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Process Development Studies

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NEW SYNTHESIS OF TATB. PROCESS DEVELOPMENT STUDIES

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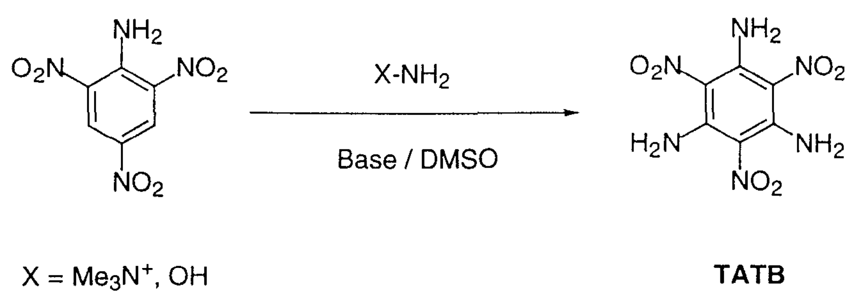
ABSTRACT

We described a new synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in 1996 at the 27th International Annual Conference of ICT. 1,1,1-Trialkylhydrazinium salts are highly reactive reagents which aminate nitroaromatic compounds through vicarious nucleophilic substitution (VNS) of hydrogen. When applied to picramide, these reagents produce TATB in high yield. Traditionally, TATB has been manufactured in the USA by nitration of the relatively expensive and domestically unavailable 1,3,5-trichlorobenzene (TCB) to give 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB) which is then aminated to yield TATB. Elevated temperatures (150° C) are required for both reactions. Our new VNS synthesis potentially affords an inexpensive and a more environmentally benign preparation of TATB. We describe in this report our progress in scaling up the synthesis of TATB from the laboratory to the pilot plant. We will discuss structure and control of impurities, changes in yield/quality with reaction conditions, choice of solvents, workup and product isolation, safety, and environmental considerations. Particle size characterizations as well as small-scale safety and performance testing will also be discussed.

INTRODUCTION

The compound 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is a reasonably powerful high explosive (HE) whose thermal and shock stability is considerably greater than that of any other known material of comparable energy.[1] The high stability of TATB favors its use in military[2] and civilian applications[3] when insensitive high explosives are required. In addition to its applications as a HE, TATB is used to produce the important intermediate benzenehexamine.[4-8] Benzenehexamine has been used in the preparation of ferromagnetic organic salts[8] and in the synthesis of new heteropolycyclic molecules such as 1,4,5,8,9,12-hexaazatriphenylene (HAT) that serve as strong electron acceptor ligands for low-valence transition metals.[5,7] The use of TATB to prepare components of lyotropic liquid-crystal phases for use in display devices is the subject of a German patent.[9]

There is a definite need for a less expensive and more environmentally benign production of TATB. Current production techniques for making TATB are expensive and rely on environmentally hazardous reagents and relatively harsh conditions. We recently reported a novel approach to the synthesis of TATB which utilizes relatively inexpensive starting materials and mild reaction conditions.[10-12] This new process relies on amination of nitroaromatic starting materials using a reaction known as Vicarious Nucleophilic Substitution (VNS) of hydrogen.[13] Scheme 1 outlines the approach.



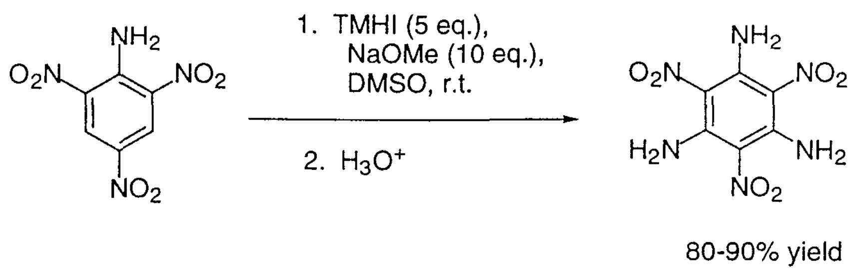
Scheme 1. VNS Synthesis of TATB from Picramide.

We have been working on the scale-up of this new synthesis with the goal of developing a new production of TATB. This paper examines the influence of aminating reagent, base, solvent, temperature, quenching, etc. on yield, purity and morphology of TATB product.

PROCESS STUDIES WITH 1,1,1-TRIMETHYLHYDRAZINIUM IODIDE AS THE VNS AMINATING REAGENT

Initial Studies

We have determined that 1,1,1-trimethylhydrazinium iodide (TMHI) is the most efficient aminating reagent available for the VNS synthesis of TATB.[10-12,14] Picramide and solid TMHI are dissolved in DMSO, and base (sodium methoxide or ethoxide) is added to initiate the reaction. The reaction is conducted at room temperature, and is complete in under 3 hours, giving TATB in 80-90% yield (Scheme 2).



Scheme 2. VNS Synthesis of TATB using TMHI

The major expected impurity is 1,3-diamino-2,4,6-trinitrobenzene (DATB), which results from incomplete amination. Under these reaction conditions, no DATB ($\leq$0.5%) was detected by FTIR spectroscopy or direct insertion solids probe mass spectrometry (DIP-MS).

