SYNTHESIS OF bis-(2-FLUORO-2,2-DINITROETHYL)NITRAMINE AND tris-(2-FLUORO-2,2-DINITROETHYL)AMINE

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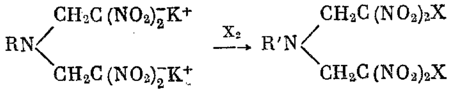
The bromination and chlorination of the dipotassium salts of bis-(2,2-dinitroethyl)amine and tris-(2,2-dinitroethyl)amine yielded satisfactory quantities of the corresponding halides [1]:



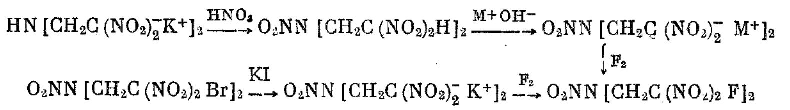
$$RN\begin{cases}CH_2C(NO_2)_2^-K^+\\CH_2C(NO_2)_2^-K^+\end{cases}\xrightarrow{X_2}R'N\begin{cases}CH_2C(NO_2)_2X\\CH_2C(NO_2)_2X\end{cases}$$

$R=H, -CH_2C(NO_2)_2H$; $X=Cl, Br$; $R'=H, -CH_2C(NO_2)_2X$

This paper is devoted to the synthesis of the 2-fluoro derivatives of these amines. In our papers [2-4] it was shown that an interaction between the alkali salts of polynitroalkanes and elementary fluorine in water and other polar solvents is a smooth reaction resulting in the formation of α-fluoropolyalkanes. This method was here used for the fluorination of the alkali salts of bis-(2,2-dinitroethyl)amine (I) and tris-(2,2-dinitroethyl)amine (II).

These salts contain two types of nucleophilic reaction centers, namely the amino group and the dinitromethyl anions. The fluorine atom may attack each of these centers. In the case of a fluorination of the dipotassium salt of (I) we might have expected the formation of N-fluoro-bis-(2-fluoro-2,2-dinitroethyl)amine and bis-(2-fluoro-2,2-dinitroethyl)amine. However, the experiments showed that in the reaction of the dipotassium salt of (I) with elementary fluorine in an aqueous solution or suspension, the initial salt dissociates and it is impossible to separate a fluoro derivative of (I). This fact proves the fluorolysis of Mannich's base, which may be connected with an attack of the fluorine atom along the polarized C – C bond. The polarization of the C – C bond in the case considered must decrease as the basicity of the amino group is reduced; this means that a replacement of the hydrogen atom of the secondary amino group by an electron-acceptor radical may yield a product which is stable against fluorolysis. For this purpose we nitrated the dipotassium salt of (I) by a mixture of concentrated HNO_3 and H_2SO_4 and obtained bis-(2,2-dinitroethyl)-nitramine, white crystals, mp 101-102°C. According to data of [5] bis-(2,2-dinitroethyl)nitramine has a melting point of 78°C; we observed that a treatment of a sample synthesized according to the method of [5] by a mixture of concentrated HNO_3 and H_2SO_4 yields bis-(2,2-dinitroethyl)nitramine mp 98-100°C. Thus the author of [5] must have described an insufficiently pure substance.

The reaction of bis-(2,2-dinitroethyl)nitramine with potassium hydroxide in an alcoholic solution results in the formation of the corresponding dipotassium salt. A fluorination of the latter by elementary fluorine in an aqueous solution yields bis-(2-fluoro-2,2-dinitroethyl)nitramine, fine white prisms, mp 86°C. The same product was obtained when we fluorinated the dipotassium salt of bis-(2,2-dinitroethyl)nitramine synthesized from bis-(2-bromo-2,2-dinitroethyl)nitramine exposed to the action of KI according to [5]



$$\begin{tikzcd}
HN[CH_2C(NO_2)_2^-K^+]_2 \arrow[r, "HNO_3"] & O_2NN[CH_2C(NO_2)_2H]_2 \arrow[r, "M^+OH^-"] & O_2NN[CH_2C(NO_2)_2^-\ M^+]_2 \arrow[d, "F_2"] \\
O_2NN[CH_2C(NO_2)_2Br]_2 \arrow[r, "KI"] & O_2NN[CH_2C(NO_2)_2^-\ K^+]_2 \arrow[r, "F_2"] & O_2NN[CH_2C(NO_2)_2F]_2
\end{tikzcd}$$

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We also obtained diammonium and disodium salts of bis-(2,2-dinitroethyl)nitramine previously not described in the literature. A fluorination of these salts in an aqueous solution showed that the nature of the cation does not influence the yield of the bis-(2-fluoro-2,2-dinitroethyl)nitramine. These salts dissolve easily in water and their use in fluorination makes it possible to work with smaller volumes of aqueous solutions.

