## Interaction of polynitro compounds with difluoroamine

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Difluoroamine does not react with tetranitromethane and fluoro-, chloro-, and bromotrinitromethanes in DMF and in acidic media (CF<sub>3</sub>COOH, ClSO<sub>3</sub>H, FSO<sub>3</sub>H, and oleum), but reacts with  $\alpha$ -fluoro- and  $\alpha$ -(difluoroamino)- $\alpha$ , $\alpha$ -dinitrotoluenes to give substitution products of the difluoroamino group for both the nitro groups, viz., PhC(NF<sub>2</sub>)<sub>2</sub>F and PhC(NF<sub>2</sub>)<sub>3</sub>, respectively.

Key words: tetranitromethane, fluoro-, chloro-, and bromotrinitromethanes,  $\alpha, \alpha$ -dinitro-  $\alpha$ -fluoro- and  $\alpha, \alpha$ -dinitro- $\alpha$ -(difluoroamino)toluenes,  $\alpha, \alpha$ -bis(difluoroamino)- $\alpha$ -fluorotoluene,  $\alpha, \alpha, \alpha$ -tris(difluoroamino)toluene, difluoroamine, difluoroamination.

In continuation of our studies of reactions of polynitroalkanes with nucleophiles, 1-4 we investigated the reaction of polynitro compounds with difluoroamine.

Earlier, similar reaction has been described only for 2-chloro- (1a) and 2-bromo-2,4,4-trinitropentane (1b). This resulted in dimethylisoxazole (2) (yield 26-34%) and a product of replacement of the halogen and the nitro groups by the difluoroamino group (3) (yield 5-8%).<sup>5</sup>



X = Cl(a), Br(b)

We found that  $C(NO_2)_4$ ,  $FC(NO_2)_3$ ,  $CIC(NO_2)_3$ , and  $BrC(NO_2)_3$  do not react with difluoroamine in DMF and in acidic media (CF<sub>3</sub>COOH, FSO<sub>3</sub>H, CISO<sub>3</sub>H, and oleum).  $\alpha$ -Fluoro- $\alpha$ , $\alpha$ -dinitro- (4a) and  $\alpha$ -(difluoroamino- $\alpha$ , $\alpha$ -dinitro)toluene (4b) smoothly react in acidic media with difluoroamine to give products of replacement of both the nitro groups by the difluoroamino group, *viz.*,  $\alpha$ , $\alpha$ -bis(difluoroamino)- $\alpha$ fluorotoluene (5a) in 92% yield (with respect to consumed 4a) and  $\alpha$ , $\alpha$ , $\alpha$ -tris(difluoroamino)toluene (5b) in 8% yield in the case of 50% and 100% conversion of 4a and 4b, respectively. PhC(NO<sub>2</sub>)<sub>2</sub>X + 2 HNF<sub>2</sub> ----- PhC(NF<sub>2</sub>)<sub>2</sub>X + 2 HNO<sub>2</sub> 4a,b 5a,b  $X = F(a), NF_2(b)$ 

Such a great difference in yields of 5a and 5b is probably due to a relatively lower stability of 5b in acidic media and more significant shift of the equilibrium

5a,b + H<sup>$$\oplus$$</sup>  $\longrightarrow$  PhC <sup>$\oplus$</sup> (NF<sub>2</sub>)X + HNF<sub>2</sub>

to the right because the NF<sub>2</sub> group stabilizes the carbocation center much better than the fluorine atom does. When the reaction mixture is diluted with water, the  $PhC^{\oplus}(NF_2)_2$  cation is transformed into benzoic acid in almost quantitative yield.<sup>6</sup>

 $PhC^{\oplus}(NF_2)_2 + 3 H_2O \longrightarrow 2 HNF_2 + PhCOOH + H_3O^{\oplus}$ 

Compound 5a has been obtained earlier<sup>6</sup> by difluoroamination of imine PhC(NF<sub>2</sub>)FC(=NF)Ph with difluoroamine in FSO<sub>3</sub>H and CH<sub>2</sub>Cl<sub>2</sub>, while compound 5b has been obtained by difluoroamination of imine PhC(NF<sub>2</sub>)<sub>2</sub>C(=NF)R (R = Me or Et) in fuming H<sub>2</sub>SO<sub>4</sub> or FSO<sub>3</sub>H.

