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NAVORD REPORT

6016

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HEAT RESISTANT EXPLOSIVES II

1, 3 - DIAMINO - 2, 4, 6 - TRINITROBENZENE, DATB

31 MARCH 1958



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U. S. NAVAL ORDNANCE LABORATORY

WHITE OAK, MARYLAND

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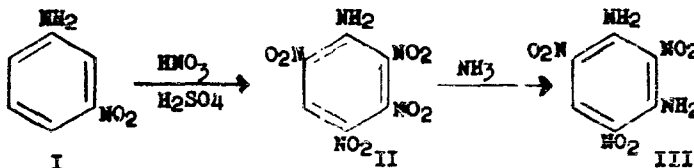
Prepared by:

K. G. Shipp and M. E. Hill

Approved by: DARRELL V. SICKMAN
Chief, Organic Chemistry Division

ABSTRACT: 1,3-Diamino-2,4,6-trinitrobenzene, III, is a high temperature resistant explosive which decomposes only slightly at 500°F (260°C). Its density is greater than that of RDX and it is less sensitive than TNT by the standard ERL drop-weight impact test. Incomplete evaluation data indicate that it is equivalent in power to TNT.

Diaminotrinitrobenzene, III, is prepared from commercially available starting materials in two steps. First m-nitroaniline, I, is nitrated by a simple nitration mixture under mild conditions to tetranitroaniline, II. The crude tetranitroaniline then is converted by methanolic ammonia to diaminotrinitrobenzene in a high degree of purity.



A conversion of 100 parts of m-nitroaniline to 110 parts of diaminotrinitrobenzene is obtained by this method, which can easily be carried out on a commercial scale.

CHEMISTRY RESEARCH REPORT

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NAVORD Report 6016

31 March 1958

This report describes the synthesis of diaminotri-nitrobenzene, a new high explosive with excellent thermal stability at high temperatures. NAVORD Report 6017 is the preceding Part I relating to high temperature resistant explosives.

42-162977

This work was performed under Task FR-44 (Explosive Synthesis). Although this work was carried out in small quantities in laboratory equipment, there is every reason to believe that larger quantities in plant equipment could be made with no loss in quality or yield. Consequently, the methods of synthesis described herein are considered worthy of adaption to plant practice.

W. W. WILBOURNE
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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HEAT RESISTANT EXPLOSIVES II
1,3-DIAMINO-2,4,6-TRINITROBENZENE, DATE

INTRODUCTION

Aerodynamic heating during the flight of a high speed missile has established the need for high temperature resistant components for the warhead. Currently used military high explosives are unusable in such warheads unless protected by thermal insulation inasmuch as their decomposition temperatures are well below the temperature which the warhead interior is expected to reach. Therefore the Organic Chemistry Division has been investigating the synthesis of new high temperature resistant explosives. So far, principal consideration has been given to explosive compounds which melt at or above 300°C, since it is well known that explosives in a molten state have a greatly increased decomposition rate over that thermally induced in the solid state.

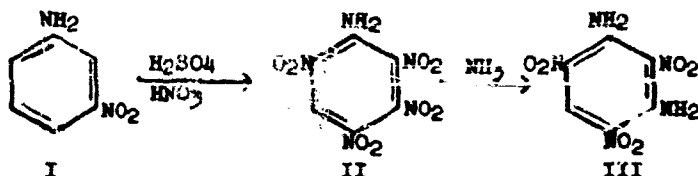
Two explosives which have both a high melting point and excellent high temperature stability are 2,4,6-trinitrobenzene and diaminotrinitrobenzene. The former compound has been known for many years. Its unusual melting point and solubility properties were redetermined in this laboratory in the course of studying the nitration of tri-bromobenzene (1). Because strong bonding between the ortho amino and nitro groups was thought to contribute to a higher fusion point and resistance to decomposition in the triamino compound, the analogous diaminotrinitrobenzene was prepared and found to have excellent high temperature thermal stability. Consequent to the successful stability test, a study of its synthesis was undertaken to develop a method which would permit pilot plant production of fifty pounds for large scale evaluation.

