isobutyrate, b.p. 87° (16 mm.), n_D^{25} 1.4179, λ(C=O) 5.71 μ, λ(NO_2) 6.46, 7.43 μ.

α-Nitroisobutyrhydrazide. Hydrazine (64% in water, 5.0 g., 0.1 mole) was added to a solution of ethyl α-nitroisobutyrate (16.1 g., 0.1 mole) in 20 ml. of methanol. The mixture was allowed to stand at 5° for 168 hr. The pale yellow solution was then evaporated to dryness at 50 mm. and below room temperature. The hydrazide separated in crystalline form. This crude material (15.5 g.) was crystallized from benzene from which it was obtained in colorless plates, m.p. 96.5–97.5°, yield 7.5 g. (51%), λ(NH) 3.00 μ, λ(C=O) 5.90 μ, λ(NO_2) 6.42, 7.41 μ. The melting point was unchanged after vacuum sublimation at 0.1 mm.

Anal. Calcd. for $C_4H_9N_3O_3$: C, 32.65; H, 6.16; N, 28.57. Found: C, 32.36; H, 6.63; N, 28.44.

α-Nitroisopropyl isocyanate. A solution of 0.69 g. (0.01 mole) of sodium nitrite in 15 ml. of water was added slowly with stirring to a mixture of 1.47 g. (0.01 mole) of sublimed α-nitroisobutyrhydrazide in 25 ml. of water, 2 ml. of concentrated hydrochloric acid, and 10 ml. of chloroform contained in an ice bath. The mixture was stirred for 0.5 hr., the organic layer was separated, and the aqueous layer was extracted with 5 ml. of chloroform. The combined extracts were dried over sodium sulfate and filtered.

When a 10% solution of α-nitroisobutyrazide in chloroform was refluxed,[8] it turned yellow, a yellow solid precipitated, and NO_2 was evolved, but even after 21 hr. of refluxing there was considerable azide left in the mixture. The precipitated solid weighed 0.25 g. after refluxing for 10 hr. and 0.35 g. at the end of 21 hr. of boiling. It did not contain a band in the nitro region but had strong bands for NH (3.10) and C=O (5.80 μ) absorption.

Anal. Calcd. for $C_4H_6N_2O_3$: C, 36.92; H, 4.65; N, 21.53. Found: C, 36.96; H, 5.28; N, 21.50.

A fresh batch of α-nitroisobutyrazide (0.005 mole) in 15 ml. of chloroform was unchanged after refluxing for 3 hr. with 5 ml. of methanol.

α-Nitroisobutyrazide (0.01 mole) was successfully rearranged by refluxing in 30 ml. of carbon tetrachloride (b.p. 68°/580 mm.) protected from light and moisture. The solution turned pink after 30 min. The azide band had largely disappeared after 4 hr. and was completely absent after 12.5 hr. Some NO_2 was evolved during the process and the polymer which was filtered at the end of the heating period weighed 0.16 g. The yellow filtrate was concentrated at 50 mm. and below room temperature. On warming the residual liquid at 1 mm. it polymerized with evolution of gas to a glassy solid which was characterized by very weak absorption in the NO_2 stretching region (6.37 μ).

Infrared absorption spectra were determined with a Perkin-Elmer Model 21 spectrophotometer, liquids as capillary films, solutions in matched cells of 0.1-mm. thickness, and solids as potassium bromide disks in 0.5% concentration, 0.5 mm. thick.

Los Alamos, N. M.

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[8] The boiling point of chloroform at this altitude is 53° (580 mm.).

[Contribution from Research Laboratory of the Aerojet-General Corp.]

Preparation and Characterization of 2,2-Dinitroethanol[1]

MARVIN H. GOLD, EDWARD E. HAMEL, and KARL KLAGER

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A new synthesis is described for the preparation of potassium *aci*-2,2-dinitroethanol. At elevated temperatures in the presence of cyclopentadiene, 2,2-dinitroethanol is apparently dehydrated and yields the Diels-Alder addition product expected from the reaction of 1,1-dinitroethylene with cyclopentadiene. Potassium *aci*-2,2-dinitroethanol, upon condensation with formaldehyde in acid medium, yields 2,2-dinitro-1,3-propanediol. This compound, upon further condensation with formaldehyde, forms the cyclic product, 5,5-dinitro-1,3-dioxan.

