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SYNTHESIS OF NEW HIGH EXPLOSIVES. IV.
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SYNTHESIS OF NEW HIGH EXPLOSIVES. IV. (U)

by

Kathryn G. Shipp
Thomas N. Hall
John C. Hoffsommer
Lloyd A. Kaplan
Howard E. Ruskie
Francis Taylor, Jr.

ABSTRACT: This report describes the results of a number of diverse preliminary investigations of the chemistry of polynitro compounds. Some of the work is concerned with the preparation of polymers from polynitro diols and acids, oxidation of amines and nitrolic acids and the amination of polynitro aromatic compounds, in some cases with negative results. The authors hope that the presentation of these negative results will serve as a guide for future research in these areas. (U)

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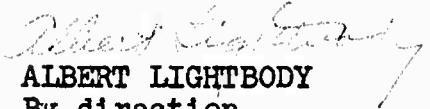
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The work described in this report was performed under Tasks FR-44 (High Energy Compounds), RUME-4E-000/212-1/F008-08-11, Problems 012 (Study of Explosives Properties), and 017 (Desensitization of Explosives).

Previous reports in this series are NavOrd Reports 2965, 4405, and 4436.

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Section A

PREPARATION OF

3-AMINO-2,2',4,4',6,6'-HEXANITROSTILBENE

by

Kathryn G. Shipp

DISCUSSION

Several of the heat resistant explosives previously prepared in this laboratory, e.g. 1,3-diamino-2,4,6-trinitrobenzene, DATB¹, 1,3,5-triamino-2,4,6-trinitrobenzene, TATB², and 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl, DIPAM³, are nitrated aromatic compounds containing amino groups. Since 3-chloro-2,2',4,4',6,6'-hexanitrostilbene, I, an intermediate in the synthesis of 2,2',4,4',6,6'-hexanitrostilbene, HNS⁴ was available, amination of the compound was undertaken in order to evaluate the product as a heat resistant explosive.

Amination of the chloro compound, I, proceeded readily in acetonitrile solution and the product was purified by crystallization from the same solvent. It melts at 291°-293°C and has an impact sensitivity of 111 cm, sigma >0.05 (ERL machine, tetryl = 32 cm). The melting point and impact sensitivity of the aminohexanitrostilbene do, indeed, place it in the class of heat resistant explosives, but it offers no advantages over DIPAM or HNS.

EXPERIMENTAL

A solution of 2.5 g of 3-chloro-2,2',4,4',6,6'-hexanitrostilbene in 75 ml of acetonitrile was prepared by heating. Ammonia gas was bubbled into the hot solution. The color of the solution changed from yellow to orange, then to brown as a yellow crystalline product formed. After about three minutes, when no more reaction was apparent, the mixture was heated to drive off excess ammonia, then chilled in an ice bath and filtered. The greenish yellow filter cake was washed with methanol and dried. It weighed 2.0 g, 83.4% of the theoretical yield. This crude product was purified by recrystallization. Bright yellow crystals were rapidly deposited from a hot solution in about 200 ml of acetonitrile diluted with an equal volume of hot methanol and then chilled; m.p. 291°-293°C.

Anal: Calc'd. for C₁₄H₇O₁₂N₇: C, 36.14% H, 1.52% N, 21.07%
Found: C, 35.92% H, 1.78% N, 21.23%
36.32% 1.71% 21.21%

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ACKNOWLEDGMENT

Impact sensitivity was determined by Mrs. Sarah Duck.

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Section B

EXPLORATORY EXPERIMENTS DIRECTED TOWARDS THE
SYNTHESIS OF 2,5-DIAMINO-4,6-DINITROPYRIMIDINE

by

Thomas N. Hall

Three explosives developed by the Naval Ordnance Laboratory, DATB¹, TATB², and DIPAM³, have one common structural feature which may contribute to their good heat resistance: two amino groups, each ortho to two nitro groups. Since the unreported 2,5-diamino-4,6-dinitropyrimidine, I, also has this structural feature, its synthesis was attempted in order to evaluate its thermal stability. Further, one would predict good thermal stability for I because aminopyrimidines in general melt without decomposition and can even be purified by sublimation under reduced pressure⁴.

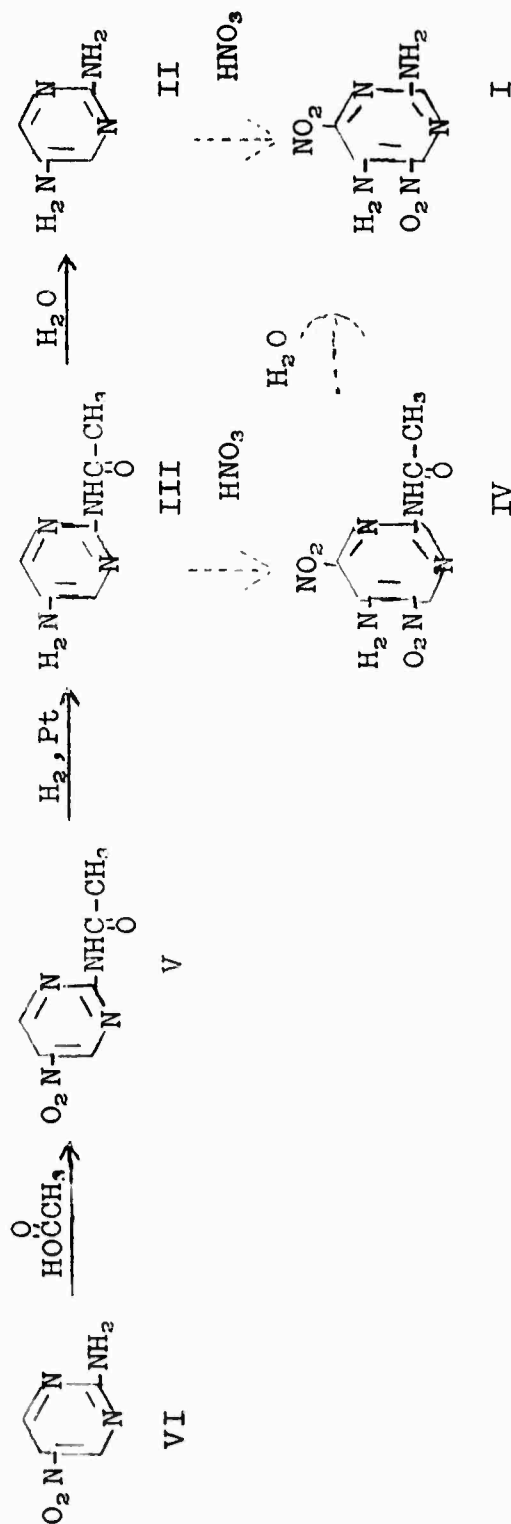
An obvious route to I involved the di-nitration of 2,5-diaminopyrimidine, II, or its mono- or di-acetyl derivatives. Tozaki⁵ has reported the synthesis of II from 2-amino-5-nitropyrimidine, VI, via 2-acetamido-5-aminopyrimidine, III, by the route shown in Figure 1. We evaluated two routes to I shown by dotted arrows in Figure 1: (i) Nitration of III to 2-acetamido-5-amino-4,6-dinitropyrimidine, IV, followed by hydrolysis to I; (ii) Direct nitration of II to I.

Route (i) above involved Tozaki's procedure H₂-Pt with acetic acid solvent, for the reduction of 2-acetamido-5-nitropyrimidine, V, to III. Following Tozaki's reduction procedure, we obtained a jet-black solution after hydrogen uptake had stopped. The black color may have been caused by colloidal platinum. Failing to clarify this solution, we did not attempt to isolate III. Instead, the black solution was digested with nitric acid, hoping to remove the black color and make III in one operation. A low yield of a brown solid was obtained by precipitation techniques, but was not characterized.

Since Tozaki's procedure did not appear practical, we decided to try route (ii): Reduction of VI to II with iron-acetic acid, followed directly by nitration to I, without attempting to isolate II. After the reduction was complete, the excess iron was removed and nitric acid added. Heating caused slow precipitation of a brown solid, finally amounting to about 80% of the weight of VI. This solid was not characterized, but

Figure 1

REACTION SEQUENCES INVOLVED IN THE ATTEMPTED SYNTHESIS
OF 2,5-DIAMINO-4,6-DINITROPYRIMIDINE



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could be I because VI and II should be soluble in HNO_3 -acetic acid.

