BRIEF COMMUNICATIONS

SYNTHESIS OF DINITRODIAZADICARBOXYLIC ACIDS

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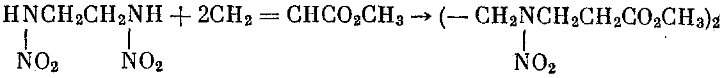
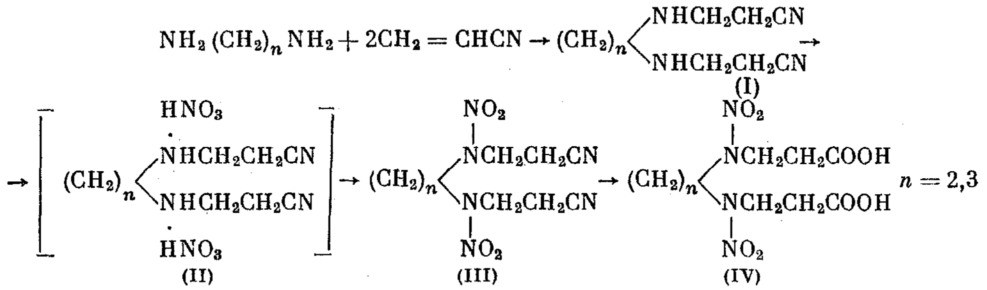
It is known that primary nitramines react with esters of α,β-unsaturated acids to yield esters of N-nitroaminocarboxylic acids, while the dinitrodiamines react with the same type of esters to yield N,N-dinitrodiazadicarboxylic acids [1]. For example, the dimethyl ester of 3,6-dinitro-3,6-diaza-1,8-octanedicarboxylic acid was obtained by the addition of ethylenedinitramine to methyl acrylate [1].

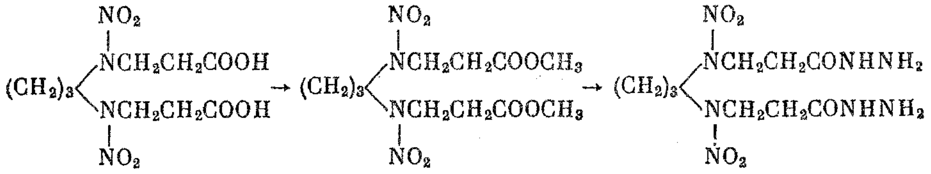


$$\underset{NO_2}{HN}CH_2CH_2\underset{NO_2}{NH} + 2CH_2 = CHCO_2CH_3 \rightarrow (-CH_2\underset{NO_2}{N}CH_2CH_2CO_2CH_3)_2$$

Since frequently the primary N-nitroamines are difficultly available, in order to synthesize such acids it seemed of interest to investigate another procedure for their preparation: to first use the well-known reaction for the addition of primary diamines to acrylonitrile [2], giving good yields, and then convert the obtained diazadinitriles to the N-nitro derivatives. We found this procedure to be a convenient way of obtaining dinitrodiazadicarboxylic acids.



The reaction of ethylenediamine with acrylonitrile [3] yields the dinitrile of 3,6-diaza-1,8-octanedicarboxylic acid, which via the nitrate was converted to the dinitrile of 3,6-dinitro-3,6-diaza-1,8-octanedicarboxylic acid. The mixed melting point of this compound with the authentic material was not depressed. The dinitrile of 3,6-dinitro-3,6-diaza-1,8-octanedicarboxylic acid was obtained by the Kissinger-Schwartz method [1], and also by our modification of the method: we propose using water as the reaction medium and diethylamine as the catalyst. With our procedure the yield of the dinitrile of 3,6-dinitro-3,6-diaza-1,8-octanedicarboxylic acid reaches 95.9% of theory, as compared to the 70% reported by the American authors. The dinitrile of the 3,6-diaza-1,8-octanedicarboxylic acid is easily converted to the acid, m.p. 142°, by refluxing with concd. hydrochloric acid. From trimethylenediamine and acrylonitrile, by a slight modification of the known Kost-Terent'ev method [4], we obtained the dinitrile of 3,7-diaza-1,9-nonanedicarboxylic acid. Then using the same procedure we obtained the dinitrodiazadinitrile, a white crystalline compound with m.p. 76°, in 88% yield. 3,7- Dinitro-3,7-diaza-1,9-nonanedecarboxylic acid was obtained in 87% yield by refluxing the corresponding dinitrile with concd. hydrochloric acid. This acid, a white crystalline compound with m.p. 141°, is soluble in water and in hot water; when heated with absolute methyl alcohol it gives the dimethyl ester with m.p. 54-55°.



