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USSR

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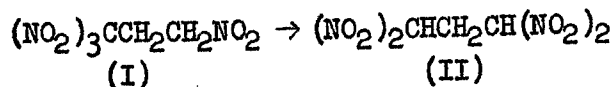
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ISOMERIZATION OF TETRANITROALKANES

[Following is a translation of an article by S. S. Novikov, A. A. Faynzil'berg, S. A. Shevelev, I. S. Korsakova, and K. K. Babiyevskiy in the Russian-language periodical Doklady Akademii Nauk SSSR (Reports of the Academy of Sciences USSR), Moscow, Vol. CXXXII, No. 4, 1 June 1960, pages 846-849.]

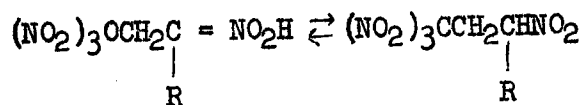
Recently we demonstrated that 1,1,1,3-tetranitropropane (I) is isomerized into symmetrical tetranitropropane (II) under the action of ammonia in an alcoholic solution (1)



In the present research it was found that 1,1,1,3-tetranitropropane is isomerized into symmetrical tetranitropropane not only in the presence of ammonia but also under the influence of some other basic agents -- potassium acetate and potassium methylate. Here should be noted that the nature of the solvent has a substantial effect on the course of the reaction. Thus, if the reaction between 1,1,1,3-tetranitropropane and potassium acetate is conducted in an alcoholic solution, isomerization occurs and 1,1,3,3-tetranitropropane is formed with a yield of 33.4%. (Here and further on the yield was calculated for the potassium salts of the corresponding nitroalkanes.) If then a mixture of acetone and alcohol is the solvent, isomerization does not take place, but only cleavage of a nitrogroup from the initial 1,1,1,3-tetranitropropane with the formation of 1,1,3-trinitropropane. In the presence of potassium methylate (in methanol) 1,1,1,3-tetranitropropane (I) is isomerized into symmetrical tetranitropropane (II) with a yield of 10.8%.

Hoping to learn whether isomerization is specific only for 1,1,1,3-tetranitropropane or whether other compounds with an analogous structure undergo it, we studied the relationship of 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane to bases. A matter of additional interest in the study of these compounds was the fact that they, in contrast to 1,1,1,3-tetranitropropane, exist in two stable forms -- the nitro and the aciform (2). A comparative study of the isomerization of these two forms could cast light upon the mode of

the reaction

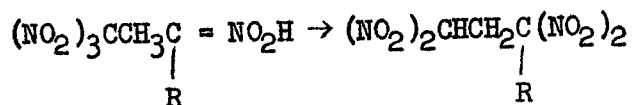


(IIIa) R = CH₃; (IVa) R = C₂H₅; (IIIb) R = CH₃; (IVb) R = C₂H₅.

It appeared that the aciform of tetranitrobutane (IIIa) is readily isomerized into 1,1,3,3-tetranitrobutane (V) under the action of potassium acetate in ethyl alcohol (yield: 34.5%), potassium methylate in methanol (yield 36.7%) and also alcoholic potassium hydroxide (yield 12.1%). Isomerization can also take place in the presence of dimethylamine but the yield of the reaction product under these conditions does not exceed several percent.

The nitro form of 1,1,1,3-tetranitrobutane (IIIb) is also isomerized into 1,1,3,3-tetranitrobutane (V) under the action of potassium acetate (yield 34.5%) and alcoholic potassium hydroxide (yield 12.8%); however, in the absence of the aciform, it is not isomerized in the presence of potassium methylate.

The aciform of 1,1,1,3-tetranitropentane (IVa), like the 1,1,1,3-tetranitropropane and 1,1,1,3-tetranitrobutane, also undergoes isomerization but the process proceeds only in the presence of potassium acetate. The yield of the isomerization product 1,1,3,3-tetranitropentane (VI) amounts to 14.5%. In the presence of other basic agents isomerization does not occur.

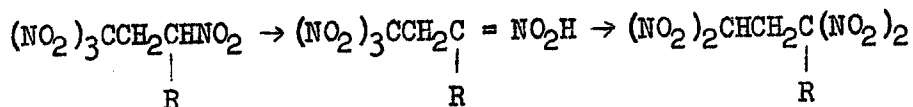


(IIIa) R = CH₃; (IVa) R = C₂H₅; (V) R = CH₃; (VI) R = C₂H₅

Finally the nitro form of 1,1,1,3-tetranitropentane (IVb) is not isomerized at all in the presence of basic agents.

