_6) δ: –40.23 (5-NO_2), –31.61 (3-NO_2). IR (KBr, ν/cm^{-1}): 1564, 1492, 1324 (C–NO_2); 872, 776 (N–F). Found (%): C, 21.03; F, 10.64; N, 31.70. Calc. for $C_6F_2N_8O_8$ (%): C, 20.58; F, 10.85; N, 32.01.

*1,1′-Difluoro-3,3′,4,4′-tetranitro-1*H,*1′*H-*5,5′-bipyrazole* **2b**: yield 34%, mp 164 °C, $T_{decomp.}$ 192 °C. ^{19}F NMR ($CDCl_3$) δ: 18.68 (N–F). ^{13}C NMR (acetone-d_6) δ: 139.77 (C^3), 127.30 (d, C^4, ^3J 11.2 Hz), 114.33 (dd, C^5, ^2J 2.2 Hz, ^3J 2.7 Hz). ^{14}N NMR (acetone-d_6) δ: –35.31 (NO_2). IR (KBr, ν/cm^{-1}): 1572, 1552, 1352, 1320 (C–NO_2); 880, 824, 776 (N–F). Found (%): C, 20.87; F, 10.60; N, 31.35. Calc. for $C_6F_2N_8O_8$ (%): C, 20.58; F, 10.85; N, 32.01.

*1,4-Difluoro-3,6-dinitropyrazolo[4,3-*c*]pyrazole* **2c**: yield 50%, $T_{decomp.}$ 177 °C. ^{19}F NMR ($CDCl_3$) δ: 16.58 (N–F). ^{13}C NMR (acetone-d_6) δ: 131.60 (C^3), 127.27 (C^4=C^5). ^{14}N NMR (acetone-d_6) δ: –33.61 (NO_2). IR (KBr, ν/cm^{-1}): 1556, 1382 (C–NO_2); 864, 824, 744 (N–F). Found (%): C, 21.03; F, 16.39; N, 36.28. Calc. for $C_4F_2N_6O_4$ (%): C, 20.52; F, 16.23; N, 35.90.

*1,7-Difluoro-3,5-dinitropyrazolo[3,4-*b*:4′,3′-*e*]pyrazine* **2d**: yield 18%, mp 132 °C (decomp.). ^{19}F NMR (acetone-d_6) δ: 16.70 (N–F). ^{13}C NMR (acetone-d_6) δ: 137.19 (d, C^3, ^3J 5.7 Hz), 135.17 (d, C^5, ^2J 7.8 Hz), 126.86 (d, C^4, J 12.5 Hz). ^{14}N NMR (acetone-d_6) δ: –32.67 (NO_2). IR (KBr, ν/cm^{-1}): 1560, 1388 (C–NO_2); 869, 830, 744 (N–F). Found (%):C, 25.64; F, 13.70; N, 42.05. Calc. for $C_6F_2N_8O_4$ (%): C, 25.19; F, 13.28; N, 39.16.

The special characteristics of new compounds[4] are signals at 16–20 ppm in the ^{19}F NMR spectra as well as the presence of spin-coupling constant $^{3}J_{C–F}$ 10–13 Hz for C^4 atoms in the ^{19}F NMR spectra. In addition to the NO_2 bands in IR spectra of products **2a**–**d**, the bands at 880–770 cm^{-1} typical[4] of N–F bond are found.

All new compounds are quite stable under ambient conditions, but they are highly sensible to the external stimuli (strike, friction). Since this, the work with such substances should be done according to the special safety regulations (*cf*. ref. 4).

In conclusion, a useful method of synthesis of bi- or tricyclic *N*-fluoropyrazoles has been elaborated.

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Received: 12th July 2010; Com. 10/3564