DISCUSSION AND RESULTS

The preparations of diaminotrinitrobenzene reported in the literature seem to have been only of academic interest for the most part and were usually carried out on a small scale. Van Duin (2) has summarized the early literature

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concerning its preparation. Considering the commercial availability of the starting materials and the simplicity of the reaction sequence, the conversion of m-nitroaniline to diaminotrinitrobenzene was investigated. The synthesis, summarized in the chemical equation below, was carried out in two steps. First, m-nitroaniline, I, was nitrated by a nitrating mixture under mild conditions to tetranitroaniline, II. The crude tetranitroaniline was aminated with ammonia in methanol to diaminotrinitrobenzene, III, which was obtained in a high degree of purity from the reaction mixture.



conversion of 100 parts m-nitroaniline to 110 parts diaminotrinitrobenzene was obtained by this method, which can easily be carried out on a commercial scale in currently available nitration plants.

Properties of Diaminotrinitrobenzene: Diaminotrinitrobenzene is a yellow crystalline compound as received from the reaction mixture. Under the optimum conditions of decomposition the crystals usually were small needles with some fine powdery particles dispersed throughout. Table I summarizes its physical properties.

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TABLE I

Physical Properties of Diaminotrinitrobenzene

Melting point	285°C
Crystal density	1.84
Impact sensitivity (50% height) (2.5 kg wt, ERL machine)	320 cm (3 explosions out of 9 trials)
Vacuum stability	
0.10 ml/g	48 hrs at 100°C
1.11 ml/g/hr	2 hrs at 260°C (500°F)
Solubility	Slightly soluble in hot glacial acetic acid, dioxane and nitrobenzene

The vacuum stability data represents approximately 0.25 per cent decomposition to gaseous products in two hours at 500°F. However, one of the primary unanswered questions about an explosive of this type was whether or not the compound would explode after subjecting it to high temperature. It is conceivable that decomposition to solid products would render the compound nonexplosive. For diaminotrinitrobenzene qualitative observations show little effect by heating. Melting points of the compound taken after two hours at 260°C showed a depression of only two degrees. After being held in the molten state at 260°C for over one hour the material again melted only two degrees below the original melting point. Resistance to decomposition in the molten state at such a high temperature is very unusual for an explosive. Therefore, it appears that in an actual situation most of the explosive is unaltered and would remain active for functioning when desired. An actual firing test to determine this point is to be made. The "cook-off" temperature was found to occur after eight minutes at 320°C (3).

Diaminotrinitrobenzene has a calculated heat of explosion of 965 cal/g compared to 980 cal/g for TNT (4). Its "shattering power" as measured by Picatinny Arsenal was 100% of that of TNT (5).

Since this report concerns a synthesis development, the following sections discuss reaction parameters primarily.

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Preparation of Tetranitroaniline: Flürscheim was the first to prepare tetranitroaniline in 1904, and the preparation by the nitration of m-nitroaniline was reported by Flürscheim and Simon (6). The method was patented in Great Britain, Germany, France, Canada and the United States from 1910 to 1913 (7). Tetranitroaniline was prepared in this country during the First World War, and nitration on a scale as large as 2500 gallon batches was carried out.

The A. D. Little laboratories (8) described the nitration of m-nitroaniline following Flürscheim's synthesis, and the method of preparation of tetranitroaniline used in this project is a development of the A. D. Little preparation.

The optimum procedure for the nitration of m-nitroaniline was found to be as follows: m-Nitroaniline is dissolved in a mixture of concentrated sulfuric acid and 30% fuming sulfuric acid. At 20°C nitric acid (assay 90%) is added slowly. The temperature of the reaction solution is maintained at 20°C for two hours and then gradually heated to 70-75°C to complete the reaction. Tetranitroaniline separates from the reaction mixture as a crystalline product, and at the completion of the reaction is filtered off and washed. It may be dried or may be used as a wet cake for the preparation of Diaminotrinitrobenzene. Tetranitroaniline is itself an explosive, having an impact sensitivity of 36 cm which is the same as that of tetryl. With proper precautions it has been found to be quite safe to handle, particularly when slightly wet. Flürscheim has published its properties in considerable detail (9, 10).

