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Reactions of (difluoroamino)trinitromethane with nucleophilic reagents

***G. Kh. Khisamutdinov*[a]* *and S. A. Shevelev*[b]**

[a]*State Research Institute "Kristall",*
6 ul. Zelenaya, 606007 Dzerzhinsk, Nizhnii Novgorod Region, Russian Federation.
Fax: +7 (831 2) 54 6501
[b]*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
47 Leninsky prosp., 119992 Moscow, Russian Federation.
Fax: +7 (095) 135 5328

Reactions of $F_2NC(NO_2)_3$ with metal fluorides (KF and CsF) in DMF yield a substitution product of the fluorine atom for one nitro group, $F_2NC(NO_2)_2F$. The reaction of $F_2NC(NO_2)_3$ with LiBr in ethanol or DMF affords $Br(NO_2)C{=}NF$ rather than the expected bromo derivative $F_2NC(NO_2)_2Br$.

Key words: (difluoroamino)trinitromethane, (difluoroamino)fluorodinitromethane, bromonitro(*N*-fluoroimino)methane, substitution reaction.

In continuation of the investigations on the reactions of polynitromethanes with nucleophiles,[1—7] we studied the reactions of (difluoroamino)trinitromethane (**1**) with fluoride and bromide ions.

The known reactions of $C(NO_2)_4$ and $XC(NO_2)_3$ (X = F, Cl, and Br) with halide and azide ions afford products in which one nitro group is replaced by the halogen atom[1—6] and by the azido group.[1,6,7] In reactions of (difluoroamino)polynitroalkanes, including compound **1**, with the azide ion it is the difluoroamino group rather than the nitro group that is replaced.[6]

Results and Discussion

We found that the direction of the reaction of compound **1** with nucleophilic reagents depends on their nature. Thus the reaction of **1** with metal fluorides (KF or CsF) in anhydrous DMF yields (difluoroamino)fluorodinitromethane (**2**), *i.e.*, a substitution product of the fluorine atom for the nitro group (Scheme 1), as is the case of other polynitromethanes.[1—3] So far this reaction remains the only one method for the preparation of compound **2**.

Scheme 1

$$\underset{\mathbf{1}}{F_2NC(NO_2)_3} + F^- \longrightarrow \underset{\mathbf{2}}{F_2NC(NO_2)_2F} + NO_2^-$$

The yield of compound **2** depends on the nature of metal fluoride. Under the same conditions, its yield varies from ~9% with KF to 40% with CsF, compound **1** being completely converted.

A relatively low yield of **2** is probably due to the reaction of the nitrite ion with the starting compound **1**, which is typical of polynitroalkanes (Scheme 2).[5,8,9]

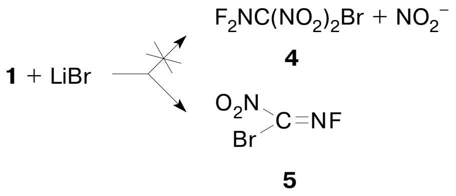
Scheme 2

$$\mathbf{1} + NO_2^- \longrightarrow \underset{\mathbf{3}}{F_2NC(NO_2)_2^-} + N_2O_4$$

Like other polynitromethane anions,[5] anion **3** decomposes in DMF to nitrogen oxides and other gases, which was observed experimentally.

The reaction of **1** with LiBr in ethanol or anhydrous DMF in the presence of CH_2Cl_2 at 30—35 °C unexpectedly did not yield the bromo derivative (**4**), giving bromonitro(*N*-fluoroimino)methane (**5**) (Scheme 3).*

Scheme 3



A pathway of the formation of compound **5** involves nucleophilic substitution of the bromine atom for the nitro group in compound **1** under the action of the bromide ion to give product **4**, which undergoes bromide-induced redox decomposition, like bromotrinitromethane,[5] to form unstable anion **3**. Elimination of the fluoride ion from **3** gives *N*-fluoroiminodinitromethane (**6**) and is followed by replacement of one nitro group by the bromine atom. Similar substitution reactions at a trigonal carbon atom bound to strong electron-acceptor

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* In the absence of CH_2Cl_2, the reaction proceeds very vigorously and is accompanied by a sharp increase in temperature. The resulting products are difficult to separate. According to the GLC data, compound **5** is also present in the mixture.

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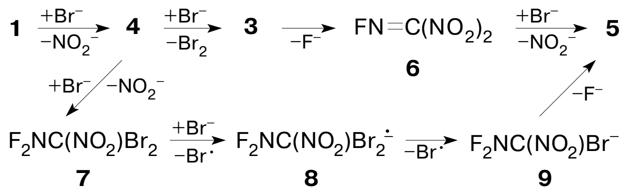
groups are well known (*cf.* reactions of phosgene, thiophosgene, and benzoyl- and *m*-nitrobenzohydroximoyl halides[10] with nucleophiles).

