**Review**

# Chemical conversion of energetic materials to higher value products

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## Abstract

The objective of this program is to develop new processes for the disposal of surplus energetic materials. Disposal through open burning / open detonation (OB / OD) is considered less attractive today due to environmental, cost and safety concerns. The use of energetic materials as chemical feedstocks for higher value products can provide environmentally sound and cost-effective alternatives to OB / OD. Our recent studies on the conversion of surplus energetic materials (Explosive D, TNT) to higher value products will be described.

*Keywords*: Energetic materials, Chemical conversion, Higher value products, 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB), Insensitive high explosive (IHE)

## 1. Introduction

The demilitarization of conventional munitions is producing millions of pounds of surplus energetic materials (propellants, high explosives and pyrotechnics). The disposal of these materials by open burning / open detonation (OB / OD) is becoming unacceptable due to public concerns and increasingly stringent environmental regulations. We have outlined scenarios utilizing surplus nitroarene explosives (Explosive D, TNT) as starting materials for industrial processes that produce higher value products (Fig. 1) [1), 2)]. We describe in this report our progress in obtaining 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), a higher value explosive, using starting materials from demilitarization inventories (Explosive D) or low-cost commodity chemicals (4-nitroaniline). In addition, we will examine the use of TNT as a starting material for the production of TATB and other higher value products.

## 2. Chemical conversion activities by earlier workers

### 2.1 Conversion of TNT to phloroglucinol

TNT (2,4,6-trinitrotoluene) has been used to produce phloroglucinol (1,3,5-trihydroxybenzene) which finds use in the pharmaceutical, cosmetics, textile-dying and photographic industries. The process to produce phloroglucinol from TNT (Fig. 2) was developed at the end of World War

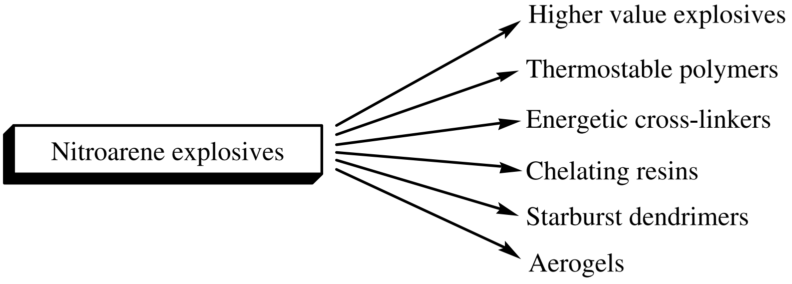

Fig. 1 Use of surplus nitroarene explosives (Explosive D, TNT) as feedstocks for higher value products.

II as a way to utilize the large surplus of TNT on hand[3]. TNT is oxidized by sodium dichromate in sulfuric acid to give 2,4,6-trinitrobenzoic acid (TNBA) which is then treated with iron and hydrochloric acid to allow simultaneous decarboxylation of TNBA to TNB and reduction of the amino groups to give 1,3,5-triaminobenzene (TAT). Acid hydrolysis (108 °C) of TAT yields phloroglucinol. The use of this process was discontinued in the USA in the 1970s due to problems associated with the waste disposal of acid liquors, iron, chromium and ammonium salts[4]. Recent improvements in the oxidation of TNT to TNBA and TNB[5] will allow us to revisit the use of TNT for the production of phloroglucinol as well as TATB.

### 2.2 Conversion of TNT to TATB

Atkins and coworkers described a conversion of TNT to TATB[6], [7] with the goal of developing a less costly production of TATB (Fig. 3). Hydrogen sulfide partially reduces TNT to 4-amino-2,6-dinitro- toluene (ADNT), which is then treated with nitric acid in sulfuric acid to provide pentanitroaniline (PNA).

Treatment of PNA with ammonia provides TATB in addition to polynitrophenol by-products (R. Atkins, personal communication). Although all of the reactants are relatively inexpensive, the cost of pollution abatement prevented the industrial scaleup of this process.

### 2.3 Disposal of munitions from the former German Democratic Republic

Wanninger has discussed the disposal of 300,000 tons of old and substandard munitions acquired when the former German Democratic Republic (GDR) was reunited with the Federal Republic of Germany (FRG) in 1989[8], [9]. Unfortunately, the disposal options available today were not available in Germany in the early 1990s when the disposal program was undertaken (Fig. 4). Particularly, the technologies for resource recovery and reuse ($R^3$) were not sufficiently developed and rotary kiln incineration was employed for the disposal of the surplus GDR munitions.

