green precipitate of a mixture of oximes was filtered, 5.99 g. (92%), m.p. 150–195°. The crude material was extracted with 600 ml. of boiling water and then with 500 ml. of boiling methanol. The light green methanol solution was filtered while still hot from an orange-green precipitate. Upon dilution with 200 ml. of water, 0.94 g. (13%), m.p. 172° (dec.) of a γ-(*amphi*) dioxime separated as a yellow powder (see above). The orange-green precipitate dissolved in 400 ml. of hot methanol over a period of 12 hr. A negligible amount of foreign material was removed by filtration and the filtrate, diluted with 100 ml. of distilled water was stored overnight at room temperature. The other γ-(*amphi*) dioxime as a flaky yellow powder, 2.22 g. (33%), m.p. 183–185° (charring at 180°) was reprecipitated from methanol and an analytical sample was dried in the vacuum oven for 12 hr. at 80–95°. A pale green precipitate was observed upon adding a drop of nickel chloride solution to an ethanol solution of this dioxime.

Anal. Calcd. for $C_{14}H_9N_3O_4$: C, 59.37; H, 3.20; N, 14.84. Found: C, 59.39; H, 3.38; N, 14.75.

Procedure B.[9] In a pressure bottle, 1.0 g. (0.004 mole) of 2-nitro-9,10-phenanthrenequinone was mixed with 10.0 g. (0.144 mole) of hydroxylamine hydrochloride, 4 ml. of pyridine, and 80 ml. of 95% ethanol. The bottle was sealed, and placed in boiling water for 4 hr. It was then cooled in a Dry Ice and acetone bath and carefully opened. Pyridine hydrochloride was removed by filtration, the filtrate was diluted with distilled water, a yellow flaky precipitate, m.p. 195–198°, 0.95 g. (85%), was removed, dissolved in 300 ml. of hot methanol and reprecipitated by the addition of 80 ml. of distilled water to the cold solution. A yellow-orange powder, after three additional reprecipitations from methanol, gave an analytical sample, m.p. 194.5–195.8° of the α-(*anti*) dioxime. In hot ethanol this dioxime reacted with one drop of a nickel salt solution with the formation of a red precipitate.

Anal. Calcd. for $C_{14}H_9N_3O_4$: C, 59.37; H, 3.20; N, 14.84. Found: C, 59.29; H, 3.29; N, 14.66.

In a pressure bottle 2.0 g. (0.008 mole) of 2-nitro-9,10-phenanthrenequinone was mixed with 20.0 g. (0.288 mole) of hydroxylamine hydrochloride in 80 ml. of 95% ethanol and 5.0 g. of potassium carbonate. The bottle was sealed and placed in boiling water for 22 hr. during which time the color of the reaction mixtures became yellow-orange. The pressure bottle was cooled in the refrigerator for a day at 15°, opened, and the precipitate was extracted twice with ether. The ether extracts were combined and evaporated over a steam bath to dryness. The residue was dissolved in 80 ml. of 95% ethanol and the solution was stored for one week in the refrigerator. A flaky pale green solid precipitated, 0.8 g. (35%), m.p. 188–189° (dec.). After three precipitations from methanol, the solid, m.p. 190–191° (dec.), gave no precipitate upon being treated with a solution of nickel chloride.

Anal. Calcd. for $C_{14}H_9N_3O_4$: C, 59.37; H, 3.20; N, 14.84. Found: C, 61.19; H, 2.67; N, 15.05.

Oxidation of 2-nitro-9,10-phenanthrenequinone dioxime. Procedure A. To 0.50 g. (0.002 mole) of each of the four isomeric 2-nitro-9,10-phenanthrenequinone dioximes, in 75 ml. of 50% ethanol, chlorine was added over a period of 10 min., during which time the temperature was held at 55–60°. As a colorless precipitate formed, the solution turned from dark red to pale yellow. The mixture was chilled and filtered. A colorless amorphous precipitate, m.p. 211–212°, was recrystallized from aqueous pyridine and washed with hot methanol, 0.45 g. (91%). An analytical sample, m.p. and mixture m.p. 211–212°, was dried in the vacuum oven for 12 hr. at 150°.

Anal. Calcd. for $C_{14}H_7O_4N_3$: C, 59.79; H, 2.50; N, 14.94. Found: C, 59.96; H, 2.48; N, 14.92.

Procedure B. With stirring 0.5 g. (0.002 mole) of each of the four isomeric 2-nitro-9,10-phenanthrenequinone dioximes, was dissolved in 100 ml. of 69% nitric acid. The solution was poured into 400 ml. of ice cold water. A colorless precipitate was collected as a powder, 0.39 g. (70%), m.p. 210–213°. The crude product was dissolved in 20 ml. of hot pyridine and the hot solution was filtered. The filtrate was chilled and diluted with 20–30 ml. of distilled water. A colorless precipitate, m.p. 211–212°, after two reprecipitations with pyridine, gave an analytical sample, m.p. and mixture m.p. 211–212°.

