

For the first mother liquor there was obtained 2.7 g. (8.9%) of an amber, non-crystallizable sirup,  $[\alpha]_D^{25} -1.0$  ( $\text{CHCl}_3$ , *c* 2).

Various modifications of the glucosylation procedure were examined in the hopes of improving the yield, but all failed to give VI. These included increasing the mole ratio of sodium acetylide to acetobromoglucose to 18:1 and adding the latter as a solid to the liquid ammonia. Attempts were also made to obtain VI by boiling acetobromoglucose with sodium acetylide in ethyl ether or in benzene.

Catalytic reduction over platinum oxide at 25° and 40 p.s.i. of 0.30 g. of compound VI in 200 ml. of ethanol, followed by filtration and evaporation, gave a sirup  $[\alpha]_D^{25} +38.2$ ,  $[\alpha]_{5461}^{25} +47.0$  ( $\text{CHCl}_3$ , *c* 1.3).

*Tetraacetyl-β-D-glucopyranosylethane* (VIII). By the general procedure described earlier 49 g. (0.12 mole) of tetraacetyl-α-D-glucosyl bromide in 600 ml. of ethyl ether was caused to react with the Grignard reagent prepared from 131 g. (1.2 moles) of ethyl bromide and 30 g. (1.2 g.-atom)

of magnesium in 200 ml. of ether. After hydrolysis, distillation of the dried ether phase gave 34 g. (72%) of 3-methyl-3-pentanol, b.p. 121–122°,  $n_D^{25}$  1.4170 (lit. b.p. 123°,  $n_D^{25}$  1.4196).<sup>19</sup> The dry residue from stripping the aqueous phase was acetylated to give 10.5 g. (24%) of sirup which slowly crystallized. Recrystallization from isopropyl ether gave 3.1 g. (7.2%) of tetraacetyl-β-D-glucopyranosylethane (VIII), m.p. 91.5–92.5°,  $[\alpha]_D^{25} -9.0$ ,  $[\alpha]_{5461}^{25} -10.5$  ( $\text{CHCl}_3$ , *c* 2).

*Anal.* Calcd. for  $\text{C}_{16}\text{H}_{24}\text{O}_9$ : C, 53.32; H, 6.71. Found: C, 53.31; H, 6.75.

The mother liquors left from crystallization of VIII were stripped of solvent at 100° in a vacuum to leave 6.1 g. of amber, non-crystallizable sirup,  $[\alpha]_D^{25} +12.2$ ,  $[\alpha]_{5461}^{25} +13.7$  ( $\text{CHCl}_3$ , *c* 2).

CHICAGO 14, ILL.

(19) R. Henry, *Rec. Trav. Chim.*, 26, 94 (1907).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF AEROJET-GENERAL CORPORATION]

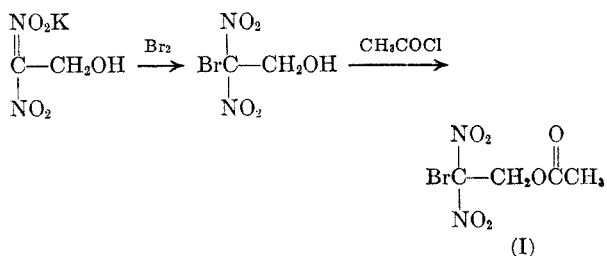
## The Dinitroethylation Reaction<sup>1</sup>

MILTON B. FRANKEL

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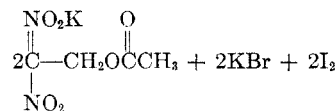
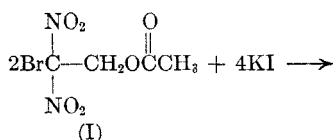
A new reaction has been discovered in the preparation of potassium 2,2,4,4-tetranitrobutyl acetate from 2-bromo-2,2-dinitroethylacetate (I) and potassium iodide. A mechanism is proposed in which 1,1-dinitroethylene is postulated as the reactive intermediate. The generality of this dinitroethylation reaction is indicated by the preparation of potassium 1,1,3,3-tetranitrobutane (VIII) and sodium 1,1-dinitro-2-phthalimidoethane (V) from I and the corresponding salts of 1,1-dinitroethane and phthalimide, respectively. Derivatives of VIII and V are reported.

