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HEAT RESISTANT EXPLOSIVES IX (U)

3 AUGUST 1960



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HEAT RESISTANT EXPLOSIVES IX (U)

Improved Procedures for the Preparation of 1,3-Dimethoxy-  
2,4,6-trinitrobenzene, DMTNB, an Intermediate in the Preparation  
of 1,3-Diamino-2,4,6-trinitrobenzene, DATB

by

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ABSTRACT: Improved procedures for the preparation of 1,3-dimethoxy-2,4,6-trinitrobenzene, DMTNB, an intermediate in the preparation of 1,3-diamino-2,4,6-trinitrobenzene are described. Foaming problems previously encountered in the preparation of this compound have been solved by using anhydrous conditions. The procedures described involve the use of anhydrous sulfuric-nitric acid and potassium nitrate-sulfuric acid mixtures as nitrating agents.

CHEMISTRY RESEARCH DEPARTMENT  
U. S. ARMY RESEARCH LABORATORY  
WHITE OAK, SILVER SPRING, MARYLAND

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NAWWEPS Report 7271

3 August 1960

This report describes improved procedures for the preparation of 1,3-dimethoxy-2,4,6-trinitrobenzene, an intermediate in a method of preparation of DATB. The work comprised an effort to overcome difficulties previously encountered in the preparation of this compound and was performed under Task No. FR-44. While laboratory preparations show excellent promise, larger scale trials would be necessary before its adoption could be recommended.

W. D. COLEMAN  
Captain, USN  
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*Albert Lightbody*  
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By direction

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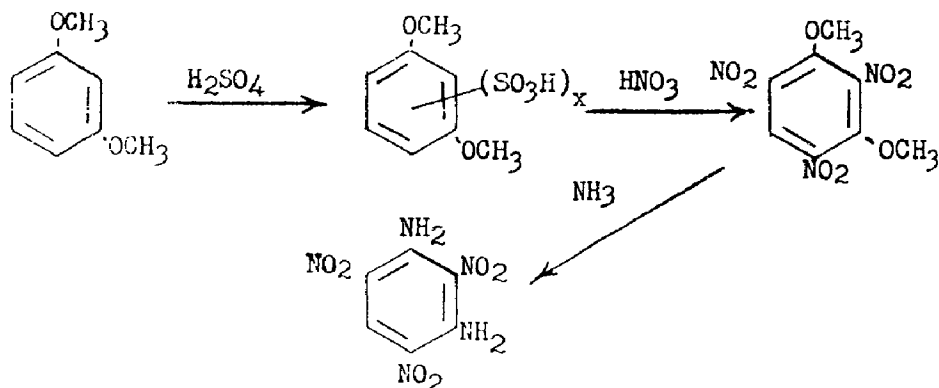
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HEAT RESISTANT EXPLOSIVES IX (U)

Improved Procedures for the Preparation of 1,3-Dimethoxy-2,4,6-trinitrobenzene, DMTNB, an Intermediate in the Preparation of 1,3-Diamino-2,4,6-trinitrobenzene, DATB

INTRODUCTION

The preparation of DATB from 1,3-dimethoxybenzene via 1,3-dimethoxy-2,4,6-trinitrobenzene, DMTNB, according to reaction I has been reported (Ref. (1)).



The excellent quality of the product (Refs. (1) and (2)) and the absence of sensitive intermediates make the process attractive. However, foaming during the nitration step created a considerable problem and dampened enthusiasm for the procedure, particularly for use in large-scale production. The foaming problem has now been solved and the procedure should be easily adaptable to large-scale syntheses.

It was suspected that the evolution of gases which caused the foaming might be due to water present in the system. To test this hypothesis several runs were made using 100% sulfuric acid, prepared by mixing 96% acid with 30% oleum, for the sulfonation and adding potassium nitrate to effect the nitration. This procedure gave yields of 81-95% of crude DMTNB without apparent gassing or foaming. Its primary drawbacks were the necessity of adding a dry ingredient and the thickness of the reaction mixture which was probably due to the precipitation of potassium bisulfate.

The use of 100% sulfuric acid in the sulfonation step followed by the addition of nitric acid-30% oleum mixtures such that the system remained approximately anhydrous at all times proved to be the better procedure (see runs 1-5, 8, 10, 11 and 12, Table I). This procedure worked well without fuming or foaming and the yields were 91-94% in the small scale runs and

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86-89% in the scale-ups. The consistency of the reaction mixture was varied by changing the volume of 100% sulfuric acid at the sulfonation stage. The product in each case was beautifully crystalline and suitable for conversion to DATB without further purification.

When an appreciable excess of oleum above that required to make anhydrous sulfuric acid was used in the sulfonation step, foaming and decomposition took place and the desired product could not be isolated. The use of an appreciable excess of oleum in the nitration step also resulted in pronounced gassing and foaming. The nature and source of the gases formed during the nitration reaction have not been determined. However, they probably arise from side reactions of the dimethoxybenzene or DMTNB, probably the former.