Anal. Calcd. for $C_{14}H_7N_3O_4$: C, 59.79; H, 2.50; N, 14.94. Found: C, 59.48; H, 2.40; N, 14.11.

Nitration and oxidation of 9,10-phenanthrenequinone dioxime. With stirring 0.50 g. (0.002 mole) of 9,10-phenanthrenequinone dioxime, m.p. 199–200°, was added to 80 ml. of 69% nitric acid at room temperature. A pale brown flaky solid formed immediately and was dissolved in 100 ml. of boiling ethanol. The solution was filtered while still hot, chilled in a Dry Ice and acetone bath, and diluted with distilled water. A colorless precipitate of 2-nitro-9,10-ψ-dinitrosophenanthrene, 0.36 g. (62%), m.p. and mixture m.p. 211–212°, was collected.

Reduction of 2-nitro-9,10-dinitrosophenanthrene. To 0.40 g. (0.002 mole) of 2-nitro-9,10-dinitrosophenanthrene in 50 ml. of hot 95% ethanol and 5 ml. of pyridine, 10.0 g. (0.144 mole) of hydroxylamine hydrochloride was added. After heating at reflux temperature for 1 hr., the solution was poured into 300 ml. of distilled water at 0°. A yellow-green precipitate, 0.30 g. (72%), m.p. 172–174° (dec.), of a γ-(*amphi*) 2-nitro-9,10-phenanthrenequinone dioxime was collected.

DEPARTMENT OF CHEMISTRY
TULANE UNIVERSITY
NEW ORLEANS 18, LA.

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(9) E. Mosettig and J. W. Krueger, *J. Am. Chem. Soc.*, **58**, 1311 (1936).

3,3-Dinitro-1-alkanols

LEVONNA HERZOG, KARL KLAGER, AND MARVIN H. GOLD

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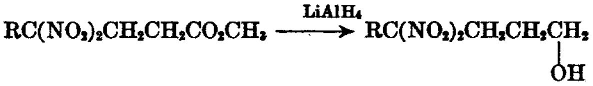
Of the aliphatic *gem*-dinitro-1-alkanols, the 2,2-dinitro-1-alkanols are readily prepared by the Henry reaction of 1,1-dinitroalkanes and formaldehyde:[1–3] The 4,4-dinitro-1-alkanols are pre-

$$RC(NO_2)_2H + CH_2O \longrightarrow RC(NO_2)_2CH_2OH$$

pared by the selective reduction of Michael adducts to 1,1-dinitroalkanes:[4,5]



$$RC(NO_2)_2H + CH_2{=}CHCO_2CH_3 \longrightarrow RC(NO_2)_2CH_2CH_2CO_2CH_3 \xrightarrow{LiAlH_4} RC(NO_2)_2CH_2CH_2\underset{\displaystyle OH}{\underset{|}{CH_2}}$$

This paper reports the synthesis of the hitherto unknown 3,3-dinitro-1-alkanols.

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(1) P. Duden and G. Ponndorf, *Ber.*, **38**, 203 (1905).

(2) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951).

(3) M. B. Frankel and K. Klager, *J. Am. Chem. Soc.*, **79**, 2953 (1957).

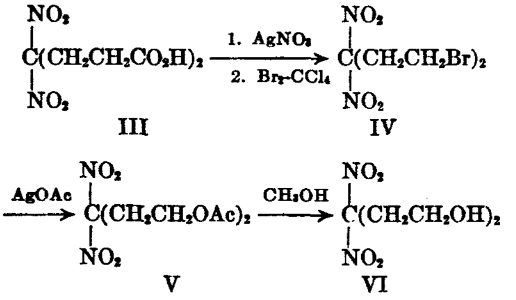
(4) H. Shechter, D. Ley, and L. Zeldin, *J. Am. Chem. Soc.*, **74**, 3664 (1952).

(5) H. Feuer and T. J. Kucera, *J. Am. Chem. Soc.*, **77**, 5740 (1955).

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).



$$\underset{\text{III}}{C(NO_2)_2(CH_2CH_2CO_2H)_2} \xrightarrow[\text{2. } Br_2\text{-}CCl_4]{\text{1. } AgNO_3} \underset{\text{IV}}{C(NO_2)_2(CH_2CH_2Br)_2} \xrightarrow{AgOAc} \underset{\text{V}}{C(NO_2)_2(CH_2CH_2OAc)_2} \xrightarrow{CH_3OH} \underset{\text{VI}}{C(NO_2)_2(CH_2CH_2OH)_2}$$

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.

Acknowledgment. We are indebted to the office of Naval Research for the financial support of this work.

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AEROJET-GENERAL CORPORATION
AZUSA, CALIF.

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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

MILTON B. FRANKEL AND CLINTON R. VANNEMAN

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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).