In continuing the work on aliphatic *gem*-dinitro compounds in this laboratory,<sup>2</sup> attempts were made to prepare potassium 2,2-dinitroethyl acetate. One of the most promising methods for preparing this salt was from the corresponding bromo compound. 2-Bromo-2,2-dinitroethyl acetate (I) was made in an unequivocal manner from potassium 2,2-dinitroethanol.



It was expected that treatment of 2-bromo-2,2-dinitroethyl acetate with potassium iodide would produce potassium 2,2-dinitroethyl acetate. An analogous reaction was reported by Meisenheimer,<sup>3</sup> who converted 2-bromo-2,2-dinitro-1-ethoxyethane

to the corresponding potassium salt by the use of potassium iodide. Klager<sup>4</sup> generalized this procedure and showed that compounds with terminal bromodinitromethyl groups react quantitatively with potassium iodide; the amount of iodine formed corresponds to the theoretical amount of bromine present in the molecule. However, treatment of I with potassium iodide did not give the expected potassium 2,2-dinitroethyl acetate, but a new salt was produced in 64% yield whose analysis was in agreement with potassium 2,2,4,4-tetranitrobutyl acetate (II). Acidification of this salt with dilute sulfuric acid gave a compound whose analysis and neutral equivalent were in agreement with 2,2,4,4-tetranitrobutyl acetate (III). The formation of potassium 2,2,4,4-tetranitrobutyl acetate can be explained as shown in the following equations:

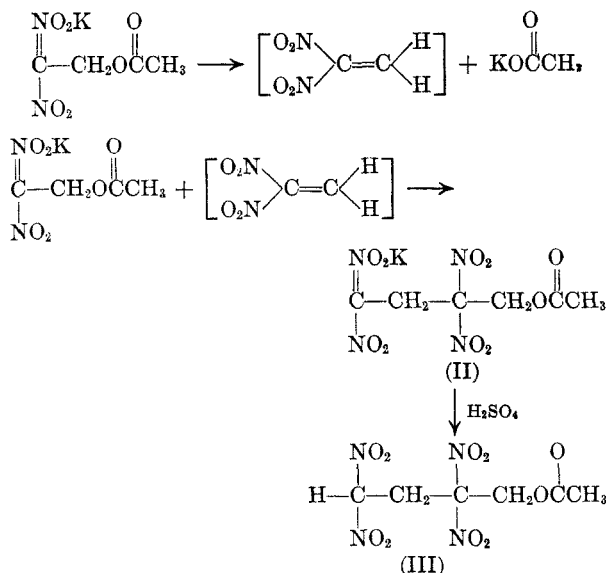


(1) Presented before the Division of Organic Chemistry at the 133rd meeting of the American Chemical Society, April 13–18, 1958, San Francisco, Calif.

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

(3) J. Meisenheimer, *Ber.*, 36, 437 (1903).

(4) K. Klager, *Anal. Chem.*, 23, 534 (1951).



All attempts to isolate potassium 2,2-dinitroethyl acetate were unsuccessful. This indicates that potassium 2,2-dinitroethyl acetate is not stable under such conditions and probably decomposes into 1,1-dinitroethylene and potassium acetate. Since 1,1-dinitroethylene also was not isolated, presumably because of its high reactivity, it must have been present as a transitory intermediate, capable of undergoing a Michael condensation with potassium 2,2-dinitroethyl acetate to form potassium 2,2,4,4-tetranitrobutyl acetate.<sup>5</sup>