The first reported synthesis of 2,2-dinitroethanol was made by Duden and Pondorff[2] who prepared it by acidification of the potassium salt with sulfuric acid. Because of the interest of these laboratories in compounds containing multiple nitro groups a reinvestigation of this work was made. In doing so several improvements were made in the synthetic methods. In Duden and Pondorff's original synthesis[2] the potassium *aci*-2,2-dinitroethanol was made by the condensation of formaldehyde with potassium *aci* dinitromethane. This latter compound was normally produced by a laborious nitration of tribromoaniline[3] in very poor yield. In this laboratory a new synthesis of 2,2-dinitroethanol was developed which is an adaptation of the method of ter Meer[4] for the synthesis of 1,1-dinitroethane. This involves the replacement of bromine in 2-bromo-2-nitroethanol by a nitro group, using a mixture of potassium nitrite and potassium hydroxide.

The 2-bromo-2-nitroethanol was most conveniently prepared by bromination of sodium *aci*-2-nitroethanol. The mode of addition of the reagents is very important because the alpha hydrogen is more acidic in the bromonitroethanol than in nitroethanol. Therefore, when bromine is added to the sodium enolate, an equilibrium mixture results:

$$Br_2 + NaO_2N = CH_2CH_2OH \longrightarrow NO_2CHBrCH_2OH + NaBr$$

$$NO_2CHBrCH_2OH + NaO_2N = CHCH_2OH \longrightarrow NaO_2N = CBrCH_2OH + NO_2CH_2CH_2OH$$

The sodium *aci*-2-bromo-2-nitroethanol then competes with the sodium *aci*-2-nitroethanol for additional bromine and consequently produces an appreciable quantity of dibromonitroethanol. In order to avoid the secondary reaction, it is necessary to

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[1] This work was performed under contract with the Office of Naval Research.

[2] P. Duden and G. Pondorff, *Ber.*, **38**, 2031 (1905).

[3] M. A. Villiers, *Bull. soc. chim. France*, [2] **41**, 281 (1884); **43**, 322 (1885); P. Duden, *Ber.*, **26**, 3003 (1893); R. A. Gotts and L. Hunter, *J. Chem. Soc.*, **125**, 442 (1924).

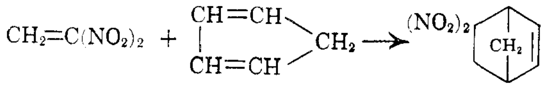
[4] E. ter Meer, *Ann.* **181**, 4 (1876).

add a slurry of sodium *aci*-2-nitroethanol to an excess of bromine. This procedure gives 2-bromo-2-nitroethanol in good yield and with a small amount of side reaction products. Previously, 2-bromo-2-nitroethanol was prepared by the condensation of formaldehyde with bromonitromethane[5] and by the deformylation of 2-bromo-2-nitro-1,3-propanediol.[6]

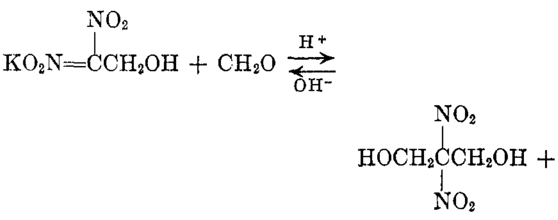
Although 2,2-dinitroethanol has been reported as an unstable liquid,[2] it was found in this laboratory to be far more stable than was previously believed. The dinitroethanol is liberated from the salt by strong acids, such as sulfuric or hydrochloric acids. It can be distilled from high boiling carrier solvents, such as the higher phthalates or sebacates, in a cyclic molecular still. This distillate upon low-temperature crystallization from ethyl chloride gives white crystals, m.p. 2–3°. The liquid alcohol may be stored for several weeks at −20°.

2,2-Dinitroethanol is apparently easily dehydrated at elevated temperatures. However, all attempts to isolate free 1,1-dinitroethylene were fruitless. Evidence of its intermediate formation was obtained by heating a mixture of cyclopentadiene with 2,2-dinitroethanol in chlorobenzene. At 100–110° the reaction proceeded rapidly to give 6,6-dinitrobicyclo[2.2.1]-2-heptene, the product expected from the Diels-Alder reaction of 1,1-dinitroethylene with cyclopentadiene. Thus it appears likely that the reaction followed the course:

$$\mathrm{HOCH_2CH(NO_2)_2 \longrightarrow CH_2C(NO_2)_2 + H_2O}$$



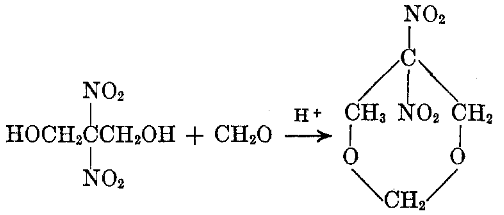
Potassium *aci*-2,2-dinitroethanol will react with aqueous formaldehyde in the presence of acetic acid to produce 2,2-dinitro-1,3-propanediol:[7]



$$\mathrm{KO_2N{=}\overset{NO_2}{C}CH_2OH + CH_2O \underset{OH^-}{\overset{H^+}{\rightleftarrows}} HOCH_2\overset{NO_2}{\underset{NO_2}{C}}CH_2OH + K^+}$$