(IV) (V) (VI)

The dihydrazide of 3,7-dinitro-3,7-diaza-1,9-nonanedicarboxylic acid (VI) was obtained in quantitative yield by reacting the methyl ester (V) with hydrazine hydrate.

EXPERIMENTAL

The cyanoethylation of ethylanediamine and 1,3-propylenediamine was run by the Kost-Terent'ev method [3, 4]. The dinitrile of 3,6-diaza-1,8-octanedicarboxylic acid has b.p. 170-180° (1.5-2 mm); n_D^{22} 1.4790. Literature data: b.p. 170° (1.5 mm); n_D^{20} 1.4793.

Preparation of nitrate of dinitrile of 3,6-diaza-1,8-octanedicarboxylic acid (II, n = 2). With stirring, a mixture of acids (2 parts of glacial acetic acid and 1 part of concd. nitric acid) was added in drops, at 15-20°, to a solution of 1.0 g of the dinitrile in 4 ml of glacial acetic acid to pH 2, in which connection a precipitate was obtained. Toward the end of the addition the temperature of the mixture was kept at 6-10°. After standing for 20 min, the precipitate was filtered and washed several times with acetone. We obtained 1.51 g (86.4%) of product with m.p. 199° (from 70% aqueous ethanol). Found: N 28.34; 28.66%. $C_8H_{16}O_6N_6$. Calculated: N 28.76%.

Nitration of nitrate of dinitrile of 3,6-diaza-1,8-octanedicarboxylic acid. With stirring, 1.16 g of the nitrate of the dinitrile of 3,6-diaza-1,8-octanedicarboxylic acid and 0.08 ml of nitric acid (d 1.5) were added at 15° to a mixture of 1.64 ml of acetic anhydride and 0.1 ml of concd. hydrochloric acid. After this the mixture was stirred for 2 hr at 15°, then cooled to 0°, and 0.3 ml of water was added. The precipitate was filtered. We obtained 0.38 g (37.4%) of product with m.p. 129° (from ethanol). The mixed melting point with the nitrile obtained by the addition of ethylenedinitramine to acrylonitrile was not depressed.

Addition of ethylenedinitramine to acrylonitrile. With stirring, 4.7 g of acrylonitrile was added in drops, at 85-90°, to a solution of 4.5 g of ethylenedinitramine in 41 ml of water, followed by the addition of 1.0 ml of diethylamine*. The stirred reaction solution was then heated on the steam bath for 10-12 hr, after which it was cooled. The obtained precipitate was filtered and washed with cold water. We obtained 6.65 g (95.9%) of the dinitrile of 3,6-dinitro-3,6-diaza-1,8-octanedicarboxylic acid (III, n = 2) with m.p. 129-130°.

Preparation of 3,6-dinitro-3,6-diaza-1,8-octanedicarboxylic acid (IV, n = 2). A mixture of 1.0 g of the dinitrile (III, n = 2) and 10 ml of concd. hydrochloric acid was heated on the steam bath for 6-8 hr. After cooling, the obtained precipitate was filtered. We obtained 0.93 g (80%) of the acid with m.p. 142°. The mixed melting point with the acid obtained from the dinitrile of 3,6-diaza-1,8-octanedicarboxylic acid was not depressed.

Preparation of nitrate of dinitrile of 3,7-diaza-1,9-nonanedicarboxylic acid (II, n = 3). A mixture of 1 volume of nitric acid (d 1.51) and 2 volumes of glacial acetic acid was added in drops, at 20°, to a solution of the nitrile (I, n = 3) in 10 ml of glacial acetic acid to pH 2. A precipitate began to deposit just as soon as the acid mixture was added, which at the end of reaction was filtered, washed with a little glacial acetic acid, and dried in the air. We obtained 2.74 g (82%) of the nitrate with m.p. 188° (after recrystallization from 70% aqueous ethanol). Found: C 35.60; 35.34; H 6.04; 5.91%. $C_9H_{18}O_6N_6$. Calculated: C 35.29; H 5.92%.