EXPERIMENTAL

Fisher reagent grade glacial acetic acid, Fisher 40 mesh iron filings, and Eastman White Label guanidine carbonate were used without further purification. Ninety percent nitric acid was taken from a drum supplied by the U.S. Naval Propellant Plant, Indian Head, Md. Sodium nitromalonaldehyde was made from mucobromic acid⁶, which was in turn prepared from 2-furoic acid⁷. Platinum oxide was made from c.p. chloroplatinic acid⁸.

Preparation of 2-amino-5-nitropyrimidine, VI. The following procedure is a modification of Tozaki's method⁵. Seventy-seven and six-tenths grams of sodium nitromalonaldehyde monohydrate (0.493 mole) and 70.2 grams (0.389 mole) of guanidine carbonate were dissolved completely in 400 ml of water ($\sim 85^\circ$) and then one ml of piperidine added. The solution became red immediately and a solid started to precipitate. The mixture was heated on the steam bath for 30 minutes, and the tan solid product collected and washed with water. The weight of the crude air-dried 2-amino-5-nitropyrimidine was 84.3 grams.

Acetylation of VI, followed by reduction with hydrogen in the presence of platinum, and then by reaction with nitric acid. Eighty-four and three-tenths grams of crude VI were dissolved in 350 ml of hot glacial acetic acid contained in a 500 ml round-bottom flask. The solution was refluxed for 15 hours following Fieser's method for acetylation⁹. The solution was cooled slightly and hydrogenated in a Paar hydrogenation apparatus as follows:

One third of the acetic acid solution was placed in the Pyrex pressure flask, and a few tenths of a gram of freshly prepared platinum oxide added. The flask was wrapped with a heating tape connected to a Variac and connected to the hydrogenation apparatus. The Variac was adjusted so that the thermometer in the well of the protective cage surrounding the pressure flask read 60° *. Hydrogenation was continued until

* At room temperature, hydrogen up-take stops abruptly after a few minutes. At 60° , hydrogen pressure decreases in the normal, smooth manner. Apparently, at room temperature, a solid product precipitates on the surface of the platinum, thus deactivating it.

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hydrogen up-take ceased. The remaining two-thirds of the acetic acid solution was hydrogenated in two batches by the same procedure. Each hydrogenation produced a jet-black solution. Unfortunately, the color could not be removed by filtration. All three acetic acid solutions, plus washings, were combined to make a total volume of 530 ml.

A 125 ml aliquot of the above 530 ml was placed in a 250 ml creased round-bottom flask fitted with a condenser and mechanical stirrer. Fifteen milliliters of 90% nitric acid was slowly added to this solution over a period of one hour, keeping the temperature under 15°. A thick solid precipitate formed after about 2 ml of the nitric acid had been added. The solution was then heated for 150 minutes at 85° to dissolve the solid. Another 15 ml portion of 90% nitric acid was added over a period of 30 minutes. The resulting solution was heated at 85° for 6 hours and then allowed to stand overnight at room temperature. One and three-hundredths grams of a brown solid was filtered off from the reaction mixture. Addition of four volumes of absolute ethanol to the red filtrate precipitated 0.59 grams of a yellow solid which was collected by filtration. Finally, the addition of anhydrous ether precipitated one gram of a light brown solid. All weights refer to solids which were washed with water after filtration and then dried to constant weight at 80°.

Reduction of VI with iron and acetic acid, followed by reaction with nitric acid. To a solution of 10 grams of crude VI in 120 ml of glacial acid contained in a 250 ml beaker were added 10 grams of iron filings. The beaker was heated on the steam bath and its contents stirred magnetically for one hour. The solution was then filtered with the aid of Celite and cooled. Four milliliters of 90% nitric acid were then added all at once to the rapidly stirred acetic acid solution. A green solid formed almost immediately and was filtered off after a few minutes. Another 4 ml portion of the 90% nitric acid was then added to the reddish-brown acetic acid solution with rapid stirring. After the acetic acid-nitric acid mixture had been stirred magnetically in an open beaker for 16 hours, a brown solid which had been slowly precipitating during this period was filtered off.

The green solid was easily ignited by a Bunsen burner flame; it continued to burn when removed from the flame, and left a rouge-colored ash (probably Fe_2O_3). The brown solid, after washing with water and drying in a vacuum dessicator, weighed 8.03 grams. The brown solid was oxidized by a Bunsen burner flame, but did not continue to burn when removed from

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the flame. Strong ignition of the brown solid in an oxidizing flame left a little ash.

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Section C

ATTEMPTED SYNTHESIS OF DINITROMALONONITRILE

By

Thomas N. Hall

Compounds of the general structure $Z(\text{NO}_2)_2\text{CCN}$ have potential use as oxidizers in propellant and explosive formulations. When Z is ionically bound, i.e., salts of dinitroacetonitrile, the pure compounds have relatively good stability and high impact sensitivity^{1a,2}. Covalently bound Z, such as alkyl groups, lower the impact sensitivity but also decrease the stability^{1b}. With the hope of improving the stability of compounds with covalently bound Z, the synthesis of dinitromalononitrile (Z = CN) was attempted. The synthetic route chosen was reaction of the salts of dinitroacetonitrile with cyanogen bromide: $\text{M}^+ + \text{NC}(\text{NO}_2)_2\text{C}^- + \text{CNBr} \rightarrow (\text{NC})_2\text{C}(\text{NO}_2)_2 + \text{MBr}$.

When M = Na, 57% of the salt was recovered unreacted after 26 hours reaction at 50-55° in acetonitrile solvent; no other organic substance was identifiable. When M = Ag, 98% of the silver was precipitated as AgBr after 168 hours reaction in acetonitrile solvent; the only organic product which could be characterized was the ammonium salt of dinitroacetonitrile (22%). The latter substance could have formed by hydrolysis of the desired product:

$(\text{NC})_2\text{C}(\text{NO}_2)_2 + 2\text{H}_2\text{O} \rightarrow [\text{NH}_4^+ \text{NC}(\text{NO}_2)_2\text{CCO}_2^-] + \text{CO}_2 + \text{NH}_4^+ + \text{NC}(\text{NO}_2)_2\text{C}^-$. In both attempted syntheses, the desired product could have been present because the fate of all of the reactant salt was not established.

EXPERIMENTAL

The sodium salt of dinitroacetonitrile was made from ethyl dinitrocyanoacetate^{1c} by the procedure developed by Rohm and Haas for the potassium salt^{1d}, and was isolated by an extraction procedure^{1e}. The silver salt of dinitroacetonitrile was precipitated by adding the calculated amount of silver nitrate in distilled water to a solution of the sodium salt in distilled water. The precipitate was washed with water, ethanol, and ethyl ether, and then air-dried in the dark. Fisher Certified Reagent Grade chemicals were used unless otherwise noted. The acetonitrile was distilled from P_2O_5 just before use. Eastman White Label cyanogen bromide and ethyl cyanoacetate were used without further purification.

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Reaction of cyanogen bromide with the sodium salt of dinitroacetonitrile. A solution of 15.9 grams (0.15 mole) of cyanogen bromide in 8 ml of acetonitrile and a solution of 15.3 grams (0.10 mole) of the sodium salt of dinitroacetonitrile in 20 ml of acetonitrile were mixed in a 100 ml round-bottomed flask fitted with a condenser and drying tube. The flask was heated for 26 hour at 50-55°³. The homogeneous orange-yellow solution was cooled to room temperature, causing hard, inorganic-appearing crystals to form. The hard crystals were collected, washed with acetonitrile, and subjected to qualitative tests for cyanide, bromide, and nitrite. Only the latter test was positive, thus inferring at least partial degradation of the cyanodinitromethide ion.

The acetonitrile solution which had been decanted from the hard crystals was not investigated. Evaporation of the acetonitrile under reduced pressure left a mixture of an orange amorphous mass and some large well-formed yellow needles. All of the residue was taken up in nitromethane. The solution was filtered to remove turbidity, concentrated by boiling, and cooled in the refrigerator. Six and twelve hundredths grams of light yellow needles separated from the yellow solution. Cooling the filtrate in the deep-freeze gave a second crop of 2.61 grams. These products had micromelting points of 227°, and so were tentatively identified as recovered sodium dinitrocyanomethide, m.p. 224-226°d.^{1e} Assuming this identification is correct, 57% of the starting sodium dinitrocyanomethide was recovered.