Studies on Varying Reaction Conditions

The initial studies of this reaction employed picramide concentrations $\leq$ 0.13 M with large excesses of TMHI and base to drive the reaction to completion. We examined the effects of decreased solvent and reagents on the reaction. Table 1 summarizes some of the results of this study.

Entry	Mole Ratio of Reagents (Picramide:TMHI: Base)	Base Used	Molarity of Picramide, mol/L	% Yield (Total Product)	Purity of TATB, %
1	1 : 5 : 10	NaOMe	0.13	89	> 99
2	1 : 4 : 8	NaOMe	0.11	82	> 99
3	1 : 4 : 8	NaOMe	0.22	86	≈ 97
4	1 : 4 : 8	NaOEt	0.22	80	≈ 97
5	1 : 2.5 : 5.6	NaOMe	0.27	86	88
6	1 : 3.1 : 8.4	NaOMe	0.11	81	> 99

Table 1. Effect on yield of TATB by varying quantities of reagents.

In general, the reaction will run efficiently up to 0.2 M picramide and using 3 eq. TMHI. The success of the reaction seems most dependent on base, requiring 8 eq. to proceed efficiently. The yield and purity of TATB drop significantly if an insufficient excess of base is used. It was also found that the reaction is very sensitive to the quality of the base, particularly in the case of sodium methoxide: older lots of the base which had been exposed to air, even while retaining the identical physical appearance of fresh material, gave reduced yields (or, in the worst case, no yield at all) of TATB.

Thus far, the largest scale attempted has been the 10 gram level. The reaction appears to scale linearly, delivering 82% yield of TATB at >99% purity. Larger scale work is currently in progress.

Methods of Quenching the Reaction

All initial studies of this reaction used either aqueous mineral acid solutions or water to quench the reaction and induce precipitation of TATB. This method results in a very small particle size, on the order of 0.2-1 μm. It was reasoned that quenching with a weak organic acid in the absence of water might result in larger particle size. We found that quenching with citric acid monohydrate in DMSO produced particles in the 1-10 μm range. A larger particle size (20 μm) has recently been obtained using other organic acids.[15] It was also noticed that the final color of the product TATB varied when different quenching solutions were used (Table 2).

Entry[1]	TMHI Addition Method[2]	Quench Method	% Yield TATB	Physical Appearance
1	solid	aq. HCl	--	Yellow powder, >99% TATB
2	solid	aq. HNO_3	82	pale tan-yellow powder, >99% TATB
3	in situ	aq. HNO_3	86	pale tan-yellow powder, >99% TATB
4	solid	citric acid/DMSO	80	yellow-maize powder, >99% TATB
5	in situ	citric acid/DMSO	86	yellow-maize powder, >99% TATB

Notes: 1 Reaction conditions were 2 mmol picramide, 4eq TMHI, 8eq NaOMe in 20 mL DMSO
2. See next section for description of TMHI addition methods.

Table 2. Effects of varying TMHI addition method and quenching method.

In Situ Generation of TMHI

Although TMHI is easy to prepare and handle[12,14] its use in the solid form requires an additional synthesis and isolation step, which would increase the overall product costs at production scale. Therefore, several experiments were conducted which examined the *in situ* generation of the reagent. To accomplish this, the precursor reagents--1,1-dimethylhydrazine and methyl iodide--were sequentially added to DMSO and allowed to react. Picramide was then added to this solution, followed by base, and the reaction was allowed to proceed as before. This method appears to give at least as good results as the original method, and in several cases gave slightly higher yields of TATB (Table 2).

Quality of Starting Materials

As mentioned earlier, the reaction appears to be very sensitive to the condition of the sodium methoxide. Several attempts at making TATB using an older lot of NaOMe failed, even though the base had been stored in a dessicator and the physical appearance of the base was no different from newer material (white, free-flowing fine powder). Analysis of this lot of NaOMe revealed that much of it had been converted to sodium carbonate by absorption of ambient CO_2 which inactivated it in the VNS reaction. Good yields (>85%) were again obtained when fresh NaOMe was employed.

In a few experiments, there was some variation in the purity of the starting picramide, and this appears to have affected the final appearance of the TATB, even though the TATB appears to be chemically >99% pure by spectroscopy. The principal impurity in the picramide was picryl chloride (vide infra). Impurity levels of greater than a few percent cause the product TATB to darken and, of course, reduce the total yield of TATB (although corrected yields are similar to those using pure picramide). High levels of impurities in starting picramide also change the crystal morphology of the product TATB.

Product Analysis

Since TATB is nearly insoluble in most solvents, simpler forms of chemical analysis such as NMR or Gas Chromatography are not practicable. Therefore, other techniques which allow analysis of the solid were investigated. The first of these attempted was Fourier Transform Infrared Spectroscopy (FTIR). The amine N-H stretching modes in TATB produce two characteristic absorptions at approximately 3225 and 3325 cm^{-1}, while those for DATB occur at 3360 and 3390 cm^{-1}. By using Nujol mull preparations for TATB samples, we have found that DATB can be reliably detected at concentrations of 1% or greater.

