3-FLUORO-3,3-DINITRO-1-AMINOPROPANE IN THE MANNICH REACTION

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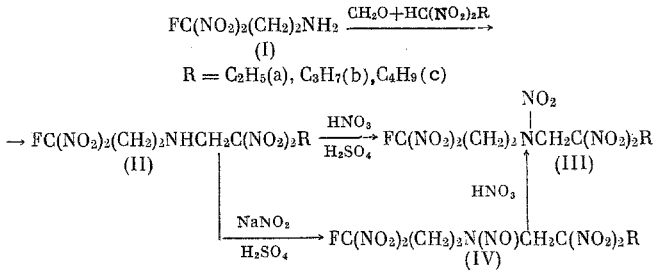
We recently described the preparation of salts of 3-fluoro-3,3-dinitro-1-aminopropane (I) [1, 2] and some of its reactions, including condensation with CH_2O and 1,1-dinitroethane [2]. In this research we investigated the physical properties of (I) and its behavior in the Mannich reaction. Amine (I) was obtained from the hydrochloride as a colorless liquid which crystallized below 0°. In the free form or in the form of salts, (I) readily condenses with CH_2O and 1,1-dinitroalkanes to form Mannich bases (II):



The condensation was carried out at pH 4-6, since the yields of (II) decrease under alkaline conditions. Treatment of the secondary nitroalkylamines (II) with HNO_3 and $NaNO_2$ in concentrated H_2SO_4 gives the corresponding N-nitroamines (III) and N-nitrosoamines (IV), respectively. The latter are readily converted to N-nitroamines by the action of concentrated HNO_3.

EXPERIMENTAL METHOD

3-Fluoro-3,3-dinitro-1-aminopropane (I). A solution of 10.3 g of the hydrochloride of (I) in 50 ml of water was neutralized to pH 8 at 0° with 18 ml of 10% NH_4OH in the presence of 50 ml of ether. The ether extract was worked up in the usual way, evaporated, and the residue was vacuum distilled to give 6.8 g (82%) of (I) as a colorless liquid with bp 57° (~0.1 mm); n_D^{20} 1.4458. Found: C 22.1; H 3.6; F 11.6; N 25.8%. $C_3H_6 \cdot FN_3O_4$. Calculated: C 21.56; H 3.62; F 11.37; N 25.15%.

1-Fluoro-1,1,6,6-tetranitro-4-azaoctane (IIa). A solution of 0.4 g of NaOH and 1.34 g of 1,1-dinitropropane in 20 ml of water was added with stirring at 18-20° to 2.03 g of the hydrochloride of (I) in 10 ml of water. A solution of 1 ml of 36% CH_2O in 5 ml of water was added dropwise to this suspension to pH 6, and the mixture was stirred for 3 h. The precipitate was filtered, washed with water, and air dried to give 2.89 g (92.2%) of (IIa) with mp 40.5-41.5° (CCl_4 with $CHCl_3$). Found: C 27.2; H 3.2; F 5.9; N 22.4%. $C_7H_{12} \cdot FN_5O_8$. Calculated: C 26.84; H 3.86; F 6.07; N 22.36%.

1-Fluoro-1,1,6,6-tetranitro-4-azanonane (IIb). A total of 2.98 g (91%) of (IIb) was obtained as white crystals with mp 45-46° (CCl_4) from 2.03 g of the hydrochloride of (I), 1.48 g of 1,1-dinitrobutane, and 1 ml of 36% CH_2O via the preceding method. Found: C 29.2; H 4.5; F 5.2; N 21.4%. $C_8H_{14}FN_5O_8$. Calculated: C 29.38; H 4.31; F 5.80; N 21.40%.