Reaction of cyanogen bromide with the silver salt of dinitroacetonitrile. A solution of 50.0 grams (0.472 mole) of cyanogen bromide in 50 ml of acetonitrile was mixed with a solution of 22.45 grams (0.0944 mole) of silver dinitrocyanomethide in 50 ml of acetonitrile in a 250 ml round-bottomed flask. Immediate turbidity was noticed when the solutions were mixed. The flask was fitted with a drying tube and stored in the dark for 167 hours at room temperature. The finely divided grey precipitate was collected on a weighed sintered glass crucible of fine porosity, washed with acetonitrile, and dried in vacuo for thirty minutes. By difference, the weight of the grey solid was 17.35 grams. X ray powder diffraction showed that the solid was silver bromide. If the grey solid is assumed to be pure silver bromide, a doubtful assumption because of the grey color, then 98% of the silver present in the silver dinitrocyanomethide was converted to silver bromide.

After the silver bromide had been removed from the reaction mixture, chloroform was added, causing a yellow solid to precipitate. Addition of chloroform was continued until

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precipitation was complete, and then the solid was collected, air-dried, and weighed (3.05 grams). Recrystallization from nitromethane gave 1.12 grams of a yellow solid which was submitted for microanalysis after another recrystallization and air-drying. The analytical data obtained were: C, 17.34, 17.06; H, 2.69, 2.83; N, 37.42, 37.86. Assuming that the product contains only C, H, N, and O, the empirical formula is $\text{CH}_{1.91}\text{N}_{1.88}\text{O}_{1.88}$. Ammonium dinitrocyanomethide, $\text{C}_2\text{H}_4\text{N}_4\text{O}_4$, is clearly consistent with this formula, and it was found that the infrared spectrum of this compound was identical to that of the yellow product. If the crude yellow solid is pure ammonium dinitrocyanomethide, the yield of the latter is 22%, based on the weight of silver dinitrocyanomethide.

ACKNOWLEDGMENTS

Grateful appreciation is expressed to Dr. L. A. Kaplan for the sample of pure ammonium dinitrocyanomethide, to Dr. J. R. Holden for the identification of the silver bromide X-ray powder diffraction, and to Professor M. H. Aldridge, Department of Chemistry, American University, Washington, D. C. for the microanalyses.

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3. Another solution made up in the same way produced brown fumes as soon as it was heated to the reflux point.

Section D

REACTION OF POTASSIUM CYANIDE WITH
sym-TRISUBSTITUTED TRINITROBENZENES

by

Thomas N. Hall

Nucleophilic attack on the halogens of sym-trisubstituted trinitrobenzene by ammonia gives excellent yields of a potentially useful, thermally stable high explosive, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)¹. It is possible that nucleophilic attack by cyanide ion on the halogens of a sym-trisubstituted trinitrobenzene would yield sym-tricyanotrinitrobenzene. The explosive properties and heat resistance of the latter compound could be compared to those of TATB, and thus provide a basis for correlating these properties with structural changes.

The reaction of potassium cyanide on sym-trichlorotrinitrobenzene, in refluxing dimethylformamide, gave a mixture of products which was partially separated by chromatography. Two of the products had a carbon to nitrogen ratio of three, indicating probable loss of a nitro group. One of these products gave analyses for C, H, N, and Cl which were consistent with those of 3,5-dinitro-2,4,6-trichlorobenzoic acid. In acetonitrile solution at room temperature, potassium cyanide and sym-trichlorotrinitrobenzene gave an unidentified solid product; a mixture of this solid with sym-trichlorotrinitrobenzene melted higher than the latter.

No solid product could be isolated from the reaction of potassium cyanide and sym-tribromotrinitrobenzene in dimethylformamide solvent. Using tetrahydrofuran as a solvent, a solid product melting at 150-160° before purification was isolated.

In summary, the reaction of potassium cyanide on sym-trisubstituted trinitrobenzenes was found to be complex. No high melting product which could be used as a thermally stable explosive was isolable. The products which have been isolated from the reaction of potassium cyanide and sym-trichlorotrinitrobenzene show little promise as explosives or explosive intermediates because their structure indicates that a nitro group, rather than a chlorine, was lost.

EXPERIMENTAL

Chemicals

Eastman White Label dimethylformamide was dried by azeotropic distillation with benzene. The forerun, boiling below 150°, contained water, benzene, and dimethylformamide, and was discarded. The clear liquid boiling from 151.0 to 151.2° was collected and stored in a tightly stoppered bottle. Samples of sym-tribromotrinitrobenzene and sym-trichlorotrinitrobenzene were made by the nitration of the appropriate sym-trihalobenzene². Fisher Certified Reagent Grade acetonitrile was distilled from phosphorus pentoxide just before use. Baker and Adams, ACS Reagent Grade, potassium cyanide was pumped for three hours in a vacuum oven set at 90° just before use. Eastman White Label tetrahydrofuran was used without further purification.

Reaction of potassium cyanide with sym-trinitrotrichlorobenzene in dimethylformamide at room temperature. To 400 ml of dimethylformamide contained in a 500 ml round-bottom flask was added 12.34 grams of potassium cyanide. After solution had been effected by magnetic stirring, 10 g. of sym-trinitrotrichlorobenzene were added all at once, producing an immediate red color. After solution was complete, the flask was stoppered and allowed to stand at room temperature* for 64 hours. The very dark reaction mixture was poured into about 1.5 liters of distilled water with rapid stirring. The resultant red-brown solution was extracted with four 200 ml portions of benzene. The combined benzene extracts were then extracted with two 50 ml portions of distilled water and then dried over anhydrous sodium sulfate for 16 hours. Evaporation of the benzene on the steam bath left a red-brown oil which was redissolved in 50 ml of benzene. This solution was then filtered with mild suction through 5 cm of 50-200 mesh silica gel contained in a 3 x 15 cm chromatographic column. The filtrate was lighter in color.

The column was then eluted with 200 ml of benzene, leaving a dark brown fluorescent band on the silica. The combined benzene eluates were concentrated to about 25 ml and poured onto a 3 x 15 cm chromatographic column made up with 50-200 mesh silica gel and benzene.

* At reflux, a solution of similar composition gave immediate evidence of degradation (extensive foaming).

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A chromatographic separation was then started, eluting with a mixture of 60% by volume benzene-40% by volume n-hexane. Eighty milliliter fractions were taken, evaporated to dryness on the steam bath, and the nature, but not the weight, of the residue noted. Fraction 5 was accidentally spilled. The following table summarizes the results:

<u>Fraction No.</u>	<u>Appearance of Residue</u>
1-4	Bright yellow, well formed needles
6-9	Fluffy light grey-yellow crystals
10-27	Mustard yellow powder, color becoming lighter in latter fractions
28-40	Bright yellow powder

The residues from fractions 1-4 were combined, recrystallized from a mixture of benzene and hexane, and dried in vacuo for 24 hours. The product, compound I, melted at 138-142° and gave the following analytical results: C, 25.09, 25.22; H, 0.37, 0.22; N, 10.06, 9.90; Cl, 35.14, 35.23. Calculating the oxygen percentage by difference, the empirical formula for I is $\text{CH}_0.133\text{N}_0.327\text{Cl}_0.455\text{O}_0.843$. This formula is about equally consistent with $\text{C}_6\text{HN}_2\text{Cl}_3\text{O}_8$ and $\text{C}_7\text{HN}_2\text{Cl}_3\text{O}_8$. Barring nuclear rearrangements, two likely structures with these formulas are 3,5-dinitro-2,4,6-trichlorophenol, and 3,5-dinitro-2,4,6-trichlorobenzoic acid. Kohn and Grun³ report that the phenol melts at 165-167°. Hence, it appears likely that compound I is the unreported benzoic acid derivative.

The residues from fractions 37-40 were combined and recrystallized from a mixture of benzene and hexane, and then submitted for microanalysis after drying in vacuo. The analytical results, C, 32.62, H, 1.57, N, 12.76, give a carbon to nitrogen ratio of 2.97, thus indicating probable loss of a nitro group.

Reaction of potassium with sym-trinitrotrichlorobenzene in acetonitrile. To 400 ml of acetonitrile contained in a 500 ml round-bottom flask were added 12.34 grams of powdered potassium cyanide. The mixture was stirred magnetically for 30 minutes to dissolve as much of the solid as possible. Addition of 10 grams of sym-trinitrotrichlorobenzene to this mixture produced an immediate yellow color. The flask was then closed off with a drying tube, and the mixture stirred magnetically at room temperature. After one hour, the acetonitrile had deepened to an orange color, even though neither the potassium cyanide or sym-trinitrotrichlorobenzene had completely

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dissolved. After 119 hours, there still remained some undissolved solid which was probably inorganic. The whole mixture was poured with rapid stirring into 1.5 liters of distilled water, causing the inorganic solid to dissolve and a tan solid to precipitate. The tan solid was filtered off and dissolved in a hot mixture of benzene-n-hexane, 5:95 by volume. After decolorization with Norite, the solution was cooled in an ice bath and two crops of light yellow needles collected. The first crop melted over the range 167-189°, and the second 182-193°. A mixture of sym-trinitrotrichlorobenzene (m.p. 190°^a) and some needles from the second crop melted over the range 193-201°. The elevation in melting point is not the common result, but does indicate that the second crop is not recovered starting material.

