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NEW SYNTHESIS OF TATB. SCALEUP AND PRODUCT CHARACTERIZATION*

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ABSTRACT

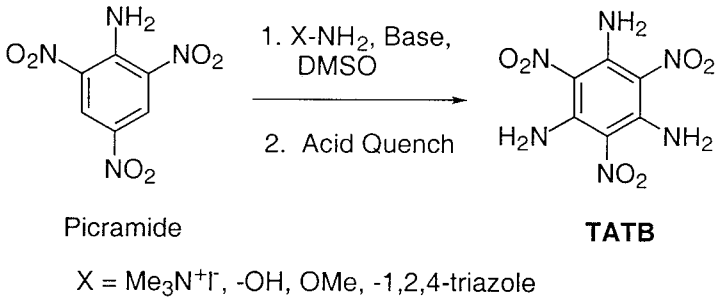
At the 29th International Annual Conference of ICT (1998), we described the results of laboratory-scale process development studies for a new synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). This new synthesis approach—which uses vicarious nucleophilic substitution (VNS) methodology—converts picramide to TATB in high yield, and potentially at lower cost and with fewer environmental effects than existing synthetic approaches. In this report we describe results of our work on producing TATB by the VNS method at the pilot plant scale. 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. Product characterization (particle size, DSC, HPLC, etc.) as well as small-scale safety and performance testing will also be discussed.

INTRODUCTION

The high degree of thermal and shock stability of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is well known, and this compound is often used as a benchmark for comparing insensitive explosives.[1] These remarkable characteristics of TATB favor its use in military[2] and

civilian applications[3] when insensitive high explosives are required. Additionally, TATB is a precursor to the intermediate benzenehexamine,[4-8] which 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 has also been described.[9]

The conventional techniques for producing TATB are expensive and relatively complex, since they rely on environmentally hazardous intermediates and use relatively harsh reaction conditions. Several years ago, we 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.

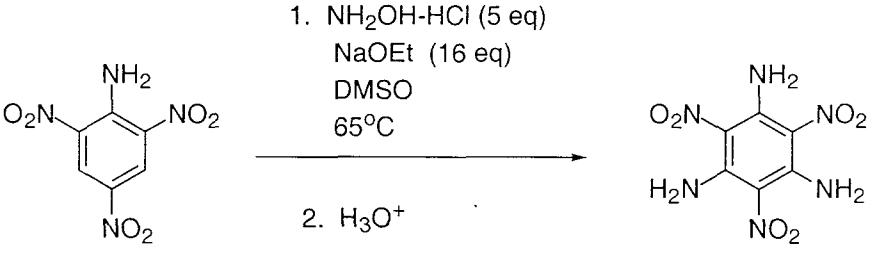
We have been working on the scale-up of this new synthesis with the goal of developing a new production of TATB. Our initial studies showed that 1,1,1-trimethylhydrazinium iodide (TMHI) was the most efficient aminating reagent available for the VNS synthesis of TATB.[10-12,14] However, use of TMHI in larger scale work proved impractical. During the process, large amounts of the corrosive, noxious gas trimethylamine are produced, and purity problems are encountered in the product TATB at higher scales.

Consequently, the use of other VNS aminating reagent--such as hydroxylamine and 4-amino-1,2,4-triazole (ATA)--was investigated. This paper examines the results of our work on the scale-up of TATB synthesis using these reagents, including the effect of reaction conditions on yield, purity, small-scale performance and morphology of the TATB product.

PROCESS STUDIES WITH HYDROXYLAMINE AS THE VNS AMINATING REAGENT

Initial Studies

Hydroxylamine is the earliest known example of a VNS aminating reagent,[15] although the term "VNS" was not coined until 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.[16] However, the low cost of hydroxylamine as an aminating reagent initiated further investigation and we found that hydroxylamine will in fact aminate picramide to TATB at elevated temperature (65-90°C. One example of successful reaction conditions is outlined in Scheme 2.[17]



Scheme 2. VNS Synthesis of TATB using Hydroxylamine Hydrochloride.

The relatively low cost of hydroxylamine salts makes this option very attractive.