The only by-product isolated during these studies was 3-methoxy-2,4,6-trinitrophenol, small amounts of which precipitate from the filtrate and washings on standing. Since this compound is considerably more soluble in water and aqueous acid than DMTNB, it is easily removed by washing. Should small amounts be carried over to the amination step, the ammonium salt of 3-amino-2,4,6-trinitrophenol would be formed. This compound is appreciably soluble in the amination solvent and would be left in solution.

TABLE I  
PREPARATION OF 2,3-DIMETHOXY-2,4,6-TRINITROBENZENE (DMTB)  
FROM 4-DIMETHOXYBENZENE (DMB) BY MIXED ACID NITRATION

Run No.	Reactor size, ml.	DMB, g.	Sulfonation <sup>a</sup>		Nitration <sup>b</sup>		DMTB Yield amt., % (m.p.)	Fuming or Foaming	Comments
			30% Oleum, ml.	96% H <sub>2</sub> SO <sub>4</sub> , ml.	30% Oleum, ml.	Nitric Acid, % (HNO <sub>3</sub> )			
1	100	2.1	9	15	11	7.5 (95.2%)	1147 g, 83% (121-3°)	YES	Best previous conditions, reac- tion mixture thick and stirring difficult.
2	100	2.1	4.5	7.5	11	7.5 (95.2%)	3.9 g, 94% (124-6°)	NO	Relatively easily stirred mixture.
3	500	10.5	45	75	55	37.5 (95.2%)	19.2 g, 92% (124-5°)	NO	Mixture thicker than 2, but still stirrable.
4	500	10.5	22.5	37.5	55	37.5 (95.2%)	19.0 g, 91% (123-4°)	NO	Scale-up of Run 1.
5	500	10.5	12.4	20.6	55	37.5 (95.2%)	18.8 g, 90% (122-4°)	NO	Scale-up of Run 2.
6	500	10.5	66	53	55	37.5 (95.2%)	No product	NO	Mixture very thick, stirring difficult.
7	500	10.5	34	56	55	37.5 (97.7%)	17.0 g, 82% (122-4°)	YES	Too much oleum in first step led to decomposition <sup>c</sup> .
8	500	10.5	22.5	37.5	12.8	37.5 (97.7%)	17.6 g, 85+ <sup>d</sup> / <sub>e</sub> (125-6°)	SLIGHT NO	Too much oleum in second step led to gassing.
9	5,000	157.5	675	1125	825	563 (97.7%)	Incomplete recov- ery (114-9°)	YES	Good conditions. Product filtered before drowning. Product filtered Scale-up of run 3 but using more concentrated HNO <sub>3</sub> . Excess oleum led to gassing and difficulty in stirring.
10	5,000	210	450	750	256	750 (97.7%)	363 g, 87% (123-4°)	NO	Scale-up of run 8 but drowning reaction mixture. Good conditions.
11 <sup>f</sup>	5,000	210	450	750	256	750 (97.7%)	357 g, 86% (123-4°)	NO	Double blade paddle, 15 min. sul- formation, 15 min. at 40-45° after nitration. Stirring good.
12	5,000	105	450	750	128	375 (97.7%)	185 g, 89% (121-3°)	NO	Thinner reaction mixture than runs 10 or 11.

<sup>a</sup> Standard conditions for sulfonation, 30 min. at 90-95°. <sup>b</sup> Nitric acid-oleum mixture added dropwise over 15-30 min. period keeping temperature below 30°. Mixture then heated to 60-65° for 30 min. <sup>c</sup> Navord Report (NOL) 6208. HNO<sub>3</sub> add'n required 150 min.; then stirred 15 min. at 30°. <sup>d</sup> Only a reddish pasty product was recovered. <sup>e</sup> Reaction mixture filtered directly. Filter cake washed first with 20% H<sub>2</sub>SO<sub>4</sub>, than with water. An additional several percent product recovered by drowning filtrate. <sup>f</sup> Described in detail in experimental section.

EXPERIMENTAL

Mixed Acids Procedure.

A three necked, round bottomed, five liter flask was fitted with thermometer, dropping funnel, air cooled condenser and a two bladed mechanical stirrer (Note 1), and charged with a mixture of 450 ml

-----  
Note 1. - Although the stirring difficulties previously encountered are very much decreased with the elimination of foaming, the reaction mixture at one stage becomes fairly thick at the surface. A simple double-bladed stirrer with one paddle near the bottom and the other at the surface allows effective stirring of the reaction mixture with a "garden variety" stirring motor.  
-----

30% oleum and 750 ml 96% sulfuric acid. Two hundred ten grams (194.4 ml) of m-dimethoxybenzene (Koppers Co.) was added to the stirred solution over a five-minute interval and the greenish mixture was heated to 90-95° for fifteen minutes (Note 2), then cooled to 5°.