The red solution, from which the tan crystals had been separated, was extracted with 3-200 ml portions of benzene. The red-brown benzene extracts were combined and dried for an hour over anhydrous sodium sulfate. Evaporation of the benzene left a black tar which was not investigated further.

Reaction of potassium cyanide with sym-trinitrotribromobenzene in dimethylformamide. To a solution of 0.25 gram of sym-trinitrotribromobenzene in 10 ml of dimethylformamide in a 25 ml flask was added 0.34 gram powdered potassium cyanide. The flask was then stoppered and its contents stirred magnetically. The initial light green color had become red-brown after 10 minutes. After eighteen hours at room temperature, the dark red-brown solution and the undissolved potassium cyanide were added to 250 ml of distilled water with rapid stirring. Since no precipitate formed, the aqueous solution was extracted with 3-50 ml portions of benzene, using a centrifuge to separate the layers. The yellow benzene extracts were combined, extracted with 25 ml of distilled water, and then dried over anhydrous sodium sulfate. After removal of the sodium sulfate, the benzene extracts were boiled with Norite to remove the yellow color, concentrated by boiling, and n-hexane added. No precipitation occurred on cooling. Evaporation of the benzene-hexane under reduced pressure left an oily film which failed to crystallize.

Reaction of potassium cyanide with sym-trinitrotribromobenzene in tetrahydrofuran. To a solution of one gram of sym-trinitrotribromobenzene in 250 ml of tetrahydrofuran in a 300 ml flask was added 0.87 gram of powdered potassium cyanide. The flask was closed off with a drying tube and its contents stirred magnetically at room temperature for 52 hours and then allowed to stand unstirred for 26 hours. The dark yellow solution was filtered to remove undissolved potassium cyanide and

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then evaporated under reduced pressure. The yellow-brown residue was extracted with boiling benzene. The yellow benzene extract was filtered and then concentrated on the steam bath. Cooling the benzene solution caused separation of grey-yellow needles, melting over the range 150-160°.

ACKNOWLEDGEMENTS

The author wishes to thank Mr. M. E. Hill for the samples of the sym-trinitrotrihalobenzenes, Mr. H. T. Simmons for the chlorine analyses, and Professor M. H. Aldridge, Department of Chemistry, American University, Washington, D. C. for the microanalyses for C, H and N.

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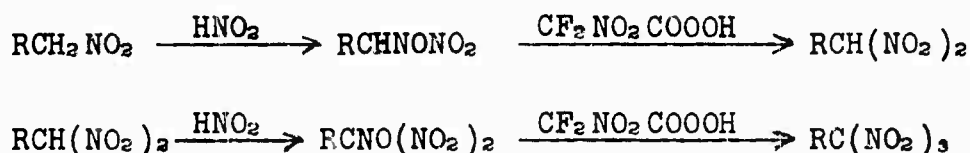
Section E

OXIDATION OF 1-NITROSO-1-NITROETHANE
(ETHYL NITROLIC ACID) TO 1,1-DINITROETHANE

by

Johr U. Hoffsommer

Early references in the literature^{1,2} indicate that ethyl nitrolic acid is oxidized by various reagents, including alkaline aqueous bromine solutions and concentrated nitric acid, to 1,1-dinitroethane. It was anticipated that difluoronitroperoxyacetic acid might be a superior reagent for the oxidation of nitrolic acids to the corresponding gem-dinitro compounds which are otherwise difficult to prepare. It was also hoped that by an extension of this line of reasoning other trinitromethyl compounds could be prepared by the following idealized sequence:



Ethyl and propyl nitrolic acids were prepared by the action of nitrous acid on the nitroalkane and used as substrates with several oxidizing agents; bromine, sodium hypochlorite, hydrogen peroxide, concentrated nitric acid (Table 1) and difluoronitroperoxyacetic acid. These results are summarized:

SUBSTRATE: $\text{CH}_3\text{CH}(\text{NO})\text{NO}_2$ (Ethyl nitrolic acid)

<u>OXIDIZING AGENT</u>	<u>RESULT (%Yield 1,1-Dinitroethane)</u>
Bromine	26
NaOCl	0
30% H_2O_2	0
Conc. Nitric Acid	12
Difluoronitroperoxy- acetic Acid	0.5

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TABLE 1

Oxidation of 1-Nitroso-1-Nitroethane to 1,1-Dinitroethane
in Aqueous and Pyridine Solutions under Basic Conditions

Run	Solvent	Molar Ratio ^a		Oxidant	% Yield ^b	
		CH ₃ CH(NO)NO ₂ /KOH/Oxidant			1,1-Dinitroethane	
1	H ₂ O	1.1/1.3/10		Br ₂		20
2	"	2.0/2.0/10		Br ₂		26
3	"	2.0/8.2/2.0		NaOCl		0
4	"	2.0/2.0/2.0		"		0 ^e
5	"	2.0/2.0/8.8		H ₂ O ₂		0
6	"	2.0/2.0/8.8 ^c		"		0
7	Pyridine	1.0/0 /2.0		"		0
8	"	1.0/2.5/10		"		0
9	"	1.3/2.5/12 ^d		"		0
10	H ₂ O	1.0/0 /15		HNO ₃ ^g		12 ^f

- Molar concentrations of 1-nitroso-1-nitroethane varied from 0.08M in run 3 to 4M in run 5.
- Yields were based on ultraviolet absorption of the K-salt of 1,1-dinitroethane ($\lambda_{\text{max}} = 380 \text{ m}\mu$ $\epsilon = 17,000$). Identification of the starting material, 1-nitroso-1-nitroethane was also based on the ultraviolet absorption of its basic solutions ($\lambda_{\text{max}} = 328 \text{ m}\mu$ $\epsilon = 6,560$).
- Base used was sodium bicarbonate.
- Base used was sodium bicarbonate.
- The 1-nitroso-1-nitroethane was completely decomposed after standing overnight.
- Concentrated nitric acid was added to the solid 1-nitroso-1-nitroethane at ambient temperatures.
- Acidic conditions.

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Analyses of the reaction mixtures for 1,1-dinitroethane and ethyl nitrolic acid were accomplished by ultraviolet absorptions of an alkaline extract at 380 mμ and 328 mμ respectively.

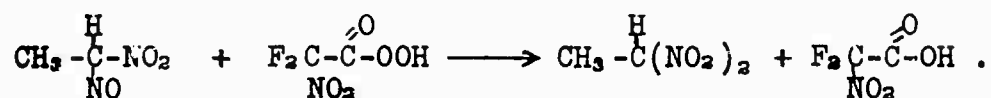
It was concluded that under the conditions employed no oxidation of nitrolic acid with difluoronitroperoxyacetic acid to dinitroethane has occurred. The main reaction appears to be the decomposition of the nitrolic acid. The mechanisms of the oxidation with bromine and concentrated nitric acid are not clear.

The oxidant was added to a mixture of 1-nitroso-1-nitroethane and base in runs 1,2,4,7,8,9 and 10 while for runs 3 and 5 the nitrolic acid was added to a mixture of the oxidant base.

Temperatures ranged from 25°C for runs 1,4,6,7,8,9 and 10 to 0°C for runs 3 and 5.

The best yield of 1,1-dinitroethane was obtained in run 2 by addition at ambient temperatures of bromine to the nitrolic acid in 1/2 the total amount of base followed by addition of the remainder of base and subsequent heat treatment at 80°C for 10 minutes.

Attempted Oxidation of 1-Nitroso-1-Nitroethane to 1,1-Dinitroethane with Difluoronitroperoxyacetic Acid under Acidic Conditions. Ten runs were carried out in an attempt to oxidize ethyl nitrolic acid according to the following equation,



Only negligible amounts, less than 0.5% of dinitroethane were formed. Yields and amounts of nitrolic acid and dinitroethane were based on the ultraviolet absorptions of their respective alkaline solutions

(λ max = 328 mμ ε = 6,560; λ max = 380 mμ ε = 17,000).

Mixtures of difluoronitroacetic acid and 90% hydrogen peroxide in methylene chloride and acetonitrile solutions were treated with solutions of the nitrolic acid at ambient, ice bath and reflux temperatures. Reverse additions were also carried out without success.

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Molar ratios of nitrolic acid/difluoronitroacetic acid/hydrogen peroxide varied from 1.0/2.0/7.0 to 2.9/3.6/24 while molar concentrations of ethyl nitrolic acid varied from 2 to 6 molar.