Studies on Varying Reaction Conditions

In an earlier report[18] we discussed the effects of decreased solvent and reagents on the synthesis of TATB using TMHI. Similar studies were done for hydroxylamine, and it was found that the reaction will run efficiently up to 0.2 M picramide and using 5 eq. of hydroxylamine hydrochloride. The reaction requires twice as much base as with other VNS aminating reagents, since the accompanying hydrochloride moiety needs to be neutralized for the reaction to work. As a result, the reaction mixture forms a rather thick slurry, which makes mixing more difficult. In small-scale tests, the reaction under these conditions produced a 70% yield of TATB, in ~97% purity.

An anomaly has been the formation of an unusual impurity at higher-scale reactions. It was found that as the reaction scale was increased, the product TATB had an increasingly green tint to it. In extreme cases, the product was a distinct drab green. Based on spectroscopic evidence (FTIR and MS) and theoretical calculations, it is believed that the impurity is 1-nitroso-3,5-dinitro-2,4,6-benzenetriamine (Figure 1). Such a compound might result from partial reduction of TATB by hydroxylamine.). It was estimated that this impurity is present in the TATB in up to 10% concentration.

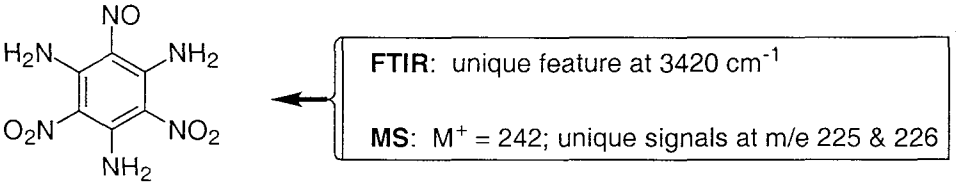


Figure 1. Structure of 1-nitroso-3,5-dinitro-2,4,6-benzenetriamine.

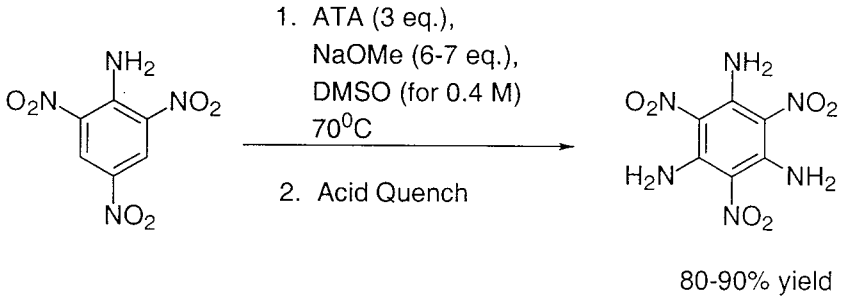
Experiments are currently being conducted to attempt to eliminate the formation of this impurity by introducing oxidants or radical scavengers to the reaction mixture.

In Situ Generation of Hydroxylamine

In order to reduce the thickness of the slurry, attempts were made to pre-neutralize the hydrochloride, filter off the resulting NaCl, and thus generate salt-free hydroxylamine for use in the reaction. Curiously, application of this method failed to produce any TATB, and in fact only small amounts of DATB were detected in the product. The reasons for this failure remain unclear.

PROCESS STUDIES WITH 4-AMINO-1,2,4-TRIAZOLE AS THE VNS AMINATING REAGENT

Due to the difficulties encountered in aminating picramide with hydroxylamine, we investigated a third VNS aminating reagent--4-amino-1,2,4-triazole (ATA). The use of ATA in the amination of nitroaromatics was first reported by Katritzky.[19] As with hydroxylamine, our initial studies using ATA were conducted at room temperature, and we similarly found that ATA only produced DATB under these conditions. However, upon reinvestigation, we found that at elevated temperature (65-70°C), ATA reacts very well with picramide to furnish TATB in excellent yield. Scheme 3 summarizes typical reaction conditions using ATA as the VNS aminating reagent.



Scheme 3. VNS Synthesis of TATB using ATA.

