(70%) of the potassium salt of ethyl α -acetoxy- β . β -dinitropropionate precipitated. The crude salt was suspended in water, acidified with 20% sulfuric acid, chilled, and the solid removed by filtration. Extraction of the solid with benzene, evaporation of the benzene, and recrystallization of the residue from hexane yielded ethyl α -acetoxy- β , β dinitropropionate, m.p. 54-55°

Anal. Caled. for C7H10N2O8: C, 33.61; H, 4.03; N, 11.20. Found: C, 32.98; H, 3.87; N, 11.16.

A sample of the purified potassium salt melted at 122° with decomposition.

Anal. Calcd. for C7H9KN2O8: K, 13.56. Found: K, 13.58

Ethyl α -acetoxy- β -chloro- β , β -dinitropropionate (XV). A solution of crude ethyl a-hydroxy-\$-chloro-\$,\$-dinitropropionate (XIV) in excess acetyl chloride was heated under reflux for 4 hr. After removal of the excess acetyl chloride, the residue was fractionated giving ethyl α -acetoxy- β chloro- β , β -dinitropropionate, b.p. 67-69°/0.01 mm., $n_{\rm p}^{25}$ 1.4484 in about 30% yield. Anal. Calcd. for C₇H₉ClN₂O₈: C, 29.54; H, 3.19; N, 9.84.

Found: C, 29.78; H, 3.29; N, 9.53.

Strong absorptions at 5.64, 5.71 μ (C=O) and 6.22 μ (NO_2) were observed in the infrared in chloroform solution.

Ethyl α -hydroxy- β -chloro- β , β -dinitropropionate (XIV). A suspension of 12.3 g. (0.05 mole) of the potassium salt of ethyl α -hydroxy- β , β -dinitropropionate in 50 ml. of methylene chloride was cooled in an ice bath while 5 g. (0.07 mole) of chlorine in 50 ml. of cold methylene chloride was added with stirring. After 15 min. the yellow salt had been replaced by potassium chloride which was removed by filtra-

tion. Crude ethyl α -hydroxy- β -chloro- β , β -dinitropropionate suitable for conversion to the α -acetoxy ester XV was obtained in 94% yield by removing the solvent under reduced pressure. An analytical sample, b.p. 70°/0.2 mm., $n_{\rm D}^{25}$ 1.4419, was obtained by fractional distillation under reduced pressure. Weak to moderate absorption at 2.80μ (OH), and strong absorption at 5.71μ (C=O) and 6.30μ (NO_2) were observed in the infrared in chloroform solution. Anal. Calcd. for C5H7ClN2O7: C, 24.75; H, 2.91; N, 11.55.

Found: C, 24.90; H, 3.04; N, 11.80. Potassium dinitromethane. An aqueous solution of 2,2-

dinitropropanediol-1.3 was treated with excess cold 35% potassium hydroxide solution and, after chilling, the resulting potassium salt of 2,2-dinitroethanol was filtered and air dried. This salt (15.1 g., 0.087 mole) was suspended in 80 ml. of water containing 6.6 g. (0.1 mole) of 85% potassium hydroxide. During a 5-min. period, 20 g. (0.18 mole) of 30% hydrogen peroxide was added with stirring. The temperature of the reaction mixture rose to 45° during the addition. After warming on a steam bath for 40 min., a second portion of hydrogen peroxide equal to the first was added during 15 min. and heating was continued for another 15 min. The reaction mixture was allowed to cool to room temperature, chilled, and the potassium salt filtered, washed with methanol, and air dried (11.3 g., 90%).

Anal. Calcd. for CHKN₂O₄: K, 27.13. Found: K, 26.91.

As a safety precaution, all potassium salts were stored only for short periods of time and were handled while moist with water or alcohol.

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[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Derivatives of Nitromethylamines. I. Nitromethyl Isocyanates

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Nitromethyl isocyanate, *a*-nitroethyl isocyanate, and *a*-nitroisopropyl isocyanate have been prepared by thermal rearrangement of the corresponding acid azides. The compounds are unstable and only α -nitroethyl isocyanate could be distilled. Infrared absorption spectra and other properties of these isocyanates are described.