-----  
Note 2. - A slight excess of oleum in the sulfonation step seems to do no harm and is not carried over to the next step as the sulfur trioxide in excess of that required to form 100% H<sub>2</sub>SO<sub>4</sub> apparently evaporates at the elevated temperature. In the presence of a large excess of oleum, however, extensive decomposition may occur (see run 6, Table I). For most of the reactions of Table I a 30 minute heating period was employed. Decreasing this to fifteen minutes apparently had no adverse effect.  
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A cold solution of 100% nitric-100% sulfuric acids, prepared by adding 750 g of Naval Propellant Plant nitric acid (assay 97.7%) to 256 g 30% oleum (Note 3) was then added dropwise to the stirred, cooled mixture at such a

-----  
Note 3. - A large excess of oleum in the nitration step leads to foaming as the temperature is raised (see runs 7 and 9, Table I); a large deficiency of oleum leads to foaming, probably due to hydrolytic-oxidative decomposition of the organic materials, as in NavOrd Report (NOL) 6208. There is probably a several percent composition range, centering around 100% nitric-100% sulfuric, within which there is no foaming.  
-----

rate as to keep the temperature below 30°. There soon formed a reddish precipitate which turned light tan in color and at the surface approached the consistency of a thick milk shake when about one third to one half of the nitric acid solution had been added (Note 4). As further nitric acid

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Note 4. - This is the critical stage as far as stirring is concerned. If gas bubbles become entrapped in the thick slurry which floats on the surface, a heavy foam forms. The foam is difficult to agitate, adheres strongly to the walls and introduces considerable problems of heat transfer. If stirring were discontinued at this point under the reaction conditions of NavOrd Report (NOL) 6208, the foam would expand to fill the reactor, then begin to climb out the top. Resumption of stirring would only hasten the process. In one run under the present conditions (run 10, Table I), stirring was intentionally discontinued several times. There was no tendency to foam and stirring could readily be resumed. A good yield of high quality product was obtained.  
-----

solution was added the reaction mixture became thinner. The addition required fifteen to thirty minutes. The contents of the flask were then heated to 40-45°, maintained at this temperature for fifteen minutes (Note 5), then cooled in an ice bath.

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Note 5. - The standard conditions of Table I involved a thirty minute heating period at 60-70°. The shorter heating period under the milder conditions had no adverse effect on yield or quality of the product.  
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The reaction mixture was drowned by pouring the slurry over 5-6000 g of crushed ice and the product filtered by suction onto a coarse sintered glass funnel, then washed with ten liters of cold water (Note 6).

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Note 6. - The first washings may come through cloudy. If the cloudy solution is allowed to stand, yellow crystals of 3-methoxy-2,4,6-trinitrophenol, m.p. 84-86°, form. There is little danger of product loss in over-washing. The solubility of DMTB in water at 25° has been determined to be in the order of 0.02-0.03 g/l.  
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After air drying, 357 g (86%) of 1,3-dimethoxy-2,4,6-trinitrobenzene, m.p. 123-124°, was obtained as a cream colored, nicely crystalline material which is probably suitable for conversion to DATB without further purification.

In an alternative procedure (run 8, Table I) the reaction mixture was filtered directly without drowning, then washed with iced 20% sulfuric acid and finally with water. A high quality product, m.p. 125-126° was obtained in 85% yield. An additional several percent of a very much poorer grade product was recovered by drowning the mother liquor.

Sulfuric Acid-Potassium Nitrate Procedure.

A 500 ml three necked round bottomed flask was fitted with a thermometer, dropping funnel, air cooled condenser and two bladed mechanical stirrer and charged with 100 ml of 100% sulfuric acid. While stirring vigorously, 10.5 g (0.076 moles) of 1,3-dimethoxybenzene was added slowly. During the addition, the solution turned dark green and the temperature rose to 45°. The mixture was heated on a steam bath to 95-100° and then cooled to 10° on an ice bath. The mixture had turned dark brown and a small amount of precipitate had formed. An amount of 35 g (0.35 moles) of potassium nitrate was added portion-wise keeping the temperature at 25° or lower. After about 2/3 of the dry salt had been added, there ceased to be an exotherm and the mixture was a reddish brown paste. When all of the potassium nitrate had been added, the mixture was heated slowly to 50° and held at about that temperature for 15 minutes during which time it became a very thick light yellow batter but no foaming was apparent. The mixture was then cooled to room temperature and drowned in approximately one liter of crushed ice and water. The product was recovered by filtration and washed with approximately one liter of cold water. After drying in air, the yield was 19.7 g (95%) of an almost white crystalline product, m.p. 123-4°. There was no further precipitation from the filtrate and washings after standing four days.

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REFERENCES

- (1) NAVORD REPORT 6208, "Heat Resistant Explosives III, 1,3-Diamino-2,4,6-trinitrobenzene, DATB, From 1,3-Dimethoxybenzene." J. C. Dacons and M. J. Kamlet, 15 December 1958.
- (2) NAVORD REPORT 6225, "Heat Resistant Explosives V, 1,3-Diamino-2,4,6-trinitrobenzene, DATB, By Ammonolysis of Methoxytrinitrobenzene Compounds." K. G. Shipp, T. N. Hall and M. E. Hill, 15 December 1958.

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