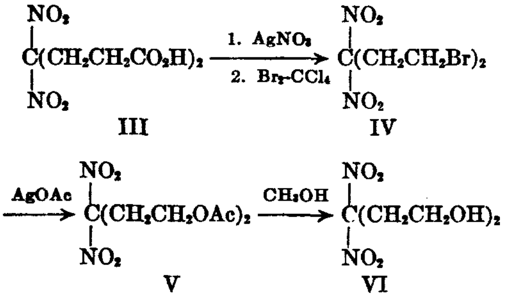
3,3-Dinitro-1-butanol (II) was prepared by diazotization of 3,3-dinitrobutylamine hydrochloride (I).

$$\underset{\text{I}}{CH_3C(NO_2)_2CH_2CH_2NH_2\cdot HCl} \xrightarrow{NaNO_2} \underset{\text{II}}{CH_3C(NO_2)_2CH_2CH_2OH}$$

3,3-Dinitro-1,5-pentanediol (VI) was synthesized from 4,4-dinitroheptanedioic acid (III). This acid was degraded by the Hunsdiecker reaction to 3,3-dinitro-1,5-dibromopentane (IV).[6] Compound IV was converted to 3,3-dinitro-1,5-pentanediol diacetate (V), which by ester interchange with methanol gave 3,3-dinitro-1,5-pentanediol (VI).



$$\underset{\text{III}}{(NO_2)_2C(CH_2CH_2CO_2H)_2} \xrightarrow[2.\ Br_2\text{-}CCl_4]{1.\ AgNO_3} \underset{\text{IV}}{(NO_2)_2C(CH_2CH_2Br)_2}$$

$$\xrightarrow{AgOAc} \underset{\text{V}}{(NO_2)_2C(CH_2CH_2OAc)_2} \xrightarrow{CH_3OH} \underset{\text{VI}}{(NO_2)_2C(CH_2CH_2OH)_2}$$

EXPERIMENTAL[7,8]

3,3-Dinitro-1-butanol (II). To a solution of 20 g. (0.1 mole) of 3,3-dinitrobutylamine hydrochloride[9] in 200 ml. of water was added a solution of 7.8 g. (0.11 mole) of sodium nitrite in 50 ml. of water. The reaction mixture was warmed to 45°, a vigorous evolution of nitrogen occurred and the temperature rose to 66°. After about 60 sec. a clear greenish solution was formed, which was kept for 10 min. at 60°. The aqueous solution was cooled and extracted twice with methylene chloride. The extracts were washed with saturated sodium chloride solution, dried, and concentrated. Distillation of the residue gave 9.2 g. (56.1%) of product, b.p. 70–80°/1μ, n_D^{25} 1.4660.

Anal. Calcd. for $C_4H_8N_2O_5$: C, 29.27; H, 4.91; N, 17.07. Found: C, 29.07; H, 4.66; N, 17.61.

3,3-Dinitro-1,5-dibromopentane (IV). The ammonium salt of 4,4-dinitroheptanedioic acid[10] was prepared by adding 50 ml. of concentrated ammonium hydroxide to a suspension of 50 g. (0.2 mole) of 4,4-dinitroheptanedioic acid in 1 liter of water. The resulting solution was boiled to evaporate the excess ammonia. The hot solution was added to a solution of 70 g. (0.41 mole) of silver nitrate in 2 liters of water. After the precipitate was digested for a short time, it was cooled, filtered, suspended in distilled water, and filtered. A slurry of the wet silver salt in 1 liter of carbon tetrachloride was heated under a Dean-Stark trap until all the water was removed. The amount of silver salt obtained (86–88%) was calculated by subtracting the weight of water collected from the weight of the wet salt.

A solution of 436 g. (2.7 moles) of dry bromine in 500 ml. of dry carbon tetrachloride was warmed to 50° and a slurry of 323 g. (0.7 mole) of silver 4,4-dinitroheptanedioate in 2 liters of carbon tetrachloride was added portionwise while the temperature of the mixture was maintained at 50–55°. After the addition was complete, the reaction mixture was stirred for two more hours, cooled, and filtered. The filtrate was decolorized by washing with sodium bisulfite solution, dried, and concentrated. Distillation of the residue gave 93.5 g. (41.8%) of a light yellow liquid, b.p. 110–120°/1 mm., n_D^{25} 1.5348.