## 3. TATB

TATB is an insensitive high explosive (IHE) whose thermal and shock stability is considerably greater than that of any other known material of comparable energy[10]. The high stability of TATB favors its use in military[11] and civilian applications[12] when insensitive high explosives are required. In addition to its applications as a HE, TATB is used to produce the important intermediate benzenehexamine[13]~[17]. Benzenehexamine has been used in the preparation of ferromagnetic organic salts[17] 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.[14]~[16] The use of

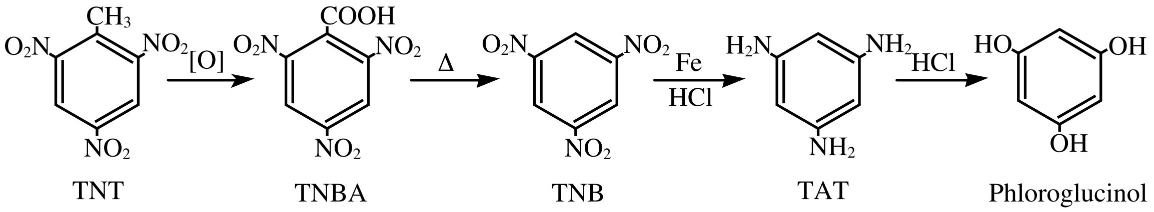

Fig. 2 Commercial production of phloroglucinol from TNT.

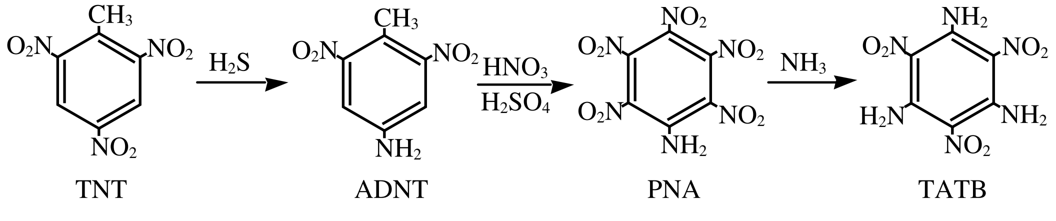

Fig. 3 Conversion of TNT to TATB.

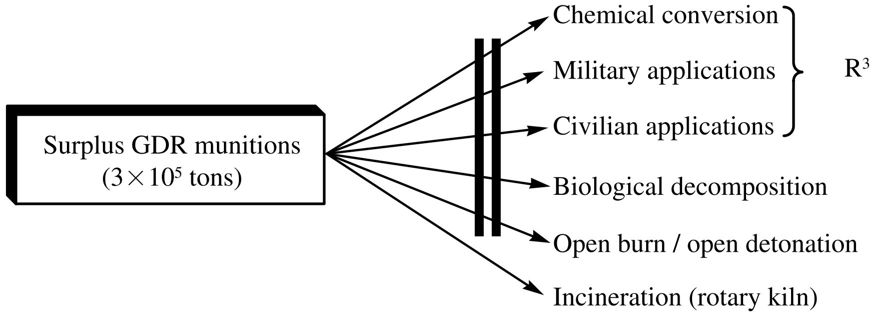

Fig. 4 Demilitarization of munitions from the former German Democratic Republic.

TATB derivatives to prepare components of lyotropic liquid-crystal phases for use in display devices is the subject of a German patent[18).

### 3.1 Current production of TATB

TATB has not been manufactured in the USA for over 15 years. TATB was formerly produced using the synthesis developed by Benziger (Fig. 5)[19), 20). The relatively expensive and domestically unavailable 1,3,5-trichlorobenzene (TCB) is nitrated 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. The major impurity encountered in this process is ammonium chloride. The inclusion of 2.5 % water during the amination step significantly reduces the ammonium chloride content of the TATB. Low levels of chlorinated organic impurities have also been identified. These impurities include 2,4,6-trichloro-1,3,5-trinitrobenzene (TCTNB), 1,3-dinitro-2,4,5,6-tetrachloro-benzene, 1,3-dinitro-2,4,6-trichlorobenzene and their partially aminated products[21). It is important to note that TATB, unlike other high explosives (RDX, HMX, TNT, HNS), cannot be purified using conventional techniques. The extremely low solubility and involatility of TATB precludes the use of recrystallization and sublimation for large-scale operations. Production batches of TATB that exceed the allowable limits for ammonium chloride and / or other impurities must be discarded. This is clearly economically and environmentally undesirable.