The only reaction which appeared to have taken place was the decomposition of the ethyl nitrolic acid.

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Section F

OXIDATION OF AMINES WITH
DIFLUORONITROPEROXYACETIC ACID

by

John C. Hoffsommer

Trifluoroperoxyacetic acid has been shown recently¹ to be a superior reagent for the oxidation of various aromatic amines to their respective nitro derivatives. For those compounds studied, the yields are quite high, usually 90% or better; however, in some cases, for example, polynuclear, heterocyclic, aliphatic, and certain alkyl aminobenzenes the method fails.

It was thought that a peroxy acid derived from a stronger acid than trifluoroacetic acid, namely difluoronitroperoxyacetic acid would be a superior oxidizing agent in those cases where trifluoroperoxyacetic acid failed. It was further anticipated that difluoronitroperoxyacetic acid amine oxidations could be extended to produce other organic nitro compounds which would be difficult to prepare by other routes. Notable in this connection would be the preparation of nitro heterocyclic compounds from the available amines.

In order to study the reaction,



p-aminobenzoic acid was chosen as the standard amine substrate and conditions were sought to optimize the formation of p-nitrobenzoic acid (Table 1, runs 1-7). From the results of this study, other amine substrates were investigated and are listed (Table 1, runs 8-21). These results are summarized:

<u>AMINE SUBSTRATE</u>	<u>PRODUCT</u>
p-Aminobenzoic acid	90% p-Nitrobenzoic acid
p-Phenylenediamine	94% p-Dinitrobenzene
Ethyl p-Aminobenzoate	84% Ethyl p-Nitrobenzoate
p-Aminonitrobenzene	81% p-Dinitrobenzene
Tetranitroaniline	No reaction
Aniline	Tars, colored products
3-Aminopyridine	Salt of Amine
2-Naphthylamine	Tars, high melting material
Melamine	1:1 Salt of Amine
3-Aminopropionic acid	Salt of Amine
d,l-Acetalaninide	Deacetylation, Salt of Amine
3-Amino-1,2,4-triazole	Salt of Amine

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Products were identified by neutralization equivalents, melting points, mixed melting points with authentic samples, and infrared absorption, in applicable cases.

As indicated by these results difluoronitroperoxyacetic acid was not found to have any advantage over trifluoroperoxyacetic acid as an amine oxidizer. The chief side reactions appear to be salt formation, partial oxidation to nitroso compounds with subsequent condensation products with unreacted amine. All attempts to "follow" the oxidation by ultra violet absorption techniques were complicated by these highly colored condensation products. Further attempts to study the kinetics of the reaction by analysis of aliquot samples for active oxygen content during the course of the reaction were likewise complicated.

It is felt that a peroxy acid derived from a weaker parent acid than difluoronitroacetic acid would be a better choice for future investigations of amine oxidations. In this connection monofluoro or difluoroperoxyacetic acid might be used to advantage.

REFERENCE

1. William D. Emmons, J. Am. Chem. Soc., 76, 3470 (1954); and other references cited therein.

TABLE I

OXIDATIONS OF VARIOUS AMINES WITH PERFLUOROPEROXYACETIC ACID

Run	Substrate	D Solvent	C H ₂ O ₂	B DFNA	Yield	Comments
1	PABA 0.00097	5 ml	0.02	0.00443	Salt formation	(a) A added to a mixture of D+C+B at room temp., stirred 1 hour. (b) Side reactions, colored products.
2	0.00945	5 ml	0.02	0.00441	50.5% p-nitroso-benzoic acid	(a) Addition as in run 1. (b) Refluxed 2-3 hrs. (c) Recovered 25% PABA along with high melting material.
3	0.00941	10 ml	0.02	0.00473	77.7% p-nitroso-benzoic acid	(a) Addition as in run 1. (b) Refluxed 1 hour.
4	0.000993	5 ml	0.02	0.00111	Identified small amount of p-nitroso-benzoic acid	(a) A added to D+C+B in one portion, stirred overnight. (b) Obtained high melting products.

Notes: (1) Quantities of reactants given in moles. (2) PABA = p-aminobenzoic acid.
 (3) Solvent is methylene chloride except where otherwise noted. (4) DFNA = difluoroperoxyacetic acid. (5) Products were identified by melting points, mixed melting points and neutralization equivalents.

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Run	A Substrate	D Solvent	C H ₂ O ₂	B DFNA	Yield	Comments
5	0.000985	5 ml	0.02	0.00104	67% p-nitro- benzoic acid	(a) A added to D+C+B gradually over 7 hrs.
6	0.00105	5 ml	0.02	0.00210	86.9% p-nitro- benzoic acid	(a) A added to D+C+B all at once; mixture stirred overnight.
7	0.00101	15 ml	0.2	0.00508	90% p-nitro- benzoic acid	(a) A added to D+C+B in small portions. (b) Also identified A and p-nitroso- benzoic acid.
8	3-aminopro- pionic acid 0.00201	5 ml	0.02	0.00430	Salt of amine.	(a) A added to D+C+B in one portion, stirred overnight.
9	d,l-acetalan- inide 0.00106	5 ml	0.02	0.00365	Deacetylation and formation of salt of amine.	(a) A added to D+C+B, stirred at ambient over weekend.

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Run	A Substrate	D Solvent	C H ₂ O ₂	B DFNA	Yield	Comments
10	p-phenylene- diamine 0.000991	5 ml	0.2	0.00652	94% p-dinitro- benzene.	(a) A added to D+C+B in one portion; stirred at ambient 3.25 hours.
11	p-phenylene- diamine 0.020	25 ml	0.020	0.0022	50% p-phenylene diamine recovered.	(a) Attempted catalytic oxidation of amine. (b) A added to D+C+B in one portion. Also recovered high melting acet- one insoluble material.
12	2-naphthyl- amine 0.000993	5 ml	0.02	0.00326	Black tars, high melting material	(a) A added to D+C+B all at once; turned black in 5 min., but went through a fleet- ing yellow color.
13	melamine 0.000992	5 ml	0.035	0.00982	Obtained only salt-like material.	(a) A added to D+C+B at room temp.; re- fluxed 3 hours.

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Run	A Substrate	D Solvent	C H ₂ O ₂	B DFNA	Yield	Comments
14	melamine 0.00101	5 ml	0.040	0.0101	Obtained 96% theoretical amount of 1:1 salt	(a) Addition as in 13; mixture stirred at room temp. for 1 week.
15	3-amino- pyridine 0.00193	5 ml	0.044	0.00669	Salt formation.	(a) Addition as in 13; stirred at ambient for 8 hrs. (b) Salt m.p. > 310°C; IR shows NH ₃ ⁺ band.
16	3-amino- pyridine 0.00198	5 ml	0.048	0.00663	Salt formation.	(a) A added to D+C+B all at once; refluxed 4 hrs.
17	3-amino- 1,2,4-tri- azole 0.00104	5 ml	0.027	0.00331	Salt formation	(a) Addition as in 16; stirred 2-3 hours at room temperature.

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Run	A Substrate	D Solvent	C H ₂ O ₂	B DFNA	Yield	Comments
18	ethyl p-aminobenzoate 0.00105	10 ml	0.021	0.00470	84% ethyl p-nitrobenzoate	(a) Product isolated as an oil; identified by acid hydrolysis to p-nitrobenzoic acid. (b) A dissolved in D was added to C+B; refluxed 2 hrs.
19	p-aminonitrobenzene 0.00104	5 ml	0.014	0.00391	81% p-dinitrobenzene	(a) A added to D+C+B; stirred overnight.
20	tetranitroaniline 0.00101	10 ml	0.0137	0.00344	No reaction	(a) A added to D+C+B; stirred at reflux 3 hrs. (b) Most of A was recovered unchanged.
21	aniline 0.00142	acetone 10 ml	0.01142	0.00318	-	(a) A added to D+C+B; stirred at room temp. 2-3 hrs. (b) Solution became red, then black.

Section G

COPOLYMERS OF 2,2,8,8-TETRANITRO-4,6-DIOXA-1,9-NONANEDIOL (DINOL)
AND 4,4-DINITROPIMELIC ACID (DNPA)

by

LLOYD A. KAPLAN

The preparation of carboxyl terminated polyester prepolymers for use as energetic binders in explosive and propellant systems has previously been described¹. The procedure utilized in this instance was to esterify a non-energetic polyol, glycerol, with a mixture of 4,4-dinitrovaleric and 4,4-dinitropimelic acids using p-toluenesulfonic acid as the catalyst. After adding about 50% bis(2,2-dinitro-2-fluoroethyl)formal, FEFO, as an oxidizing plasticizer, the prepolymer was crosslinked to give the final oxidizer-binder composition. The use of a nitro polyol in place of glycerol was considered. This would increase the oxygen balance of the prepolymer and thereby enable one to reduce the quantity of high energy plasticizer added. Lower plasticizer content should give better physical properties in the final crosslinked polymer. However, the esterification of polynitro alcohols by this procedure was not practical because of the feeble basicity of these alcohols.

