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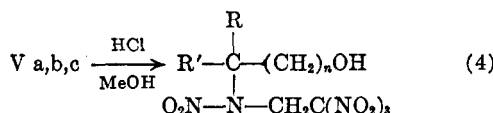
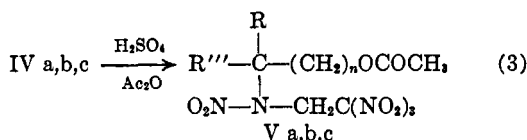
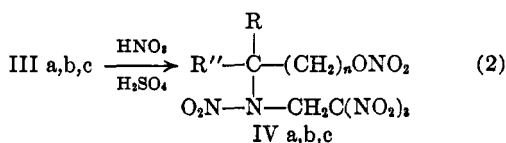
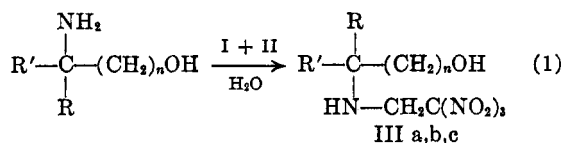
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## Chemistry of Trinitromethane. IV. Preparation of *N*-Nitro-*N*-trinitroethylamino Alcohols

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*N*-Nitro-*N*-trinitroethylamino alcohols, representing a novel class of compounds, were prepared by treating amino alcohols with a mixture of trinitromethane (I) and formaldehyde (II) (step 1) followed by nitration (step 2), acetolysis (step 3), and hydrolysis (step 4).



- (a) R, R', R'', R''' = H; n = 1.  
(b) R, R', R'', R''' = H; n = 2.  
(c) R = CH<sub>3</sub>; R' = CH<sub>2</sub>OH; R'' = CH<sub>2</sub>ONO<sub>2</sub>; R''' = CH<sub>2</sub>OCOCH<sub>3</sub>; n = 1.

2-(*N*-Trinitroethylamino)ethanol (IIIa), and 3-(*N*-trinitroethylamino)-1-propanol (IIIb) were obtained as yellow solids, while 2-methyl-2-(*N*-trinitroethylamino)-1,3-propanediol (IIIc) was isolated as an oil, when I and II were condensed with the appropriate amino alcohol in a minimal amount of water. Since IIIa and IIIb decomposed slowly at ambient temperatures with the formation of I, they were treated with a mixture of concentrated sulfuric and fuming nitric acids at 10–25°.

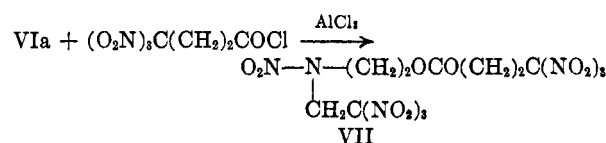
(1) (a) Abstracted from the Ph.D. thesis of W. A. Swarts, Purdue Univ., 1955. (b) This research was supported by the Office of Naval Research.

This afforded the stable 2-(*N*-nitro-*N*-trinitroethylamino)ethyl nitrate (IVa) and 3-(*N*-nitro-*N*-trinitroethylamino)-1-propyl nitrate (IVb).<sup>2</sup> When the unstable IIIc was nitrated with a mixture of acetic anhydride and fuming nitric acid, the dinitrate (IVc) was obtained as an oil which was used directly in subsequent reactions.

Direct hydrolysis, in acidic medium, of these nitrates led only to decomposition. Basic hydrolysis could not be applied because of the well-known<sup>3</sup> instability of the trinitroethyl group in this medium. The desired alcohols, 2-(*N*-nitro-*N*-trinitroethylamino)ethanol (VIa), 3-(*N*-nitro-*N*-trinitroethylamino)-1-propanol (VIb) and 2-methyl-2-(*N*-nitro-*N*-trinitroethylamino)-1,3-propanediol (VIc) were, however, obtained by following the method of Wolfrom,<sup>4</sup> which involved acetolysis with a mixture of acetic anhydride and concentrated sulfuric acid of the nitrate esters, followed by the acid hydrolysis of the acetates with methanolic hydrochloric acid.

The alcohols VIa and VIb reacted readily with phenyl isocyanate to give phenylurethanes, which had correct analyses, but which decomposed on standing at ambient temperatures. The reaction of the diol VIc with phenyl isocyanate gave a gummy solid which could not be purified.