### 3.2 VNS synthesis of TATB

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 have described a novel approach to the synthesis of TATB which utilizes relatively inexpensive starting materials and mild reaction conditions.[2), 22)~24) This new process relies on amination of nitroarene starting materials using a reaction known as Vicarious Nucleophilic Substitution (VNS) of hydrogen[25). Figure 6 outlines the general approach. We have been working on the scale-up of this new synthesis with the goal of developing a new production of TATB that is less expensive and more environmentally benign than the existing process illustrated in Fig. 5. The VNS aminating reagents that we have most extensively examined are shown in Fig. 7. The reagents in order of increasing reactivity and cost are hydroxylamine[26), 4-amino-1,2,4-triazole(ATA)[23) and 1,1,1-trimethylhydrazinium iodide(TMHI)[24). We will chiefly focus on results obtained with TMHI and hydroxylamine after a consideration of starting materials.

### 3.3 Starting materials for synthesis of TATB

#### 3.3.1 Conversion of Explosive D to picramide

Our synthesis of TATB has been designed so that either surplus energetic materials or inexpensive, commercially available chemicals can be used to make the necessary starting materials. Several million pounds of Explosive D (ammonium picrate) are available for disposal in the USA. Ammonium picrate can be converted to 2,4,6-trinitroaniline (picramide) by the pathways shown in Fig. 8. There is one report describing the direct conversion of picric acid to picramide[27).

Molten picric acid and urea were heated at 173 °C for 36 hours to produce a mixture of picramide, urea and cyanuric acid. Removal of the urea and cyanuric acid by extractions with the appropriate solvents (water, acetone) afforded picramide in 88 % yield. This procedure has major drawbacks, as molten picric acid, especially at such an elevated temperature (173 °C), is a recognized hazard. Furthermore, the picramide is produced as a solid glass product which cannot be safely and efficiently removed from an industrial scale reactor. What about the direct conversion of Explosive D to picramide? We have not found any reports in the chemical literature describing such a conversion. There are suggestions, however, that the reaction of Explosive D with urea at elevated temperature has been attempted and little or no picramide was produced[28). The

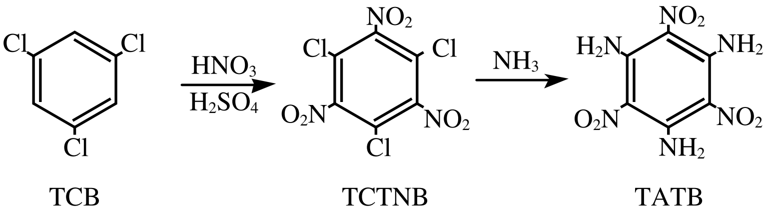

Fig. 5 Benziger synthesis of TATB.

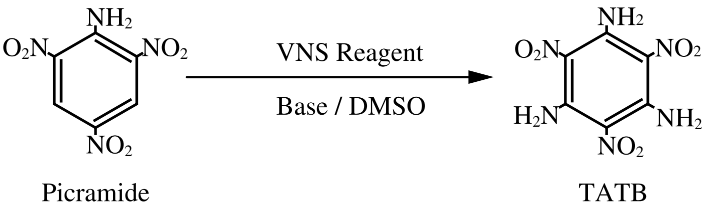

Fig. 6 VNS synthesis of TATB from picramide.

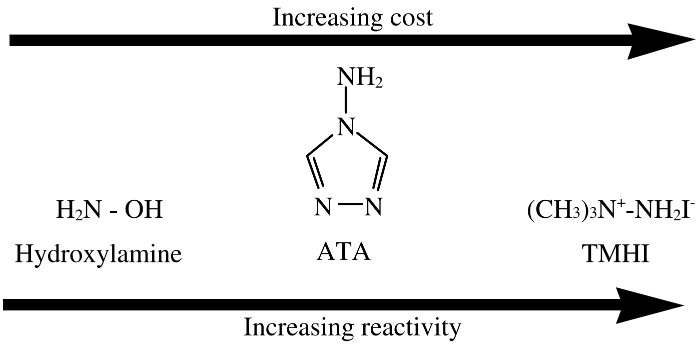

Fig. 7 VNS amination reagents.

reaction of picric acid and urea was reinvestigated and conditions were discovered that promoted the reaction of either Explosive D or picric acid with urea to provide picramide. Good yields (> 90 %) were obtained irrespective of the starting material. In each case, however, cyanuric acid was present as an unwanted by-product formed from excess urea in the reaction mixture. We have recently described conditions under which both Explosive D and picric acid are directly converted to picramide (Fig. 8, dotted arrow) in over 90 % yield without the formation of cyanuric acid[29].

