Soviet-era science, translated into English

Chemistry

S. S. Novikov, A. A. Fainzil' berg, S. A. Shevelev,

1960

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196001.15510

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

SovietRxiv

Abstract

Full Text

Chemistry

S. S. Novikov, A. A. Fainzil' berg, S. A. Shevelev,
I. S. Korsakova, and K. K. Babievskii

Isomerization of Tetranitroalkanes

(Presented by Academician A. V. Topchiev, January 9, 1960)

Recently we showed that 1,1,1,3-tetranitropropane (I) isomerizes to symmetrical tetranitropropane (II) under the action of ammonia in an alcoholic solution (1)

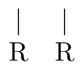
$$(NO_2)_3CCH_2CH_2NO_2 \rightarrow (NO_2)_2CHCH_2CH(NO_2)_2.$$

(I) (II)

In the present work it was found that 1,1,1,3-tetranitropropane isomerizes to symmetrical tetranitropropane not only in the presence of ammonia, but also under the influence of certain other alkaline agents—potassium acetate and potassium methylate. It should be emphasized here that the nature of the solvent has a substantial influence on the course of the reaction. Thus, if the interaction of 1,1,1,3-tetranitropropane with potassium acetate is carried out in an alcoholic solution, isomerization occurs and 1,1,3,3-tetranitropropane is formed in 33.4% yield*. If, however, the solvent is a mixture of acetone with alcohol, isomerization does not take place, and only cleavage of a nitro group from the initial 1,1,1,3-tetranitropropane occurs, with formation of 1,1,3-trinitropropane. In the presence of potassium methylate (in methanol), 1,1,1,3-tetranitropropane (I) isomerizes to symmetrical tetranitropropane (II) in 10.8% yield.

Wishing to determine whether isomerization is specific only to 1,1,1,3-tetranitropropane or whether other analogously constructed compounds also undergo it, we studied the behavior toward bases of 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane. The study of these compounds was of additional interest in that, unlike 1,1,1,3-tetranitropropane, they exist in two stable forms —the true and the aci-form (2). A comparative study of the isomerization of these two forms could shed light on the reaction mechanism

$$(NO_2)_3CCH_2C = NO_2H \rightleftarrows (NO_2)_3CCH_2CHNO_2,$$



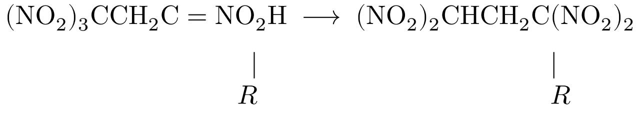
$$\begin{array}{cc} | & | \\ \mathrm{R} & \mathrm{R} \end{array}$$

(IIIa) $R = CH_3$; (IVa) $R = C_2H_5$ (IIIb) $R = CH_3$; (IVb) $R = C_2H_5$.

It turned out that the aci-form of tetranitrobutane (IIIa) readily isomerizes to 1,1,3,3-tetranitrobutane (V) under the action of potassium acetate in alcohol (yield 34.5%), potassium methylate in methanol (yield 36.7%), and also alcoholic caustic potash (yield 12.1%). Isomerization can also be effected in the presence of dimethylamine; however, the yield of the reaction product under these conditions does not exceed a few percent.

The true form of 1,1,1,3-tetranitrobutane (IIIb) also isomerizes to 1,1,3,3-tetranitrobutane (V) under the action of potassium acetate (yield 34.5%) and alcoholic caustic potash (yield 12.8%); however, unlike the aci-form, it is not isomerized in the presence of potassium methylate.

The aci-form of 1,1,1,3-tetranitropentane (IVa), like 1,1,1,3-tetranitropropane and 1,1,1,3-tetranitrobutane, also undergoes isomerization, but the process takes place only in the presence of potassium acetate. The yield of the isomerization product—1,1,3,3-tetranitropentane (VI)—is 14.5%. In the presence of other alkaline agents, isomerization does not occur.



$$(NO_2)_3CCH_2\underset{R}{\underset{|}{C}} = NO_2H \longrightarrow (NO_2)_2CHCH_2\underset{R}{\underset{|}{C}}(NO_2)_2$$

(IIIa) $R = CH_3$; (IVa) $R = C_2H_5$ (V) $R = CH_3$; (VI) $R = C_2H_5$.