The reaction of VIa with 4,4,4-trinitrobutanoyl chloride in the presence of aluminum chloride gave the expected ester VII.



## EXPERIMENTAL

2-(*N*-Nitro-*N*-trinitroethylamino)ethyl nitrate (IVa). A mixture of 15.1 g. (0.1 mole) of trinitromethane (I), dissolved in 25 ml. of distilled water, 6.1 g. (0.1 mole) of ethanolamine and 8 ml. of 37% formalin solution (0.1 mole of formaldehyde) was stirred at about 5° for 1.5 hr. Since no precipitate appeared, the reaction mixture was placed overnight in the freezing compartment of the refrigerator.

The mixture was then allowed to melt slowly in the refrigerator, and 7.5 g. of a yellow solid was filtered off and dried on porous tiles. Repetition of the freezing and thawing process afforded only 0.1 g. more of 2-(*N*-trinitroethylamino)ethanol (IIIa); the total of 7.6 g. represented a 33.9% yield of IIIa.

A 100-ml. 3-necked round-bottomed flask equipped with a thermometer and a "Tru-Bore" stirrer was charged with a mixture of 25 ml. of concd. sulfuric acid and 25 ml. of fuming nitric acid, and cooled to approximately 15°. The dried IIIa was added to the mixture in fairly large

(2) CARE should be taken in handling these compounds for the impact sensitivity of IVa was found to be equal to that of lead azide and that of IVb to pentaerythritol tetranitrate.

(3) H. Feuer, E. H. White, and S. M. Pier, *J. Org. Chem.*, **26**, 1639 (1961).

(4) M. L. Wolfrom, R. S. Bower, and G. G. Maher, *J. Am. Chem. Soc.*, **73**, 874 (1951).

batches; a white sludge formed during this operation. After the mixture had been stirred at 15–25° for approximately 2 hr., it was poured over crushed ice to produce a solid (or occasionally an oil that soon solidified) that could be purified either by dissolution in fuming nitric acid followed by precipitation over crushed ice, or by recrystallization from ethylene dichloride once the solid had been washed free of the mixed acids. Drying *in vacuo* at 25–30° and recrystallization from 30 ml. of ethylene dichloride afforded 4.6 g. (14.6%) of product. Addition of 50 ml. of hexane to the filtrate gave another 1.0 g. of product, making a total of 5.6 g. (17.8% based on ethanolamine) of 2-(*N*-nitro-*N*-trinitroethylamino)ethyl nitrate (IVa). Evaporation of the solvents in an air stream left only a small amount of crude colored matter which was discarded. Either method of purification afforded approximately the same recovery of pure compound that softened at 101°, and decomposed at 105–106°.

*Anal.* Calcd. for  $C_4H_8N_6O_{11}$ : C, 15.28; H, 1.91; N, 26.75. Found: C, 15.55, 15.70; H, 1.71; N, 26.40.

2-(*N*-Nitro-*N*-trinitroethylamino)ethyl acetate (Va). Three grams (9.55 mmoles) of IV was dissolved in approximately 30 ml. of acetic anhydride. The flask was cooled in a crushed ice bath, and the solution stirred vigorously. Three milliliters of concd. sulfuric acid was added portionwise so that the temperature never exceeded 15°. After the addition was complete, the mixture was allowed to stir for approximately 5 hr. at 0–5°, and then for another hour while the temperature rose to about 30°. Pouring the mixture over crushed ice afforded an oil which was taken up in 100 ml. of ether. The solution was washed with four 50-ml. portions of distilled water, dried over magnesium sulfate, and the ether was then removed *in vacuo* leaving a slightly colored oil. Addition and removal of several 10–15 ml. portions of anhydrous ether *in vacuo* at 30° failed to cause solidification of this oil.

2-(*N*-Nitro-*N*-trinitroethylamino)ethanol (VIa). The oil obtained in the previous experiment was dissolved in a mixture of 30 ml. of methanol and 3 ml. of concd. (37%) hydrochloric acid, and the solution refluxed for about 2 hr. Removal of the solvents *in vacuo* left an oil that solidified when two 10–15 ml. portions of ether were added and subsequently removed *in vacuo*. After two more such treatments, a total of 1.12 g. (43.3% based on IVa) of 2-(*N*-nitro-*N*-trinitroethylamino)ethanol (VIa) was obtained. Recrystallization from carbon tetrachloride gave a white solid, m.p. 74°.