### 3.3.2 Conversion of 4-nitroaniline to picramide

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[30]. Early studies in our laboratories 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. The removal of such impurities would require expensive recrystallization processing, since they affect the quality of TATB produced, as discussed earlier. We have modified the workup and have obtained picramide in high yields (90 %) and purity (> 99.5 %) without recourse to crystallization.

## 3.4 Process studies with TMHI as the VNS aminating reagent

### 3.4.1 Initial studies

We have determined that 1,1,1-trimethylhydrazinium iodide (TMHI) is the most efficient nucleophilic aminating reagent available for the VNS synthesis of TATB.[2), 22)~24)] 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 less than 3 hours, giving TATB in 80-90 % yield (Fig. 9). The major expected impurity is 1,3-diamino-2,4,6-trinitrobenzene (DATB), which results from incomplete amination. Under these reaction conditions, no DATB (≤ 0.5 %) was detected by FTIR spectroscopy or direct insertion solids probe mass spectrometry (DIP-MS).

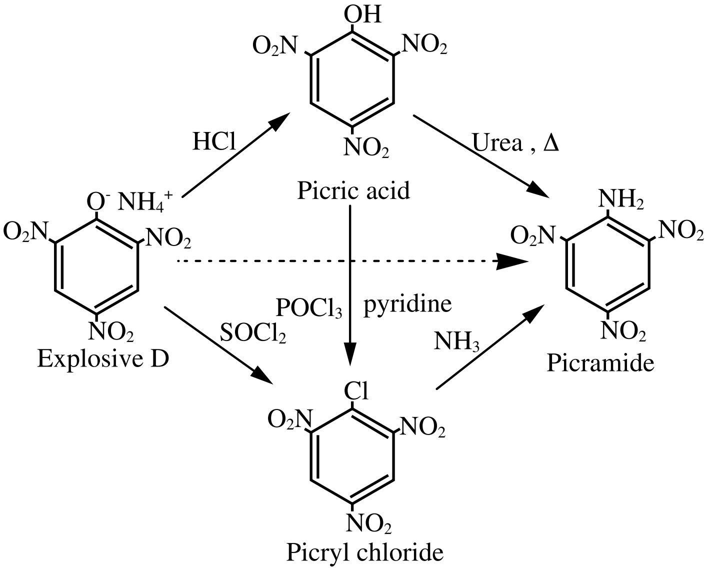

Fig. 8 Pathways to picramide from Explosive D.

### 3.4.2 Studies on varying reaction conditions

The initial studies of this reaction employed picramide concentrations ≤ 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. 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 100-gram level. The reaction appears to scale linearly, delivering 82 % yield of TATB at > 99 % purity.

### 3.4.3 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 (30 μm) has recently been obtained using other organic acids. It was also noticed that the final color of the product TATB varied when different quenching solutions were used.

### 3.4.4 In situ generation of TMHI

Although TMHI is easy to prepare and handle[22), 24)] its use in the solid form requires an additional synthesis and isolation step, which would increase the overall 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. We have also used the relatively inexpensive and halogen-free dimethyl sulfate to generate the methosulfate salt of 1,1,1-trimethylhydrazine in situ for use in VNS aminations of nitroarenes[26)].

### 3.4.5 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 desiccator 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 the surface material 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 (see above). 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.

### 3.4.6 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 employed 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 that 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 %.

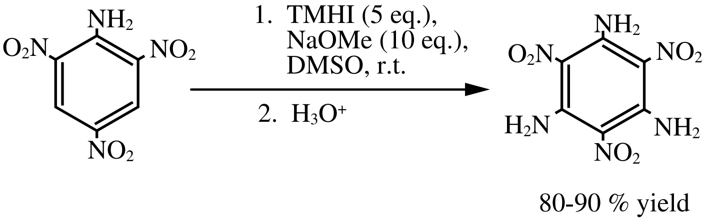

Fig. 9 VNS synthesis of TATB using TMHI.