Alternatively, the reaction pathway can include two-step nucleophilic substitution of the bromine atom for the nitro group in compound **1** under the action of the bromide ion, which gives intermediate **4** and then dibromo(difluoroamino)nitromethane (**7**), which is similar to the formation of dibromodinitromethane from tetranitromethane;[5] a single-electron transfer from the bromide ion to compound **7** and generation of a radical anion of dibromo(difluoroamino)nitromethane (**8**); its decomposition into the bromo(difluoroamino)nitromethane anion (**9**) and a bromine radical, as in the formation and decomposition of the radical anion of chlorofluorodinitromethane into anion **3** and a chlorine radical;[11] and the decomposition of anion **9** into product **5** and the fluoride ion (Scheme 4).

Scheme 4



Experimental

KF, CsF, LiBr, and DMF of "chemically pure" grade were used. KF, CsF, and LiBr were ground and calcined in a glass reaction vessel equipped with a magnetic stirrer, thermometer, and a dropping funnel *in vacuo* (10 Torr) at 300 °C for 2 h prior to each experiment; after cooling to ~20 °C, anhydrous DMF was added from the dropping funnel (DMF was dried over molecular sieves for 10 days).

IR spectra were recorded on a UR-10 instrument in a thin film between germanium plates. ^{19}F NMR spectra were recorded on a Varian DP-60 instrument (56.4 MHz) with CF_3COOH as the external standard.

GLC analysis was carried out on an LKhM-8 chromatograph with a katharometer (column length 3.3 m, QF fluorosilicon (10%) on Chromosorb P (150—200 mesh) as the stationary phase, helium as the carrier gas, temperature 53 °C).

(Difluoroamino)fluorodinitromethane (2). A solution of compound **1** (20.2 g, 0.1 mol) in 10 mL of anhydrous DMF was added dropwise with stirring to a freshly prepared (see above) and cooled (10 °C) suspension of CsF (20 g, 0.11 mol) in 30 mL of anhydrous DMF over ~30 min (the reaction temperature was maintained below 50—55 °C because the reaction is highly exothermic and is accompanied by evolution of nitrogen oxides and other gases). The reaction mixture was stirred at 50—55 °C for 2.5 h, cooled to 10 °C, and poured into 400 mL of ice water. The oily product that formed was separated from the aqueous layer (the latter was retained), washed with water (3×10 mL), dried with $MgSO_4$, and distilled. The yield of product **2** was 5 g, b.p. 54—55 °C (760 Torr), m.p. −85 °C, n_D^{20} 1.3515, d_4^{20} 1.5925, purity ~99% (GLC). Found (%): C, 6.83; F, 32.73. $CF_3N_3O_4$. Calculated (%): C, 6.85; F, 32.56. Molecular mass, found (cryoscopic measurements in nitrobenzene): 185. Calculated: 175. IR, ν/cm^{-1}: 803, 1303, 1630 ($FC(NO_2)_2$); 683, 933 and 955 (NF_2). ^{19}F NMR, δ: −105 (br.s, NF_2); +33.8 (quint, C—F). The organic material was extracted from the aqueous layer (see above) with chlorobenzene (3×30 mL), and the extracts were combined, washed with water (2×30 mL), and dried with $MgSO_4$. Twofold distillation additionally gave product **2** (2 g), b.p. 55—56 °C (765 Torr). The total yield of **2** was 40%. In the case of KF, the yield of product **2** was 9%.

Bromonitro(*N*-fluoroimino)methane (5). A solution of compound **1** (4.04 g, 0.02 mol) in 10 mL of CH_2Cl_2 was added with stirring and cooling with ice water to a solution of freshly calcined LiBr (6.95 g, 0.08 mol) in 30 mL of 96% EtOH over 15 min, so that the reaction temperature was 25—30 °C (the reaction is extremely exothermic, and the solution turns red-brown). The reaction mixture was stirred at 30—35 °C for 2.5 h, cooled to 10 °C, and poured into 200 mL of ice water. The organic layer was separated, and the products were extracted from the aqueous layer with CH_2Cl_2 (2×30 mL). The organic layers were combined, washed with 2% Na_2CO_3 (40 mL) and water (2×40 mL), and dried with $MgSO_4$. Dichloromethane was distilled under atmospheric pressure using a fractionating column, and the residue was distilled twice to give a light yellow liquid. The yield of product **5** was 0.9 g (26.5%), b.p. 101.5—103.0 °C (760 Torr), purity ~98% (GLC, the product contains up to 2% of CH_2Cl_2). Found (%): F, 11.02; Br, 45.88; N, 14.86. $CFBrN_2O_2$. Calculated (%): F, 11.12; Br, 46.75; N, 16.39. IR, ν/cm^{-1}: 796 (C—Br); 966, 1025 (=NF); 1316 and 1576 (NO_2); 1730 (C=N). The CH_2Cl_2 that distilled contains product **5** and trace amounts of the starting compound **1**. The reaction in anhydrous DMF in the presence of CH_2Cl_2 gave product **5** in 21.6% yield.

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