Syntheses based on (*N*,*N*-difluoroamino)dinitroacetonitrile

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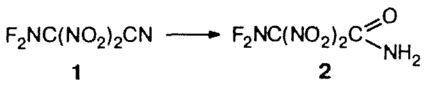
High reactivity of the nitrile group in (*N*,*N*-difluoroamino)dinitroacetonitrile was demonstrated. Based on its reaction with HN_3, a new preparative method for the synthesis of 5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazole was developed; some derivatives of the latter compound have been obtained.

Key words: reactivity, synthesis, (*N*,*N*-difluoroamino)dinitroacetonitrile, 5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazole.

(*N*,*N*-Difluoroamino)dinitroacetonitrile (**1**)[1] is a highly energetic compound[2] and is of interest as a polyfunctional synthon.

Nitrile **1** is miscible with N_2O_4 and almost does not react with it; it is virtually insoluble in H_2O, H_2SO_4, FSO_3H, or conc. HCl and almost does not change when kept with acids at 20 °C for 3—5 days without stirring. However, nitrile **1** can be hydrated to the corresponding amide (**2**) by intense stirring in 98 % H_2SO_4 at 20—47 °C, or by treatment with an equivalent amount of H_2O in Et_2O saturated with HCl at −10 to 0 °C (Scheme 1).

Scheme 1



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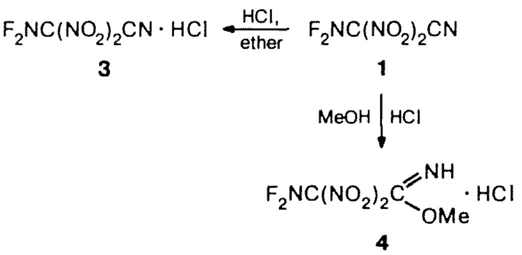
In both cases, the yield of the amide does not exceed 30—35 %, which is apparently due to destructive side processes.

In anhydrous ether saturated with dry HCl, nitrile **1** is converted into highly hygroscopic crystals of an adduct of **1** with HCl (**3**), whereas in the presence of anhydrous MeOH, the imidate hydrochloride (**4**) is formed (Scheme 2).

Scheme 2



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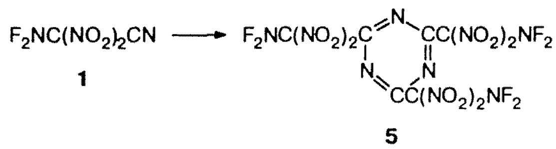
Compound **4** is relatively unstable; in some cases, during its isolation from solutions by evacuation, the residue exploded.

We studied the possibility of trimerization of nitrile **1** under the action of dry HCl, an alcoholic solution of HCl, or catalytic amounts of BF_3, $AlCl_3$, AlF_3, $ZnCl_2$, or $POCl_3$. The best results were obtained by prolonged maintenance in the cold of ethereal solutions of nitrile **1** in the presence of ethanolic solutions of HCl or solutions of BF_3 in $CHCl_3$ (Scheme 3).

Scheme 3



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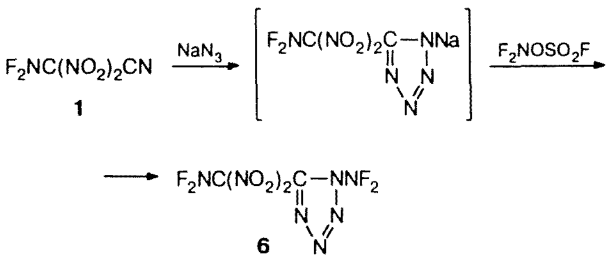
However, the reproducibility of these experiments is quite low, and the yields of triazine **5** are 1—30 %.

When we attempted to obtain 1-*N*,*N*-difluoroamino-5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazole (**6**) without isolation of the intermediate salt (Scheme 4), an extremely explosive liquid was isolated by distillation under a high vacuum (0.01 Torr), which could not be

Scheme 4



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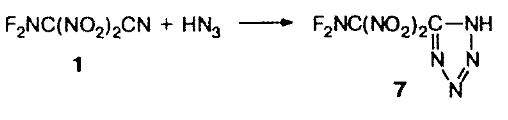
analyzed, because it exploded upon contact with a capillary.

Later we found that nitrile **1** reacts with HN_3 in ether (but not in CH_2Cl_2) at ~20 °C giving 5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazole (**7**) in an almost quantitative yield (Scheme 5).

Scheme 5



Such high activity of nitriles with respect to HN_3 was not observed in previous studies.[3,4] When tetrazole **7** is stored without a solvent, the evolution of gaseous products is observed after 1.5—2 weeks, and a new signal arises in its ^{19}F NMR spectrum at −106.5 ppm in addition to the signal at −121 ppm, which is due to compound **7**. In an ethereal solution, compound **7** is stable over a period of several months.