In an attempt to utilize these alcohols for the preparation of prepolymers, it was felt that they would esterify the acid chlorides of carboxylic acids since this reaction is essentially irreversible under the usual synthetic conditions. The resulting prepolymers would be hydroxy terminated if excess diol is used and acid chloride terminated with excess acid chloride. The hydroxy terminated prepolymer could be crosslinked with a difunctional isocyanate to yield a polyester-polyurethane. With the acid chloride terminated prepolymers, several approaches are available. Hydrolysis of the acid chloride end groups to the carboxylic acid could be effected and the resulting carboxyl terminated prepolymer crosslinked as described previously¹. A more reasonable approach seemed to be either capping the acid chloride end group with a reactive polyfunctional derivative such as trimethylol propane to give a hydroxy terminated prepolymer or reaction with an imine to form the bis acylaziridine terminated prepolymer which would be crosslinked with a dibasic acid such as 4,4-dinitropimelic acid.

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The preparation of 4,4-dinitropimeloyl chloride, DNPCl, which was selected as the model dibasic acid chloride, was readily achieved by reacting DNPA with phosphorus pentachloride in carbon tetrachloride. The acid chloride was isolated as a crystalline solid melting at 58-9°. Preliminary experiments involved melting together mixtures of anhydrous DINOL and DNPCl. On raising the temperature of the melt to about 100°, the evolution of hydrogen chloride became quite vigorous. Continued heating increased the viscosity of the melt. This was further indication that polyester formation was taking place. The product from this reaction was a clear glass when cold. However, the addition of 50 weight percent FEFO to the prepolymer gave a homogeneous, viscous liquid which could readily be handled.

The prepolymer from this preliminary run was utilized for surveying the various methods of converting the acid chloride end groups to usable crosslinking functions. Attempts to hydrolyze the acid chloride end groups to the carboxylic acid were not completely successful in that the resulting hydrolysate still had residual chlorine. The possibility of converting the acid chloride end groups to the acylaziridine function was tested by utilizing DNPCl as a model compound. Several attempts to isolate the bis acylaziridine from the reaction of DNPCl with ethyleneimine met with failure and in one instance a fume-off. This approach was therefore abandoned.

The most successful procedure was reacting the acid chloride terminated prepolymer with a polyol to form a hydroxy terminated prepolymer. Thus, the reaction of the prepolymer containing 50 weight percent FEFO with trimethylol propane proceeded smoothly and rapidly as evidenced by the evolution of hydrogen chloride. The resulting hydroxy terminated prepolymer was cured to a rubbery solid with hexamethylene diisocyanate using 4,4-dinitropimelic acid as a catalyst.

Under more quantitative conditions, the reaction of 0.02 moles of DINOL with 0.025 moles of DNPCl evolved 96% of the theoretical quantity of hydrogen chloride after 2.7 hours at 100-30°. The addition of 50 weight percent FEFO and the requisite amount of trimethylol propane to the prepolymer yielded a colorless viscous liquid which set up to a waxy solid on cooling. This prepolymer could be cured with hexamethylene diisocyanate to give rubbery products.

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EXPERIMENTAL

4,4-Dinitropimeloyl Chloride was prepared by adding 0.089 moles (22.2 g) of 4,4-dinitropimelic acid to a solution of 0.2 moles (41.6 g) of phosphorus pentachloride in 150 ml of carbon tetrachloride at reflux temperatures. During the addition of the acid, rapid evolution of hydrogen chloride occurs. After the addition of the acid was complete, the mixture was refluxed for additional 30 minutes at which time the evolution of hydrogen chloride had ceased. The resulting pale green solution was stripped to under vacuum to yield a semi-solid residue. This was extracted with three 100 ml portions of petroleum ether to remove the phosphorus chlorides and about 150 ml of carbon tetrachloride was added to the petroleum ether insoluble residue. The residue crystallized on stirring, and this solid was collected on a Buchner funnel, washed with 50 ml of carbon tetrachloride, and dried. The crude product was protected from atmospheric moisture with a rubber dam during the drying operation.

The crude product was recrystallized from a large volume of carbon tetrachloride to give a white crystalline solid melting at 58-9°. There was obtained two crops of the acid chloride totalling 18.6 g (65%).

Anal. Calcd. for $C_7H_8Cl_2N_2O_6$: %C, 29.3; %H, 2.8; %N, 9.8; %Cl, 24.7.
Found: %C, 30.4, 30.4, 29.7; %H, 2.9, 3.5; %N, 10.1, 10.1;
%Cl, 24.7, 24.5.

Preparation of DINOL-DNPA Polyester. In a typical run, 0.02 mole (6.88 g) of anhydrous DINOL and 0.025 mole (7.18 g) of DNPCl were placed in a cylindrical, flat-bottomed glass reactor constructed from the socket member of a 50/30 spherical joint so as to have a volume of about 50 ml. A 5 mm gas take-off side arm was sealed to the wall of the reactor just below the joint. The ball joint member was sealed off as close to the top of the joint as possible so as to minimize the dead volume and about 1 inch of 6 mm tubing sealed in the center of the ball member to act as a stirrer bearing. The reactor was fitted with a stirring rod having two glass flats sealed at right angles to each other at one end so as to be able to scrape the bottom and walls of the reactor. This rod fitted through the bearing in the ball joint member and was made gas tight by a rubber sleeve fitting over the rod and bearing. The sleeve was lubricated with a small amount of Fluorolube. Due to the relatively high viscosity of the polymer melt, the stirrer was turned by hand.

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The charged reactor was placed in an oil bath at about 120-30° and the gas take-off side tube was arranged so as to deliver any gases evolved into a 250 ml beaker containing about 75 ml of distilled water. The solid mixture melted and stirring was begun. Gas evolution (hydrogen chloride) commenced shortly after the reactants melted, as evidenced by the appearance of Schlieren lines in the water in the beaker. At various intervals, the hydrogen chloride evolved was measured by titrating the solution in the beaker to a phenolphthalein end point with 0.492N sodium hydroxide. A cumulative record of the milliliters of sodium hydroxide required versus time is given in the following table.

<u>Time, min.</u>	<u>Temp. °C^a</u>	<u>ml 0.492N NaOH</u>	<u>% Theoretical HCl^b</u>
0.0	100	---	---
20	118	40.5	50
35	118	57	70.4
50	118	65	81.1
65	119	69	85.2
80	118	70	86.4
110	raise to 125	72	89
125	128	73	90.1
150	130	73.5	90.4
160	130	73.8	90.8

^a Oil bath temperature.

^b The theoretical yield of hydrogen chloride based on DINOL is 0.04 moles. This is equivalent to 81.3 ml of 0.492N sodium hydroxide.

After 2.7 hours, 90.8% of the theoretical quantity of hydrogen chloride had been evolved. When corrected for the dead volume of the apparatus, this figure becomes 96%. Hence, the reaction was essentially complete at the end of this time. The resulting polyester was a sirupy liquid while hot.

The product was cooled to 60-70° and 13.47 g (50% by weight) of FEFO was added to the polyester with stirring, to yield a homogeneous sirupy liquid. This product was transferred to a 150 ml beaker and the residual acid chloride functions reacted by stirring in 0.01 mole (1.34 g) of trimethylol propane. A

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vigorous reaction ensued with the evolution of hydrogen chloride. The viscous mixture was then heated at 70-80° until the evolution of hydrogen chloride had ceased. While still warm, the polymer was pumped at 10-20 mm to remove any residual hydrogen chloride. The resulting product was a clear, colorless liquid that set to a waxy solid on cooling.

A sample of the polymer was cured as follows: 5.41 g of the polymer and 0.34 g of hexamethylene diisocyanate were thoroughly mixed while heating at 80°. Then, about 20 mg of DNPA was added as a catalyst. The clear melt was placed in a Teflon coated aluminum dish, out-gassed by pumping at 20 mm and placed in a 65° oven for 18 hours. The product was a light amber, rubbery material which appeared to have good tensile strength, but could have had better elongation. A sample, on ignition, sustained its flame and burned at a uniform rate.

