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USE OF POTASSIUM SULFAMATE IN THE SYNTHESIS OF HETEROCYCLIC NITRAMINES

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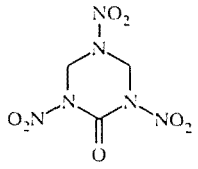
A preparative method for the synthesis of heterocyclic nitramines, containing the methylene tetramine fragment, has been proposed. The method is based on the nitration of the condensation products of urea, guanidine, 3,4-diaminofurazan, and 5-aminotetrazole with formaldehyde and potassium sulfamate.

A method for the synthesis of 1,3,5-trinitrohexahydro-1,3,5-triazine (hexogen) by the nitration of the condensation product of potassium sulfamate with formaldehyde has been described in [1]. In the present study an attempt was made to expand the field of application of this reaction. For this purpose urea, guanidine, 3,4-diaminofurazan (DAF), and 5-aminotetrazole were condensed with potassium sulfamate and formaldehyde.

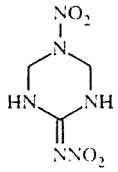
It is known that the condensation with urea and formaldehyde depends strongly on the reaction conditions [2-5] and that in many instances it leads to a large range of products [2, 3, 5]. Cyclic condensed structures are formed in the reaction of N-monosubstituted ureas with N-methylene-tert-butylamine [6].

In all instances the condensation led to crystalline compounds which did not have a well-defined melting point. Attempts to isolate individual products in pure form were unsuccessful. The structure of the obtained compounds and the factors influencing the course of the above reaction were therefore assessed on the basis of data obtained in the nitration of its products.

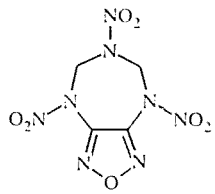
Nitration gave the individual cyclic nitramines I-III [7] by using urea, guanidine, or DAF at the condensation stage.



I

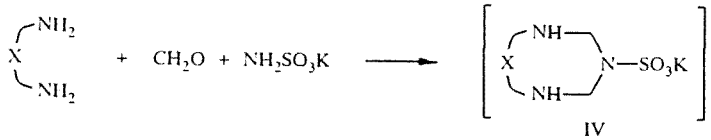


II



III

The structure of compounds I-III indicates that the sulfamate (IV) is the most probable condensation product.



IV

X = C=O, C=NH, 3,4-

5-Aminotetrazole gave the nitramines V and VI.

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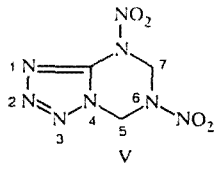
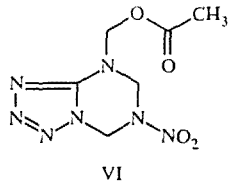
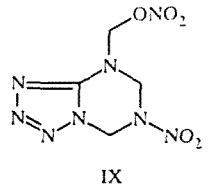


V

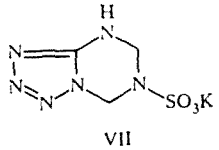


VI

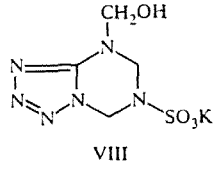


IX

The fact that nitration produced predominantly the compounds V or VI leads to the conclusion that, depending on the pH of the medium, the sulfamate VII (pH = 4.0) or VIII (pH = 6.5) is formed in the condensation step.



VII



VIII

The maximum yield of the heterocyclic nitramines (18-36%) is obtained when the condensation is carried out in a virtually neutral medium (pH = 6.5-7.5); only in the instance of compound V the reaction is performed in an acidic medium (pH = 4.0). The stoichiometric ratio of the initial components gives the optimum yield (only in the synthesis of compound III a change in the stoichiometry by using the molar ratio DAF:CH_2O:NH_2SO_3K = 1:3:2 increases the yield of the nitroproduct).

Of the different nitration methods [8, 9], we have selected those which gave the highest yields of the nitramines I-III, V, and VI (see Experimental). The concrete examples for the preparation of the nitramines, given in the further text, and the nitration conditions of the corresponding condensation products differ from each other; this is probably due to the different stability of the sulfamates IV, VII, and VIII, as well as of the nitramines in the nitration medium. In particular, the presence of the acetate VI and the absence of the corresponding nitrate IX indicates that the former is more stable than the latter at the given conditions for the nitration of the sulfamates and isolation of the nitramines.

In distinction from the optimum conditions for the nitration of the condensation products, based on urea or guanidine, where a mixture of nitric acid and oleum (fuming sulfuric acid) was used, a mixture of nitric acid and acetic anhydride must be used in the synthesis of compounds III, V, and VI, as well as catalysis by chloride ions (~15 wt.% methylamine hydrochloride is added to the nitration mixture, together with the condensation products).

Thus, the nitration of the condensation products, formed in the reaction of potassium sulfamate, formaldehyde, and the component, containing the NH_2 (or NH) fragment — urea, guanidine, DAF, or 5-aminotetrazole — leads to the corresponding heterocyclic nitramines.

EXPERIMENTAL

The PMR spectra were obtained on Bruker AM-300 (δ, ppm) and Tesla BS-467 (60 MHz) spectrometers. The chemical shifts (δ, ppm) are cited with respect to tetramethylsilane. The IR spectra were taken on a UR-20 spectrometer in KBr tablets. The elemental analysis data (C, H, N) of compounds I, V, and VI correspond to the calculated values.