While nitromethylamine is apparently unknown, two types of related compounds have been described. The nitromethylurethan I was believed to be obtained when the azide of nitrocyanoacetic acid (II) was refluxed with ethanol. The urethan I has not been isolated and its structure is based on the products of hydrolysis of crude material which

include one mole of carbon dioxide, one mole of hydrogen cyanide, ethanol, and ammonium chloride.¹ The stable crystalline compounds IIIa have been prepared by coupling aryl diazonium salts with active methylene compounds and IIIb result from the analogous coupling reaction with secondary nitro-

(1) A. Darapsky and D. Hillers, J. prakt. Chem., 92, 305 (1925).

paraffins or their methylol derivatives.^{2,2a} COOMe, CN, CONH₂, SO₂Ar, SOAr, NO₂. R = H or alkyl.

$$X = H$$
, COOMe, CN, CONH₂, SO₂Ar, SOAr, NO₂
ArN=NC(NO₂)R₂
IIIb

 $\mathbf{R} = \mathbf{H}$ or alkyl

(2) S. Hünig and O. Boes, Ann., 579, 28 (1953); E. Bamberger, O. Schmidt, and H. Levenstein, Ber., 33, 2059 (1900); H. E. Baumgarten and M. R. DeBrunner, J. Am. Chem. Soc., 76, 3489 (1954); C. F. Feasly and E. F. Degering, J. Org. Chem., 8, 13 (1943); Z. Eckstein and T. Urbanski, Bull. acad. polon. Sci., Classe III, 3, 433 (1955)

⁽²a) Other analogs of nitromethylamine which are reported in the literature, probably owe their stability to special structural features, as for instance, the α -nitro-pyrroles [H. Fischer and W. Zerweck, *Ber.*, 55, 1949 (1922)] and the 3-nitrocinnolines [H. E. Baumgarten and M. R. DeBrunner, J. Am. Chem. Soc., 76, 3490 (1954)].

In the present investigation the Curtius reaction of nitro-substituted acid azides has been studied in some detail for the preparation of other derivatives of nitromethylamine.

 $CRR'(NO_2)CON_2 \longrightarrow CRR'(NO_2)N=C=O$ R, R' = H or alkyl

The required hydrazides can be prepared from α nitro esters by the action of hydrazine. Thus methyl nitroacetate gives a solvated hydrazine salt of nitroacethydrazide (IV, R = H) with hydrazine hydrate in methanol. The intermediate hydrazine salt of the methyl ester cannot be isolated but the corresponding salt of the ethyl ester is formed in good yield from molar equivalents of ester and hydrazine hydrate in ethanol. It is converted to IV (R = H) by reaction with aqueous hydrazine hydrate at 25°. When this salt (IV, R = H) is treated with dry hydrogen chloride in ethanol, it is converted to the hydrazide hydrochloride (V, R = H) in 58% yield.

$$\begin{array}{c} H_2 N\dot{N} H_3 NO_2 \overline{C} RCONHNH_2 + HCl \longrightarrow \\ IV \\ NO_2 CHRCONHNH_3 Cl^{-1} \\ V \end{array}$$

R = H or Me

Ethyl α -nitropropionate yields a crystalline hydrazine salt which is converted to the salt of the hydrazide (IV, R = Me) by heating with excess hydrazine hydrate. Cold aqueous hydrochloric acid converts the salt to a product devoid of nitro groups as evidenced by its infrared spectrum. The hydrochloride V (R = Me) is obtained by using dry hydrogen chloride. Ethyl α -nitroisobutyrate is converted to the hydrazide by reaction with an equimolar amount of hydrazine hydrate at 5°, while heating with an excess of hydrazine hydrate causes the nitro group to be eliminated.

The nitroacid hydrazides (or their hydrochlorides) are completely converted to acid azides by nitrous acid at 0°. The solutions of the acid azides in chloroform or carbon tetrachloride show characteristic bands for N₃, C=O, and NO₂ in the infrared (Table I). After refluxing of the solutions, the first two bands disappear and a new intense band (N=C=O) occurs in the 4.4- μ region. Some slight decomposition occurs during the rearrangement of all the nitroacid azides. Nitromethyl and α -nitroethyl isocyanate have been obtained free from solvent and the latter has been distilled under reduced pressure. The rearrangement product of α nitroisobutyrazide, on the other hand, is formed only at the higher temperatures of boiling carbon tetrachloride and decomposes when the solvent is removed.

