SYNTHESIS OF 3-FLUORO-3,3-DINITRO-1-AMINOPROPANE AND SOME OF ITS DERIVATIVES

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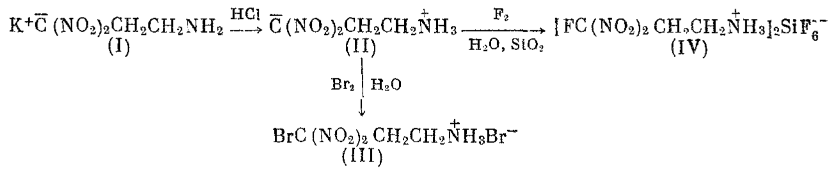
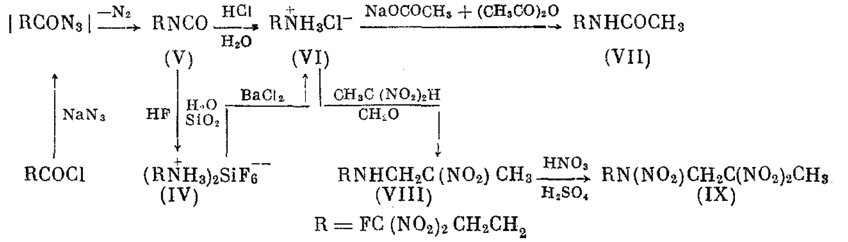
3-Fluoro-3,3-dinitro-1-aminopropane can be synthesized by basically different methods, viz. by fluorination of salts of 3,3-dinitro-1-aminopropane or by the reaction of Schmidt and Curtius, starting from a carbonyl compound containing the 3-fluoro-3,3-dinitropropyl group. For the synthesis of the first type, we have used the method of fluorination in water, which has been recently widely studied. The internal salt of 3,3-dinitro-1-aminopropane was used as the starting compound.*



The potassium salt (I) was produced from 3,3,3-trinitro-1-aminopropane described in [2]. The reactivity of salt (II) was previously checked by bromination in water, which gave a good yield of 3-bromo-3,3-dinitro-1-aminopropane hydrobromide (III); mp 167° with decomposition. Fluorination of salt (II) in a glass reactor resulted in the formation of 3-fluoro-3,3-dinitro-1-aminopropane hexafluorosilicate (IV) in a 66% yield. Thus, under conditions selected by us, the first stage of the process, i.e., the fluorine attack on the anion center of salt (II), is prominent. It should be pointed out that such a selectivity essentially depends on the degree of dilution of fluorine with nitrogen and on the ratio of fluorine to the salt being fluorinated. The separation of the reaction product in the form of a hexafluorosilicate is obviously due to the reaction between glass silicates and HF formed during the reaction.

For the synthesis of the second type, we have used 4-fluoro-4,4-dinitrobutyryl chloride [3] in the Curtius reaction.



We did not isolate the azide of 4-fluoro-4,4-dinitrobutyric acid from the reaction mixture, but boiled it in chloroform to convert it into the isocyanate (V). The latter was isolated, distilled in vacuo and hydrolyzed in a quartz flask with HCl or HF to obtain hydrochloride (VI) or hexafluorosilicate (IV) of 3-fluoro-3,3-dinitro-1-aminopropane. When salt (IV) was treated with a $BaCl_2$ solution, the hydrochloride (VI) was quantitatively formed; this reaction was also used for the determination of the SiF_6^{2-} anion. We have

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* We have published the preliminary results in [1].

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investigated some reactions of 3-fluoro-3,3-dinitro-1-aminopropane. When hydrochloride (VI) was heated with acetic acid anhydride in the presence of CH_3COONa, N-(3-fluoro-3,3-dinitropropyl) acetamide (VII) was formed. Condensation of salt (VI) with formaldehyde and 1,1-dinitroethane gave 1-fluoro-1,1,6,6-tetranitro-4-azaheptane (VIII), which can be easily nitrated with a mixture of concentrated HNO_3 and H_2SO_4 to 1-fluoro-1,1,4,6,6-pentanitro-4-azaheptane (IX).

EXPERIMENTAL

Internal Salt of 3,3-Dinitro-1-aminopropane (II). A solution of 7.48 g of potassium-3,3-dinitro-1-aminopropane (decomposition temp. 156-159°) in 150 ml of water was acidified with conc. HCl to pH 6 and cooled to −5°; the precipitated salt was separated by filtration, washed with ice water, alcohol, and ether, and air-dried. The yield of (II) was 4.48 g (75% theor.) the yellow crystals melted with decomposition at 150° (after recrystallization from water). Found: C 23.33; H 3.98; N 27.70%. $C_3H_7N_3O_4$. Calculated: C 24.16; H 4.69; N 28.19%.

3-Fluoro-3,3-dinitro-1-aminopropane Hexafluorosilicate (IV). A mixture of 3.80 g F_2 with N_2 (volume ratio 1:18) was passed for 1.5 h through a stirred suspension of 9.66 g of (II) in 150 ml of water. Then the solution was evaporated to 1/3 volume at 40-50° under vacuum, and the residue was cooled to −5°. The precipitated crystals were separated by filtration, washed with ice water, alcohol, and ether, and dried; 8.14 g of (IV) were obtained. A further 2.77 g were recovered by evaporating the filtrate to dryness and recrystallizing the residue from water. The total yield was 65.9%; (IV) was obtained in the form of white platelets melting at 208° (with decomposition). Found: F 31.67; N 17.60; SiF_6^{2-} 24.48%. $C_6H_{14}F_8N_6O_8Si$. Calculated: F 31.80; N 17.57; SiF_6^{2-} 29.71%.

