FLUORINATION OF BIPOLAR ION OF 2,2-DINITROAMINOETHANE WITH ELEMENTAL FLUORINE

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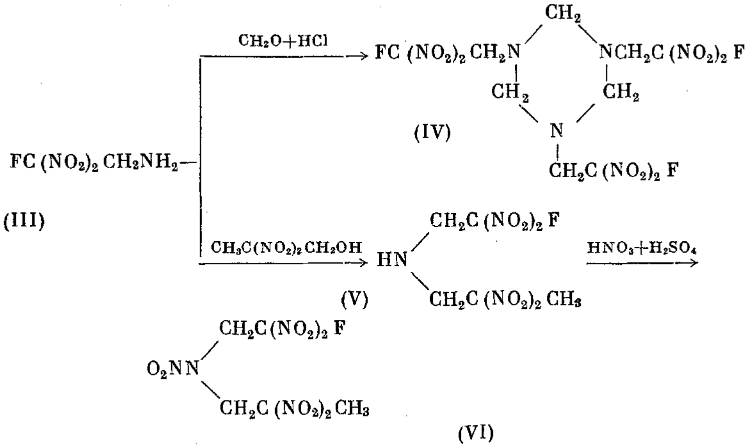
In one of our papers [1] it was shown that the bipolar ion of 3,3-dinitro-1-aminopropane can be fluorinated only at the anionic reaction center to give 3-fluoro-3,3-dinitro-1-aminopropane. It was interesting to study the direct fluorination of the bipolar ion of 2,2-dinitroaminoethane (I), described in [2], with elemental fluorine in order to ascertain the generality of the character of the progress of this reaction in the series of ω,ω-dinitro-α-aminoalkanes. It is indicated that the bipolar ion of (I) cannot be fluorinated with perchloryl fluoride in a medium that contains methanol, water, or ether [3]. Our attempts to fluorinate (I) with elemental fluorine in water under the conditions described in [1], and also in methanol, have as yet also proved unsuccessful. However, when the reaction is run in CCl_4 medium at low temperature it proved possible to obtain 2-fluoro-2,2-dinitroaminoethane (III) and to isolate it as the free base after treating the reaction product with alcoholic ammonia solution:

$$\underset{(I)}{(NO_2)_2^{\ominus}CCH_2NH_3^{\oplus}} \xrightarrow[CCl_4]{F_2+N_2} \underset{(II)}{FC(NO_2)_2CH_2\overset{\oplus}{N}H_3} \xrightarrow[CH_3OH]{NH_3} \underset{(III)}{FC(NO_2)_2CH_2NH_2} + NH_4^{\oplus}$$

We studied some of the reactions of amine (III). Amine (III) when reacted with formaldehyde in the presence of HCl forms tris-1,3,5-(2'-fluoro-2',2'-dinitroethyl)-1,3,5-triazacyclohezane (IV). The reaction of (III) with nitroalcohols, on the example of 2,2-dinitropropanol, leads to the condensation product (V), which is converted to nitramine (VI) by treatment with a mixture of conc. H_2SO_4 and HNO_3:



EXPERIMENTAL

2-Fluoro-2,2-dinitroaminoethane (III). With stirring, 38 g of F_2, diluted with N_2 in a 1:10 volume ratio, was passed through a suspension of 14.4 g of (I) in 100 ml of CCl_4 at $-20°$ in 6 h. The mixture of unreacted (I) and salt (II) was rapidly filtered at a temperature below 0°, transferred to 100 ml of a 1:1 mixture of CH_2Cl_2 and CH_3OH, and a solution of excess NH_3 in methanol was added. The insoluble products were filtered, and the solution was washed with water, dried over $MgSO_4$, and the solvent was distilled off. The

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residue was vacuum-distilled. We obtained a liquid with a greenish tinge, bp 29.5° (0.1 mm); yield 4.9 g (32.1%); n_D^{20} 1.4405. NMR spectrum at 20° (δ, ppm): broad singlet 1.78 (NH_2), doublet 4.00, J_{HF} 19.2 Hz (CH_2). From [4]: bp 38-41° (0.3 mm).