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Section H

THE AMINATION OF POLYNITROAROMATIC COMPOUNDS WITH HYDROXYLAMINE

by

Howard Ruskie

The amination of hexanitrobiphenyl (HNB) was explored as a direct route to DIPAM (diaminohexanitrobiphenyl). It has been reported¹ that hydroxylamine aminates s-trinitrobenzene in basic medium, giving picramide in high yield. This reaction appeared to offer a new and more convenient preparation of DIPAM. It might even be useful for preparing other thermally stable high explosives related to DIPAM. The procedure for the aminations with hydroxylamine reported in the literature is vague. Although m-dinitrobenzene could be successfully aminated, the preparation of picramide could not be duplicated, and the method appears to be completely unsuccessful for aminating HNB, 2,4,2',4'-tetra-nitrobiphenyl, and 4,4'-dinitrobiphenyl.

Meisenheimer reports that hydroxylamine can aminate m-dinitrocompounds. m-Dinitrobenzene was aminated to 2,4-dinitroaniline, or to dinitro-m-phenylenediamine. By varying the reaction conditions, he obtained each compound in good yield. 2,6-Dinitrotoluene was aminated to 2,6-dinitro-m-toluidine in only 15% yield. Under similar conditions, picramide was obtained from s-trinitrobenzene in about 90% yield. Dinitrocompounds with ortho or para substitution do not undergo amination². Reduction occurs instead, and a mixture of products is obtained. For instance, o-dinitrobenzene³ gives a mixture of o-nitronitrosobenzene, o-nitrophenol, o-nitroaniline, nitrobenzene, and tar.

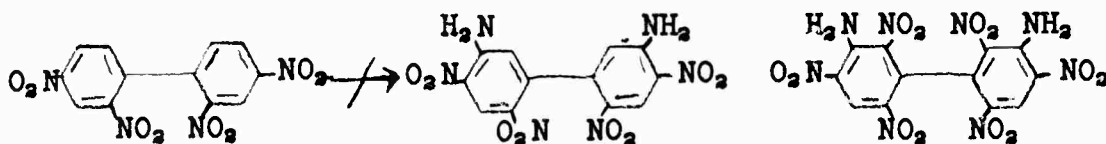
The procedures used by Meisenheimer are not reported¹ in detail, and several attempts were necessary to determine the conditions under which m-dinitrobenzene could be aminated. This compound reacts with neither methanolic hydroxylamine nor methanolic sodium methoxide alone, but when all three are mixed, a deep red solution is formed. After dilution with ice-water and acidification, 2,4-dinitroaniline precipitates in almost quantitative yield. Replacement of some of the solvent methanol by dioxane had no effect upon the reaction. If insufficient base is used, the reaction proceeds more slowly, and unreacted dinitrobenzene is recovered.

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Attempts to prepare picramide from s-trinitrobenzene in the same manner were unsuccessful. The reaction conditions were varied over a wide range, but the only evidence for the formation of picramide was obtained from ultraviolet spectra of the reaction products. No pure picramide could be isolated from these products.

Hexanitrobiphenyl was expected to behave similarly. But, because of the slight solubility of DIPAM in most solvents, it should be easier to isolate than picramide. In one series of experiments, HNB was dissolved in methanolic sodium methoxide. Hydroxylamine solution was added to this dark red solution, and it immediately turned dark brown and evolved small amounts of gas. After dilution with ice water and acidification, some brown color remained. Alternatively, the HNB was dissolved in a small amount of dioxane and methanol was then added. Thus, varying amounts of base could be added to a solution of HNB and hydroxylamine. In either case, the amount of base used seemed to have a marked effect upon the reaction. When only small amounts of base were used, some of reaction took place, but only unreacted HNB could be isolated from the reaction mixture. In one attempt, an unidentified solid product was obtained. This brown substance was quite soluble in methanol, in which neither HNB nor DIPAM is even moderately soluble.

Since the amination of m-dinitrobenzene had been successful, perhaps it would also be possible to aminate 2,4,2',4'-tetranitrobiphenyl. Nitration of the resulting diamine should furnish another route to DIPAM. The results from attempted aminations, however, were the same as were obtained when HNB was used.



This behavior of HNB and the tetranitrobiphenyl appeared similar to that reported for ortho and para nitrocompounds. If reduction was occurring when these biphenyl compounds were treated with hydroxylamine, then 4,4'-dinitrobiphenyl might also be expected to undergo such reduction under the same conditions. This was found to be the case. The same behavior was shown by 4,4'-dinitrobiphenyl as had been shown by the other two biphenyl compounds.

EXPERIMENTAL

Amination of m-dinitrobenzene. m-Dinitrobenzene (1 g) was dissolved in 25 ml of methanol, and 8 ml of 4 N sodium methoxide in methanol was added. The solution was chilled in an ice-bath, and a methanolic solution of hydroxylamine (prepared from 1 g of hydroxylamine hydrochloride) was added. A red color immediately appeared, but no precipitate formed. After 30 minutes, the solution was poured into approximately 100 ml of ice water and made slightly acid with acetic acid. The reaction product crystallized from the solution. This substance m.p. 180° (Lit.⁵, 180°), was identified as 2,4-dinitroaniline by comparison of its ultraviolet spectrum with that reported in the literature⁴.

Hydroxylamine solutions were prepared as needed by dissolving the required amount of hydroxylamine hydrochloride in methanol, neutralizing with sodium methoxide solution, and filtering off the precipitated sodium chloride.

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Section I

PURIFICATION OF BIS(2-FLUORO-2,2-DINITROETHYL)FORMAL, FEFO

by

Francis Taylor, Jr.

Several pounds of FEFO, prepared on Contract NOW-60-0745-c, were received by the laboratory. The FEFO as received was straw yellow in color, had an acrid odor, and appeared to be gassing at ambient temperatures. The melting points of these lots of FEFO varied over a wide range; 5.4 to 10.1°. FEFO, as prepared in our laboratories, is a colorless, odorless liquid with a melting point of 10.7°. A sample of FEFO prepared by the Aerojet-General Corporation, using a different synthetic route, had similar visual characteristics and melted at 12.7°.

In order to check the purity of the above lots of FEFO, we attempted to prepare a pure sample of FEFO so as to ascertain the true melting point of this compound. From past experience in purifying liquids³, our first trials involved fractional crystallization of the Aerojet-General sample of FEFO since this had the highest melting point. Three crystallizations of this material only raised the melting point 0.2°.

The next task was to determine the purity of the recrystallized material. Vacuum stability measurements did not give conclusive results. A measurement of the melting point depression would have given the desired result, but it was difficult to find a suitable compound that was soluble in FEFO. It appeared that bis(2-fluoro-2,2-dinitroethyl)carbonate was somewhat soluble in FEFO at ambient temperatures, but it may well have separated from solution at lower temperatures. Thus, the addition of 3.53×10^{-5} mole of the bis-carbonate to 0.355 mole of FEFO gave a 0.2° depression in the melting point. An additional 3.53×10^{-5} mole of the bis-carbonate was added and the resulting depression was now only 0.3° instead of the expected 0.4°.

At this point we resorted to vapor phase chromatography. With this technique, we were able to resolve the components in the various samples of FEFO. Since a pure sample of FEFO was not available for calibrating the instrument, it was not possible to assign absolute purities to the various FEFO

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samples. However, it was possible to make some estimates of the purity by normalizing the peak areas in the chromatogram. Table I gives the melting point and estimated purity as determined by vapor phase chromatography.

TABLE I
MELTING POINTS AND ESTIMATED PURITY OF FEFO SAMPLES
BY VAPOR PHASE CHROMATOGRAPHY

<u>Sample</u>	<u>m.p., °C</u>	<u>Purity, %</u>
5A	5.4	79
3A	6.4	84
6A	7.5	85
2A	8.4	92
6705-6	11.3	>95
6705-1	12.9	>95

The fractional crystallization procedure was satisfactory for purifying small lots of FEFO, but it was costly in terms of material. Starting with 100 ml of FEFO, only 12.5 ml were recovered after three fractional crystallizations. Because of the large losses, this method was not considered practical for purifying large lots of FEFO.

As an alternative procedure, we investigated washing the crude FEFO with concentrated sulfuric acid and bicarbonate solution, slurring with Darco decolorizing charcoal and chromatographic grade silica, and pumping at reduced pressure. A combination of these techniques raised the melting point of one sample of FEFO from 9.6° to 11.3°. The purity of the product obtained by this procedure was estimated to be 95% or better by vapor phase chromatography. After refining the above procedure, it consistently gave FEFO with a melting point of 11° or higher regardless of the purity of the starting crude⁴. The recovery from this procedure was excellent, since it was possible to treat 3.4 pounds of FEFO in this manner and obtain 3.3 pounds of purified material. The major loss in this procedure is due to the solubility of FEFO in concentrated sulfuric acid.