All three nitromethyl isocyanates are extraordinarily reactive toward water and alcohols, and polymerize to unstable solids even below room temperature and, in part, during their formation. A chloroform solution of α -nitroethyl isocyanate (VI) reacts

TABLE I

CHARACTERISTIC INFRARED ABSORPTION BANDS FOR AZIDES AND ISOCYANATES IN CHLOROFORM

	N ₃	C=0	N== C==0	NO2 as	NO2 sym
NO ₂ CH ₂ CON ₃ NO ₂ CHM ₆ CON ₃ NO ₂ CM ₆₂ CON ₃ NO ₂ CH ₂ N=C=O NO ₂ CHM ₆ N=C=O NO ₂ CM ₆₂ N=C=O	4.64 4.64 4.66 	5.78 5.78 5.81	4.41 4.42 4.44	$\begin{array}{c} 6.36 \\ 6.36 \\ 6.44 \\ 6.33 \\ 6.36 \\ 6.45 \end{array}$	$\begin{array}{c} 7.25 \\ 7.36 \\ 7.47 \\ 7.30 \\ 7.37 \\ 7.45 \end{array}$

exothermically with methanol. The oil, obtained after removing the solvents, has an infrared spectrum corresponding to VII.

Its structure is established by hydrolysis with cold water, which gives an excellent yield of acetaldehyde (based on acetaldimethone). By analogy, the alcoholysis product of nitrocyanoacetazide is probably also an imine (CNCH=NCOOEt) rather than the urethan I.¹ The reported hydrolysis products¹ allow for either structure. The loss of nitrous acid seems to be characteristic for nitromethylamines with a hydrogen on the nitrogen.

EXPERIMENTAL³

Hydrazine salt of ethyl nitroacetate. Hydrazine hydrate (1.64 g., 0.032 mole) was added to a solution of ethyl nitroacetate (4.36 g., 0.032 mole) in 20 ml. of 95% ethanol. The warm solution was cooled immediately and kept at 5° for 15 hr. The crystalline precipitate was filtered, washed with benzene and petroleum ether, and dried at 60°; total yield (2 crops) 4.41 g. (81%). Recrystallization from 95% ethanol and then from methanol gave pale yellow plates, m.p. 104-105° (dec.).

Anal. Calcd. for $C_4H_{11}N_3O_4$: C, 29.09; H, 6.71; N, 25.45. Found: C, 28.95; H, 6.90; N, 25.60.

Hydrazine salt of nitroacethydrazide. The hydrazine salt of ethyl nitroacetate (1.65 g., 0.01 mole) was dissolved in 10 ml. of cold water. To this solution was added hydrazine hydrate (0.5 g., 0.01 mole) and the mixture was allowed to stand at 25° for 3.5 hr. The aqueous solution was evaporated at 25° (50 mm.) giving 1.5 g. of a yellow solid which was crystallized from 95% ethanol. The first crop (0.76 g.) was recrystallized from the same solvent; yield 0.73 g., m.p. 115-116° (dec.). The second crop of slightly less pure crystals melted at 113-114° (dec.). The over-all yield was 1.04 g. (60%). After several recrystallizations from 95% ethanol the salt melted at 117-118° (dec.).

Anal. Caled. for C₂H₉N₅O₈.¹/₂C₂H₅OH: C, 20.69; H, 7.59; N, 40.23. Found: C, 19.78; H, 5.91; N, 40.93.

A solvate⁴ with nearly identical infrared spectrum was obtained by adding hydrazine hydrate (2.0 g., 0.04 mole) with shaking to a solution of methyl nitroacetate (4.76 g., 0.04 mole, n_D^{25} 1.4238) in 25 ml. of methanol. The solution

(3) All temperatures uncorrected. Analyses by M. Naranjo and C. Esquibel.

(4) The composition of these solvates varied on crystallization. Analyses are reported for representative solvates which do not necessarily correspond to definite compounds.

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was cooled to 5° and the colorless salt was filtered with suction, yield 5.73 g., m.p. 131-132° (dec.). Recrystallization from methanol gave colorless needles, m.p. 125° (dec.), yield 2.76 g. (70%).

Anal. Caled. for C2H9N5O3.11/2CH3OH: C, 21.09; H, 7.59; N, 35.17. Found: C, 21.25; H, 7.05; N, 35.99.

On recrystallization from 95% ethanol, the methanol solvate (m.p. 125°, dec.) was converted to the ethanol solvate, m.p. 117-118° (dec.).

Nitroacethydrazide hydrochloride. The hydrazine salt of nitroacethydrazide (1.51 g., 0.0087 mole, ethanol solvate, m.p. 117-118°), suspended in 25 ml. of 95% ethanol, was treated with a slow stream of hydrogen chloride while cooled in an ice bath. The colorless precipitate weighed 2.0 g. and the ethanol filtrate furnished an additional 0.2 g. The combined solids were digested with hot acetonitrile from which the sparingly soluble hydrochloride crystallized on cooling in colorless needles. Repeated digestions gave a total of 0.90 g. (66%) of hydrochloride, m.p. 124° (dec.), λ (C=O) 5.85 μ , λ (NO₂) 6.39, 7.26 μ .

