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

Reaction of Potassium 2,2-Dinitroethanol and Ammonia

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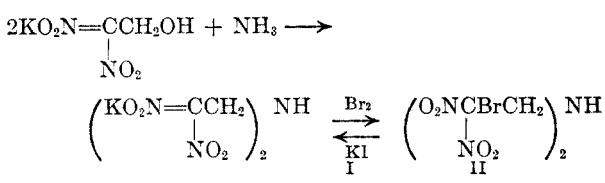
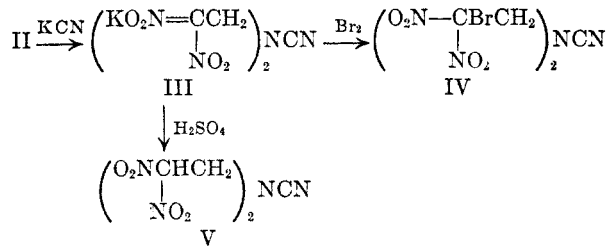
The Mannich condensation of potassium 2,2-dinitroethanol and ammonia gave the dipotassium salt of 2,2,2′,2′-tetranitrodiethylamine (I), which was brominated to 2,2′-dibromo-2,2,2′,2′-tetranitrodiethylamine (II). The reaction of II with potassium iodide and potassium cyanide yielded I and the dipotassium salt of *N*-cyano-2,2,2′,2′-tetranitrodiethylamine, respectively. II was converted to the corresponding *N*-nitroso and *N*-nitro derivatives. Treatment of I with methyl acrylate gave dimethyl 4,4-dinitroheptanedioate.

It was previously reported that the Mannich condensation of 2,2-dinitro-1-alkanols with ammonia yielded the corresponding bis-substituted amines.[1] In continuing this work, the reaction of potassium 2,2-dinitroethanol and ammonia was studied. Heating an aqueous suspension of potassium 2,2-dinitroethanol and ammonia at 55–65° yielded the dipotassium salt of 2,2,2′,2′-tetranitrodiethylamine (I).



Bromination of I gave 2,2′-dibromo-2,2,2′,2′-tetranitrodiethylamine (II). Iodometric titration[2] of II with potassium iodide indicated the presence of two bromodinitromethyl groups and gave I again, showing the reversibility of these reactions. Attempts to isolate 2,2,2′,2′-tetranitrodiethylamine by the acidification of I were unsuccessful since the product ignited spontaneously.

The reaction of II was entirely different when potassium cyanide was used in place of potassium iodide. In this case cyanogen bromide was formed and reacted *in situ* with the secondary amino group to give the dipotassium salt of *N*-cyano-2,2,2′,2′-tetranitrodiethylamine (III).



Bromination of III gave *N*-cyano-2,2′-dibromo-2,2,2′,2′-tetranitrodiethylamine (IV) while acidification with dilute sulfuric acid yielded *N*-cyano-2,2,2′,2′-tetranitrodiethylamine (V).

The behavior of II toward nitric acid was of particular interest. When this compound was heated to 60° with 70% nitric acid, nitrogen oxides were evolved and a crystalline compound, m.p. 118–119°, was formed whose elemental analyses corresponded to *N*-nitroso-2,2′-dibromo-2,2,2′,2′-tetranitrodiethylamine (VI). The same product was also formed by treatment of a solution of II in sulfuric acid with sodium nitrite. Compound VI was converted into the disodium or dipotassium salts (VII) by reaction with the alkali iodides in methanol solution. From these salts the free *N*-nitroso-2,2,2′,2′-tetranitrodiethylamine (VIII) was prepared. Compound VIII is an unstable crystalline compound which exploded violently after a few days storage at −20°.

When fuming nitric acid was allowed to react with II at 60–70°, *N*-nitro-2,2′-dibromo-2,2,2′,2′-tetranitrodiethylamine (IX), m.p. 168°, was formed. The same compound was also prepared by treating VI with fuming nitric acid. Treatment of IX with potassium iodide gave the dipotassium salt of *N*-nitro-2,2,2′,2′-tetranitrodiethylamine (X). Acidification and chlorination of X yielded the unstable *N*-nitro-2,2,2′,2″-tetranitrodiethylamine (XI) and the stable *N*-nitro-2,2′-dichloro-2,2,2′,2′-tetranitrodiethylamine (XII), respectively. Compound XII was also formed by the chlorination of I, followed by nitration with fuming nitric acid.

The reactions involving the nitrosation and nitration of II are summarized in Chart I.

The Michael reaction of I with methyl acrylate was studied. Under the conditions of this reaction the amine appeared to undergo a reversal of the Mannich condensation yielding dinitromethane which reacted with methyl acrylate forming dimethyl 4,4-dinitroheptanedicate, in the manner described by Herzog, Gold, and Geckler.[3] Similar results were obtained with the *N*-substituted derivatives of I. In addition, contrary to other primary or secondary nitro compounds, I or its *N*-substituted derivatives did not undergo reaction when treated with formaldehyde.

