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A VERSATILE SYNTHESIS OF 1,3,5-TRIAMINO-2,4,6-TRINITROBENZENE (TATB)

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ABSTRACT

A safe and versatile synthesis of high-purity 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) based on vicarious nucleophilic substitution (VNS) chemistry has now been achieved. The starting material can be selected from a variety of inexpensive nitroarenes obtained from commercial suppliers (4-nitroaniline, picric acid) or U.S. stockpiles (ammonium picrate, TNT). The use of picric acid and ammonium picrate (Explosive D) is preferred as both compounds are directly converted to picramide in the presence of ammonium salts (diammonium hydrogen phosphate, ammonium carbamate) in sulfolane at elevated temperature. The picramide resulting from this process is directly converted to TATB using an optimized VNS reaction employing inexpensive hydroxylamine as the nucleophilic aminating reagent. A crucial element in our synthesis is a novel and efficient purification of TATB.

INTRODUCTION

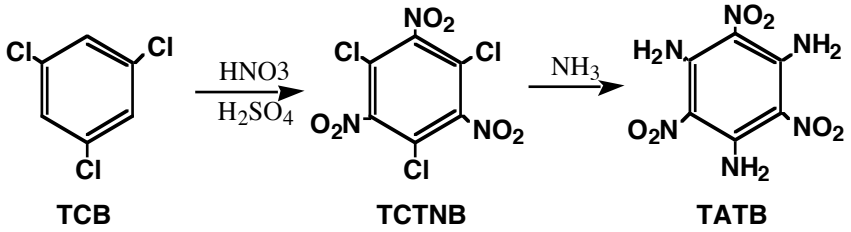
The high degree of thermal and shock stability of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) is well known[1], and this compound provides a benchmark for comparing insensitive explosives used in military applications.[2] In the civilian sector, perforating guns containing TATB have been designed for use in deep oil well explorations where heat-insensitive explosives are required.[3] TATB is also used to produce benzenehexamine, an intermediate in the synthesis of new, advanced materials.[4]

SURVEY OF TATB SYNTHESES

The first reported synthesis of TATB was in 1888 when Jackson and Wing described the ammonolysis of 1,3,5-tribromo-2,4,6 –trinitrobenzene (TBTNB) to produce TATB.[5] Although four significant synthetic routes to TATB have emerged since then, only one route has been utilized for industrial scale production. It is instructive to compare the advantages and drawbacks of each approach.

Benziger Synthesis of TATB

TATB was formerly produced on an industrial scale in the USA by the Benziger process (Figure 2)[6,7] The relatively expensive and domestically unavailable 1,3,5-trichlorobenzene (TCB) is nitrated to give 2,4,6-trichloro-1,3,5-trinitrobenzene



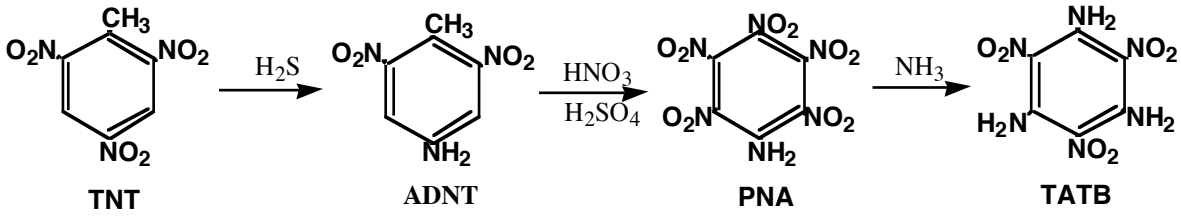
Scheme 1. Preparation of TATB using the Benziger process.

(TCTNB) which is then aminated to yield TATB. Elevated temperatures (150^{O}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.[8] There is a desire to develop a synthesis of TATB that does not require such harsh reaction conditions (elevated temperature, strong acid). In addition, there is mounting environmental pressure to abandon the use of halocarbons such as TCB in favor of more benign and "greener" feedstocks in industrial processes.