As indicated by the above equilibrium, the salt of 2,2-dinitroethanol can be regenerated in good yield from the dinitropropanediol by heating the diol with an aqueous-alcoholic solution of potassium hydroxide. This is similar to the equilibrium between potassium *aci*-dinitromethane and potassium *aci*-2,2-dinitroethanol described by Duden and Pondorff.[2]

The hydroxy groups of 2,2-dinitro-1,3-propanediol are difficult to replace in substitution reactions due to their proximity to the nitro groups.[8] However, the glycol does undergo some of the reactions attributed to the hydroxyl group. With formaldehyde in equimolecular quantities, it forms the corresponding 1,3-dioxan:



and the Schotten-Bauman reaction with benzoyl chloride produces the dibenzoate.

EXPERIMENTAL

2-Bromo-2-nitroethanol. 2-Nitroethanol[6] (637 g.) and 1500 ml. of methanol were placed in a 5-liter, three-necked flask fitted with a thermometer, stirrer, dropping funnel, and a bottom drain. The solution was cooled to −10° and a solution of 290 g. of U.S.P. sodium hydroxide in 2100 ml. of methanol was added slowly with stirring, maintaining the temperature between −10 and 0°.

In another 5-liter, three-necked flask placed below the first reaction flask and fitted with stirrer, dropping funnel, thermometer, and connection to the bottom drain of the upper flask, was placed 300 ml. of methanol. The methanol was cooled to −10°, and while being stirred, 350 ml. of bromine and the slurry of sodium *aci*-2-nitroethanol were added simultaneously. An excess of bromine was maintained at all times and the temperature was maintained below 0°. After the addition, the reaction mixture was allowed to warm to room temperature, then filtered to remove sodium bromide. The sodium bromide was washed with 200 ml. of methanol, and the combined filtrates concentrated under reduced pressure. The resulting concentrate was treated with 1 liter of ether, the precipitated salt washed with 200 ml. of ether, and the combined filtrates again concentrated under reduced pressure. The residue was vacuum distilled and the fraction boiling at 83°/2 mm. collected. The yields averaged 1083 g. (91%) based on 2-nitroethanol with a purity of 87–95%. The product thus obtained was found to be satisfactory for use in the next step of the synthesis.

Potassium aci-2,2-dinitroethanol. A solution of 1020 g. of 2-bromo-2-nitroethanol and 1500 ml. of methanol was maintained at 0° by means of a Dry Ice–acetone bath and with stirring, a solution of 620 g. of 96% potassium nitrite in 900 ml. of water was added in a fine stream. When the addition was complete, a solution of 492 g. of 85% potassium hydroxide was added, also in a fine stream. The temperature was maintained at 0° until crystallization began, then it was allowed to rise slowly to 7–10°. When this addition was complete, the solution was again cooled to 0° and filtered. The yellow salt was washed with 100 ml. of methanol and then suspended in 900 ml. of water and stirred at 25° for 15 min. to remove inorganic material. The purified salt was again filtered, washed twice with 100-ml. portions of methanol, and partially dried by means of an aspirator. The yield of moist salt (77–87% solids) from several preparations weighed 423–450 g. It was stored at −20° in brown bottles without further drying.

This salt was easily converted into the corresponding bromo-derivative, *2-bromo-2,2-dinitroethanol*, by dropping bromine into a cooled suspension of the salt in ether. It is a solid when dry, m.p. 63–65°, and is extremely hygroscopic,

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(5) M. J. Maas, *Chem. Zentr.*, **1899 I,** 179; *Rec. trav. chim.*, **17,** 386 (1898).

(6) R. Wilkendorf and M. Trenel, *Ber.*, **56B** 611 (1923).

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

(8) To be reported in subsequent publications.

liquefying when exposed to the atmosphere. It can be distilled, having a boiling point of 85–90° at 2 mm.

Anal. Calcd. for $C_2H_3BrN_2O_5$: Br, 37.23. Found: Br, 36.85.

The acetate, b.p. 59–60°/1 mm., and the *p*-nitrobenzoate, m.p. 76°, of the bromo compound were prepared in the usual manner.

Anal. Calcd. for $C_4H_5BrN_2O_6$: N, 10.90. Found: N, 10.59.

Anal. Calcd. for $C_9H_6BrN_3O_8$: C, 29.67; H, 1.65; Br, 21.98; N, 11.54. Found: C, 30.20; H, 1.74; Br, 21.75; N, 10.85.