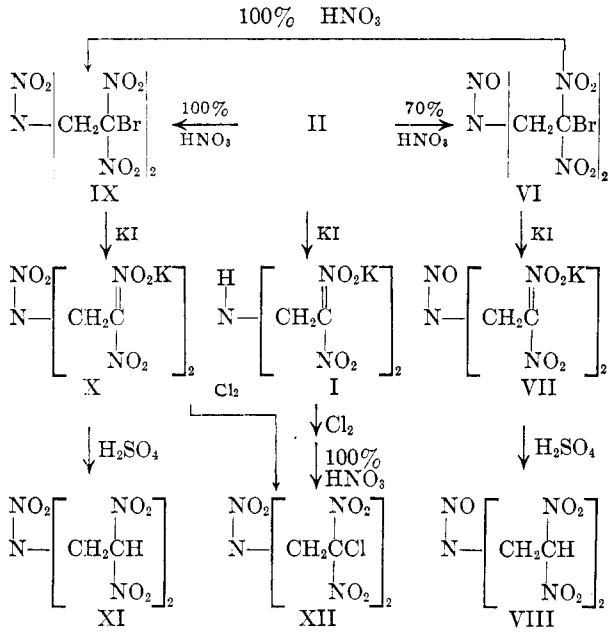
Primary amines appeared to react similarly to ammonia when treated with potassium 2,2-dinitroethanol. Crystalline salts were obtained with *n*-bu-

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

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

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

CHART I



tylamine, *n*-amylamine, and aniline. A thorough study of these reactions was not made. All melting points are uncorrected.

EXPERIMENTAL[4]

Dipotassium 2,2,2',2'-tetranitrodiethylamine (I). A mixture of 375 ml. of water, 125 ml. of 28% aqueous ammonia, and 300 g. of potassium 2,2-dinitroethanol was slowly heated to 55–60°. After about 30 min. stirring at this temperature, all of the salt had dissolved and a yellowish brown solution was obtained. After additional stirring for 2 hr. at 55–60° a yellow precipitate separated which soon increased in quantity. One hundred ml. of 28% ammonia was added and the stirring was continued for 1.5 hr. The total reaction time was 4 hr. The mixture was cooled to room temperature and the yellow crystals were filtered and washed first with 50% aqueous methanol and then with methanol. The yield of dipotassium salt of 2,2,2',2'-tetranitrodiethylamine was 275 g.

2,2'-Dibromo-2,2,2',2'-tetranitrodiethylamine (II). A mixture of 64.5 g. of methanol damp dipotassium salt of 2,2,2',2'-tetranitrodiethylamine and 200 ml. of ice water was cooled in an ice bath. With rapid agitation, 16 ml. of bromine was added dropwise until the bromine color persisted. A white solid formed which after filtration and washing with ice water was immediately covered with isopropyl ether, whereupon it dissolved. The crude solid could not be dried. It melted and decomposed when drying was attempted. After a second extraction and separation of the water, the isopropyl ether solution was dried with sodium sulfate and concentrated *in vacuo*. The remaining oil crystallized and was filtered, then washed with cold (about −50°) isopropyl ether. A total of 49.1 g. of white crystals was obtained. After recrystallization from isopropyl ether the melting point of the nearly colorless crystals was 70°.

Anal. Calcd. for $C_4H_5O_8N_5Br_2$: C, 11.68; H, 1.22; N, 17.03; Br, 38.93; M.W., 411. Found: C, 11.98; H, 1.45, N, 17.25; Br, 38.83; M.W. 397.

Conversion of 2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine into its salts. Five g. of 2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine was dissolved in 50 ml. methanol and cooled to 0°. Then a concentrated aqueous solution of 15 g. of potassium iodide was dropped into the flask with rapid stirring. A yellow precipitate of the dipotassium salt of 2,2,2',2'-tetranitrodiethylamine was formed and iodine liberated. After stirring for 30 min. the precipitate was collected on a filter and washed with methanol and ether until free from iodine. When sodium iodide was used the corresponding disodium salt was obtained.

N-cyano-2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine (IV). A solution of 16.5 g. of 2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine and of 150 ml. methanol was cooled to 0–10° and a solution of 11 g. potassium cyanide, 20 ml. methanol and 22 ml. water, was added dropwise. A yellow precipitate was formed. After stirring for an additional 50 min. at 0°, the salt was filtered and washed with methanol to yield 20 g. of damp salt.