Anal. Calcd. for C2H6CIN3O3: C, 15.45; H, 3.89; Cl, 22.79. Found: C, 15.24; H, 3.39; Cl, 24.36.

Nitromethyl isocyanate. A solution of 0.345 g. (0.005 mole) of sodium nitrite in 7.5 ml. of water was added dropwise with stirring to a mixture of 5 ml. of alcohol-free chloroform and a solution of 0.775 g. (0.005 mole) of nitroacethydrazide hydrochloride and 0.5 ml. of concentrated hydrochloric acid in 12.5 ml. of water at 0°. After completed addition the mixture was stirred at 0° for 0.5 hr. The chloroform layer was separated, the aqueous layer was extracted with 5 ml. of alcohol-free chloroform, and the combined extracts were dried over sodium sulfate.

The dry chloroform solution of nitroacetazide with infrared characteristics given in Table I was refluxed from a steam bath for 5 hr. The solution was filtered from 0.015 g. of unidentified tan solid. The isocyanate remained as pale yellow oil (0.08 g.) when the solvent was removed under reduced pressure.

Anal. Calcd. for C₂H₂N₂O₃: N, 27.46. Found: N, 27.52.

It started to decompose at room temperature within 10 min., forming a tan solid which also decomposed at room temperature.

The remaining oil (0.060 g.) was quickly dissolved in carbon tetrachloride and allowed to stand at room temperature. Infrared spectra, taken at intervals during 28 hr., showed that the isocyanate band at 4.41 μ disappeared and a new one appeared at 4.30 μ , while the nitro band was greatly diminished in intensity.

Hydrazine salt of ethyl a-nitropropionate. A colorless precipitate formed immediately when 0.5 g. (0.01 mole) of 65% hydrazine hydrate was added to 1.5 g. (0.01 mole) of ethyl α -nitropropionate (b.p. 75°/6 mm., n_D^{25} 1.4190) in 5 ml. of 95% ethanol. The mixture was brought to boiling, diluted with sufficient ethanol (5 ml.) to bring the salt into solution, and allowed to cool. The colorless salt which crystallized weighed 1.2 g. (75%). On recrystallization from 20 ml. of 95% ethanol, it was obtained in colorless needles, m.p. 131-133° (dec.), (lit. m.p. 120°),⁵ yield 0.6 g. (33%). Anal. Calcd. for $C_{5}H_{15}N_{5}O_{4}$: C, 33.52; H, 7.31; N, 23.46. Found: C, 33.21; H, 7.19; N, 23.87.

The salt burned slowly in a flame and was insensitive to

impact.

Hydrazine salt of α -nitropropionhydrazide. The hydrazine salt of ethyl α -nitropropionate (4.0 g., 0.022 mole) was heated on a steam bath with 1.5 g. (0.03 mole) of hydrazine hydrate for 20 min. The clear yellow liquid solidified on cooling. It was stirred with 95% ethanol, filtered, and washed with ethanol. The dry salt weighed 3.5 g. (95%). After recrystallization from ethanol it melted at 139-140°.

Anal. Caled. for C3H11N5O3: C, 21.82; H, 6.70; N, 42.40. Found: C, 21.77; H, 6.53; N, 41.42.

(5) A. K. Macbeth and D. Traill, J. Chem. Soc., 897 (1925).

An over-all yield of 85% was obtained from ethyl α nitropropionate when its crude moist hydrazine salt was heated with a slight excess of hydrazine hydrate. The compound melted and burned in a flame and was not sensitive to impact.

 α -Nitropropionhydrazide hydrochloride. Dry hydrogen chloride reacted with a suspension of 12.8 g. (0.077 mole) of the above hydrazine salt in 75 ml. of methanol at 0° to give a colorless precipitate of hydrazine dihydrochloride, which was filtered with suction. The filtrate was heated on a steam bath under reduced pressure to remove the solvent. The glassy residue was dissolved in 100 ml. of boiling acetonitrile, the solution was filtered from a trace of hydrochloride, and allowed to cool. The crystalline hydrazide hydrochloride was filtered with suction; yield 8.0 g. (61%), m.p. 120-121° (dec.). A second crop of slightly less pure material weighed 4.0 g. (30%). Anal. Calcd. for C₃H₃ClN₃O₃: C, 21.25; H, 4.75; Cl,

20.91; N, 24.78. Found: C, 21.49; H, 4.88; Cl, 20.83; N, 24.88

 α -Nitroethyl isocyanate. α -Nitropropionhydrazide hydrochloride (1.69 g., 0.01 mole) was converted to the azide as described for the lower homolog. The chloroform layer was separated and the aqueous layer was extracted with 5 ml. of chloroform. The combined chloroform solutions of α nitropropionazide (15 ml.) were dried over sodium sulfate, filtered, and refluxed for 3 hr.