2,2-Dinitroethanol. To 1 liter of ice water at 3° was added 300 g. of damp potassium *aci*-2,2-dinitroethanol. The slurry was stirred and cooled by means of an ice bath while a solution of 33 ml. of concentrated sulfuric acid in 320 ml. of water was added. The reaction mixture was maintained below 3° during the addition. After the addition was complete, the aqueous solution was extracted five times with ice-cold 20-ml. portions of ether. The ether solutions were combined and dried over sodium sulfate while being stored at −20°. Then, after filtering to remove the hydrated salts, the ether was removed from the solution under vacuum, leaving a light yellow liquid residue weighing 65 g. To this residue were added 2 drops of sulfuric acid and 75 ml. of dibutyl sebacate. This mixture was then further evacuated to remove the last traces of volatiles, after which it was transferred to a Distillation Products CMS-5 cyclic molecular still, degassed, and distilled at 50–60°/0.2 mm. Two fractions were obtained weighing 11 g. and 2 g., respectively. The first fraction had n_D^{20} 1.4717 while the second fraction had n_D^{20} 1.4710. Fraction 1 was extracted with petroleum ether (b.p. 30–60°) and then crystallized from ethyl chloride at Dry-Ice temperature. The white crystalline solid was collected on a precooled Buchner funnel and then quickly transferred to a cooled flask. The residual solvent was removed at a vacuum of 0.5 micron while maintaining the flask at −15°. A sample which was thus crystallized twice, melted at 2–3° and was analyzed on the same day.

Anal. Calcd. for $C_2H_4N_2O_5$: C, 17.64; H, 2.94; N, 20.59. Found: C, 17.98; H, 2.97; N, 21.08.

6,6-Dinitrobicyclo[2.2.1]-2-heptene. A solution of 4 g. (0.05 mole) distilled cyclopentadiene in 15 ml. of chlorobenzene was heated to reflux (100–110°) and a mixture of 3 g. of distilled 2,2-dinitroethanol in 15 ml. of chlorobenzene was added dropwise over a period of 10 min. Reflux was continued for an additional 20 min., and during this time the reaction mixture darkened and some polymer was deposited on the walls of the flask. The reaction mixture was clarified with charcoal and the solvent and excess cyclopentadiene were removed under reduced pressure. The residue was transferred to a small cold-finger distillation apparatus and distilled under vacuum. This operation was conducted behind a safety glass shield, as an earlier preparation had decomposed violently, spraying hot oil in all directions. The product sublimed at 145°/2 mm. and solidified on the cold-finger as a crystalline compound. The waxy crystals after recrystallization from ether melted at 117–118°.

Anal. Calcd. for $C_7H_8N_2O_4$: C, 45.6; H, 4.35; N, 15.21. Found: C, 44.96; H, 4.38; N, 15.21.

2,2-Dinitro-1,3-propanediol. A solution of 37% formaldehyde (460 g.) was added during a 1-hr. period to a suspension of 870 g. of pure potassium *aci*-2,2-dinitroethanol in 2 liters of water. When the addition was complete, 333 g. of glacial acetic acid was added dropwise during a 2.5-hr. period, and the resulting mixture stirred for an additional 2 hr. It was then extracted five times with 1-liter portions of ether and the extracts dried over sodium sulfate. The ether was removed under reduced pressure and the concentrate dissolved in 1 liter of 1-chloro-1-nitroethane and subsequently cooled to induce crystallization. The white crystals of 2,2-dinitro-1,3-propanediol which separated were filtered and washed with two 100-ml. portions of chloroform, and finally dried in a vacuum oven at 50°/30 mm. for 4 hr. There was obtained 630 g. (76%) of product melting at 139–140°.

Anal. Calcd. for $C_3H_6N_2O_6$: C, 21.69; H, 3.64; N, 16.89. Found: C, 21.97; N, 3.90; N, 17.09.

The dibenzoate was prepared in the usual manner, m.p. 79°.

Anal. Calcd. for $C_{17}H_{14}N_2O_8$: N, 7.49. Found: N, 7.64.

5,5-Dinitro-1,3-dioxan. A mixture of 10 g. of 2,2-dinitro-1,3-propanediol, 2.0 g. of paraformaldehyde, 10 ml. of acetic acid, and 0.1 ml. of sulfuric acid was heated on a steam bath for nearly 8 hr. The mixture was filtered and then concentrated under reduced pressure. The sirup that remained was distilled in a micro distillation apparatus. At an oil-bath temperature of 140° and a pressure of 2–3 mm., 8 g. of clear distillate was obtained which partially crystallized in the receiver. About 2 g. of liquid was decanted and then the solid residue was dissolved in chloroform. To this solution was added petroleum ether (b.p. 30–60°) and a crystalline product was recovered which, after several recrystallizations from the same solvent, melted at 53–53.5°. According to the analysis the compound is the 1,3-dioxan.

Anal. Calcd. for $C_4H_6N_2O_6$: N, 15.73; Found: N, 15.90.

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