When tetrazole **7** was treated with an ethereal solution of CH_2N_2, the 2-methyl derivative (**8**) was obtained containing a minor amount of the 1-methyl derivative (ratio 16 : 1, according to ^1H NMR). The ammonium salt (**9**) and hydrazinium salts (**10** and **11**) were synthesized from tetrazole **7** (Scheme 6).

The crystalline compounds, namely the substituted tetrazole **8** and the ammonium salt **9**, are fairly stable during storage, whereas the liquid salts of hydrazine **10** and **11** are relatively unstable and slowly decompose with evolution of gaseous products and formation of a solid incombustible residue.

Salt **9** (m.p. 131—132 °C, flash point 135 °C) is readily soluble in H_2O, EtOH, Et_2O, Me_2CO, and MeCN and is insoluble in CH_2Cl_2, CCl_4, or Freons. It is highly sensitive to external influences; during evacuation of ethereal solutions, the residue, as a rule, explodes. Salt **9** can be isolated only when tetra- or pentachloroethane is added to its solution prior to evacuation.

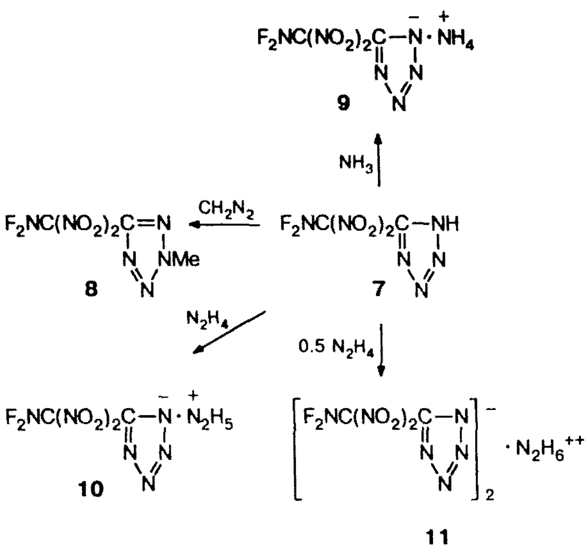
The properties of the compounds obtained are presented in Table 1.

Experimental

Warning. Compounds **1**—**11** are very sensitive to external influences and handling them requires the corresponding precautions.

(*N*,*N*-Difluoroamino)dinitroacetamide (2). (*N*,*N*-Difluoroamino)dinitroacetonitrile (**1**) (1 g, 5.5 mmol) was added dropwise at 20 °C to an intensely stirred 98 % H_2SO_4 (15 g). The mixture was stirred for 1 h, then the temperature was raised to 47 °C over a period of 2 h, and the mixture was kept at this temperature over a period of 4 days. Then it was evacuated under 1 Torr for 5 h, and cooled to 2—3 °C. Ice water (20 mL) was added to it dropwise. The product was extracted with CH_2Cl_2 (3×25 mL), and the extract was washed with 50 mL of ice water, dried with $MgSO_4$, and concentrated *in vacuo* to give 0.36 g (33 %) of colorless crystals of **2** (m.p. 86 °C).

Scheme 6



Methyl (*N*,*N*-difluoroamino)dinitroacetimidate hydrochloride (4). At 0—15 °C, HCl was passed for 4 days through a solution containing (*N*,*N*-difluoroamino)dinitroacetonitrile (**1**) (8.4 g, 46 mmol) and anhydrous MeOH (1.5 g, 46 mmol) in 30 mL of anhydrous ether. Half of the resulting mixture was separated from the precipitate (mostly NH_4Cl) and concentrated under a vacuum varying from 100 to 10 Torr. The residue consisted of 0.3 g (~5 %) of a colorless highly hygroscopic solid, m.p. 112 °C (decomp.). In an attempt to remove the solvent from the other half of the mixture, the residue exploded.

Adduct ol (*N*,*N*-difluoroamino)dinitroacetonitrile with HCl (3) was obtained under the conditions of the previous procedure, but without MeOH. Yield ~7 %, m.p. 84 °C.

1,3,5-Tris[*N*,*N*-(difluoroamino)dinitromethyl]-*symm*-triazine (5). At −20 °C, dry gaseous HCl (0.4 L) was slowly introduced into a mixture of (*N*,*N*-difluoroamino)dinitroacetonitrile (**1**) (3 g, 16.5 mmol), anhydrous ether (7 mL), and MeOH (0.53 g, 16.6 mmol). The mixture was kept with exclusion of moisture for 5 days at −78 °C, for 2 days at 0 °C, and for 3 days at ~20 °C. The precipitate was separated and washed with ether, and the filtrate was concentrated under a vacuum of 15 to 1 Torr to give 0.8 g (27 %) of a very viscous liquid, which crystallized upon standing, m.p. 55—56 °C.