### 3.5 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[31) although the term “VNS” was coined many decades later[25). Our earliest work in aminating picramide with hydroxylamine was disappointing since the reaction only provided DATB in low yield containing trace amounts of TATB at best[23). The poor reactivity of hydroxylamine was independently confirmed by Seko and Kawamura who were unable to aminate nitrobenzene using hydroxylamine[32).

The low cost of hydroxylamine as an aminating reagent warranted further investigation and recent work in our laboratories showed that hydroxylamine will aminate picramide at elevated temperature to furnish TATB (Fig. 10)[26). 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.

### 3.6 Purification of TATB

One of the drawbacks associated with the earlier production of TATB was the inability to recycle or purify preparations of TATB with levels of ammonium chloride and / or other impurities that exceeded specifications (see Section 3.1). Because TATB is nearly insoluble in even the strongest solvents, it is not practical to purify it on a large scale using standard purification methods (chromatography, crystallization). In response to the impurities seen in our earlier TATB synthesis studies, we have developed effective methods for the purification of TATB[29). The general procedure is schematically outlined in Fig. 11. The ability to purify batches of TATB that normally would have been discarded should significantly lower the cost of TATB production.

## 4. Feedstocks for future chemical conversion activities

This project originated in response to the need to demilitarize Explosive D. The demilitarization inventory of TNT is much larger, which makes the use of TNT attractive for the production of higher value products. Production of phloroglucinol from TNT (Fig. 2) was stopped in this country in the 1970s due to the polluting nature of the process, especially during the oxidation of TNT to TNBA. Workers in Sweden and Russia have described improved oxidations of TNT to TNBA and TNB[5).

These developments make the conversion of TNT to phloroglucinol (Fig. 2) or TATB (Fig. 12) via TNB more attractive. The direct conversion of TNB to TATB using VNS chemistry has been described.[22), 23)

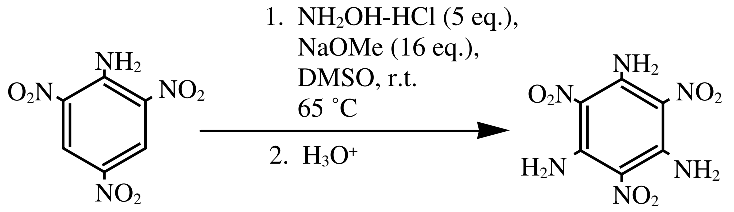

Fig. 10 VNS synthesis of TATB using hydroxylamine hydrochloride.

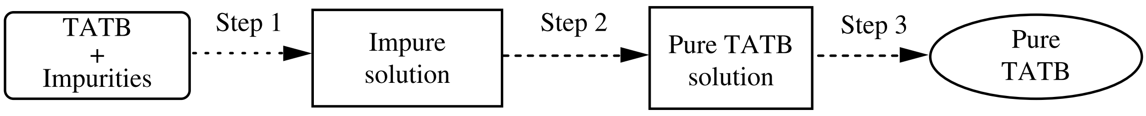

Fig. 11 Scheme for purification of TATB.

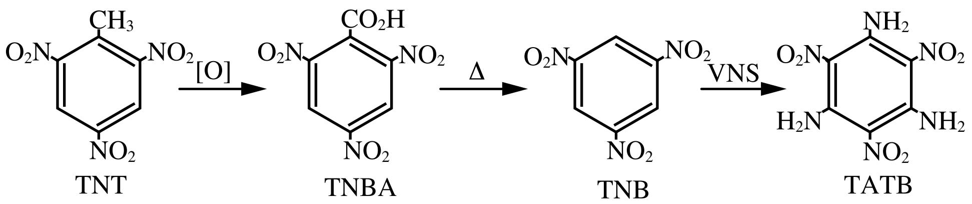

Fig. 12 Improved conversion of TNT to TATB.

## 5. Conclusions

Chemical conversions of surplus energetic materials (high explosives, propellants) offer constructive alternatives to destruction. Explosives containing nitroarenes (TNT, Explosive D) are especially useful as feedstocks for industrial processes that produce higher value products.

## Acknowledgements

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