Nitration of nitrate of dinitrile of 3,7-diaza-1,9-nonanedicarboxylic acid. With stirring, 0.18 ml of nitric acid (d 1.51) and 3.26 g of the nitrate of the dinitrile of 3,7-diaza-1,9-nonanedicarboxylic acid were added in portions, at 15°, to 4.8 ml of freshly distilled acetic anhydride, containing 1 drop of concd. hydrochloric acid. Then the reaction mixture was stirred for 2 hr at 15°, allowed to stand overnight at room temperature, after which it was cooled to 0°, diluted with a little water (0.5-1 ml), and the precipitate was filtered. We obtained 1.66 g (88%) of crystalline substance with m.p. 77° (after recrystallization from ethyl alcohol). Found: C 39.19; 39.40; H 5.27; 5.43%. $C_9H_{14}O_4N_6$. Calculated: C 40.00; H 5.22%.

Preparation of 3,7-dinitro-3,7-diaza-1,9-nonanedicarboxylic acid (IV, n = 3). A mixture of 2.0 g of the dinitrile of 3,7-dinitro-3,7-diaza-1,9-nonanedicarboxylic acid and 20 ml of concd. hydrochloric acid was heated on the

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* The yield of the reaction product reaches 91% when triethylamine is used as the catalyst.

steam bath for 5 hr. White crystals deposited from the reaction mixture on cooling, which were filtered and dried in the air. We obtained 1.95 g (87%) of product with m.p. 141° (after recrystallization from water). Found: C 35.05; 35.04; H 5.14; 5.27%. $C_9H_{16}O_8N_4$. Calculated: C 35.07; H 5.23%.

Preparation of dimethyl ester of 3,7-dinitro-3,7-diaza-1,9-nonanedicarboxylic acid (V). To 1.2 g of 3,7-dinitro-3,7-diaza-1,9-nonanedicarboxylic acid in 17 ml of absolute methyl alcohol was added 0.1 ml of concd. sulfuric acid. The mixture was heated under reflux on the water bath for 17 hr, after which it was cooled and poured into cold water. The obtained precipitate was filtered, washed with water, and dried in the air. We obtained 0.56 g (42.5%) of white substance with m.p. 54-55° (after recrystallization from carbon tetrachloride). Found: C 39.40; 39.44; H 6.11; 6.11%. $C_{11}H_{20}O_8N_4$. Calculated: C 39.28; H 5.99%.

Preparation of dihydrazide of 3,7-dinitro-3,7-diaza-1,9-nonanedicarboxylic acid (VI). To 0.1 ml of hydrazine hydrate was gradually added 0.32 g of dimethyl 3,7-dinitro-3,7-diaza-1,9-nonanedicarboxylate. The obtained precipitate was filtered, washed with a little cold methyl alcohol, and dried in the air. We obtained 0.3 g (quantitative yield) of a white crystalline compound with m.p. 151° (after recrystallization from ethyl alcohol). Found: C 31.96; 32.01; H 6.05; 6.03%. $C_9H_{20}O_6N_8$. Calculated: C 32.14; H 5.99%.

SUMMARY

A convenient method was proposed for the preparation of dinitrodiazadicarboxylic acids and some of their chemical transformations were studied.

LITERATURE CITED

1. L. W. Kissinger and M. Schwartz, J. Organ. Chem. 23, 1342 (1958).
2. A. P. Terent'ev and A. N. Kost, Reaktsii Organich. Soed. 2, 47 (1952).
3. A. P. Terent'ev and A. N. Kost, Zhur. Obshchei Khim. 20, 2069 (1950).
4. A. P. Terent'ev, A. P. Kost, and K. I. Chursina, Zhur. Obshchei Khim. 21, 268 (1951).

BEHAVIOR OF TRIETHYLOXONIUM FLUOBORATE TOWARD HYDRIDE-ION DONORS

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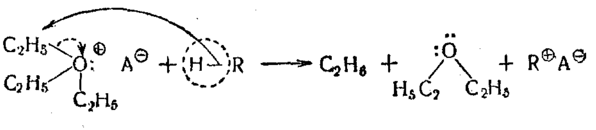
It is known that oxonium salts are capable of nucleophilic substitution reactions. It could be expected that in the decomposition of oxonium salts the electrophilic group cleaved from the oxonium ion will react with a hydride-ion donor.



We investigated the reaction of triethyloxonium fluoborate with various hydride-ion donors. If the hydride shift takes place, then ethane should be formed as a reaction result.

As possible hydride-ion donors we took: dioxane, ethyl alcohol, benzyl alcohol, sodium ethylate in ethyl alcohol solution, cycloheptatriene, sodium borohydride and lithium aluminum hydride. The reaction was run at room temperature and at temperatures up to 90° in various solvents: dioxane, chloroform, nitromethane, nitrobenzene, etc. However, we were able to obtain ethane only in the reaction with sodium borohydride and lithium aluminum hydride. Under