

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.

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, IND.

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

D. C. MORRISON

Received November 2, 1961

Of the nitro derivatives of Martius Yellow (2,4-dinitro-1-naphthol), the 5-, 7-, and 8-mono-nitro derivatives are known.^{1–5} The 5-nitro derivative (naphthopicric acid) is formed in the direct nitration of Martius Yellow, together with some of the 7-nitro compound.^{3,4} 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.^{2,4} 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-naphthol⁶ or of 4,6-dinitro-1-naphthol,⁷ 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.^{1,2,4} 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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(4) P. Friedlander, *Ber.*, **32**, 3528 (1899).

(5) R. Conden and J. Kenyon, *J. Chem. Soc.*, 1591 (1935).

(6) V. Vesely and K. Dvorak, *Bull. Soc. Chim.*, **IV**, **33**, 319 (1923).

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ease of formation of compounds of the Martius Yellow type.

The 2,4,6-trinitro-1-naphthol is an acidic compound and generally resembles its isomers in most properties. A pyridine salt was prepared and analyzed. This reacted with phosphorus oxychloride (8) to form 2,4,6-trinitro-1-chloronaphthalene.

EXPERIMENTAL

Melting points are uncorrected and were taken on a melting point block.

6-Nitro-1,4-naphthaquinone 4-oxime. While cooling to 5–10°, 5 g. (0.023 mole) of 1,7-dinitronaphthalene was added slowly, with stirring, to 100 ml. of 30% oleum and the solution left 19 hr. on ice. It was then poured slowly onto 1 kg. of ice and the precipitate filtered and washed. The product was extracted a number of times with dilute sodium carbonate solution and filtered from some insoluble material. On acidifying the combined filtrates, the nitroquinone oxime was precipitated and filtered, washed, and dried; yield 4.4 g., 88%. The compound was treated with charcoal in aqueous isopropyl alcohol and recrystallized from this solvent mixture. On heating, it sintered at 165–170° and darkened above 195°, with partial fusion and decomposition at 204–207°, forming a black mass.

Anal. Calcd. for $C_{10}H_6N_2O_4$; N, 12.84. Found: N, 12.8.

This conversion of 1,7-dinitronaphthalene into an alkali-soluble nitroquinone oxime allows a separation to be made from 1,3,5-trinitronaphthalene (the product of further nitration of 1,7-dinitronaphthalene), as the trinitro compound is unaffected by oleum under the conditions used.

2,4,6-Trinitro-1-naphthol. (a) *From 6-nitro-1,4-naphthaquinone 4-oxime.* A mixture of 1.2 g. (0.0055 mole) of the nitroquinone oxime and 40 ml. of acetic acid was warmed for solution and cooled to about 30°. To this solution, was added dropwise 3 ml. of 70% nitric acid. The first half of the acid caused considerable heating, and the temperature was kept below 45°. After mixing, the solution was kept at room temperature for 6 hr. and then diluted with 6–8 volumes of water. Next day, the yellow crystalline deposit was filtered, washed, and dried; yield 1.2 g., 78.2%. The product was recrystallized from aqueous methanol and then from water. It sintered 151–152° with m.p. 155.5–157°.

Anal. Calcd. for $C_{10}H_6N_3O_7$; C, 43.01; H, 1.79; N, 15.05. Found: C, 43.01; H, 2.12; N, 15.11.

(b) *From 6-nitro-1-naphthol.* A solution of 0.2 g. (1.06 mmoles) of this nitronaphthol in 2 ml. of acetic acid was treated dropwise (spontaneous warming) with 0.5 ml. of 70% nitric acid while keeping the temperature below 30°. The color soon lightened and the mixture was left to stand. After 1.5 hr., a considerable amount of crystalline material had deposited, and water (8 ml.) was added during 0.5 hr. to precipitate the remainder in crystalline form. The mixture was left to stand 8 hr. and the product filtered, washed with water, and dried. The yield was 0.22 g., 74.5%. A little is lost in washes.

(c) *From 4,6-dinitro-1-naphthol.* The nitration of this compound was similar to the preceding and gave a comparable yield.

The infrared spectra of the three nitration products were the same. Like the 2,4,7-trinitro-1-naphthol, this isomer gives a sparingly soluble sodium salt which may be used in its purification or recovery.

2,4,6-Trinitro-1-naphthol, pyridine salt. A solution of 1.05 g. (0.00376 mole) of the trinitronaphthol in 100 ml. of benzene was mixed with a solution of 2 ml. of anhydrous pyridine in 50 ml. of benzene, giving an immediate bright yellow precipitate. This was washed thoroughly with benzene and dried under vacuum; yield 1.20 g., 91.7%. It was not recrystallized but was analyzed directly. On heating, it melted at 160–185° dec.

Anal. Calcd. for $C_{10}H_6N_3O_7$; C, 50.28; H, 2.79; N, 15.64. Found: C, 50.41; H, 2.91; N, 15.61.

2,4,6-Trinitro-1-chloronaphthalene. This was prepared from the pyridine salt by the method of Gray, Schmidt, and Smith.⁸

Phosphorus oxychloride (15 ml.) was treated slowly with 6.3 g. (0.00176 mole) of the pyridine salt and the mixture stirred 10 min. at 45–50°. It was then cooled and poured onto an excess of ice, and stirred until the product was solid. After filtering and washing, it was dissolved in acetone, filtered, and re-precipitated by water. When washed and dried, this material weighed 5.0 g., 95.5%. The compound was recrystallized four times from methanol and then had m.p. 132–133°.

Anal. Calcd. for $C_{10}H_5N_3O_6Cl$; Cl, 11.9. Found: Cl, 11.5.

HYMAN LABORATORIES INC.

2840 EIGHTH ST.

BERKELEY, CALIF.

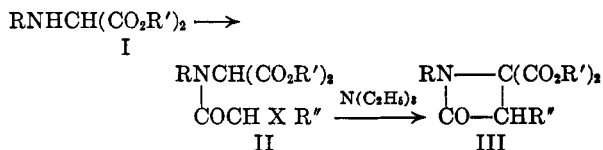
(8) D. N. Gray, J. J. E. Schmidt, and C. D. Smith, *J. Chem. Soc.*, 2243 (1960).

Studies on Lactams. II.¹ A Simplified Synthesis

AJAY K. BOSE, M. S. MANHAS, AND
B. N. GHOSH-MAZUMDAR

Received October 10, 1961

A general method for the synthesis of β -lactams of type III has been described by Sheehan and Bose² which involves the acylation of a substituted aminomalonate I to the amidomalonate II followed by its cyclization to III in the presence of a weak base such as triethylamine.



The acylation step has usually been carried out under nonbasic conditions³ using a halo acid and phosphorus trichloride in benzene solution at the reflux temperature.

Further work has now shown that the conversion of a substituted aminomalonate I to the corresponding β -lactam III can be carried out in one operation. When to a benzene solution of I there are added the appropriate α -haloacyl halides and then an excess of triethylamine, heat is evolved and a solid starts to separate. This reaction mixture may either be allowed to stand at room temperature for about three days or heated under reflux for

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