1-Fluoro-1,1,6,6-tetranitro-4-azadecane (IIc). Similarly, (IIc) was obtained as an oil from 2.03 g of the hydrochloride of (I), 1.62 g of 1,1-dinitropentane, and 1 ml of 36% CH_2O. The oil was dissolved in 40 ml of CH_2Cl_2, washed with water (two 20 ml portions), and dried over $MgSO_4$. The CH_2Cl_2 was air evaporated, and the solid residue was pressed on a filter and washed with n-hexane to give 2.87 g (84%) of (IIc) with

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mp 22-23° (CCl_4 with $CHCl_3$). Found: C 31.8; H 4.5; F 5.6; N 20.6%. $C_9H_{16}FN_5O_8$. Calculated: C 31.67; H 4.72; F 5.56; N 20.52%.

1-Fluoro-1,1,4,6,6-pentanitro-4-azaalkanes (IIIa-c). A total of 12 ml of 94% H_2SO_4 was added to a solution of 2 g of (IIa) in 8 ml of 98% NHO_3, and the mixture was stirred at 65° for 30 min and cooled to −20°. The crystals were washed with ice water and air dried to give 2.1 g (91%) of (IIIa) with mp 82-83° ($CHCl_3$ with CCl_4). Found: C 23.6; H 3.5; F 5.4; N 23.5%. $C_7H_{11}FN_6O_{10}$. Calculated: C 23.47; H 3.09; F 5.30; N 23.46%. (IIIb) and (IIIc) were similarly obtained. The yield of (IIIb) with mp 66.5-67.5° ($CHCl_3$ with CCl_4) was 2.04 g (89.7%). Found: C 25.1; H 3.3; F 4.5; N 22.5%. $C_8H_{13}FN_6O_{10}$. Calculated: C 25.81; H 3.52; F 5.10; N 22.58%. The yield of (IIIc) with mp 58.5-59.5° ($CHCl_3$ with CCl_4) was 2.03 g (90%). Found: C 28.0; H 3.9; F 5.2; N 21.9%. $C_9H_{15}FN_6O_{10}$. Calculated: C 27.98; H 3.91; F 4.92; N 21.76%.

1-Fluoro-4-nitroso-1,1,6,6-tetranitro-4-azaalkanes (IVa-c). A total of 1 g of (IIa) followed by 0.66 g of $NaNO_2$ was sprinked with stirring into 15 ml of 94% H_2SO_4 at −10°, and the temperature was allowed to rise to 20° after 30 min. The mixture was stirred at 18-22° for 3 h and poured into 150 g of crushed ice. The resulting precipitate was filtered, washed with water, and dried to give 0.97 g (89%) of white crystals with mp 50-51° (CCl_4 with $CHCl_3$). Found: C 24.2; H 2.9; N 24.5%. $C_7H_{11}FN_6O_9$. Calculated: C 24.57; H 3.24; N 24.56%. (IVb) was similarly obtained [0.95 g (88.5%)] and had mp 52-53° (CCl_4). Found: C 26.6; H 3.8; N 23.8%. $C_8H_{13}FN_6O_9$. Calculated: C 26.98; H 3.67; N 23.59%. (IVc) was obtained in 92.6% yield and had mp 50-51° ($CHCl_3$ with CCl_4). Found: C 29.2; H 4.5; N 22.9%. $C_9H_{15}FN_6O_9$. Calculated: C 29.19; H 4.08; N 22.69%.

Nitration of N-Nitrosoamines (IVa-c). A total of 0.1 g of (IVa) was sprinkled at 18-22° into 5 ml of 98% HNO_3, and the mixture was stirred for 1 h and poured over ice. The resulting precipitate was filtered, washed with water, and dried to give 0.09 g (86.5%) of (IIIa) with mp 82-83° (from CCl_4 with $CHCl_3$). Similarly, (IIIb) and (IIIc) were obtained in 77 and 82% yields from (IVb) and (IVc).

CONCLUSIONS

3-Fluoro-3,3-dinitro-1-aminopropane condenses with CH_2O and 1,1-dinitroalkanes to form Mannich bases which are readily converted to the corresponding N-nitro- and N-nitroso derivatives.

LITERATURE CITED

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