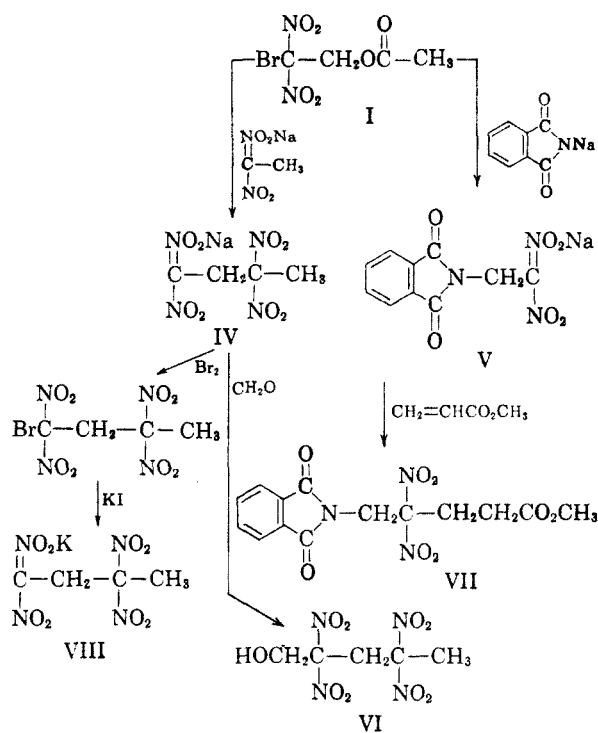
If these assumptions are valid, then the metallic salts of a variety of organic and inorganic compounds which are weak acids are capable of reacting with 2-bromo-2,2-dinitroethyl acetate. One mole of the salt would liberate 1,1-dinitroethylene which would immediately condense with a second mole of the salt, forming a compound containing a dinitro-

ethyl grouping  $\left( \begin{array}{c} \text{NO}_2\text{M} \\ \parallel \\ -\text{CH}_2-\text{C} \\ \parallel \\ \text{NO}_2 \end{array} \right)$ . Several ex-

amples of this general reaction were realized. When potassium iodide was replaced with the salt of an organic nitro compound or a phthalimide salt, the corresponding salts containing the dinitroethyl grouping were formed. Thus, treatment of I with sodium 1,1-dinitroethane and sodium phthalimide yielded the corresponding salts of 1,1,3,3-tetranitrobutane (IV) and 1,1-dinitro-2-phthalimidoethane (V).

This evidence indicates that the process of dinitroethylation is a general type of reaction, with 2-bromo-2,2-dinitroethyl acetate functioning as a source of 1,1-dinitroethylene which can participate in a Michael type of reaction with other compounds.

(5) L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, **79**, 4708 (1957), recently reported that the reaction of 1,1,1-trinitroethane with certain bases caused elimination of nitrous acid to give 1,1-dinitroethylene, a reactive intermediate, which underwent addition of the base to yield β-substituted derivatives of 1,1-dinitroethane.



In the reactions of 2-bromo-2,2-dinitroethyl acetate (I), both the sodium and potassium salts of the organic compounds were used. The sodium salts gave higher yields because of their greater solubility; however, the potassium salts of the products were more readily isolated and purified. Thus, treatment of I with sodium 1,1-dinitroethane gave sodium 1,1,3,3-tetranitrobutane (IV) which was difficult to purify, so it was brominated and then treated with potassium iodide to give potassium 1,1,3,3-tetranitrobutane (VIII), which was easily crystallized.

The salts formed in the Michael condensation can react further as illustrated in the preparation of 2,2,4,4-tetranitro-1-pentanol (VI) from IV and formaldehyde and also methyl 4,4-dinitro-5-phthalimidopentanoate (VII) from V and methyl acrylate.