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

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

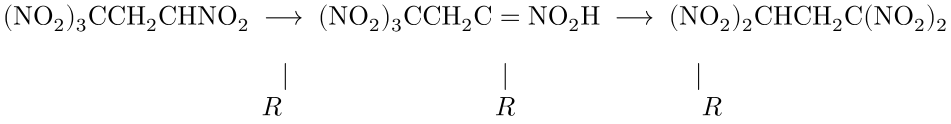
Comparing the results obtained in the study of the aci- and true forms of 1,1,1,3-tetranitrobutane and 1,1,1,3-tetranitropentane, it is not difficult to observe

---

* Here and below, the yield was calculated with respect to the potassium salts of the corresponding nitroalkanes.

SovietRxiv

that the aci-forms isomerize more readily than the corresponding true forms. On the basis of this fact it may be assumed that the isomerization of 1,1,1,3-tetranitroalkanes proceeds through the stage of formation of the aci-form:



$$(\mathrm{NO_2})_3\mathrm{CCH_2}\underset{\substack{|\\ R}}{\mathrm{C}}\mathrm{HNO_2} \longrightarrow (\mathrm{NO_2})_3\mathrm{CCH_2}\underset{\substack{|\\ R}}{\mathrm{C}} = \mathrm{NO_2H} \longrightarrow (\mathrm{NO_2})_2\mathrm{CHCH_2}\underset{\substack{|\\ R}}{\mathrm{C}}(\mathrm{NO_2})_2$$

$$R = \mathrm{H},\ \mathrm{CH_3},\ \mathrm{C_2H_5}$$

The isomerization products—1,1,3,3-tetranitroalkanes (II), (V), and (VI)—were isolated in the form of their potassium salts, which were analyzed for potassium.

The potassium salts were converted by the action of bromine into 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, it may be concluded that isomerization with migration of the nitro group is a general reaction for 1,1,1,3-tetranitroalkanes possessing 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, with stirring and cooling with ice, there was added dropwise a solution of 4.9 g (0.05 mole) of fused potassium acetate in 25 ml of alcohol, maintaining the temperature at 0°. After addition of the potassium acetate, the mixture was stirred for 2.5 hours at 0° and for 1 hour at room temperature. The precipitate that formed was filtered off, washed with a small amount of ice water, then with acetone, with a small amount of dry ether, and dried in air. There was obtained 2.5 g (33.4%) of the dipotassium salt of 1,1,3,3-tetranitropropane. M.p. 221° (with decomposition) (after recrystallization from water).

$$\mathrm{C_3H_2N_4O_8K_2}.\quad \begin{array}{ll} \text{Found, \%:} & K\ 26.41;\ 26.22 \\ \text{Calculated, \%:} & K\ 26.03 \end{array}$$

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, pri-

was added dropwise with stirring and ice cooling to 40 ml of a 1 N solution of potassium methylate (0.04 mole), keeping the temperature no higher than

SovietRxiv

0°. After the addition of the potassium methylate, the mixture was stirred for 1 hour at 0° and 1 hour at 10°. The precipitate that formed was filtered off and washed repeatedly with acetone. The residue was washed with a small amount 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

From this salt, 1,3-dibromo-1,1,3,3-tetranitropropane (I) was obtained.

Isomerization of the aci-form of 1,1,1,3-tetranitrobutane (IIIa) to 1,1,3,3-tetranitrobutane (V).

a) **In the presence of potassium acetate.** 4 g (0.0168 mole) of the aci-form of 1,1,1,3-tetranitrobutane was dissolved at 0° in 24 ml of alcohol. To the resulting solution there was added dropwise, with stirring and ice cooling, a solution of 1.7 g (0.0174 mole) of fused potassium acetate in 20 ml of alcohol, keeping the temperature at 6–8°. The mixture was then stirred for 4 hours at room temperature. The solution was decanted; to the remaining precipitate a little ice water was added, the crystalline reaction product was filtered off, washed with a small amount of cold alcohol and ether, and dried in air. 1.6 g (34.5%) of the potassium salt of 1,1,3,3-tetranitrobutane was obtained. M.p. 118° (with decomposition) (after recrystallization from 50% methanol). Literature data: m.p. 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.** To 7.5 ml of a 1 N solution of potassium methylate (0.0075 mole) and 3 ml of absolute methanol, the salt of 1.8 g (0.0075 mole) of the aci-form of 1,1,1,3-tetranitrobutane was added in several portions with stirring and ice cooling, keeping the temperature below −5°. The mixture was then stirred at −10° for 45 min; the precipitate that formed was filtered off, washed with small amounts of ice water, cold 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.