*Anal.* Calcd. for  $C_4H_7N_6O_9$ : C, 17.84; H, 2.60; N, 26.0. Found: C, 17.66; H, 2.84; N, 16.7.

The phenylurethane of VIa was prepared by adding excess phenyl isocyanate to the alcohol, and allowing the solution to stand overnight at about 25°. Pouring the solution into excess hexane afforded an oil that solidified when placed in the freezing compartment of the refrigerator overnight. Two recrystallizations from carbon tetrachloride furnished a buff colored solid, m.p. 88.5–89° (decompn.).

*Anal.* Calcd. for  $C_{11}H_{12}N_6O_{10}$ : C, 34.02; H, 3.09; N, 21.64. Found: C, 33.82; H, 3.48; N, 22.0.

3-(*N*-Nitro-*N*-trinitroethylamino)-1-propyl nitrate (IVb). 3-Amino-1-propanol (7.5 g., 0.1 mole), a solution of 15.1 g. (0.1 mole) of I in 25 ml. of water, and 8.5 ml. of 37% formalin solution (3.14 g., slightly over 0.1 mole of formaldehyde) were stirred together at 0–5° for about 5 hr. A total of 13.4 g. (56.4%) of 3-(*N*-trinitroethylamino)-1-propanol (IIIb) was filtered off and dried on porous tiles. Further stirring at about 0°, and freezing the mixture and subsequently allowing the ice to melt slowly in the refrigerator, failed to produce more of the Mannich condensate.

A 100-ml. flask was charged with a mixture of 25 ml. of concd. sulfuric acid and 25 ml. of fuming nitric acid. The mixture was cooled to approximately 10° and 13.4 g. of IIIb was added to the nitration mixture in moderate size batches, in about 40 min. The temperature never rose above 20° during the nitration; a white sludge formed during this nitration. The reaction mixture was stirred at 10–20° for

5 hr. after addition was completed, and it was then poured over crushed ice to afford a white solid material that could be purified either by dissolution in fuming nitric acid followed by precipitation over crushed ice, or by recrystallization from ethylene dichloride. The former method was the preferred one since the recrystallization technique usually affords a somewhat smaller yield of slightly impure 3-(*N*-nitro-*N*-trinitroethylamino)-1-propyl nitrate (IVb). The pure compound softened at about 97° and decomposed at 101–102°. Recrystallization from ethylene dichloride of a sample already treated with fuming nitric acid did not raise the decomposition point. The yield of IVb purified by the fuming nitric acid technique was 8.9 g. (27.1% based on 3-amino-1-propanol).

*Anal.* Calcd. for  $C_8H_{11}N_6O_{11}$ : C, 18.29; H, 2.43; N, 25.60. Found: C, 18.05; H, 2.26; N, 25.94.

3-(*N*-Nitro-*N*-trinitroethylamino)-1-propyl acetate (Vb). One gram (3.4 mmoles) of IVb was dissolved in approximately 10 ml. of acetic anhydride and placed in a 100 ml. flask. The flask was cooled in a crushed ice bath, the solution stirred vigorously, and 1 ml. of concd. sulfuric acid added in small portions over 15–20 min. The mixture was stirred at approximately 0° for 5 hr. and then the temperature was allowed to rise to almost 30° in an hour. The acetolysis mixture was poured over crushed ice, the precipitated oil taken up in 100 ml. of ether, the ethereal solution washed with four 50-ml. portions of anhydrous ether. Two more such treatments yielded a white solid, m.p. 40–42.5°. The yield of Vb was 0.47 g. (47.5%).

*Anal.* Calcd. for  $C_7H_{11}N_6O_{10}$ : C, 25.84; H, 3.38; N, 21.55. Found: C, 26.40; H, 3.78; N, 21.89.

3-(*N*-Nitro-*N*-trinitroethylamino)-1-propanol (VIb). Inasmuch as the parent alcohol was isolated from an experiment in which the acetolysis mixture was heated, and yielded a liquid acetate,<sup>5</sup> the preparation is described *in toto* starting from the nitrate ester.