The salt was suspended in 250 ml. of water and brominated at 0–10° until excess bromine was present. When the bromine color persisted for 15 min., the white precipitate was filtered and washed with ice water. The nearly dry compound was suspended in chloroform and the mixture distilled until all water was removed. The crystals were separated by filtration and washed with cold chloroform. The product weighed 9.1 g.; m.p. 154–155°. Recrystallization from chloroform raised the melting point to 158°.

Anal. Calcd. for $C_5H_4N_6O_8Br_2$: Br, 36.7. Found: Br, 36.52; 36.23; 36.22.

N-cyano-2,2,2',2'-tetranitrodiethylamine (V). A solution of 13.1 g. of *N*-cyano-2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine in 130 ml. of methanol was cooled to 0–10°. A solution prepared from 4.3 g. of potassium cyanide, 10 ml. of water, and 10 ml. of methanol was added dropwise while stirring rapidly. A yellow precipitate formed. After all the potassium cyanide had been added the stirring was continued for 15 min. The dipotassium salt of *N*-cyano-2,2,2',2'-tetranitrodiethylamine was separated and washed with methanol. The yield of dry salt was 10.5 g. and this material was very sensitive to impact.

Two and six-tenths grams of *N*-cyano-2,2'-dibromo-2,2,-2',2'-tetranitrodiethylamine was converted into the dipotassium salt as described above. The salt was suspended in 75 ml. of water and acidified with 16% sulfuric acid to a *p*H of 2. The white precipitate which formed was collected and washed with water and dried on a porous plate, m.p. 88° with decomposition.

Neutral equivalent weight calcd. 139. Found: 140.2.

The stability of this compound is poor, after standing for two days it had completely decomposed.

N-nitroso-2,2,2',2'-tetranitro-2,2'-dibromodiethylamine (VI). Three grams of 2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine was dissolved in 30 ml. concentrated sulfuric acid, and within 60 min., 1.5 g. of sodium nitrite was added in small portions. The solution was allowed to stand for 4 hr. at room temperature. The sulfuric acid solution was then added to 300 g. ice water. The precipitate was collected and washed with water. After crystallization from isopropyl ether and hexane and recrystallization from isopropyl ether, white needles were obtained having a melting point of 118°.

Anal. Calcd. for $C_4H_4N_6O_9Br_2$: C, 10.92; H, 0.92; N, 19.10; Br, 36.33. Found: C, 11.28; H, 0.99; N, 18.89; Br, 36.2.

Dipotassium salt of N-nitroso-2,2,2',2'-tetranitrodiethylamine (VII). A solution prepared from 2.6 g. of potassium cyanide, 15 ml. of methanol and 15 ml. of water was added to a solution of 9.16 g. of 2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine in 50 ml. of methanol. The temperature was kept at 0–10°. After stirring for an additional 30 min., the precipitated dipotassium *N*-nitroso-2,2,2',2'-tetranitrodiethylamine was filtered and washed with methanol yielding 11.2 g. of damp salt.

Eleven g. of the dipotassium salt obtained above was suspended in 100 ml. ice water and 4 ml. of bromine was addep dropwise with good agitation. The temperature was maintained between 0° and 10°. After filtration and washing with

(4) Microanalyses by Dr. A. Elek, Elek Microanalytical Laboratory, 4763 W. Adams Blvd., Los Angeles, Calif.

ice water, the crystals were dried to yield 7.93 g., m.p. 117–118°. The mixed melting point with the starting material showed no depression.

N-nitroso-2,2,2',2'-tetranitrodiethylamine (VIII). To a mixture of 8 g. of the dipotassium salt of *N*-nitroso-2,2,2',2'-tetranitrodiethylamine, 35 ml. of water, 100 ml. of methylene chloride, and 50 ml. of ether, was added 15 ml. of 20% sulfuric acid. The temperature was kept at 0°. The yellow salt disappeared quickly and an organic phase separated. The organic layer was washed once with 10% sodium chloride solution and dried over sodium sulfate. The solvent was evaporated *in vacuo*, and the remaining yellow oil (4.2 g.) was cooled to −70°. The white crystals which formed were collected and washed with methylene chloride (precooled to −70°). After recrystallization from methylene chloride at −70°, 2.2 g. of white crystals were obtained having a melting point of 60–61° with decomposition.

Neutral Equivalent weight calcd. 141. Found: 139.

At room temperature, the material decomposed after one day. After two days storage at −20°, the compound exploded.

N-nitro-2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine (IX). (a) From 2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine. Fifty ml. of fuming nitric acid (d = 1.5) was heated to 50°. Five g. of 2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine was added in small portions, and the stirring was continued for 30 min. at 65–70°. At 60°, a white precipitate formed which increased in quantity upon cooling to room temperature. It was collected, washed with 70% nitric acid, and then with water until neutral. The yield was 5.5 g., m.p. 165–167°.