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A recent communication from the contractor reported that it was possible to recrystallize the FEFO from methylene chloride. One recrystallization of the crude reaction mixture by this procedure gave material melting at 12.5C⁵.

EXPERIMENTAL

Purification by Washing

One volume of crude FEFO was dissolved in three volumes of reagent grade methylene chloride and dried over anhydrous magnesium sulfate. The solution was filtered from the drying agent and washed with 25 grams of concentrated sulfuric acid for each 500 ml of solution. The mixture was thoroughly mixed in a separatory funnel and the sulfuric acid drawn off at the bottom after it had all settled. The washing with sulfuric acid was repeated three times and the third washing gave almost colorless sulfuric acid. The acid was drained off completely and then the organic phase was washed three times with cold tap water. The volume of water used was equal to one-third the volume of the organic phase. The organic phase was next washed three times with 10% sodium carbonate, the volume equal to one-third the volume of the organic phase. The organic phase was washed again with three volumes of water as above. The last water washed was checked with pH paper to make sure that the last wash was neutral. The organic phase was dried over anhydrous magnesium sulfate, filtered from the drying agent, and stirred with activated Darco, 25 grams for each 500 ml of solution. The mixture was stirred for one hour and then filtered through a pad of celite on a Buchner funnel. The FEFO solution was concentrated to one-half its volume on a steam bath. The resulting concentrate was pumped on a Rinco (rotary) evaporator at 40-50° with a water pump until a constant pressure was obtained. The water pump was replaced by an oil vacuum pump and the residual organic phase was pumped at 0.5 mm or less for one hour at 40-50°. The FEFO recovered was a very pale straw color to colorless liquid and melted at 11.5°. The purity was estimated by vapor phase chromatography to be greater than 95 mole percent. The recovery from the above procedure was 90% or better, depending upon the quality of the crude FEFO with which one started.

We do not have definite proof that FEFO reacts with glass, but it is felt that the FEFO is best stored in polyethylene.

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Purification by Recrystallization

The crude FEFO from the reaction mixture was dissolved in distilled methylene chloride, treated with Darco G-60 and filtered. There was a 9% loss in weight at this point and the resulting FEFO melted above 10°. After treatment with Darco, the FEFO was dissolved in methylene chloride in a volume ratio of 1:3 and the solution cooled in a dry-ice acetone bath and seeded. The FEFO crystallized and was collected on a cold Buchner funnel. The product was transferred to a round bottom flask and pumped on a Rinco (rotary) evaporator at 65° with a water pump until a constant pressure was obtained. The recoveries were between 70-85% and the FEFO melted up to 12.5°. Attempts to recover second crops were unsuccessful. The solids separated from the second crops melted at 6°. The FEFO melting at 12.5° was estimated to be greater than 95 mole percent pure from analysis using the gas chromatograph.

The melting points of the various lots of FEFO were measured as follows: A 15-20 ml sample of FEFO was poured into an unsilvered Dewar jacketed tube, fitted with a narrow range mercury thermometer, and the tube immersed in an ice-salt bath. The sample was agitated with the thermometer and the curve plotted. The samples always supercooled, the higher the melting point of the FEFO, the less the sample supercooled. The temperature where the plot leveled off was taken as the melting point of the FEFO sample.

The purity of the various FEFO samples were estimated from the plot obtained using an F and M Scientific Corporation Model 300 Programmed Temperature Gas Chromatograph. The instrument was fitted with a thirty-six inch column containing 10% May-Baker Silicone oil on 30-60 mesh Haloport F. The temperature of the column was programmed at 9°/minute starting at 75° and held at 220° until the FEFO came off of the column. The injection port was heated at 210°, the block at 240°, the current at 140 milliamps., and the flow rate of helium was 30 ml/minute. Under the above conditions the impurities were resolved and FEFO has a retention time of 18 minutes.

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Section J

PREPARATION OF TRINITROPHLOROGLUCINOL

by

Francis Taylor, Jr.

INTRODUCTION

A method was developed in these laboratories for the analysis of 2,4-diamino-2,4,6-trinitrobenzene (DATB)¹. The amino groups of DATB were quantitatively displaced by hydrolysis with boiling aqueous sodium hydroxide. The ammonium formed in the reaction was collected using a modified Kjeldahl distillation procedure. Quantitative recoveries were obtained on both DATB and ammonium perchlorate with the method. During the development of the analytical procedure a single sample of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) was analyzed by the general method used for DATB and it was demonstrated that the analytical method was feasible for the analysis of TATB. The products resulting from the alkaline hydrolysis were separated and identified. The products were trinitroresorcinol and trinitrophloroglucinol from the DATB and TATB respectively.

DISCUSSION AND RESULTS

It was suggested that we investigate the feasibility of adapting the analytical procedure for the preparation of trinitrophloroglucinol. The preparation of trinitrophloroglucinol by hydrolysis of both TATB and 1,3,5-trichloro-2,4,6-trinitrobenzene were reported in the literature². The hydrolysis was carried out using alcoholic sodium hydroxide. The yields reported were 55% and 70% starting with 1,3,5-trichloro-2,4,6-trinitrobenzene and TATB respectively. It has also been reported that 1,3,5-trifluoro-2,4,6-trinitrobenzene hydrolyzes in water alone to give trinitrophloroglucinol, but no yields were reported³.

We attempted the hydrolysis of both TATB and 1,3,5-trichloro-2,4,6-trinitrobenzene using an excess of 1.5 N aqueous sodium hydroxide. The samples were heated at the reflux temperature for varying lengths of time and hydrolysis progressed as follows:

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<u>Samp</u>	<u>Time, hrs.</u>	<u>% Yield, trinitro- phloroglucinol</u>
TATB	5.5	72.8
TATB	6.0	80.0
TATB	7.0	83.0
1,3,5-trichloro- 2,4,6-trinitrobenzene	5.0	62.6

The impact sensitivity of the pure trinitrophloroglucinol using type 12 tools on sandpaper with a 2.5 kilogram weight was 27 cm., (σ , 0.10).

EXPERIMENTAL

A mixture of 3.0 g (0.011 mole) of TATB in 300 ml. of 1.5 N aqueous sodium hydroxide was refluxed for seven hours. After the reflux period the mixture was allowed to cool to room temperature and then neutralized with concentrated HCl. The crude trinitrophloroglucinol was extracted from the aqueous phase with ether and the ether solution dried over anhydrous magnesium sulfate. After filtering off the magnesium sulfate, the ether was removed under reduced pressure and gave 2.5 grams (83%) of crude trinitrophloroglucinol. The crude material was recrystallized from ethanol and gave trinitrophloroglucinol which melted at 166°.

When 1,3,5-trichloro-2,4,6-trinitrobenzene was substituted for TATB and the mixture refluxed for five hours, trinitrophloroglucinol was obtained in a 52% yield.

SUMMARY

We feel that anyone interested in the preparation of large laboratory samples of trinitrophloroglucinol would do well to consider the alkaline hydrolysis of 1,3,5-trichloro-2,4,6-trinitrobenzene. It appears to have many advantages over the trinitration of phloroglucinol. The s-trichlorobenzene can be purchased for \$2.60/pound and we estimated that the materials cost to make one pound of the trinitro derivative was \$2.24 based on an 85% yield⁴.

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DOCUMENT CONTROL DATA - R&D		
(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)		
1. ORIGINATING ACTIVITY (Corporate author) U. S. Naval Ordnance Laboratory White Oak, Silver Spring, Maryland		2a. REPORT SECURITY CLASSIFICATION CONFIDENTIAL
		2b. GROUP 4
3. REPORT TITLE SYNTHESIS OF NEW HIGH EXPLOSIVES. IV. (U)		
4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Technical Report		
5. AUTHOR(S) (Last name, first name, initial) SHIPP, Kathryn G., HALL, Thomas N., HOFFSOMMER, John C., KAPLAN, Lloyd A., RUSKIE, Howard E., TAYLOR, Francis, Jr.		
6. REPORT DATE 26 May 1965	7a. TOTAL NO. OF PAGES 49	7b. NO. OF REFS 35
8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S) NOLTR 64-211	
b. PROJECT NO. FR-44, RUME-4E, Probs. 012 and 017		
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
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13. ABSTRACT This report describes the results of a number of diverse preliminary investigations of the chemistry of polynitro compounds. In some cases the results reported are negative. The authors hope that the presentation of these negative results will serve as a guide for future research in these areas. (U)		

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