A part of the chloroform solution (5 ml.) was diluted with 5 ml. of methanol. The mixture warmed exothermically and then was refluxed from a steam bath for 30 min. The solvents were removed under reduced pressure leaving a yellow oil, λ (C—O) 8.1–8.25 μ , λ (C=O) 5.80, λ (C=N) 5.92, $\lambda(CON=)$ 6.60 μ . The oil, mixed with 5 ml. of water, was allowed to stand at 25° for 12 hr. The aqueous solution was filtered from traces of insoluble material, treated with a solution of 1.4 g. of dimethyldihydroresorcinol in 5 ml. of acetic acid and 50 ml. of water, and allowed to stand for 3 hr. The precipitated acetaldehyde dimethone was filtered and dried to constant weight at 60°; yield 1.01 g. (91%), m.p. 140-141° (lit. value 140.2°).6 It was converted to the anhydride, m.p. 176-177° (lit. value 175°),⁶ by refluxing with acetic anhydride.

The remaining chloroform solution of the isocyanate (10 ml.) was distilled at 40 mm. to remove the solvent. The products from a number of runs, obtained in the same way, were distilled at pressures between 1 and 32 mm. The distillate, b.p. 69° (32 mm.), $n_{\rm D}^{25}$ 1.4317, was obtained in yields of 45% as a colorless oil accompanied by a yellow amorphous solid and nitrogen oxides. It reacted vigorously with water, ethanol, and methanol, and was unstable even when refrigerated in the dark. Under these conditions, as well as on heating or exposure to light and air, it was converted to a yellow solid which decomposed between 25 and 90° with evolution of gas on slow heating. On one occasion it decomposed explosively at room temperature. In view of this instability of the compound it was not possible to obtain good analytical data. It was established, however, that the yellow solid still had the approximate composition of the isocyanate. It was insoluble in chloroform, benzene, and ether, unlike the isocyanate, initially dissolved in acetonitrile but precipitated on standing. Its infrared spectrum was devoid of nitro absorption.

Ethyl α -nitroisobutyrate. The reaction of ethyl α -bromoisobutyrate (58.5 g., 0.3 mole) with sodium nitrite (41.4 g., 0.6 mole) and urea (40 g.) in dimethylformamide (500 ml.) at room temperature⁷ gave 32.8 g. (68%) of ethyl α -nitro-

(6) D. Vorlander, Z. anal. Chem., 77, 321 (1929); Ann., 309, 370 (1899); W. Stepp and R. Feulgen, Z. physiol. Chem., 114, 301 (1921).

(7) N. Kornblum, H. O. Larsen, D. D. Mooberry, R. K. Blackwood, E. R. Oliveto, and C. E. Graham, Chemistry & Industry, 443 (1955); N. Kornblum and J. H. Eicher, J. Am. Chem. Soc., 78, 1496 (1956).

isobutyrate, b.p. 87° (16 mm.), n_D^{25} 1.4179, λ (C=O) 5.71 μ , λ (NO₂) 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 (NO₂) 6.42, 7.41 μ . The melting point was unchanged after vacuum sublimation at 0.1 mm.

Anal. Calcd. for $C_4H_9N_8O_8$: 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 pre-

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

cipitated, and NO₂ 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=0 (5.80 μ) absorption.

NH (3.10) and C=O (5.80 μ) absorption. Anal. Calcd. for C₄H₆N₂O₈: 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 NO₂ 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 NO₂ 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.

[CONTRIBUTION FROM RESEARCH LABORATORY OF THE AEROJET-GENERAL CORP.]

Preparation and Characterization of 2,2-Dinitroethanol¹

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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 Pondorff² 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 synthesis² 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 tribromoaniline³ 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 Meer⁴ 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*-2nitroethanol. 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

⁽¹⁾ This work was performed under contract with the Office of Naval Research.

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⁽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).