The only representative of 2,4-dinitrophenylalkanols known before this study was 2,4-dinitrobenzyl alcohol synthesized from benzyl chloride via a multistage process [2–5].

In continuation of earlier work [6], we have investigated the action of concentrated sulfuric acid upon nitroesters of 4-nitrobenzyl (I) and β-(4-nitrophenyl)ethyl (II) alcohols.

It was established that these compounds, in contrast to the nitroesters of α-nitrophenylalkylcarbinols [6], exhibit the autonitration reaction at 28–42°C in a 93–96% sulfuric acid. The reaction takes place at position 2 of the benzene ring and leads to the formation of 2,4-dinitrophenylalkylsulfuric acids (C). The hydrolysis of compounds C in a dilute sulfuric acid yields 2,4-dinitrobenzyl and β-(4-dinitrophenyl)ethyl alcohols (III, IV).

The fast stage in this process is apparently the hydrolysis of nitroesters I and II leading to the corresponding alcohols (A) and nitric acid.

Alcohols A react with sulfuric acid to form its esters—4-nitrophenylalkylsulfuric acids B (as is known, 4-nitrobenzylsulfuric acid forms upon dissolution of 4-nitrobenzyl alcohol in concentrated sulfuric acid [2]).

Finally, the intermediate aralkylsulfuric acids B are subjected to nitration under the reaction conditions (30–40°C) with the formation of 2,4-dinitrophenylalkylsulfuric acids C.

As described previously [4, 5], 2,4-dinitrobenzylsulfuric acid forms upon dissolution of 2,4-dinitrobenzyl alcohol in 87–93% sulfuric acid.

Previously unreported β-(2,4-dinitrophenyl)ethylsulfuric acid (C, n = 2) was isolated in the form of ammonium salt upon completion of the autonitration process of nitroester II. The salt is readily hydrolyzed to form alcohol IV on heating in a 10% sulfuric acid.

There is no need to isolate the intermediate acids C in order to obtain 2,4-dinitrophenylalkanols III and IV. After termination of the autonitration process, the reaction mass is diluted with water, so as to provide for a 10–30% sulfuric acid concentration, and heated at 100°C for 3–4 h. Upon cooling of the reaction mass, the target alcohols are separated by filtration or extracted with an organic solvent at a yield of 70–87%.

To simplify the process, the reaction can be performed using a mixture of isomeric nitrobenzyl nitrates (VI) or α-(nitrophenyl)ethyl nitrates (VII), rather than the individual p-isomers.

Similarly, a mixture of α-(nitrobenzyl)ethyl nitrates (VIII) was used to obtain α-(2,4-dinitrobenzyl)ethyl alcohol (IX). The proposed structure was confirmed by the oxidation with potassium permanganate, which yielded 2,4-dinitrobenzoic acid.

It should be noted that the reaction involving mixed isomeric nitroesters leads to a mixture of 2,4-, 2,6-, and 3,5-dinitrophenylalkanols with a dominating fraction of 2,4-dinitro isomers. Fractional crystallization of these mixtures from water or aqueous ethanol (for alcohol IX—vacuum distilla-
tion followed by crystallization from aqueous ethanol) gives pure 2,4-dinitrophenylalkanols (III, IV, IX) at a 20–56% yield.

Once the sequence of stages in the transformation of nitroesters I, II into dinitrophenylalkanols III, IV was established, we proceeded to study nitration of 4-nitrobenzyl (X), 15-(4-nitrophenyl)ethyl (XI), benzyl (XII), and 13-phenylethyl (XIII) alcohols with mixed concentrated nitric and sulfuric acids.

In contrast to the procedures described in [7-9], we have used the following molar ratios of nitric acid to substrate: 2:1 for phenylalkanols (XII, XIII) and 1:1 for 4-nitrophenylalkanols (X, XI).

The nitration process was conducted at 4-8°C and terminated at 30-32°C. The conditions of hydrolysis of the intermediate dinitrophenylalkylsulfuric esters were the same as described above for the autonitration of nitroesters I and II.

The nitration of phenylalkanols XII, XIII leads to the mixtures of isomeric dinitrophenylalkanols (E). The fractional crystallization of compounds E yields pure alcohols III and IV.

EXPERIMENTAL PART

The experiments were performed with 93.6–95.6% sulfuric acid (“high-purity” grade, State Standard GOST 4204-77) and 97.5–98.6% nitric acid (“concentrated” grade, GOST 701-89).

The purity of compounds was checked by TLC on Silufol UV-254 plates; the spots were developed by exposure to iodine vapors.

The data of elemental analyses for the previously unreported compounds agree with the results of calculations according to the empirical formulas.

The initial compounds were as follows: 4-nitrobenzyl nitrate (I) [10]; a nitrobenzyl nitrate mixture (VI) [10]; 4-nitrobenzyl alcohol (X); freshly distilled benzyl alcohol (XII); β-(4-nitrophenyl)ethyl nitrate (II) [1]; a mixture of β-(nitrophenyl)ethyl nitrites (VII) [1]; β-(4-nitrophenyl)ethyl alcohol (XI); freshly distilled β-phenylethyl alcohol (XIII); and freshly distilled α-phenylethyl alcohol (XIV).

Mixed α-(nitrobenzyl)ethyl nitrites (VIII). The nitrate mixture VIII was obtained by nitrating alcohol XIV with concentrated nitric acid under the same conditions as described for the nitration of alcohol XIII [1]. Compound VIII was obtained at a 97% yield in the form of a viscous yellow liquid (not crystallized upon cooling to -5°C). The product was used in the synthesis of alcohol IX without separating the β-isomer.

β-(2,4-Dinitrophenyl)ethylsulfuric acid ammonium salt (V). To 192 ml of sulfuric acid heated to 39–40°C was added by small portions during 30 min with intensive stirring 36.0 g of nitroester II, so as to maintain the temperature within 40–42°C (by periodically cooling the flask with water). Then the solution was stirred at this temperature for another 30 min, cooled, and poured onto 50 g of pure crushed ice, and adjusted to pH 8 by adding 25% aqueous ammonia. The precipitate was filtered, washed with cooled water and acetone, and dried to obtain 32.0 g (61%) of compound V in the form of pale-yellow crystals; m.p., 197–201°C, upon recrystallization from ethanol m.p., 201–202°C; the crystals are soluble on heating in water and ethanol; C₉H₆N₃O₇S.

2,4-Dinitrobenzyl alcohol (III).

(a) To 12 ml of sulfuric acid was gradually added (for 8–10 min) with stirring 4.0 g of nitroester I; the temperature was maintained within 32–36°C by cooling the flask with water. Then the solution was stirred at this temperature for another 30 min, cooled, poured into 70 ml of water, and boiled for 4 h. Upon cooling, the solution was extracted with methylene chloride (4 × 40 ml). The extracts were washed with water and dried over Na₂SO₄. Finally, the solvent was distilled off to obtain 3.2 g (80%) of compound III; m.p., 108–110°C. Crystallization from water (150 ml, 2% activated charcoal) yielded 2.8 g (70%) of pure alcohol III; m.p., 114–115°C (published m.p., 114–115°C [2, 3]; 115–116°C [4, 5]).