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Abstract

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As is known, nitrate esters of polyhydroxy compounds are of interest because some of them exhibit vasodilating action. Thus, for example, dinitrate of sorbitan is a very valuable medicinal substance, used in the treatment of hypertension, angina pectoris, and other diseases of the cardiovascular system. In this connection we have synthesized a series of nitrate esters of carbon-substituted carbohydrates, which in their chemical structure are anhydrides of substituted polyhydric alcohols.

Among the various methods for the synthesis of nitrate esters of polyhydroxy compounds, in our case the most convenient proved to be the reaction with concentrated nitric acid in acetic anhydride. This method was previously proposed for sugars ([1]-[4]). We have synthesized nitrate esters of glucopyranosyl-, galactopyranosyl-, rhamnopyranosyl-, xylopyranosyl-, and arabopyranosylbenzene. The last compound was obtained by us for the first time from the corresponding acetyl derivative.

The nitrate esters of C-substituted carbohydrates obtained by us are, for the most part, snow-white crystalline substances, soluble in ether, benzene, lower alcohols, acetone, chloroform, and ethyl acetate, and insoluble in water and petroleum ether. They have a tendency to burn with a flash.

Experimental Part

Tetranitro-glucopyranosylbenzene. To a solution of 3 g (0.125 mole) of glucopyranosylbenzene in 20 ml of acetic anhydride, with external cooling by ice, there was added a solution of 6 ml of fuming nitric acid in 10 ml of acetic anhydride. The mixture was allowed to stand at room temperature for 15 min, and then was poured into ice water and neutralized with potash. 4.2 g of crude product was obtained. The substance was purified by treating its ethereal solution with anhydrous sodium sulfate and activated charcoal. After distilling off the ether, 2.14 g (41% of theory) of a snow-white crystalline product with m.p. 102–104° was isolated. The substance is described for the first time. Its structure is represented by the formula tetranitro-glucopyranosylbenzene

$$\text{Found, \%:}\quad N\ 13.13,\ 13.00$$
$$C_{12}H_{12}O_{13}N_4.\quad \text{Calculated, \%:}\quad N\ 13.33$$

Tetranitro-galactopyranosylbenzene. To a solution of 1.3 g (0.054 mole) of the previously described galactopyranosylbenzene (^{5}) in 10 ml of acetic anhydride, with cooling, there was added a solution of 3 ml of fuming nitric

nitric acid in 6 ml of acetic anhydride. Further processing was carried out by the method described above. After removal of ether, 1.48 g of a transparent syrup was obtained. On brief storage in a vacuum desiccator over phosphorus pentoxide the syrup solidified; after recrystallization from isopropanol, 0.6 g (26% of theory) of snow-white crystals with m.p. 108–110° was isolated. The substance is described for the first time.

$C_{12}H_{12}O_{13}N_4$. Found, %: N 13.57
Calculated, %: N 13.33

Trinitro-rhamnopyranosylbenzene. For the synthesis, rhamnopyranosylbenzene, described by us earlier (^{6}), was taken. To 1.5 g (0.067 mole) of the substance in 7 ml of acetic anhydride was added 4 ml of fuming nitric acid in 8 ml of acetic anhydride. Further processing was carried out by the method indicated above. 1.5 g (62.5% of theory) of a light, transparent syrup was obtained, which could not be crystallized. The substance is described for the first time.

$C_{12}H_{13}O_{10}N_3$. Found, %: N 11.48
Calculated, %: N 11.69

Trinitro-xylopyranosylbenzene. For the synthesis, xylopyranosylbenzene (^{5}), previously obtained by us, was used. To a solution of 1 g (0.047 mole) of the substance in 7 ml of acetic anhydride was added dropwise a solution of 3 ml of fuming nitric acid in 4 ml of acetic anhydride. Further processing was as usual. 1.45 g of a light syrup was obtained, which after recrystallization from *n*-butyl and isopropyl alcohols gave 0.9 g (55% of theory) of a white crystalline product with m.p. 74–76°. On rapid heating the substance explodes. The substance is described for the first time.

$C_{11}H_{11}O_{10}N_3$. Found, %: N 11.98
Calculated, %: N 12.17

Trinitro-arabopyranosylbenzene. The triacetyl-L-arabopyranosylbenzene described by us earlier (^{7}) was subjected to deacetylation with ammonia in absolute methanol. As a result, the previously undescribed L-arabopyranosylbenzene was obtained in the form of a syrup.

To a solution of 2 g (0.094 mole) of arabopyranosylbenzene in 8 ml of acetic anhydride was carefully added, with cooling, 3 ml of fuming nitric acid in 7 ml of acetic anhydride. Further processing was as described above. After purification, 1.9 g (58% of theory) of a snow-white crystalline product with m.p. 138–140° was obtained. On heating above the melting point the substance explodes. The substance is described for the first time.

$C_{11}H_{11}O_{10}N_3$.	Found, %:	N 11.79; 11.84
	Calculated, %:	N 12.17

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REFERENCES

1. L. Brissaud, *Mém. Serv. chim. état* (Paris), **30**, 120 (1943).
2. G. Fleury, L. Brissaud, *C.R.*, **222**, 105 (1946).
3. J. Honeyman, J. W. W. Morgan, *Chem. and Ind.*, 1953, 1035.
4. J. Honeyman, J. W. W. Morgan, *Advances Carbohydr. Chem.*, **12**, 117 (1957).
5. Yu. A. Zhdanov, G. V. Bogdanova, A. I. Chuvileva, *DAN*, **128**, 953 (1959).
6. Yu. A. Zhdanov, G. A. Korol' chenko, L. A. Kubasskaya, *DAN*, **128**, 1185 (1959).
7. Yu. A. Zhdanov, T. N. Dorofeenko, *DAN*, **113**, 601 (1957).

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