For the inverse synthesis of bis-(2-fluoro-2,2-dinitroethyl)nitramine we used the condensation of 2-fluoro-2,2-dinitroethanol with ammonia and subsequent nitration of the secondary amine formed. According to data of [6, 7], fluorodinitromethane has a pK_α of 7.8. This means that the dissociation constant of 2-fluoro-2,2-dinitroethanol according to the equation

$$FC(NO_2)_2CH_2OH \rightleftarrows FC(NO_2)_2H + CH_2O$$

must be of the same order of magnitude as in the case of the β-mononitro alcohols. It is well known that a Mannich condensation of the latter requires conditions guaranteeing a dissociation of the alcohol on nitroalkane and formaldehyde. Usually the reaction takes place in an alkaline medium, in certain cases heating is necessary.

The optimum conditions for a condensation of 2-fluoro-2,2-dinitroethanol with ammonia are a temperature of 50°C and a pH of the medium of 7.5-8.0. When the reaction takes place in water the condensation product falls out in the form of an oil which crystallizes slowly when stored. Bis-(2-fluoro-2,2-dinitroethyl)amine forms white crystals melting at 42-43°C. Exposure to the action of concentrated HNO_3 or its mixture with concentrated H_2SO_4 results in the formation of the corresponding nitramines which are identical as to the melting point, the infrared spectrum, and other properties with the alkali salts of bis-(2,2-dinitroethyl)nitramine obtained by fluorination.

The structure of the dipotassium salt of (II) proven in [1] does not arouse any doubts as regards the sucessful synthesis of its fluoro derivatives. In this substance the basicity of the amino group must be much lower because of the I-effect of the 2,2-dinitroethyl radical, which must reduce the polarization of the C — C bonds.

In fact, the fluorination of the dipotassium salt of (II) in an aqueous solution or suspension results in the formation of tris-(2-fluoro-2,2-dinitroethyl)amine (mp 78°C) with a yield of 75%. It should be noted that, in spite of the presence of only two anionic reaction centers in the initial substances, the reaction product is a trifluoride.

EXPERIMENTAL

The dipotassium salts of (I) and (II) were obtained by a condensation of the ammonium salt of dinitromethane with formaldehyde in the presence of potassium chloride [1]. 2-Fluoro-2,2-dinitroethanol was synthesized in the reaction of fluorodinitromethane with formaldehyde [4].

bis-(2,2-Dinitroethyl)nitramine. The dipotassium salt of (I) (39.8 g) prewashed with alcohol and ether and dried on the filter, was admixed in small quantities to a mixture consisting of 200 g HNO_3 (sp. gr. 1.5) and 50 g H_2SO_4 (sp. gr. 1.84), at a temperature between −5 and −10°C. Thereafter, at 0-5°C, 850 g H_2SO_4 (sp. gr. 1.84) was added and mixed at this temperature for 1 h. The crystals precipitated were filtered off and washed by H_2SO_4 of decreasing concentration (80-60-40-20-5%); the yield was 27 g (90%). After a double recrystallization from dichloroethane white crystals were obtained, mp 100-101°C (with decomposition). Found: C 16.87; H 1.40; N 28.36%. $C_4H_6N_6O_{10}$. Calculated: C 16.9; H 1.35; N 28.31%.

Dipotassium Salt of bis-(2,2-Dinitroethyl)nitramine. bis-(2,2-Dinitroethyl)nitramine (3 g) was dissolved in 10 ml methanol at 20°C. To this solution a solution of 1.4 g KOH in 50 ml alcohol was added and mixed at 18-20°C. Half an hour later the precipitate was filtered off, washed with alcohol and ether, and dried on the filter. We obtained yellow crystals, mp 128° (with decomposition); yield 3.57 g (95%).

Disodium Salt of bis-(2,2-Dinitroethyl)nitramine. The salt was obtained by means of the above method, using NaOH. Yellow crystals were separated; mp 121°C (with disintegration), yield 3.35 g (97%).

Diammonium Salt of bis(2,2-Dinitroethyl)nitramine. To 10 ml of a 6% alcoholic solution of NH_3 at 20° a solution of 3 g bis-(2-dinitroethyl)nitramine in methanol was admixed. After 20 min the precipitate was filtered off, washed with alcohol and ether, and dried in air. Yellow crystals were obtained, mp 99°C (with decomposition), yield 3.2 g (96.3%).

bis-(2-Fluoro-2,2-dinitroethyl)nitramine. Fluorine (2.5 g) diluted by N_2 in a ratio of 1 : 20 was blown through a solution of 6 g disodium salt of bis-(2,2-dinitroethyl)nitramine in 240 ml water at 0-5°C and mixed. The precipitate formed was filtered off, washed with water, and dried. After recrystallization from a mixture of dichloroethane and petroleum ether in a ratio of 1 : 10 (25 ml per gram) 2.64 g (45%) fine white prisms were obtained; mp 86°C. Found: C 14.79; H 1.25; F 11.22; N 25.37%; mol. wt. 337 (benzene). $C_4H_4F_2N_6O_{10}$. Calculated: C 14.36; H 1.20; F 11.36; N 25.23%; mol. wt. 334.