Several advantages with using ATA soon became apparent. First, the concentration of picramide in the reaction solution can be significantly increased while still retaining excellent

yield and product quality. We have conducted successful, small-scale experiments at up to 0.6M picramide using ATA. Second, the reagent is free of halides, thus ensuring the elimination of such contaminants from the product TATB. Third, the conversion of picramide is complete, and the purity of the product TATB is >99.9%. Product color is also very good, without any trace of the green tint found with hydroxylamine, nor the brown coloration sometimes seen with TMHI. The single disadvantage with ATA at this time is its relatively high cost. However, this is due to a low market demand; when ATA was made in large quantities, its cost was around $13/lb, and synthesis of ATA is simple.[20,21]

Because of these many advantages, ATA was selected as the reagent that we would use in our scale-up of the VNS TATB synthesis. In the lab, we conducted reactions of up to 100 grams, with high yields (92%) and very good product quality (>99.5% pure, golden yellow TATB). Small scale performance testing indicated that this TATB was essentially identical to that produced by traditional methods: highly insensitive to spark, friction and impact; sharp DSC exotherm at 370°C; and satisfactory CRT measurement.

With these results in hand, the process was repeated at our pilot plant facility at a 1 kg scale. Initial results at this scale were encouraging, although some technical difficulties were encountered which resulted in green discoloration (as seen with hydroxylamine) and a somewhat reduced yield. A subsequent experiment resolved most of these problems, and further trials are in progress. Details of these experiments will be presented.

METHODS OF QUENCHING THE REACTION

Upon completion, the reaction solution must be quenched with an acid or other proton source to induce precipitation of TATB. In early work, it was found that use of either aqueous mineral acid solutions or water to quench the reaction results in TATB with a very small particle size, on the order of 0.2-1 μm[18] . Use of organic acids, and quenching at elevated temperature, both increase the product TATB particle size. Thus far, the largest TATB

particles have been obtained by quenching the reaction at 65°C with a solution of salicylic acid in DMSO. See Table 1 for summary of results.

Entry[1]	Acid	Temperature	Particle Size
1	Mineral Acids, Water	25°C	< 1μm[1]
2	Acetic Acid	25°C	1-5 μm[1]
3	Acetic Acid (vapor)	25°C	10-30 μm[1]
4	Citric Acid/DMSO	25°C	5-10 μm[1]
5	Salicylic Acid/DMSO	25°C	5 μm[2]
6	Salicylic Acid/DMSO	65-70°C	25-29 μm[2]

Notes: 1. Particle size estimated by Scanning Electron Microscope photographs.
2. D[v, 0.5], as measured by Malvern Particle Analyzer.

Table 1. Effects of quenching method on TATB particle size.

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 or KBr pellet preparations ofTATB samples, we have found that DATB can be reliably detected at concentrations of 1% or greater. Additionally, as mentioned above, the green impurity found in some product TATB samples (suspected to be the mononitroso-analogue of TATB) can be detected by its N-H stretch absorption at 3420 cm^{-1}.

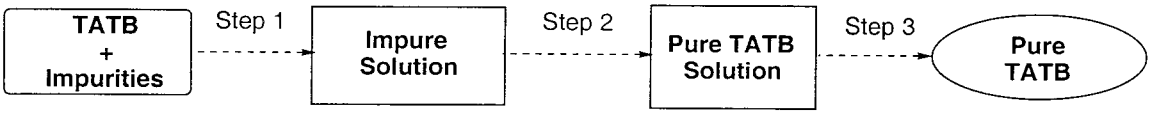
Another technique for TATB product analysis which we are using is direct insertion solids probe mass spectrometry (DIP-MS). In this technique, a solid sample of TATB is placed in a sample holder at the end of a probe. The probe tip is inserted into a mass spectrometer, and is heated to cause the solid 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%.

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. The results of these measurements compare favorable with TATB produced by the traditional methods.

PURIFICATION OF TATB

Because TATB is nearly insoluble in even the strongest solvents, it is not practical to purify it on a large scale using standard recrystallization methods. However, because of the impurities seen in our earlier TATB synthesis studies, we developed a new method for the purification of TATB. A very general procedure is outlined in scheme 4.



Scheme 4. Purification of TATB by derivatization.

At this time, the details of this method have been submitted for patent protection, and so cannot be included in this paper. However, we hope to be able to present these details in the near future.

ACKNOWLEDGEMENTS

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