#### EXPERIMENTAL<sup>6,7</sup>

*2-Bromo-2,2-dinitroethyl acetate* (I). A slurry of 215 g. of damp potassium 2,2-dinitroethanol<sup>2</sup> (equivalent to 1 mole of dry salt) and 500 ml. of water was cooled to 0° and 176 g. (1.1 mole) of bromine was added during a 40 min. period. The reaction mixture was extracted 4 times with 100 ml. portions of ether. The ether extracts were combined, washed twice with water, and dried over sodium sulfate overnight at 0°. The ether solution was concentrated and distilled from a Claisen flask at 88–93° (2 mm.). The distillate, 2-bromo-2,2-dinitroethanol, was a white mushy solid which liquefied on contact with moist air. It was treated directly with a solution of 86 g. (1.1 mol.) of acetyl chloride in 500 ml. of dry chloroform. The solution was refluxed for 3.5 hr., the solvent was evaporated under reduced pressure leaving a light yellow liquid which was distilled from a Claisen

(6) All melting points are uncorrected.

(7) Microanalyses by Elek Micro Analytical Laboratories, Los Angeles, Calif.

flask. The overall yield of 2-bromo-2,2-dinitroethyl acetate was 193.4 g. (75%), b.p. 70–71°/0.35 mm.,  $n_D^{25}$  1.4728.

*Anal.* Calcd. for  $C_4H_5N_2O_6Br$ : Br, 31.10; N, 10.90. Found: Br, 30.96; N, 10.59.

*Potassium 2,2,4,4-tetranitrobutyl acetate* (II). A solution of 25.7 g. (0.10 mole) of 2-bromo-2,2-dinitroethyl acetate in 100 ml. of methanol was cooled to 0° and a solution of 83 g. (0.50 mole) of potassium iodide in 150 ml. of 50% methanol was added dropwise. The purple reaction mixture was filtered and the yellow solid was washed thoroughly with ether to remove the iodine liberated in the reaction. The yield of potassium 2,2,4,4-tetranitrobutyl acetate was 24.0 g. (equivalent to 21.5 g. or 64.5% of dry salt). The salt was recrystallized 3 times from water, m.p. 174° explodes.

*Anal.* Calcd. for  $C_8H_8N_4O_{10}K$ : C, 21.56; H, 2.11; N, 16.76. Found: C, 21.89; H, 2.27; N, 16.67.

*2,2,4,4-Tetranitrobutyl acetate* (III). A slurry of 12 g. (0.035 mole) of potassium 2,2,4,4-tetranitrobutyl acetate and 150 ml. of water was cooled to 0° and a solution of 5 ml. of concentrated sulfuric acid in 30 ml. of water was added. At the end of the addition the reaction mixture turned from orange to yellow. Stirring was continued for another hour and the reaction mixture was filtered. The cream colored solid was collected, washed well with water, and air dried. The yield of 2,2,4,4-tetranitrobutyl acetate was 7.0 g. (67.5%), m.p. 57–58°. The product was recrystallized twice from ethyl chloride at –70° to give a white crystalline solid, m.p. 58–59°.

*Anal.* Calcd. for  $C_6H_8N_4O_{10}$ : C, 24.33; H, 2.72; N, 18.92; neut. equiv., 296. Found: C, 24.62; H, 2.89; N, 18.50; neut. equiv., 297, 298.

*Potassium 1,1,3,3-tetranitrobutane* (VIII). 1,1-Dinitroethane,<sup>8</sup> 12.0 g. (0.10 mole), was cooled in an ice bath and a solution of 4.2 g. (0.10 mole) of 95% sodium hydroxide in 30 ml. of water was added. Then a solution of 12.85 g. (0.05 mole) of 2-bromo-2,2-dinitroethyl acetate in 25 ml. of methanol was added dropwise while the sodium 1,1-dinitroethane solution was maintained at 10°. Stirring was continued while the solution warmed to room temperature. The reaction mixture was extracted with ether to remove any starting material. The aqueous layer was cooled to 5° and treated with 8.0 g. (0.05 mole) of bromine. The solution was extracted with ether, dried, and concentrated to give 4.4 g. of 1-bromo-1,1,3,3-tetranitrobutane. One and seven-tenths g. of this orange liquid was dissolved in 3 ml. of methanol and cooled to 0°, then a solution of 1.78 g. of potassium iodide in 6 ml. of 50% methanol was added. The

purple reaction mixture was filtered and the yellow salt was washed with ether, wt. 1.0 g. The salt was recrystallized 3 times from ethanol, m.p. 137–138° dec.