Tetranitroaniline is recrystallized from glacial acetic acid, but requires large volumes of the acid for this purpose. Thus, it is important that the tetranitroaniline be pure enough to use as it comes from the reaction mixture. This was held clearly in mind as the nitration of m-nitroaniline to tetranitroaniline was studied, and was successfully accomplished.

It is interesting to note that the crude tetranitroaniline appears quite green in some preparations and orange in others. This agrees with Flürscheim's observations. It is also interesting that the green tetranitroaniline always has a slightly higher melting point than the orange product. The isomerism has not been investigated as yet, but the study

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of the X-ray patterns for the two forms is planned for the future. The recrystallized tetranitroaniline is yellow, although it may have a greenish tinge, and the green form tends to become less green and more orange on standing in light. In one instance, several grams of the green product mixed with two grams of orange material in the presence of 2% water and kept in a tightly closed container over night appeared completely orange in the morning.

Because the previous preparations of tetranitroaniline involved very large volumes of concentrated sulfuric acid and fuming sulfuric acid, 1000 parts of acid for 50 parts of m-nitroaniline, this was the first variable to be studied. It was found that the volumes could be reduced by 1/3 each and still get a very good product from the reaction. However, when the volumes were reduced by 1/2, the reaction was less smooth, the product being orange and obtained in slightly lower yield. When the volumes were drastically reduced to 1/4 the reaction "fumed-off". Two experiments have been carried out using concentrated sulfuric acid unfortified by the addition of fuming sulfuric acid. A yield comparable to that from the more acidic medium was obtained when an equivalent volume of concentrated sulfuric acid was used. Again reduction of acid volume was detrimental. Although the product in these cases was orange and had a lower melting point than the green product from the sulfuric acid-fuming sulfuric acid mixture, diaminotrininitrobenzene prepared from it was very satisfactory in the high temperature vacuum stability test. The spent acid from the nitration reaction may also be fortified with fuming sulfuric acid and re-used at least once in further nitration reactions. This has been carried out in the laboratory.

Potassium nitrate and 100% nitric acid were tried as nitrating agents in the reaction and neither one showed any advantage over the 90% nitric acid. As a note on the color isomer, the product was orange whenever potassium nitrate or 100% nitric acid was used.

Reversing the addition procedure, that is, adding the m-nitroaniline to the nitrating mixture instead of adding nitric acid to its solution in the sulfuric acid-fuming sulfuric acid mixture, was tried and found to have no advantage. Since the addition of the acid is easier to handle this was the procedure adopted.

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The temperature of the reaction mixture during the addition of the nitric acid was varied: 0-20°C, 20-25°C, 45-50°C, and 60-65°C. The reaction proceeded to a satisfactory conclusion from any addition temperature with the exception of the last range of addition. In this experiment there were small explosions within the reaction mixture, "flashes of fire" as Plüschke expressed it. The ones carried out at room temperature or below gave more reproducible results without untoward incident as to amount, color and melting point of the product.

It was necessary to maintain the reaction mixture at 20-25°C for a period after the addition of the nitric acid. A mild exothermic reaction always occurred when the nitration mixture was heated too soon after the addition of the nitric acid. However, when an exothermic reaction did occur it was always slight and readily controlled by a bath at ambient tap-water temperature or lower. When the "post-addition" reaction period was followed by a slow warming period to 70°C, the exotherm was not apparent. The nitration on a half mole scale required about five hours overall.

The nitration is thought to proceed not only by direct nitration but also by the production and rearrangement of intermediate nitramines, i.e. the Bamberger rearrangement (11, 12). Such intermediate nitramines, e.g. metadinitrophenylnitramine, are known to be formed in the preparation of pentanitroaniline. Their precipitation must be avoided because, in this case, their rearrangement is accompanied by "flashes of fire" by using large volumes of sulfuric acid in which the nitramines are soluble. When large volumes of sulfuric acid-fuming sulfuric acid mixture were used there was no evidence of any precipitate in the reaction mixture until the tetranitroaniline separated as a crystalline product. When the volume of acid was reduced, however, there was usually a flocculent precipitate at some point. This precipitate might dissolve completely before the tetranitroaniline appeared, or the character of the precipitate might change to the characteristic tetranitroaniline crystalline product, depending on the conditions of the experiment. In one experiment carried out in 100% sulfuric acid the flocculent precipitate was filtered off and found to be water soluble and unstable in water solution, which is true of the nitramines of such character. Further identification of the nitramine was not made, but all observations bear

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out the theory that the nitration proceeds, at least in part, by the formation of the nitramine which then rearranges to the nitro-aniline after an initial direct nitration by electrophilic substitution at the para position.