Anal. Calcd. for $C_5H_8Br_2N_2O_4$: Br, 49.95; N, 8.76. Found: Br, 49.37; N, 8.17.

3,3-Dinitro-1,5-diacetoxypentane (V). A mixture of 65 g. (0.2 mole) of 3,3-dinitro-1,5-dibromopentane, 100 g. (0.6 mole) of silver acetate, and 600 ml. of glacial acetic acid was refluxed for 24 hr. The solution was diluted with ether to precipitate the dissolved salts, filtered, and the filtrate concentrated to about 200 ml. The filtrate was diluted with more ether, washed with dilute sodium bicarbonate solution until neutral, and treated with charcoal. The ether was then evaporated and the residue was crystallized from ethanol at −15° to give 41.6 g. (74%) of white crystals, m.p. 34–34.5°.

Anal. Calcd. for $C_9H_{14}N_2O_8$: C, 38.85; H, 5.07; N, 10.07. Found: C, 39.24; H, 5.12; N, 10.29.

3,3-Dinitro-1,5-pentanediol (VI). A solution of 40.4 g. (0.14 mole) of 3,3-dinitro-1,5-diacetoxypentane, 250 ml. of methanol, and 0.5 g. of anhydrous hydrogen chloride was refluxed for 14 hr. The methanol solution was then treated with charcoal and concentrated. The residue was recrystallized from benzene to give 25 g. (88.6%) of white needles, m.p. 72–73°.

Anal. Calcd. for $C_5H_{10}N_2O_6$: C, 30.93; H, 5.19. Found: C, 31.05; H, 4.98.

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[6] A similar reaction was reported for the conversion of 4,4-dinitropentanoic acid to 3,3-dinitro-1-bromobutane, H. Shechter and L. Zeldin, *J. Am. Chem. Soc.*, **73**, 1276 (1951).

[7] All melting points are uncorrected.

[8] Microanalyses by Elek Microanalytical Laboratories, Los Angeles, Calif.

[9] The preparation of this compound will be described in a future publication.

[10] L. Herzog, M. H. Gold, and R. D. Geckler, *J. Am. Chem. Soc.*, **73**, 749 (1951).

Preparation of Aliphatic Secondary Nitramines

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In connection with our work on the preparation of aliphatic secondary nitramines containing a nitrile group,[1] a simple, economical synthetic method was needed. Inasmuch as Chute, Herring, Toombs, and Wright[2] reported the preparation of nitriminodipropionitrile in 71% yield from iminodipropionitrile, it was decided to study this reaction in detail in order to find the optimum conditions for this conversion. In their procedure both nitric acid and acetic anhydride were employed in large excess. This is disadvantageous because of (*a*) waste of nitric acid and acetic anhydride, (*b*) the neces-

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[1] M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **78**, 5428 (1956).

[2] W. J. Chute, K. G. Herring, L. E. Toombs, and G. F Wright, *Can. J. Research*, 26B, 89 (1948).

sity in large scale operation of recovering the excess acetic and nitric acids, and (*c*) the potential hazard since tetranitromethane is formed from the reaction of nitric acid and acetic anhydride.[3]

Using essentially the same procedure as employed by Chute *et al.*,[2] that is, the simultaneous addition of iminodipropionitrile, nitric acid, and hydrochloric acid to acetic anhydride, a systematic study of this nitration was undertaken to determine the conditions and reactant ratios for optimum yields. Using one mole of iminodipropionitrile and varying the molar quantities of nitric acid, acetic anhydride, and hydrochloric acid, it was found that an optimum yield of 73.1% was obtained with 1.1 moles of nitric acid, 1.4 moles of acetic anhydride, and 0.05 mole of hydrochloric acid. Several more runs were made with these quantities and consistent yields of 70–73% were obtained. On scaling the nitration up to a 15.0 mole batch, it was found that the yield decreased to 43.2%. This was substantiated in subsequent runs. In the larger run the addition of amine, nitric acid, and hydrochloric acid was carried out over a greater length of time than in the smaller run. Thus the amine was exposed to a large excess of acetic anhydride for a greater length of time in the larger run; this resulted in a reduced yield apparently owing to acetylation of the amine. In order to keep the concentration of the acetic anhydride at a minimum, the addition procedure was reversed. The amine was added to the nitric acid followed by the addition of acetic anhydride and hydrochloric acid. A yield of 77% of the nitramine was then obtained on a 15.0 mole batch. Subsequent runs substantiated this yield.