c) **In the presence of caustic potash.** 2.5 g (0.0105 mole) of the aci-form of 1,1,1,3-tetranitrobutane was dissolved at 0° in 10 ml of alcohol. To the resulting solution there was added, with stirring and ice cooling, a solution of 0.6 g (0.0107 mole) of caustic potash in 10 ml of alcohol, keeping the temperature no higher than 10°. The mixture was then stirred at room temperature for 3.5 hours, the solution was decanted, and to the remaining precipitate a little ice water was added; the crystalline reaction product was filtered off, washed with a small amount of cold alcohol and 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, with stirring and ice cooling, the calculated amount of bromine was added. The ethereal solution was filtered and dried with calcium chloride. After removal of the ether, 3 g (100%) of crystalline 1-bromo-1,1,3,3-tetranitrobutane was obtained. M.p. 46° (after recrystallization from hexane at 40° followed by freezing out).

$C_4H_5N_4O_8Br$. Found, %: Br 25.13; 25.26
Calculated, %: Br 25.22

* In this and in subsequent experiments, the potassium salt of 1,1,3,3-tetranitrobutane was analyzed for potassium and was also identified by its melting point. These data are not given in order to avoid repetition.

Isomerization of the true form of 1,1,1,3-tetranitrobutane (IIIb) to 1,1,3,3-tetranitrobutane (V).

a) **In the presence of potassium acetate.** To a solution of 4 g (0.0168 mole) of the true form of 1,1,1,3-tetranitrobutane in 32 ml of alcohol, a solution of 1.65 g (0.0168 mole) of fused potassium acetate in 18 ml of alcohol was added dropwise with stirring and cooling with cold water, maintaining the temperature at 15–18°. The mixture was then stirred at room temperature for 4.5 hours; the precipitate that had separated was filtered off, washed with small amounts of ice water, cold alcohol, and ether, and dried in air. There was obtained 1.6 g (34.5%) of the potassium salt of 1,1,3,3-tetranitrobutane.

b) **In the presence of caustic potash.** To a solution of 1 g (0.0042 mole) of the true form of 1,1,1,3-tetranitrobutane in 8 ml of alcohol, a solution of 0.25 g (0.0045 mole) of caustic potash in 4 ml of alcohol was added with stirring and cooling with ice water, maintaining the temperature not above 10°. The mixture was then stirred for 3 hours at room temperature and left for 3 days. The solution was decanted; a little ice water was added to the remaining precipitate; the crystalline reaction product was filtered off, washed with cold alcohol and ether, and dried in air. There was obtained 0.15 g (12.8%) of the potassium salt of 1,1,3,3-tetranitrobutane.

Isomerization of the aci-form of 1,1,1,3-tetranitropentane (IVa) to 1,1,3,3-tetranitropentane (VI). 3 g (0.012 mole) of the aci-form of 1,1,1,3-tetranitropentane was dissolved in 12 ml of alcohol at 0°. To the resulting solution, with stirring and cooling with ice water, a solution of 1.2 g (0.0123 mole) of fused potassium acetate in 12 ml of alcohol was added dropwise. After the addition of the potassium acetate, the mixture was stirred for 2 hours at

0°, then for 3 hours at room temperature, and left for 5 days. The precipitate that had separated was filtered off, washed with small amounts of ice water, cold alcohol, and ether, and dried in air. There was obtained 0.5 g (14.5%) of the potassium salt of 1,1,3,3-tetranitropentane. M.p. 135° (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 with stirring and cooling with ice water the calculated amount of bromine was added. The ethereal solution was filtered and dried over calcium chloride. After removal of the ether, 1.1 g (88%) of liquid 1-bromo-1,1,3,3-tetranitropentane was obtained, n_D^{20}1.5060 (purified by dissolution in hexane followed by freezing out).

$C_5H_7N_4O_8Br$.	Found %: Br 24.16; 24.02
	Calculated %: Br 24.14

Institute of Organic Chemistry named after N. D. Zelinsky
Academy of Sciences of the USSR

Received
9 I 1960

REFERENCES CITED

1. S. S. Novikov, A. A. Fainzil' berg, S. A. Shevelev et al., DAN, **124**, 589 (1959).

2. S. S. Novikov, K. K. Babievskii, I. S. Korsakova, DAN, **125**, 560 (1959); Izv. AN SSSR, OKhN, 1959, 1847.

3. M. Frankel, J. Org. Chem., **23**, 913 (1958).

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.