*Anal.* Calcd. for  $C_4H_5N_4O_8K$ : C, 17.39; H, 1.83; N, 20.29. Found: C, 17.71; H, 1.83; N, 20.69.

*2,2,4,4-Tetranitro-1-pentanol* (VI). 1,1-Dinitroethane, sodium hydroxide, and 2-bromo-2,2-dinitroethyl acetate were treated in the same amounts and in the same manner as above. The reaction mixture was extracted with ether to remove any unreacted starting material. At room temperature, 4.1 g. of 37% formalin was added to the aqueous layer, the solution was stirred for 1 hr., and 3 g. of glacial acetic acid was added dropwise. The orange solution was extracted 3 times with ether, the ether extracts were combined, washed with water, dried, and concentrated leaving 2.5 g. of a yellow liquid. The liquid was heated in a bulb tube at 70–110° (1 micron), 0.5 g. of the liquid distilled leaving a viscous yellow liquid which solidified. This residue was recrystallized from carbon tetrachloride to give 0.3 g. of a white crystalline solid, m.p. 66–67°.

*Anal.* Calcd. for  $C_5H_8N_4O_8$ : C, 22.40; H, 3.01; N, 20.90. Found: C, 22.44; H, 2.87; N, 21.31.

*Sodium 1,1-dinitro-2-phthalimidoethane* (V). To a solution of 110.0 g. (0.65 mole) of sodium phthalimide in 500 ml. of 60% methanol, at room temperature, was added a solution of 83.7 g. (0.325 mole) of 2-bromo-2,2-dinitroethyl acetate in 150 ml. of methanol. A yellow solid separated in about 5 min.; stirring was continued for an additional 30 min. The yellow solid was collected, washed with ether, and air dried. The yield of sodium 1,1-dinitro-2-phthalimidoethane was 60.0 g. (64.3%), m.p. 238° explodes.

*Methyl 4,4-dinitro-5-phthalimidopentanoate* (VII). A mixture of 3.0 g. (0.01 mole) of sodium 1,1-dinitro-2-phthalimidoethane, 30 ml. of water, and 2.6 g. (0.03 mole) of methyl acrylate was heated at 50° for 3.5 hr.; the solid dissolved and an oil separated. On cooling, the oil solidified, and the tan solid was collected and dried. The yield of methyl 4,4-dinitro-5-phthalimidopentanoate was 1.7 g. (48.4%), m.p. 107–113°. The product was recrystallized 3 times from absolute ethanol to give a white crystalline solid, m.p. 113–115°.

*Anal.* Calcd. for  $C_{14}H_{18}N_2O_8$ : C, 47.87; H, 3.73; N, 11.96. Found: C, 47.95; H, 3.74; N, 12.12.

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

AZUSA, CALIF.

(8) E. ter Meer, *Ann.*, 181, 1 (1876).

[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

## Derivatives of Nitromethylamine. II. Nitromethyl Imides<sup>1</sup>

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*N*-Nitromethylphthalimide and *N*-nitromethylsuccinimide have been prepared from the corresponding *N*-bromomethyl imides and silver nitrite in acetonitrile. The new imides are crystalline solids which are stable at temperatures up to their melting points. They react with bases by displacement of the nitro group and decompose on heating with acids to mixtures from which nitromethylamine could not be isolated.

In the course of further investigations of nitromethylamine derivatives in this laboratory,<sup>2</sup> it

(1) (a) This work was performed under the auspices of the U. S. Atomic Energy Commission. (b) Presented before the Organic Section of the American Chemical Society at the 133rd Meeting, San Francisco, Cal., April 1958.

has been found that *N*-nitromethyl imides can be prepared in fairly good yield by the reaction of *N*-bromomethyl imides with silver nitrite in aceto-

(2) Paper I: H. E. Ungnade and L. W. Kissinger, *J. Org. Chem.*, 22, 1662 (1957).