One gram (3.05 mmoles) of IVb was dissolved in 8 ml. of acetic anhydride, and the solution was cooled. One milliliter of concd. sulfuric acid was added portionwise while the solution was stirred by hand. The temperature never rose above 40° during this addition; it was then gradually raised to 60°, held there for 15 minutes, and then raised to 80°. It was held at 80° for 3 min. until bubbling slowed down and the solution turned very slightly yellow. After the solution had cooled to 30°, it was poured over crushed ice producing an oil that was dissolved in about 70 ml. of ether. After the ethereal solution was washed with water and dried over magnesium sulfate, the ether was removed *in vacuo*. The remaining oil was dissolved in a mixture of 10 ml. methanol and 1 ml. of concd. hydrochloric acid, and the solution refluxed for 3.5 hr. Removal of the solvents *in vacuo* left an oil that solidified when three 10-ml. portions of ether were added and subsequently removed *in vacuo*. Precipitation of the alcohol from the ethereal solution by means of hexane furnished 0.36 g. (41.7% based on IVb), of white 3-(*N*-nitro-*N*-trinitroethylamino)-1-propanol (VIb), m.p. 50–50.5°.

*Anal.* Calcd. for  $C_6H_9N_6O_9$ : C, 21.20; H, 3.18; N, 24.73. Found: C, 21.17; H, 3.38; N, 24.32.

The phenylurethane of VIb was prepared by heating the alcohol and excess phenyl isocyanate in a soft flame for about 10 sec. and allowing the solution to cool to 25°. When the solution was poured into excess hexane, an oil precipitated that solidified on standing in the freezing compartment of the refrigerator. Two recrystallizations from carbon tetrachloride produced slightly yellow crystals, m.p. 91–92° (decompn.).

*Anal.* Calcd. for  $C_{12}H_{14}N_6O_{10}$ : C, 35.83; H, 3.51; N, 21.89. Found: C, 35.60; H, 3.62; N, 21.55.

2-Methyl-2-(*N*-nitro-*N*-trinitroethylamino)-1,3-propanediol

(5) Heating an acetolysis mixture always yielded the acetate as an oil.

diacetate (Vc). A solution composed of 10.5 g. (0.1 mole) 2-methyl-2-amino-1,3-propanediol, 15.1 g. (0.1 mole) I, and 8.5 ml. 37% formalin solution (0.105 mole, slight excess of formaldehyde) in 35 ml. of distilled water was stirred at ice bath temperature for a few hours. Neither this treatment nor the freezing and thawing technique afforded a precipitate of any sort. Consequently the water was removed by playing a stream of air over the solution at 25°. The residual oil was taken up in ethanol, and the solution dried over magnesium sulfate. Removal of the ethanol *in vacuo* left an unchecked amount of 2-methyl-2-(*N*-trinitroethylamino)-1,3-propanediol as a heavy oil. It was then dissolved in 50 ml. of acetic anhydride and cooled to 5°. A total of 30 ml. of fuming nitric acid was added to the cooled solution over a period of 1.5 hr., the temperature being kept below 20° at all times. The nitration mixture was stirred at 5–15° for two hours and then poured over crushed ice.

The precipitated oil was dissolved in 100 ml. of ether, the ethereal solution washed with two 100-ml. portions of distilled water, and then dried with magnesium sulfate. After the magnesium sulfate had been filtered off, and the ether removed *in vacuo*, the remaining oil was dissolved in 100 ml. of acetic anhydride. The solution was cooled to 5° in an ice bath and stirred vigorously while 6 ml. of concd. sulfuric acid was added in small portions keeping the temperature below 20°.

The cooling bath was removed and stirring was discontinued shortly after the addition of sulfuric acid was completed. When the temperature reached approximately 20°, a violent exothermic reaction accompanied by much gas evolution set in. Prompt reapplication of the ice bath and stirring kept the temperature from rising above 50°. After the reaction had been brought under control and cooled to 30° (a procedure that required half an hour), the mixture was cautiously reheated to 45° while it was vigorously stirred. There was no evidence of further reaction as evinced by lack of bubbling, and temperature decrease as soon as heating was discontinued. Pouring the mixture over crushed ice afforded a red oil. It was dissolved in about 100 ml. of ethylene dichloride, and the solution washed with one 100-ml. portion of distilled water, two 100-ml. portions of 1% aqueous sodium bicarbonate (which caused a small loss of product due to decomposition of the trinitroethyl group), and finally with three 100-ml. portions of distilled water. The ethylene dichloride solution was dried with magnesium sulfate, and the solvent removed *in vacuo* to give 8.2 g. (21.7% based on 2-methyl-2-amino-1,3-propanediol) of a reddish impure solid. Approximately 1 g. of this solid was triturated with methanol at 25°. The 200 mg. of diacetate that remained was filtered off, and washed by dropwise addition of a small amount of ether. Approximately 60–70 mg. of white 2-methyl-2-(*N*-nitro-*N*-trinitroethylamino)-1,3-propanediol diacetate (Vc), m.p. 75–75.5°, was left after the solid was dried *in vacuo* at 25° for 12 hr.