Amination of Tetranitroaniline: Of the many preparations of diaminotrinitrobenzene recorded in the literature, the ammonolysis of tetranitroaniline to the diamino compound used by Plüschke (13) was the most direct. Although he did not obtain a pure compound according to his reported melting point, it was decided to investigate this method because its simplicity would make scaling up to pilot plant production easier. The investigation of the amination had the objective of using successfully crude tetranitroaniline to produce crude diaminotrinitrobenzene which was pure enough as received from the reaction mixture to use in explosive compositions. The low solubility of tetranitroaniline and diaminotrinitrobenzene in the usual solvents made it imperative to avoid recrystallization of either compound.

The vacuum thermal stability test because of its sensitivity to impurities was used almost exclusively to determine the purity of the final product of the amination. The test consisted essentially of heating a sample in an evacuated tube for two hours at 260°C (500°F) and measuring the volume of the decomposition gases evolved. Previous experience had indicated that approximately four ml of gas per gram per hour would correspond to 1% decomposition, the maximum amount that could be accepted for the intended use of the explosive. The diaminotrinitrobenzene samples prepared by the optimum procedure outlined below varied from 1.1 ml to 2.90 ml per gram per hour or roughly one-fourth to three-fourths of one per cent decomposition. Qualitatively, melting point determinations were helpful as an indication of purity of the various reaction products. Carefully recrystallized diaminotrinitrobenzene from nitrobenzene melted at 285°C. The "production" materials which had good thermal stability melted at 282°C. Discoloration while heating the melting point tube, sharpness of melting point, and actual observed melting points were all used to screen out obviously unstable samples and consequently speeded up the survey of reaction conditions.

The study of the direct amination proceeded in three phases: The feasibility of direct amination was tested with

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purified starting material, crude tetranitroaniline was substituted for pure, and the reaction volume was reduced for efficient scale-up. To test the feasibility of direct amination of tetranitroaniline, the purified compound was dissolved in Cellosolve and added dropwise to a dilute solution of ammonia in 97% methyl alcohol at room temperature. The product precipitated from solution within a few minutes after addition began. Stable crude diaminotrinitrobenzene was obtained by this procedure which became the basis of subsequent experimental work. Various solvents were substituted for methyl alcohol with no improvement and, in some cases, decided detriment. Alcohol solutions containing 50% water worked reasonably well but reaction solutions with a lower water content gave better and more reproducible vacuum stability tests. In general, polar solvents worked best experimentally as might be expected from the nature of the reaction. Cellosolve was found to be the best solvent for introduction of the tetranitroaniline.

In order to eliminate a recrystallization step, solutions of crude tetranitroaniline were substituted for solutions of the purified material. Crude diaminotrinitrobenzene of excellent stability was obtained as easily as with the purified material. However in considering the necessary steps to scale up the method to large laboratory scale prior to pilot plant scale-up, it became apparent that the reaction volume resulting from the combined alcohol Cellosolve solutions would have to be reduced. Since a time lag had been observed between the addition of the tetranitroaniline solution and precipitation of the diamino product, it was thought that the sequence of reaction after addition of solid tetranitroaniline to ammoniacal alcohol would be solvation, reaction, and then precipitation of the product until all starting material was consumed. After successful trial experiments the conversion of crude solid tetranitroaniline to diaminotrinitrobenzene was scaled up from one to fifty gram runs.

Within certain limits the amount of ammonia relative to the amount of tetranitroaniline could be varied. The best products were obtained in reactions having an ammonia-tetranitroaniline ratio of 0.40-1.0 part to one. Less stable products were obtained when reactant ratios outside this range were used.

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Although stable products were obtained in many cases at room temperature, more reproducible results were obtained by aminating at 50°C. The product crystals formed were larger and more uniform than the sometimes amorphous solids obtained at the lower temperature. Wet tetranitroaniline can be substituted for the dry material, thereby decreasing the handling hazard for the entire synthesis.