The reaction we studied can serve as a route for synthesis of difficultly available aliphatic-aromatic compounds with the *gem*-difluoroamine and tris-difluoroamine groups.

## Experimental

Experiments with difluoroamine were carried out in an atmosphere of inert gas in a special-purpose remote-controlled

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protective box. Difluoroamine was obtained according to the known procedure<sup>7</sup> and dried by passing over  $P_2O_5$ .

IR spectra were recorded on a UR-10 instrument (thin film between germanium glasses). <sup>1</sup>H NMR spectra were recorded on a Perkin—Elmer 12 instrument (60 MHz) (HMDS as the internal standard), and <sup>19</sup>F NMR spectra were recorded on a Varian DP-60 instrument (56.4 MHz) (CCl<sub>3</sub>F as the external standard).

GLC analysis was carried out on an LKhM-8 chromatograph equipped with a katharometer on a 30-cm long column with fluorosilicone QF-1 (10%) on Chromosorb P (150– 200 mesh) as the stationary phase and helium as the carrier gas at 70 °C).

Difluoroamination of a,a-dinitro-a-fluoro- and a,a-dinitroa-(difluoroamino)toluene (general procedure). DMF (10 mL) or a mixture of CISO<sub>3</sub>H (7 mL) and dry CH<sub>2</sub>Cl<sub>2</sub> (7 mL) was placed in a glass reactor (preliminarily purged with an inert gas) equipped with a magnetic stirrer and a Staedeler condenser cooled with solid CO2 with CHCl3 and saturated with difluoroamine at -5 to 0 °C (in the reactor) for 60-80 min. A solution of the corresponding polynitro compound (0.02 mol) in 8 mL of CH<sub>2</sub>Cl<sub>2</sub> was added at -15 to -10 °C over 10 min. The reaction mixture was stirred for 3 h, and the temperature was raised to 7-8 °C with gradual addition of difluoroamine to the reaction mixture. Then the system was purged with an inert gas, and the reaction mixture was poured dropwise onto crushed ice (100 g). The organic layer was separated, and the aqueous layer was extracted with CH2Cl2 (2×15 mL). The combined organic layers were washed with 5% NaHCO3 and water to neutral reaction and dried with MgSO4. The solvent was removed at atmospheric pressure, and the residue was distilled.

 $\alpha, \alpha$ -Bis(difluoroamino)- $\alpha$ -fluorotoluene (5a) was obtained from  $\alpha, \alpha$ -dinitro- $\alpha$ -fluoro'oluene (4a). After removal of the solvent, the residue was distilled *in vacuo*. Product 5a was first distilled off followed by the unconsumed starting compound 4a. The yield of product 5a was 1.95 g (92% with respect to the consumed 4a), b.p. 70 °C (45 Torr),  $n_D^{20}$  1.4339,  $d_4^{20}$  1.4001. Purity according to GLC data is 99%. Found (%): C, 39.40; H, 2.30; N, 13.40; F, 44.80.  $C_7H_5F_5N_2$ . Calculated (%): C, 39.60; H, 2.38; N, 13.20; F, 44.70. Molecular weight, found (cryoscopy in benzene): 199. Calculated: 212. IR,  $v/cm^{-1}$ : 890–955 (NF<sub>2</sub>). <sup>1</sup>H NMR,  $\delta$ : 7.98–8.22 (m, 5 H, Ph). <sup>19</sup>F NMR,  $\delta$ : 152.4 (t, C--F,  $J_{F,NF_2} = 4$  Hz); -23.7 (q, AB system, NF<sub>2</sub>).

α,α,α-**Tris(difluoroamino)toluene (5b)** was obtained from α-(difluoroamino)-α,α-dinitrotoluene (4b). After removal of the solvent, the residue was distilled at reduced pressure to give product 5b (0.2 g, 8%), b.p. 47 °C (25 Torr). According to GLC data, the product contains 2% CH<sub>2</sub>Cl<sub>2</sub>. IR,  $\nu/cm^{-1}$ : 890–955 (NF<sub>2</sub>). <sup>1</sup>H NMR, δ: 7.78–8.02 (m, 5 H, Ph). <sup>19</sup>F NMR, δ: -27.8 (s, NF<sub>2</sub>).

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