Anal. Calcd. for $C_4H_4N_6O_{10}Br_2$: Br, 35.05. Found: Br, 34.42; 34.53. This material is quite sensitive to shock.

(*b*) From *N*-nitroso-2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine. Fifty ml. of fuming nitric acid (d = 1.5) was heated to 60° and 5 g. of *N*-nitroso-2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine was introduced in small portions. Upon dissolution of the nitroso compound the temperature was raised to 75° for 25 min., after which the evolution of nitric oxide was very slow. Upon cooling to 10°, the white precipitate which separated was filtered, washed with 70% nitric acid, and then with water. The yield was 4.95 g., m.p. 168° with decomposition. The mixed melting point with the compound prepared under (*a*) showed no depression.

Anal. Calcd. for $C_4H_4O_{10}N_6Br_2$: Br, 35.05. Found: Br, 35.07; 34.72.

Dipotassium salt of N-nitro-2,2,2',2'-tetranitrodiethylamine (X). A solution consisting of 15 g. of potassium iodide, 15 ml. of water, and 10 ml. of methanol was added dropwise to 7.6 g. of *N*-nitro-2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine at 0–5°, with stirring. A dark brown solution formed, and yellow crystals precipitated. After filtering and washing out the free iodine with methanol, the damp salt weighed 11 g. The mother liquor and washings were collected and diluted to 500 ml. A 25-ml. portion was titrated with sodium thiosulfate. It was found that 93.7% of the bromo compound was converted into the dipotassium salt. The dry salt was found to be *extremely* sensitive to shock.

N-nitro-2,2,2',2'-tetranitrodiethylamine (XI). One g. of damp dipotassium *N*-nitro-2,2,2',2'-tetranitrodiethylamine was suspended in 10 ml. of water. Dilute sulfuric acid was added until the color changed from yellow to white and a white precipitate formed. The white crystals were filtered and washed free of sulfuric acid and weighed 0.4 g. After drying on a porous plate, the *N*-nitro-2,2,2',2'-tetranitrodiethylamine had a melting point of 78°.

Neutral equivalent weight calcd. 149. Found: 147.

This compound became yellow after one day staying at room temperature and decomposed quickly.

N-nitro-2,2'-dichloro-2,2,2',2'-tetranitrodiethylamine (XII). (*a*) From dipotassium salt of 2,2,2',2'-tetranitrodiethylamine. A slow stream of chlorine was introduced into a suspension of 20 g. of dipotassium salt of 2,2,2',2'-tetranitrodiethylamine and 100 ml. of water, while a temperature of 0–10° was maintained. The yellow salt was converted gradually into a white oily material. The oil was separated in a separatory funnel and dropped into 75 ml. white-fuming nitric acid at room temperature. The oil dissolved immediately and the temperature rose slowly to 33°. The solution was warmed to 60–65°, maintained at that temperature for 30 min., and a slow evolution of NO_2 was noticed. The mixture was cooled with ice and white crystals precipitated. The crystals were collected and washed with water. A product with a melting point of 146–147° was obtained.

(*b*) From *N*-nitro-2,2'-dibromo-2,2,2',2'-tetranitrodiethylamine. A solution of 10 g. *N*-nitro-2,2'-dibromo-2,2,-2',2'-tetranitrodiethylamine and 100 ml. of methanol was cooled to 0° and a solution of 25 g. potassium iodide, 25 ml. of water, and 10 ml. of methanol was introduced into it. Iodine was liberated and a yellow salt precipitated. After filtration, the salt was washed with methanol until free of iodine. Then the salt was suspended in 100 ml. of ice water and a slow stream of chlorine was passed into the suspension. A white precipitate replaced the yellow salt. The crystals were collected, washed with water, and, after drying in a desiccator, had a melting point of 147°. They did not give a depression in a mixed melting point determination with the compound described above.

Anal. Calcd. for $C_4H_4N_6O_{10}Cl_2$: C, 13.09; H, 1.10; N, 22.90. Found: C, 12.72; H, 1.63; N, 21.95.

Reaction between the dipotassium salt of 2,2,2',2'-tetranitrodiethylamine and methyl acrylate. A suspension of 40 g. of the dipotassium salt of 2,2,2',2'-tetranitrodiethylamine in 100 ml. of water was slowly mixed with 34 g. of methyl acrylate. A color change was noted and the temperature rose to 28°. After one day of stirring, two layers had formed and the *p*H of the water layer was 7. The organic layer was taken up in ether then washed with water. After drying over sodium sulfate, the ether was evaporated. A yield of 26.8 g. of oil was obtained, which crystallized from absolute ether. After decolorizing and recrystallizing from methanol, crystals were isolated, m.p. 45–46°. A mixed melting point with dimethyl 4,4-dinitroheptanedioate[3] showed no depression.

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