It should be noted that 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane (both the aci- and nitro forms) are not isomerized in the presence of ammonia in contrast to 1,1,1,3-tetranitropropane.

Comparing the results obtained during the study of the aci- and nitro forms of 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane, it is not difficult to observe that the aciforms are not isomerized more easily than the corresponding nitro forms. On the basis of this fact it can be assumed that the isomerization of 1,1,1,3-tetranitroalkanes passes through a stage of aciform formation:



R = H, CH₃, or C₂H₅.

The isomerization products -- 1,1,3,3-tetranitroalkanes (II), (V) and (VI), were separated as their potassium salts which were analyzed for potassium.

The potassium salts reacted with bromine to yield the corresponding bromides -- 1,3-dibromo-1,1,3,3-tetranitropropane, 1-bromo-1,1,3,3-tetranitrobutane and 1-bromo-1,1,3,3-tetranitropentane.

On the basis of the results obtained in the present work the conclusion can be made that isomerization with transferred nitrogroups is a general reaction for 1,1,1,3-tetranitroalkanes which possess a straight chain of carbon atoms.

Experimental Part

Isomerization of 1,1,1,3-tetranitropropane (I) into 1,1,3,3-tetranitropropane (II).

a) In the presence of potassium acetate. To a solution of 5.6 g (0.025 mole) of 1,1,1,3-tetranitropropane in 35 ml of alcohol, 4.9 g (0.05 mole) of melted potassium acetate in 25 ml of alcohol, which is held at 0° C, are added dropwise with stirring and cooling with ice. After adding the potassium acetate, stirring is continued for 2.5 hours at 0° and for 1 hour at room temperature. The precipitate is separated, washed with a small quantity of ice water, later by acetone and by a small quantity of dry ether, and dried in air. 2.5 g (33.4%) of the dipotassium salt of 1,1,3,3-tetranitropropane was obtained. Boiling point 221° (with decomposition) (after recrystallization from water).

C₃H₂N₄O₈K₂ -- Found %: K 26.41, 26.22
Calculated T: K 26.03

b) In the presence of potassium methylate. To a solution of 4.5 g (0.02 mole) of 1,1,1,3-tetranitropropane in 15 ml of absolute methanol, 40 ml of 1 N solution of potassium methylate (0.04 mole) are added dropwise with stirring and cooling with ice. The temperature being held at 0° C. After adding the potassium methylate stirring is continued for 1 hour at 0° and 1 hour at 10°. The precipitate is separated and repeatedly washed with acetone. The precipitate is washed with a small quantity of dry ether and dried in air. 0.65 g (10.8%) of the dipotassium salt of 1,1,3,3-tetranitropropane was obtained.

$C_3H_2N_4O_8K_2$ -- Found %: K 26.26, 26.17
Calculated %: K 26.03

1,3-Dibromo-1,1,3,3-tetranitropropane (1) was obtained from this salt.

Isomerization of the aciform of 1,1,1,3-tetranitrobutane (IIIa) into 1,1,3,3-tetranitrobutane (V).

a) In the presence of potassium acetate. 4 g (0.0168 mole) of the aciform of 1,1,1,3-tetranitrobutane was dissolved in 24 ml of alcohol at 0° C. To the solution obtained, a solution of 1.7 g (0.0174 mole) of melted potassium acetate in 20 ml of alcohol kept at 6-8° are added dropwise with stirring and cooling with ice. After this, stirring was continued for 4 hours at room temperature. The solution was decanted, a small amount of ice water was added to the remaining deposit; the crystalline reaction product was separated, washed with a small quantity of chilled alcohol and ether and dried in air. 1.6 g (34.5%) of the potassium salt of 1,1,3,3-tetranitrobutane was obtained. Melting point: 118° (with decomposition) (after recrystallization from 50% methanol). Literature melting point: 137-138° (3).

$C_4H_5N_4O_8K$ -- Found %: K 14.09, 14.17
Calculated %: K 14.16

b) In the presence of potassium methylate. 1.8 g (0.0075 mole) of the aciform of 1,1,1,3-tetranitrobutane, maintained below -5°, was added in several portions to 7.5 ml of a 1 N solution of potassium methylate (0.0075 mole) and 3 ml of absolute methanol, with stirring and cooling with ice and salt. Stirring was continued at 10° for 45 minutes; the precipitate was drawn off, washed with a small amount of ice water, chilled alcohol and dry ether, dried in air and recrystallized from 50% methanol. 0.75 g (36.7%) of the potassium salt of 1,1,3,3-tetranitrobutane was obtained. (In this and the following experiments the potassium salt of 1,1,3,3-tetranitrobutane was analyzed for potassium and was also identified by melting point. These data are not presented to avoid repetition.)