Tris-1,3,5-(2'-fluoro-2',2'-dinitroethyl)-1,3,5-triazacyclohexane (IV). To a solution of 7.65 g of amine (III) in 60 ml of CH_2Cl_2 was added a neutral solution of 1.5 g of paraform in 10 ml of methanol. The reaction mixture was refluxed for 1 h in a flask connected to a water separator, in which connection 0.95 ml of water was collected. A vigorous stream of anhydrous HCl was passed through the solution at 0 to −5° for 30 sec, in which connection a white crystalline precipitate was obtained. The reaction mixture was heated under reflux for 2 h until the precipitate had dissolved. The reaction product was isolated by distilling off the solvent to give 5.28 g (64%) of (IV) as white crystals with mp 141-142° (decompn.) (from $CHCl_3$). Found: C 21.68; H 2.56; F 11.67; N 25.56%. $C_9H_{12}F_3N_9O_{12}$. Calculated: C 21.82; H 2.42; F 11.51; N 25.45%. NMR spectrum in deuteroacetone at 20° (δ, ppm): singlet 3.90 (CH_2 in the ring), doublet 4.18, J_{HF} 19.2 Hz (CH_2 in the side chain).

1-Fluoro-1,1,5,5-tetranitro-3-azahexane (V). To a solution of 7.65 g of amine (III) in 60 ml of CH_2Cl_2 were added 6.0 g of 1,1-dinitroethane and 3.75 ml of 40% aqueous formaldehyde solution, and the mixture was stirred at 30-35° for 3 h. The organic layer was separated, and the aqueous layer was extracted with 5 ml of CH_2Cl_2. The combined solutions in CH_2Cl_2 were washed with water and dried over $MgSO_4$. The solvent was vacuum-distilled. To the residual clear, yellowish, viscous liquid was added 4 ml of $CHCl_3$, and then 6 ml of CCl_4 after solution.

The solution was allowed to stand at −10 to −12° for 20 h. The obtained precipitate was filtered and washed with chilled CCl_4. We obtained 3.55 g (25.1%) of (V) as white crystals with mp 52-54°. Found: C 21.23; H 2.77; F 6.73; N 24.64%. $C_5H_8FN_5O_8$. Calculated: C 21.05; H 2.82; F 6.63; N 24.48%.

1-Fluoro-1,1,3,5,5-pentanitro-3-azahexane (VI). With stirring, 3.5 g of (V) was added at 0° in 15 min to 20 ml of 94% H_2SO_4 solution. Then 10 ml of 98% HNO_3 solution was added dropwise at 0° in 10 min. The reaction mixture was stirred at 20-25° for 2 h and then poured on 250 g of cracked ice. The obtained precipitate was filtered, washed with water (5 × 50 ml) on the filter, and dried. We obtained 3.42 g (84.5%) of (VI) as white crystals with mp 125-125.5° (from $CHCl_3$). Found: C 18.05; H 2.17; F 5.96; N 25.66%. $C_5H_7 \cdot FN_6O_{10}$. Calculated: C 18.18; H 2.12; F 5.76; N 25.45%.

The addition of 10 ml of conc. HNO_3 and 20 ml of conc. H_2SO_4 to the mother liquor, obtained from the isolation of crystalline (V) in the preceding experiment, gave an additional 5.45 g of (VI) with mp 123-125°. The total yield of (VI), when based on the starting (III), was 53.8%.

CONCLUSIONS

1. It was shown that the bipolar ion of 2,2-dinitroaminoethane can be fluorinated with elemental fluorine to give 2-fluoro-2,2-dinitroaminoethane.

2. The end reaction product of 2-fluoro-2,2-dinitroaminoethane with formaldehyde in the presence of HCl is tris-1,3,5-(2'-fluoro-2',2'-dinitroethyl)-1,3,5-triazacyclohexane.

LITERATURE CITED

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