Many of the experiments made investigating the parameters of the amination produced diaminotrinitrobenzene which was too unstable to be acceptable. To determine if recovery could be made of production material which did not meet the stability requirement, various methods of reworking the crude product were investigated. Material which evolved up to 12 ml of gas per hour was improved enough for acceptance by brief slurring with acetone, methyl alcohol, ammoniacal methyl alcohol, or hot water. Therefore, should a plant run produce unstable material, recovery of the run is easily made by a simple reworking procedure.

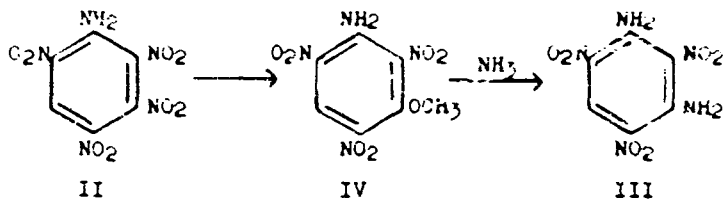
The conversion of tetranitroaniline to diaminotrinitrobenzene was accompanied by side reactions, principally the formation of trinitroaminophenol ammonium salt by the reaction of water and then ammonia. In addition, a small amount of dark red material soluble in water and alcohol was isolated from some of the mother liquors by evaporation. This material, possibly a phenazine reduction product similar to the type described by Gagnon et al (14), has not been identified as yet. Higher yields of the diamine were obtained in 50% aqueous methanol but in most cases the thermal stability was not as good as with 97% methanol. However, the improved workup procedure developed later was not used in these experiments. The amino phenol formation was eliminated by aminating under strictly anhydrous conditions but without improving the yield of diaminotrinitrobenzene. Two products were obtained, the reduction product in 40% yield, and the diamine.

Tetranitroaniline reacts almost exclusively at the three position by nucleophilic substitution, a possible exception being the formation of the reduction product. In the structure of tetranitroaniline the three position is highly activated by two ortho-nitro groups and a para-nitro group. It undergoes nucleophilic substitution with water and

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alcohol less easily than with ammonia as might be expected from the relative nucleophilicity of these reagents. Burnett (15) has published an excellent review of nucleophilic aromatic substitution which obviates our discussion here of an additional example. Note, however, that the reaction of ammonia with tetranitroaniline is one of only a few known examples of substitution of a nitro group which is ortho, ortho, para activated by nitro groups. A more basic study of this interesting reaction is to be made and will be discussed elsewhere.

Because of the susceptibility of groups at the three position to nucleophilic substitution, an alternative route to dianilinotrinitrobenzene was briefly explored. Tetranitroaniline, II, in refluxing methanol converted nearly quantitatively to trinitroethoxyaniline, IV. The anisole was easily converted to the diamine, III, in 93% yield by its reaction with ammonia in methanol.



The product diamine was a light yellow finely crystalline, needle like material but less pure than that obtained by direct amination of tetranitroaniline. The product in vacuum thermal stability tests at 200°C evolved 8-10 ml of gas per gram per hour compared with the acceptable 4.0 ml per gram.

Study of this reaction is in progress with the aim of providing an alternative synthesis in which the diamine can be made in the same vessel in two stages: reaction of tetranitroaniline with methanol, followed by introduction of ammonia to produce the end product in high yield with little more effort than by direct amination.

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Another route which was tried in the laboratory was the direct nitration of m-phenylene diamine sulfate and of the diaceto derivative. The conversion of styphnic acid to trinitrodichlorobenzene and then to diaminotrinitrobenzene by the method of Haas and Feuer (1c) was too involved to offer an advantage over the present synthesis. Other literature methods were surveyed and not adopted because of lack of simplicity for large scale production.

ACKNOWLEDGMENT

Mr. Herbert Simmons measured the crystal density and the vacuum stability of the experimental products during the course of this work.

Mrs. Sarah P. Duck measured the impact sensitivities.

Dr. Darrell V. Sickman suggested that the explosive and stability properties of diaminotrinitrobenzene be tested.