c) In the presence of potassium hydroxide. 2.5 g (0.0105 mole) of the aciform of 1,1,1,3-tetranitrobutane was dissolved in 10 ml of alcohol at 0°. A solution of 0.6 g (0.0107 mole) of potassium hydroxide in 10 ml of alcohol, maintained below 10°, was added to the obtained solution, while it was stirred and cooled with ice. After this, stirring was continued for 3.5 hours at room temperature; the solution was decanted; a little ice water was added to the resulting precipitate; the crystalline reaction product was separated, washed with a small amount of chilled alcohol, and with ether, and dried in air. 0.35 g (12.1%) of the potassium salt of 1,1,3,3-tetranitrobutane was obtained.

1-Bromo-1,1,3,3-tetranitrobutane. 2.6 g (0.0094 mole) of the potassium salt of 1,1,3,3-tetranitrobutane was covered with a layer of ether and during mixing and cooling with ice, a determined quantity of bromine was added. The ether solution was filtered and dried with calcium chloride. After distilling the ether off 3 g (100%) of crystalline 1-bromo-1,1,3,3-tetranitrobutane was obtained. Melting point 46° C (after recrystallization from hexane at 40° with subsequent freezing out).

$C_4H_5N_4O_8Br$ -- Found %: Br 25.13, 25.26
Calculated %: Br 25.22

Isomerization of the nitro form of 1,1,1,3-tetranitrobutane (IIIb) into 1,1,3,3-tetranitrobutane (V).

a) In the presence of potassium acetate. A solution of 1.65 g (0.0168 mole) of melted potassium acetate in 18 ml alcohol, maintained at $15-18^{\circ}$ C, are added dropwise with stirring and cooling with ice water into a solution of 4 g (0.0168 mole) of the nitro form of 1,1,1,3-tetranitrobutane in 32 ml of alcohol. Stirring was continued for 4.5 hours at room temperature; the precipitate was separated, washed with a small quantity of ice water, chilled alcohol, and ether, and dried in air. 1.6 g (34.5%) of the potassium salt of 1,1,3,3-tetranitrobutane was obtained.

b) In the presence of potassium hydroxide. A solution of 0.25 g (0.0045 mole) of potassium hydroxide in 4 ml of alcohol, maintained at a temperature below 10° C was added with stirring and cooling with ice water to a solution of 1 g (0.0042 mole) of the nitro form of 1,1,1,3-tetranitrobutane in 8 ml of alcohol. After this, the solution was stirred for 3 hours at room temperature and left for 3 days. The solution was decanted; a small quantity of ice water was added to the remaining deposit; a crystalline reaction product was separated, washed with cooled alcohol and ether, and dried in air. 0.15 g (12.8%) of the potassium salt of 1,1,3,3-tetranitrobutane was obtained.

Isomerization of the aciform of 1,1,1,3-tetranitropentane (IVa) into 1,1,3,3-tetranitropentane (VI). 3 g (0.012 mole) of the aciform of 1,1,1,3-tetranitropentane was dissolved in 12 ml of alcohol at 0° C. To the solution obtained are added dropwise, while stirring and cooling with ice water, a solution of 1.2 g (0.0123 mole) of melted potassium acetate in 12 ml of alcohol. After adding the potassium acetate the solution was stirred for 2 hours at 0° , then 3 hours at room temperature and left for 5 days. The precipitate was separated, washed with a small quantity of ice water, cold alcohol, and ether, and dried in air. 0.5 g (14.5%) of the potassium salt of 1,1,3,3-tetranitropentane was obtained. Melting point 135° C (with decomposition) (after recrystallization from 50% methanol).

$C_5H_7N_4O_8K$ -- Found %: K 13.15, 13.35
Calculated %: K 13.47

1-Bromo-1,1,3,3-tetranitropentane. 1.1 g (0.0038 mole) of the potassium salt of 1,1,3,3-tetranitropentane was covered with ether and, while stirring and cooling with ice water, a determined amount of bromine was added. The ether solution was filtered and dried with calcium chloride. After eliminating the ether 1.1 g (88%) of liquid 1-bromo-1,1,3,3-tetranitropentane was obtained; n_D^{20} 1.5060 (purified by dissolving in hexane with subsequent freezing out).

$C_5H_7N_4O_8Br$ -- Found %: Br 24.16, 24.02
Calculated %: Br 24.14

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