A mixture of 9.65 g of (V) and 25 ml of 40% HF was heated for 2.5 h at 95-100° in a quartz flask equipped with a reflux condenser. The reaction mixture was cooled to −5°, and filtered. The precipitated crystals were washed with ice water, alcohol, and ether; 11.15 g of the salt were obtained. A further 0.72 g were recovered by evaporating the filtrate to dryness and recrystallizing the residue from water. The total yield was 99.33%; mp 208° (with decomposition). When this product was mixed with (IV) produced as above there was no depression of the melting point. The IR spectra of both substances were identical.

3-Fluoro-3,3-dinitro-1-isocyanatopropane (V). A solution of 51.8 g of 4-fluoro-4,4-dinitrobutyryl chloride [3] in 36 ml of $CHCl_3$ was added at 10-15° with vigorous stirring to a solution of 31.4 g of NaN_3 in 95 ml water. The mixture was kept at 30° for 30 min, then the $CHCl_3$ layer was separated, and the aqueous layer was extracted with 35 ml of $CHCl_3$. The chloroform solutions were combined, washed with water (2 × 20 ml), dried over Na_2SO_4, and boiled under reflux until N_2 ceased to evolve. Then $CHCl_3$ was evaporated and the resultant (V) was distilled under vacuum. The yield of (V) was 35 g (75.6%); it was a colorless liquid; $bp_{2mm} = 83-84°$; $n_D^{20} = 1.4521$; $d_4^{20} = 1.498$. Found: C 24.68; H 2.09; F 9.92; N 21.76%; mol. wt. 189. $C_4H_4FN_3O_5$. Calculated: C 24.88; H 2.09; F 9.92; N 21.60; mol. wt. 193.

3-Fluoro-3,3-dinitro-1-aminopropane Hydrochloride (V). To 40 ml of conc. HCl (d_4^{20} 119) were added with stirring 23.4 g of (V). The solution was heated for 2 h at 95-100°; then evaporated to dryness at a pressure of 15-20 mm. The yield of (VI) was 24.1 g (98%); it formed white crystals melting at 168-170°. Found: C 17.70; H 3.47; F 8.33; N 20.64%. $C_3H_7ClFN_3O_4$. Calculated: C 17.58; H 3.78; F 8.53; N 20.65%.

Solutions of 4.78 of (IV) in 50 ml water and 2.29 g of $BaCl_2$ in 20 ml water heated to 90°, were mixed together with stirring. The resultant suspension was stirred for 30 min, and then cooled to 0°. The precipitate was separated by filtration, washed with water, methanol, and absolute ether, and dried; 2.771 g (99.22%) of $BaSiF_6$ were obtained. The filtrate was evaporated to dryness. After recrystallization of the residue, 2.00 g (98.3%) of (VI) were obtained. When this product was mixed with (VI) produced as above there was no depression of the melting point.

N-(3-Fluoro-3,3-dinitropropyl)acetamide (VII). A mixture of 10.2 g of (VI), 10.2 g of $CH_3COONa \cdot 3H_2O$, and 47 ml of $(CH_3CO)_2O$ was stirred for 2 h at 70-75°. The acetic acid and its anhydride were driven off at 15-20 mm; the residue was dissolved in 150 ml of CH_2Cl_2; the solution was filtered, washed with 2% Na_2CO_3 solution, then with water, and dried over Na_2SO_4. After evaporation of the solvent the residue was distilled under vacuum. The yield of (VII) was 6.8 g (65%); it formed a yellowish oil; $bp_{1mm} = 119-121°$; $n_D^{20} = 1.4613$. Found: C 28.78; H 3.91; F 8.71; N 20.30%. $C_5H_8FN_3O_5$. Calculated: C 28.71; H 3.87; F 9.09; N 20.09%. (According to [4], $bp_{2mm} = 125-130°$; $n_D^{20} = 1.4603$.)

1-Fluoro-1,1,6,6-tetranitro-4-azaheptane (VIII). To a solution of 2.04 g of (VI) in 50 ml water were added 2.61 g of 1,1-dinitroethane and 2.64 g of 25% solution of formaldehyde in water. The pH was adjusted to 7 by adding crystalline Na_2CO_3 with stirring. The mixture was kept at 18-25° for 24 h; the separated oil crystallized on trituration. The precipitate was separated by filtration, washed with water and dried. The yield of (VIII) was 5.52 g (92.3%); the compound formed white crystals melting at 51-52° (after crystallization from CCl_4 and $CHCl_3$). Found: C 24.08; H 3.34; F 6.35; N 23.41%. $C_6H_{10}FN_5O_8$. Calculated: C 23.90; H 3.29; F 6.16; N 23.63%.

1-Fluoro-1,1,4,6,6-pentanitro-4-azaheptane (IX). Compound (VIII) (1.5 g) was dissolved at 15° in 15 ml HNO_3 (sp. gr. 1.50) and 30 ml H_2SO_4 (sp. gr. 1.84) were added; the mixture was kept at 15-20° for 2 h, and then poured onto crushed ice. The crystals formed were separated by filtration, washed with water and air-dried. The yield of white crystals of (VIII) was 1.69 g (99.4%); mp 85-86° (after recrystallization from $CHCl_3$). Found: C 20.93; H 2.61; F 5.51; N 24.41%. $C_6H_9FN_6O_{10}$. Calculated; C 20.81; H 2.84; F 5.36; N 24.51%.

CONCLUSIONS

1. On the example of the fluorination of the internal salt of 3,3-dinitro-1-aminopropane in water, it was shown that a selective fluorination of the anion center in nitroalkylamines, with preservation of the amino group, is possible.

2. Salts and some N-substituted derivatives of 3-fluoro-3,3-dinitro-1-aminopropane were synthesized.

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