EXPERIMENTAL

The optimum procedures only are given in this section.

Nitration of m-Nitroaniline.

Procedure: A solution of 69 g (0.5 mole) m-nitroaniline (Note 1) in 600 ml of concentrated sulfuric acid and 240 ml of 30% fuming sulfuric acid was prepared in a 2 liter, 3-neck, round bottom flask with a thermometer, mechanical stirrer and dropping funnel, keeping the temperature at 20-25°C by means of a tap-water bath (20°C). To this solution, still at 20-25°C, 105 ml of concentrated nitric acid (90%) was added from a dropping funnel over a period of thirty minutes. The solution was light amber colored after the addition of the acid and there were bubbles of gas in the solution (Note 2). The reaction solution was held at 20°C by means of the tap-water bath for two hours, then heated gradually to 70°C with a water bath during one hour and held at 70-75°C for one-half hour. The color of the solution, which was orange red at the end of the two hours at 20°C, became cherry red during heating. The first crystals

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appeared at 35°C and the flask was quite thick with crystals when the temperature of the mixture had reached 45°C (Note 3). At the end of the heating period the mixture was chilled and the product was filtered on a sintered glass funnel (Note 4), washed with 50% sulfuric acid and cold water. After drying, the green crystalline product weighed 102 g or 75% of the theoretical yield. The melting point of this product was 215-217°C (dec.). It can be recrystallized from glacial acetic acid, from which it crystallizes in yellow needles melting at 217-220°C with decomposition.

Note 1. The m-nitroaniline used was from an 85 pound lot purchased from the Verona Chemical Co. It was in well formed yellow needles which melted at 114°C, which is the melting point given in the literature for the pure product (17).

Note 2. The gas evolution was never such as to cause foaming with this volume of sulfuric acid-fuming sulfuric acid mixture. With reduced volume of acid foam almost filled the flask.

Note 3. The temperature at which the first crystals of product appeared varied from 35-45°C, and seemed to be connected with the rate of heating, appearing at the lower temperature when the reaction had been heated slowly. A flocculent precipitate appeared in some instances. As had been stated in the discussion, this precipitate is presumed to be the nitramine. During the heating period, the flocculent precipitate would gradually disappear and the characteristic crystals of tetranitroaniline would form in the reaction flask.

Note 4. The filtrate was orange red in color. No additional product was obtained by drowning the filtrate in flaked ice-water. This spent acid can be fortified with fuming sulfuric acid and reused for nitration of m-nitroaniline.

TABLE II
Nitration of m-Nitroaniline (2 ml)

Expt. No.	Anti. m-Na	V ₂ O ₅	Acid SO ₃ H ₂ SO ₄	Nitrating Agent	Add. Method	Temp.	Reactor Cycle	Yield	m.p. Crude	Δ
5253-60	5g	50 ml	0 ml	ES03	ES03	0-20°C	No. 111 at low T. Exo. at 45° (to 80°)	70.0	205	0
" 61	5g	33 "	15 "	"	"	45-50°	" " " "	51.0	200	0
" 62	5g	50 "	20 "	"	"	50-55°	55° for 20 min. Heat to 15°C	70.5	206-209	0
" 63	5g	50 "	20 "	"	"	60-65°	60-65° 10 min. Then "flasher of fire"	60.0	208-210	0
" 64A	5g	50 "	18 "	100% ES03	Acid to ES03	45-50°	1 1/2 hr. for add. online 70°C for 45 min.	67.7	212-213	0
" 64A	5g	50 "	20 "	90% ES03	Acid to ES03	0-20°	Heated rapidly to 60° 60-70° for 1 1/2 hr.	62.6	212-213	0
" 86	5g	40 "	20 "	"	"	0-10°	1 1/2 hr. to 20°C Exo. at 30° 70-75° 1 1/2 hr.	72.0	212-215	0
" 91	50g	500 "	200 "	"	"	0-5°	1 hr. to 20°C 40 min. to 50°C 21. exotherm.	71.0	217-218	0
5437-10	5g	25 "	0 "	"	"	0-5°	35 min. to 70° Pump off.			
" 11	5g	70 "	0 "	"	"	0-5°	50 min. to 20° Exo. at 50°	72.2	212-214	0
" 30	10g	100 "	40 "	"	"	20-25°	1 hr. at 20°C 1 hr. to 70° No exotherm.	71.7	215-216	0
" 33A	10g	Heune 30	20 "	"	"	20-25°	1 hr. at 20°C 1 1/2 hr. to 75° 31. exotherm.	70.0	210-214	0
" 33B	10g	Heune 30A	40 "	"	"	20-25°	1 hr. at 20°C 1 1/2 hr. to 70° 31. exo. flash.	505	209-212	0
" 36	10g	200 "	40 "	Excess ES03	"	20-25°	1 hr. at 20°C Rapid to 40° Exo. "flasher"	70.0	210-212	0
" 37	10g	400 "	40 "	ES03	"	20-25°	1 hr. at 20°C 1 hr. to 70° No exotherm.	75.0	215-217	0