This procedure was then applied to improve the synthesis of *N*-methyl-3-nitraminopropionitrile, which was previously prepared by isolating the nitric acid salt of *N*-methyl-3-aminopropionitrile and then dehydrating the salt with an excess of nitric acid and acetic anhydride; the over-all yield was 50.7%.[1] Using a modification of the improved procedure, the direct nitration of *N*-methyl-3-aminopropionitrile gave *N*-methyl-3-nitraminopropionitrile in yields of 87–89%. This modification consisted in using methylene chloride as a solvent for the nitration reaction. In the preparation of nitriminodipropionitrile, the product precipitated when the reaction mixture was quenched with water. In the case of a liquid product, such as *N*-methyl-3-nitraminopropionitrile, a solvent was desirable to extract the nitramine from the acid mixture. Accordingly, the nitration was carried out in methylene chloride, which served not only as a solvent for the starting amine and the product but also as a diluent for the reaction. The importance of keeping the concentration of acetic anhydride at a minimum during the nitration was shown again. By reversing the mode of addition, that is adding the *N*-methyl-3-aminopropionitrile, nitric acid, and hydrochloric acid to acetic anhydride, the yield of *N*-methyl-3-nitraminopropionitrile was decreased to 43–57%.

EXPERIMENTAL

Nitriminodipropionitrile. To 694.5 ml. (16.5 moles) of 98–99% nitric acid was added in 30 min. 900 ml. (7.5 moles) of iminodipropionitrile, keeping the temperature at 0–10° by external cooling. The reaction mixture consisted of a yellow slurry which still could be stirred uniformly. (If all of the amine is added at this point, the mixture becomes too thick for stirring.) The temperature of the reaction mixture was allowed to rise to 15° and the simultaneous addition of 900 ml. (7.5 moles) of iminodipropionitrile, 1980 ml. (21.0 moles) of acetic anhydride, and 62.6 ml. (0.75 mole) of 37% hydrochloric acid was made dropwise in 2.5 hr., keeping the temperature at 15–20° by external cooling. The amine and acetic anhydride were added at the same rate, so as to ensure that the addition of the amine will be completed while only about half of the acetic anhydride has been added. The addition of the acetic anhydride and hydrochloric acid were completed at about the same time. The reaction mixture was stirred for 3 hr. at 25–30°, intermittent cooling being required during this period in order to stay within this temperature range. The mixture was then cooled to 5–10° and quenched with 4 liters of ice water. The white solid was collected, washed thoroughly with ice water, and dried to give 1940.4 g. (77.0%), m.p. 54–55° (lit. value, 53.5–55.5°[2]).

N-Methyl-3-nitraminopropionitrile. A solution of 84.1 g. (1.0 mole) of *N*-methyl-3-aminopropionitrile in 100 ml. of methylene chloride was cooled to 0–10° and 46.3 ml. (1.1 moles) of 98–99% nitric acid was added dropwise in 30 min., keeping the temperature at 0–10°. The temperature of the reaction mixture was allowed to rise to 20° and 132 ml. (1.4 moles) of acetic anhydride and 2.5 ml. (0.03 mole) of 37% hydrochloric acid was added dropwise in 30 min., keeping the temperature at 20–25° by external cooling. The reaction mixture was stirred at 25–30° for 2.5 hr., cooled to 5–10° and quenched by the addition of 100 ml. of ice water. The methylene chloride layer was separated and the aqueous layer was extracted with two 100-ml. portions of methylene chloride. The combined methylene chloride extracts were washed with saturated sodium carbonate solution until the aqueous phase reached a *p*H of 8. After a final wash with water, the methylene chloride solution was concentrated *in vacuo* leaving 115.2 g. (89.2%) of light yellow liquid, n_D^{25} 1.4855 (lit. value of distilled product, n_D^{25} 1.4863).[1]

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(3) P. Liang, *Org. Syntheses*, Coll. Vol. III, (1955).

Derivatives of *N*-Methylnitraminoacetonitrile

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The preparation of *N*-methyl-3-nitraminopropionitrile and its conversion to *N*-methyl-3-nitraminopropionyl chloride, *N*-methyl-2-nitraminoethyl