1,3,5-Trinitrohexahydro-1,3,5-triazin-2-one (I, $C_3H_4N_6O_7$). NH_2SO_3K (10 mmoles), urea (10 mmoles) and formaldehyde (20 mmoles) (33% aqueous solution) are dissolved in 20 ml of water. The solution is adjusted to pH 6.5-7.0 and evaporated on a rotary evaporator at 80-120°C; 2 g of the crystalline residue is added to a mixture of 6 ml 98% HNO_3 and 5 ml 20% oleum at −5 to −10°C. The mixture is stirred at this temperature for 1 h and poured onto 50 g of ice. The precipitate formed is filtered off, washed with water, dried, and recrystallized from acetic acid; mp 190-192°C. IR spectrum: 1255, 1700, 1560, 2885 cm^{-1}. PMR spectrum (acetone-D_6): 6.32 ppm (4H, s, $2CH_2$). Yield 18%.

4-Nitrimino-1-nitrohexahydro-1,3,5-triazine (II, $C_3H_6N_6O_4$*). The condensation is carried out by using the method described above and replacing urea by guanidine nitrate. The nitration is carried out at 15-20°C; after pouring the reaction mixture onto ice, the nitroproduct is extracted with ethyl acetate and the extract washed with water (2 × 20 ml), 3% aqueous soda solution (1 × 20 ml, and water (1 × 20 ml), and dried over $MgSO_4$. The residue after evaporation is recrystallized from acetone; mp 215-216°C. M^+ 190. IR spectrum: 1120, 1310, 1565, 1600, 2960, 3120, 3220, 3325 cm^{-1}. PMR spectrum (acetone-D_6): 5.30 ppm (4H, s, $2CH_2$). Yield 30%.

4,6,8-Trinitro-4,5,7,8-tetrahydro-6H-2,1,5-oxadiazolo[3,4-*f*]-1,3,5-triazepine (III, $C_4H_4N_8O_7$). The synthesis is carried out as described for compound II by using DAF instead of guanidine. The nitration is performed at 5-15°C in HNO_3-Ac_2O (5:1 by vol.) by taking 6 ml of the nitrating mixture for 1 g of crystalline residue and adding ~15 wt.% of methylamine hydrochloride. The obtained product III is recrystallized from ethanol; mp 151°C. IR spectrum: 1110, 1280, 1310, 1610, 3070 cm^{-1}. PMR spectrum (acetone-D_6): 6.42 ppm (4H, s, $2CH_2$). Yield 36%.

6,8-Dinitro-5,6,7,8-tetrahydrotetrazolo[4,5-*a*]-1,3,5-triazine (V, $C_3H_4N_8O_4$). 5-Aminotetrazole (3.63 g, 0.03 mole) and 4.05 g, (0.03 mole) NH_2SO_3K is dissolved in 30 ml water; 5.9 ml (0.06 mole) of aqueous formaldehyde solution is added, the pH of the solution is brought to 4.0 and the reaction mixture evaporated on a rotary evaporator at 80-90°C.

A solution of 15 ml 98% HNO_3 (d = 1.506) and 10 ml AcOH is treated at the lowest temperature which permits stirring (approximately −5 to −10°C) with 7.1 g of the crystalline residue mole of $CH_3NH_2 \cdot HCl$; 20 ml Ac_2O is then added. The reaction mixture is kept at 5-8°C for 2-2.5 h and poured onto 100 g of ice. The product is extracted with ethyl acetate (3 × 80 ml), the extract is washed with water (1 × 30 ml), and stirred for 0.5 h with a 3% soda solution, by adding the Na_2CO_3 solution in portions until the pH of the aqueous phase reached 7.5-8.0. The organic layer is separated, washed with water (1 × 30 ml), dried over $MgSO_4$, and evaporated. Yield 2.34 g of residue; chromatography of the residue on a column packed with Silpearl (mobile phase hexane−ethyl acetate 1:3) gives 1.43 g (24%) of compound V, R_f 0.5; mp 154-155°C (from acetone). IR spectrum 1280, 1580, 2995 cm^{-1}. PMR spectrum (DMSO-D_6): 6.42 ppm (2H, s, 5-H), 6.43 ppm (2H, s, 7-H).

8-Acetoxymethyl-6-nitro-5,6,7,8-tetrahydrotetrazolo[4,5-*a*]1,3,5-triazine (VI, $C_6H_9N_7O_4$). The synthesis is carried out as described for compound V, but the condensation is performed at pH 6.5 and the fraction with R_f 0.26 is collected in the chromatographic separation; mp 138-139°C (from ethanol). The molecular mass obtained by ebullioscopy was 246, calculated 243. IR spectrum: 1270, 1560, 1750, 2290 cm^{-1}. PMR spectrum (DMSO-D_6): 6.33 ppm (2H, s, 5-H), 5.57 ppm (2H, s, 7-H), 5.46 ppm (2H, s, CH_2O), 2.14 ppm (3H, s, CH_3). Yield 21%.

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*The compound II was synthesized earlier by O. A. Luk'yanov and T. G. Mel'nikova by using a different method which will be published separately.