5-[(*N*,*N*-Difluoroamino)dinitromethyl]tetrazole (7). (*N*,*N*-Difluoroamino)dinitroacetonitrile (**1**) (2.7 g, 14.8 mmol) was added dropwise to a solution of HN_3 (0.86 g, 20 mmol) in 25 mL of ether (an exothermal reaction). The mixture was kept for 2 days at 20 °C with exclusion of moisture and concentrated *in vacuo* under a pressure of 10 to 15 Torr and then under 10^{-3} Torr to give 3.2 g (97 %) of a very viscous colorless liquid, which crystallized upon standing, m.p. 58—60 °C.

5-[(*N*,*N*-Difluoroamino)dinitromethyl]-2-methyltetrazole (8). An ethereal solution of CH_2N_2 was added dropwise to a solution of tetrazole **7** (1.2 g, 5.3 mmol) in 2 mL of ether until a yellow color persisted. The mixture was kept for 12 h and concentrated under a vacuum of 10 to 15 Torr and then

Table 1. Characteristics of the compounds synthesized

Compound	M.p. /°C	IR, ν/cm^{-1}	^{19}F NMR, δ (CF_3COOH as the external standard)	Found/Calculated (%)				Molecular formula
				C	H	F	N	
2	86	3450 (NH); 1717 (CO); 1598, 1340 (NO_2); 1015, 945 (NF)	−120	12.24 12.00	0.81 1.00	18.80 19.00	27.94 28.00	$C_2H_2F_2N_4O_5$
3*	84	—	—	11.10 10.90	0.61 0.45	17.34 17.39	25.41 25.63	$C_2F_2N_4O_4 \cdot HCl$
4**	112	—	—	14.83 14.33	2.16 1.99	15.35 15.17	22.23 22.35	$C_3H_5ClF_2N_4O_5$
5	55—56	1550 (*symm*-triazine); 1598, 1295, 817 (NO_2); 1018, 945 (NF)	−125	13.04 13.19	—	20.43 20.88	30.55 30.77	$C_6F_6N_{12}O_{12}$
7	58—60	3105 (N—H); 1600, 1377 (NO_2); 1288, 1044 (tetrazole); 945, 908 (NF)	−121.5	11.26 10.67	1.04 0.44	17.42 16.89	42.95 43.56	$C_2HF_2N_7O_4$
8***	49—50	2990—2860 (CH); 1612, 1266 (NO_2); 1299 (tetrazole); 945, 914 (NF)	−118.5	15.28 15.06	1.17 1.25	15.46 15.90	41.36 41.00	$C_3H_3F_2N_7O_4$
9	130—132	3300—2800 (NH); 1608—1595, 1300 (NO_2); 1040 (tetrazole); 945, 920, 900 (NF)	−118.5	9.77 9.92	1.49 1.65	15.65 15.70	46.09 46.28	$C_2H_4F_2N_8O_4$
10	Oil	—	−121	9.17 9.34	2.03 1.94	14.61 14.78	49.27 49.03	$C_2H_5F_2N_9O_4$
11	Oil	—	−121	9.77 9.96	1.32 1.24	15.71 15.77	46.12 46.47	$C_4H_6F_4N_{16}O_8$

* Found (%): Cl, 18.31. Calculated (%): Cl, 18.25. ** Found (%): Cl, 14.78. Calculated (%): Cl, 14.17. *** ^{1}H NMR, δ: 4.60 (s, HMDS); contains ~6.2 % 1-methyl-5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazole, ^{1}H NMR, δ: 4.33 (t, HMDS), J_{HF} = 0.7 Hz.

under 10^{-3} Torr to give 1.2 g (98 %) of a viscous colorless liquid, which crystallized upon standing, m.p. 49—50 °C.

Ammonium salt of 5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazole (9). NH_3 (0.15 L) was slowly passed through a solution of tetrazole **7** (1.4 g, 6.2 mmol) in 25 mL of anhydrous ether. Tetrachloroethane (4 mL) was added to the mixture, the precipitate was separated, and the filtrate was concentrated *in vacuo*. The residue was dissolved in 8 mL of anhydrous ether, the precipitate was separated, the filtrate was diluted with 50 mL of anhydrous CH_2Cl_2, and the precipitate was separated and washed with 10 mL of CH_2Cl_2 to give 1.5 g (~100 %) of colorless crystals, m.p. 130—132 °C.

Monohydrazinium salt of 5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazole (10). A solution of N_2H_4 (0.228 g, 7.12 mmol) in a mixture of MeOH (3 mL) and H_2O (0.5 mL) was added with intense stirring to a solution of tetrazole **7** (1.6 g, 7.12 mmol) in 15.6 mL of anhydrous ether and 5 mL of tetrachloroethane. The solvent (10 mL) was evaporated *in vacuo* and the residue was kept for 10 h under 0.5—1 Torr to give 1.8 g of a viscous yellowish oil, which permanently evolved gas bubbles.

Hydrazinium bis{5-[(*N*,*N*-difluoroamino)dinitromethyl]tetrazolide} (11) was obtained under the conditions described in the following procedure, yellowish oil, d_4^{20} 2.001.

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