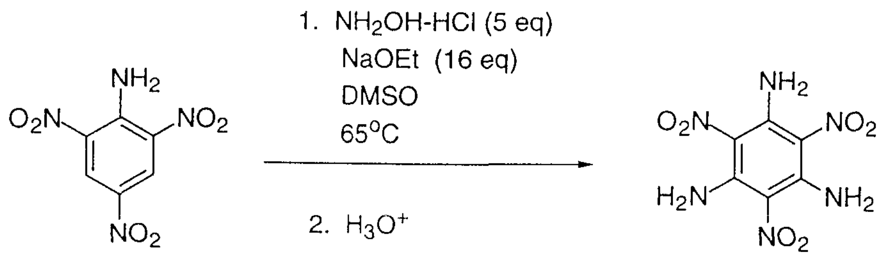
Another technique for TATB product analysis which we are using is direct insertion solids probe mass spectrometry (DIP-MS). In this technique, a solid sample of TATB is placed in a sample holder at the end of a probe The probe tip is inserted into a mass spectrometer, and is heated to cause the solid sample to evaporate into the MS ion volume, thereby allowing analysis of solids. Compounds with differing volatilities will evaporate at different times (a process known "probe distillation") and can thus be resolved to some extent by the MS detector. We have found that DATB can be reliably detected in a TATB sample at 1% concentration, and in some cases in concentrations as low as 0.1%.

Selected samples were submitted for elemental analysis. In early samples, the elemental analysis revealed that the product TATB was contaminated with 1-2% iodine. Unreacted TMHI as a source of iodine contamination was ruled out as TMHI could not be detected in the TATB samples using mass spectroscopy We are examining the effects of quenching methods on impurities such as iodine, chlorine, etc

In order to compare the TATB from this VNS process to that from more traditional processes, we have also conducted DSC, CRT, DH_{50}, spark and friction sensitivity tests on this material. In general, results are similar to those observed for TATB, except that thus far, the DSC values run consistently low by about 20-30 degrees. This may be an artifact of the much finer particle size produced by this process, although to confirm this more tests will be needed.

PROCESS STUDIES WITH HYDROXYLAMINE AS THE VNS AMINATING REAGENT

Due to the relative toxicity and cost of reagents used to make TMHI, we reinvestigated the use of hydroxylamine as a VNS aminating reagent. Hydroxylamine is in fact, the earliest known example of a VNS aminating reagent,[16] although the term "VNS" was coined many decades later.[13] Our earliest work in aminating picramide with hydroxylamine was disappointing since the reaction only provided DATB containing trace amounts of TATB at best.[11] The poor reactivity of hydroxylamine was independently confirmed by Seko and Kawamura who were unable to aminate nitrobenzene using hydroxylamine.[17] The low cost of hydroxylamine as an aminating reagent initiated further investigation and recent work in our laboratories showed that hydroxylamine will aminate picramide to TATB at elevated temperature (65-90°C) to furnish TATB (Scheme 3). [18]

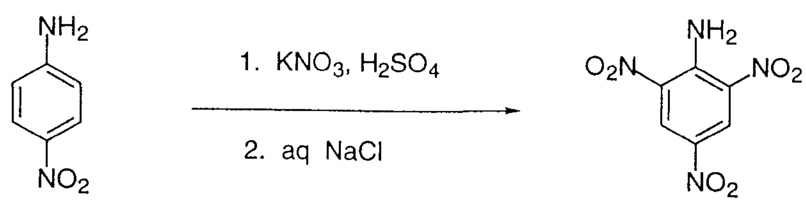


Scheme 3. VNS Synthesis of TATB using Hydroxylamine Hydrochloride.

Although the work with hydroxylamine is preliminary, satisfactory yields of TATB at approximately 97% purity have been achieved. Thus far the best results were obtained using NaOEt as the base in DMSO at 65°C for 6-12 hours. We are in the process of testing other hydroxylamine salts and anticipate the purity of the product will increase to over 99%. The relatively low cost of hydroxylamine salts makes this option very attractive.

STUDIES OF PICRAMIDE SYNTHESIS

As mentioned earlier, picramide is no longer commercially available. Therefore, as part of this project, we were required to reinvestigate methods for its production. One simple method is nitration of 4-nitroaniline, an inexpensive commodity chemical (Scheme 4). [19]



Scheme 4. Synthesis of Picramide.

Early studies in our laboratories using similar conditions gave good results, although some impurities were noted, the most significant being picryl chloride. (The workup of picramide is facilitated by the addition of brine, which apparently gives rise to the picryl chloride impurity.) In one case, picryl chloride was present in up to 20% impurity. Such impurities would require expensive recrystallization processing, since they affect the quality of TATB produced, as discussed earlier. However, our project collaborators at Pantex (Mason & Hanger Corporation, Amarillo, Texas) have improved the process and have prepared picramide in high yields (90%) and purity (>99.5%).

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