Δ 0 = Green colored crystals
0 = Green colored crystals

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Preparation of Diaminotrinitrobenzene from Tetranitroaniline.

Apparatus: 3 liter, 3-neck, round bottom flask fitted with mechanical stirrer, dropping funnel and addition funnel for solids.

Procedure: A solution of 100 ml of concentrated ammonium hydroxide in 2 liters of methanol was prepared. A portion, 500 ml, of this solution was poured into the flask and it was heated with a water bath at 50°C. Tetranitroaniline, 50g, was added in small portions during 75 minutes, with simultaneous addition of the remaining alcoholic ammonia solution. The first portions of tetranitroaniline dissolved to a red-orange solution which became cloudy after two minutes and then a fine yellow crystalline precipitate appeared while the liquid remained orange colored. These color changes were repeated as the tetranitroaniline was added, although the initial red color was considerably masked by the precipitate as the reaction progressed. After all the tetranitroaniline was added the reaction mixture was stirred for two hours, the temperature of the water bath being maintained at 50°C. The reaction mixture was then chilled and the product filtered off, washed with methanol, acetone and water. It was dried in a vacuum oven at 100°C for 20 hours, and weighed 32.75 g, which is 72% of theory. It consisted of very fine needles, orange yellow in color, and melted at 280-282°C. It can be recrystallized from glacial acetic acid, dioxane, or nitrobenzene (lit. 288°C).

The ammonium salt of 2,4,6-trinitro-3-aminophenol was found as the main by-product of the reaction. This was obtained by evaporation of the filtrate from the diaminotrinitrobenzene. Approximately 9 gms of a crystalline solid were obtained. This was recrystallized from water with Norite as yellow needles which melted with decomposition at 248°C. Acidification of an aqueous solution of this product produced a yellow crystalline product which was recrystallized from alcohol and melted at 179-181°C.

2,4,6-Trinitro-3-aminophenol, for reference purposes, was prepared by dissolving 10 gms tetranitroaniline in 60 ml acetone containing 5 ml water on a hot plate (about 15 minutes), then distilling off the acetone until the first crystals appeared (about 20 ml solution remaining). The product recrystallized from alcohol in yellow leaflets melting at 179-181°C (2).

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Melting point determinations of mixtures of 2,4,6-trinitro-3-aminophenol thus prepared and the product isolated from the reaction above showed no depression of the melting point, nor was there any depression of melting point on mixing the ammonium salt isolated from the reaction mixture with that prepared from the free phenol.

About two grams of a dark red, water soluble, crystalline product were also isolated from the filtrate from the preparation of diaminotrinitrobenzene. This product was not identified, but is assumed to be a reduction product of tetranitroaniline.

Thus, about 96% of the tetranitroaniline used in the reaction is accounted for.