Fluorine (1.66 g) diluted by N_2 in a ratio of 1 : 20 was blown through a solution of 6.6 g diammonium salt of bis-(2,2-dinitroethyl)nitramine in 200 ml water at 0-5°C, and mixed. The white precipitate was washed with water and dried. We obtained 2.7 g (40%) bis-(2-fluoro-2,2-dinitroethyl)nitramine, mp 85-86°C. A sample obtained when mixing with bis-(2-fluoro-2,2-dinitroethyl)nitramine according to the above method showed no depression of the melting point.

Fluorine (4.6 g) diluted by N_2 (volume ratio 1 : 50) was blown through a solution of 18.8 g dipotassium salt of bis-(2,2-dinitroethyl)nitramine in 2 liter water at a temperature of 0-5°, and mixed for 2 h. We obtained 15.9 g (44%) of bis-(2-fluoro-2,2-dinitroethyl)nitramine, mp 86°C.

bis-(2-Fluoro-2,2-dinitroethyl)amine. 2-Fluoro-2,2-dinitroethanol (15.4 g) was dissolved in 150 ml water; 34 ml of a 5% aqueous solution of NH_3 was added dropwise (at 50°C) to this solution; it was mixed for 4 h, keeping the pH at 7.5-8.0. The reaction mixture was then mixed at 50° for another 30 min. The oil formed was separated, washed with water, and dried. We obtained 10.32 g of a heavy liquid with n_D^{20} 1.4695. The product crystallized slowly when it was left standing. The solid substance of bis-(2-fluoro-2,2-dinitroethyl)amine formed white prisms, mp 42-43°C* (tetrachloromethane). Found: N 24.26%; mol. wt. 289 (benzene). $C_4H_5F_2N_5O_8$. Calculated: N 24.20%; mol.wt. 289.

bis-(2-Fluoro-2,2-dinitroethyl)nitramine. bis-(2-Fluoro-2,2-dinitroethyl)amine (10.0 g), mp 42-43°C, was dissolved in 110 g concentrated H_2SO_4 (sp. gr. 1.84) cooled to 0°C. To this solution we added dropwise 36 g concentrated HNO_3 (sp. gr. 1.5), stirring constantly, then the solution was left standing at room temperature for 2 h. Thereafter the reaction mixture was poured out on 600 g ice. The residue was filtered off, washed with water until neutrality of reaction, and dried. After recrystallization from a mixture of petroleum ether and dichloroethane we obtained 8.1 g (70%) of fine white prisms, mp 86°C. The mixture of the substance with bis-(2-fluoro-2,2-dinitroethyl)nitramine obtained from the disodium salt of bis-(2,2-dinitroethyl)nitramine melted without depression.

tris-(2-Fluoro-2,2-dinitroethyl)amine. The disodium salt of (II) (22.35 g) was dissolved in 2.8 liters water. Fluorine (7.6 g) diluted by N_2 (ratio 1 : 50) was blown through the solution at 2-6°C within 30 min, stirring constantly; the precipitate was filtered off, washed with water until neutrality of reaction, and dried. After recrystallization from CCl_4 we obtained 16 g (75%) of a white crystalline product, mp 78°C. Found: C 16.81; H 1.63; F 13.72; N 22.97%; mol. wt. 417 (benzene). $C_6H_6F_3N_6O_{12}$. Calculated: C 16.95; H 1.41; F 13.60; N 23.08%; mol. wt. 425.

CONCLUSIONS

1. By means of a fluorination of salts of bis-(2,2-dinitroethyl)nitramine and tris-(2,2-dinitroethyl)-amine in aqueous solutions by elementary fluorine, we obtained for the first time bis-2-fluoro-2,2-dinitroethyl)nitramine and tris-(2-fluoro-2,2-dinitroethyl)amine.

2. We made a counter-synthesis of bis-(2-fluoro-2,2-dinitroethyl)nitramine through condensation of 2-fluoro-2,2-dinitroethanol with ammonia and nitration of the Mannich base obtained.

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*When this article had already been submitted to the editorial office, paper [8] was published in which this substance, with the same melting point, is described.

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