*Anal.* Calcd. for  $C_{10}H_{15}N_5O_{12}$ : C, 30.22; H, 3.77; N, 17.63. Found: C, 30.15; H, 3.86; N, 17.84.

2-Methyl-2-(*N*-nitro-*N*-trinitroethylamino)-1,3-propanediol (VIc). Crude Vc, 7.2 g., was dissolved in a mixture of 100 ml. of methanol and 5 ml. of concd. hydrochloric acid, and the solution refluxed for 2 hr. Removal of the solvents *in vacuo* afforded a solid that was recrystallized from about 1000 ml. of carbon tetrachloride to yield 2.85 g. (50.3% based on Vc), of white 2-methyl-2-(*N*-nitro-*N*-trinitroethylamino)-1,3-propanediol, m.p. 116–117° (dec.). Concentration of the carbon tetrachloride solution to approximately 100 ml. followed by addition of 200 ml. of hexane afforded only highly impure gummy matter which was discarded.

*Anal.* Calcd. for  $C_8H_{11}N_5O_{10}$ : C, 23.00; H, 3.51; N, 22.36. Found: C, 23.40; H, 3.67; N, 22.20.

2-(*N*-Nitro-*N*-trinitroethylamino)ethyl 4,4,4-trinitrobutyrate (VII). 2-(*N*-Nitro-*N*-trinitroethylamino)ethanol, 1.07 g. (0.004 mole), 4,4,4-trinitrobutyryl chloride, 1.00 g. (slight

excess) and aluminum chloride, 0.55 g. (slight excess) were dissolved in 30 ml. of ethylene dichloride and the solution was heated at about 50° for about 18 hr. It was then poured over a mixture of 15 ml. of concd. hydrochloric acid and 30 g. of crushed ice. After the ice had melted, the aqueous layer was washed with six 15-ml. portions of ethylene dichloride and the washings were combined with the ethylene dichloride layer. Washing with three 20-ml. portions of water, drying with magnesium sulfate and concentrating *in vacuo* to 15 ml. afforded an oil which after addition of hexane and keeping at –10° solidified after five days. Washing with carbon tetrachloride and hexane and drying *in vacuo* gave the ester VII, m.p. 40–43° (decompn.). *Anal.* Calcd. for  $C_{26}H_{31}N_5O_{16}$ : C, 20.25; H, 2.11; N, 23.62. Found: C, 19.86; H, 2.40; N, 23.20.

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## 2,4,6-Trinitro-1-naphthol and Derivatives

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Of the nitro derivatives of Martius Yellow (2,4-dinitro-1-naphthol), the 5-, 7-, and 8-mono-nitro derivatives are known.<sup>1–5</sup> The 5-nitro derivative (naphthopicric acid) is formed in the direct nitration of Martius Yellow, together with some of the 7-nitro compound.<sup>3,4</sup> The 8-nitro analog can be prepared from 8-nitro-4-nitroso-1-naphthol(8-nitro-1,4-naphthaquinone 4-oxime) by a combined oxidation and nitration.<sup>2,4</sup> The present work describes the synthesis of the 6-nitro derivative or 2,4,6-trinitro-1-naphthol. This substance can be obtained by the further nitration of 6-nitro-1-naphthol<sup>6</sup> or of 4,6-dinitro-1-naphthol,<sup>7</sup> and also by the oxidation-nitration of 6-nitro-4-nitroso-1-naphthol (6-nitro-1,4-naphthaquinone 4-oxime). The products from these three nitrations were identical by infrared spectra.

The 6-nitro-1,4-naphthaquinone 4-oxime is formed by the isomerization of 1,7-dinitronaphthalene in the presence of oleum, a reaction which has previously been found to occur also with 1,5-, 1,6-, and 1,8-dinitronaphthalenes.<sup>1,2,4</sup> This nitroquinone oxime completes the series of heteronuclear mononitro derivatives of 1,4-naphthaquinone monooxime. All of the nitroquinone oximes can be converted into the corresponding nitro Martius Yellows by nitric acid treatment. These various nitrations would seem to indicate again the great

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