TABLE 227
Reaction of Anisole with Tetranitroaniline (TNA)

Expt. No.	Addition Method/ ^a	Reaction Solvent/ ^b	Al NH ₃ /g	Reaction Time	Yield	m.p.	Stability	Temp. Reaction
5453-70A	Recryst	Sol. A	50% CH ₃ OH	3	1 hr.	78.6%	262	2.3 Room T.
" 73A	"	" A	50% C ₂ H ₅ OH	3	1-1/2 hr.	83	282-3	2.7 Room T.
" 84A	Crude	" B	H ₂ O	3	45 min.	74		3.84 Room T.
" 87C	"	Solid	50% CH ₃ OH	1.5	40 min.	92	282-283	3.63 50°C
" 88A	"	Sol. B	50% CH ₃ OH	3	1 hr.	60	282-283	2.5 Room T.
" 90B	"	Solid	50% CH ₃ OH	1.5	35 min.	87.6	282	4.82 70-75°C
" 92A	"	Solid	50% Cellulosolve	1.5	45 min.	77.0	280-282	15.5 50°C
" 92C	"	Sol. B	50% CH ₃ OH	1.5	20 min.	73.0	280-282	9.63 50°C
" 93A	"	Solid	CH ₃ OH	1.5	45 min.	70.2	280-282	2.12 50°C
" 93B	"	Solid	95% C ₂ H ₅ OH	1.5	40 min.	63.0	280-282	2.23 50°C
" 93C	"	Solid	50% CH ₃ OH	2.0	1-1/4 hr.	69.0	280-282	5.75 50°C
5437-1B	"	Solid	CH ₃ OH	1.0	110 min.	70.0	278-280	9.7 50°C
" 2	"	Solid	CH ₃ OH	2.0	110 min.	60.5	280-282	2.11 50°C
" 15A	50 g	Solid	CH ₃ OH	2.0	3-1/4 hr.	72.0	280-282	2.90 50°C
" 15B	50 g ^{1/2}		CH ₃ OH	2.0	3-1/4 hr.	80.0	278-280	5.90 50°C

^a Addition method.

Solution A - Recrystallized TNA in Cellulosolve solution.

Solution B - Crude TNA in Cellulosolve solution.

^b Other solvents, worked less well: dioxane, tetrahydrofuran, dimethoxy ethane, acetonitrile, acetone and liquid ammonia.

^c Volume CH₃OH reduced by 1/2 from 5437-15A

^d Stability is cc/g : hour; at 26°C for 2 hours.

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Preparation of 2,4,6-Trinitro-3-Methoxyaniline: Crude tetranitroaniline 10 g was added to 50 ml methanol in a 100 ml round bottom flask fitted with a reflux condenser, and the mixture was heated to reflux, by means of a water bath, for an hour. At that time the tetranitroaniline had all dissolved. When the orange colored solution was allowed to cool to room temperature, a mass of well formed yellow needles separated. This product was filtered off, washed with a little alcohol and dried. It weighed 0.1 g. A second crop of 0.4 g was obtained by concentration of the filtrate. The total yield was 0.5 g or 90% of the theoretical. The melting point of the product was 135°C, (lit. 131°C), (2).

Preparation of Diaminotrinitrobenzene from 2,4,6-Trinitro-3-Methoxyaniline: A solution of 2,4,6-trinitro-3-methoxyaniline (1.35 g) in 50 ml of methanol was prepared in a 100 ml, 3-neck, round bottom flask with a mechanical stirrer and dropping funnel. This solution was heated to 50°C in a water bath while a solution of 10 ml of methanol and 4 ml of concentrated ammonium hydroxide was added dropwise during ten minutes. The solution became red-orange followed by a yellow precipitate in two minutes. The mixture was stirred for two hours at 50°C. Then the produce was filtered, washed with methanol and dried. It weighed 1.12 g, or 95.8% of theoretical, and melted at 278-280°C, darkening above 250°C.

Solid 2,4,6-trinitro-3-methoxyaniline was added to a solution of methanol and concentrated ammonium hydroxide as in the preparation of diaminotrinitrobenzene from tetranitroaniline. The product formed was similar in color, crystal structure, yield and melting point to that above.

Adding ammonia (gas) to a solution of 2,4,6-trinitro-3-methoxyaniline produced well formed crystals (needles) of good clear yellow color, in excellent yield, 93%, melting at 280-282°C without darkening. This last method would be most suitable for the preparation of diaminotrinitrobenzene via the methoxy derivative and should avoid the phenolic by-product which is formed in the direct amination of tetranitroaniline. However, as yet, vacuum stability of the preparations from the methoxy compound has not been acceptable. Work is being continued on this preparation.

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