Atkins Synthesis of TATB

Atkins and coworkers described a conversion of TNT to TATB[9,10] with the goal of developing a less costly production of TATB (Scheme 2). Hydrogen sulfide partially reduces TNT to 4-amino-2,6-dinitrotoluene (ADNT), which is then treated with nitric acid in sulfuric

acid to provide pentanitroaniline (PNA) via an unanticipated oxidative nitration of ADNT. Treatment of PNA with ammonia provides TATB in addition to polynitrophenol by-products (R. Atkins, personal communication). Although the starting material and reactants are relatively inexpensive, the cost of pollution abatement ultimately prevented the industrial scale-up of this process.

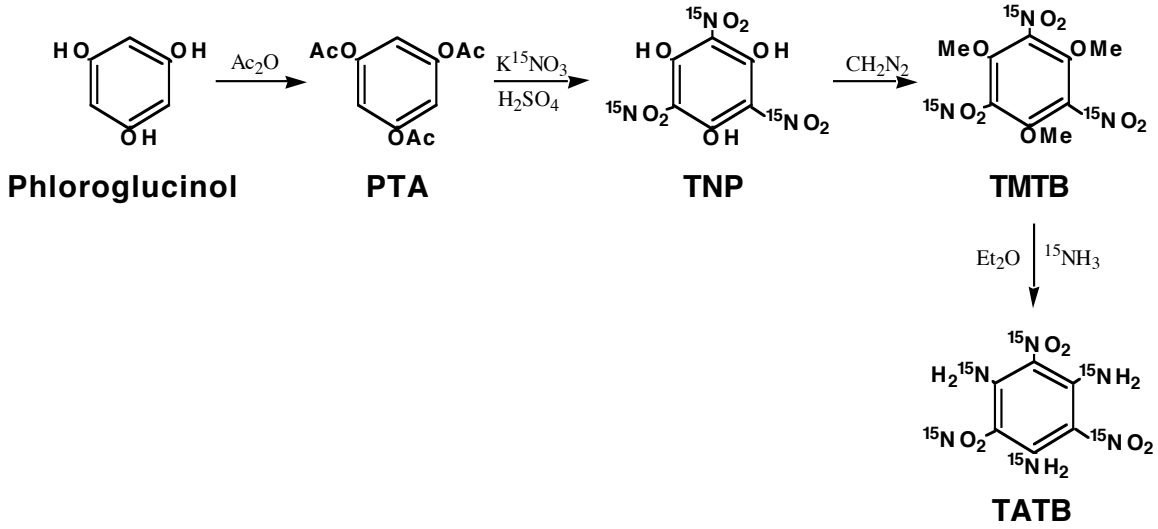


Scheme 2. Atkins synthesis of TATB from TNT.

Conversion of Phloroglucinol to TATB

Two groups have described the conversion of phloroglucinol (1,3,5-trihydroxybenzene) to TATB. Wolff and Limbach described the efficient conversion of phloroglucinol to ^{15}N-labelled TATB for use in the preparation of ^{15}N-labeled benzenehexamine derivatives (Scheme 3).[11] Due to the relatively high cost of ^{15}N-labeled precursors ($^{15}NH_4Cl$, $Na^{15}NO_3$), the Benziger synthesis (Scheme 1), which requires excess nitric acid (TCB -> TCTNB) and ammonia (TCTNB -> TATB), would be prohibitively expensive with ^{15}N-labeled reagents. Phloroglucinol is converted to phloroglucinol triacetate (PTA) which is then nitrated to trinitrophloroglucinol (TNP, 93%) using a stoichiometric quantity of potassium nitrate in sulfuric acid at room temperature. Excess diazomethane converted TNP to 1,3,5-trimethoxy-2,4,6-trinitrobenzene (TMTB, 100%) which is then ammonolyzed using a 1.6-fold excess of ammonia in ether with warming from-78^o to 70^o C to give TATB (97%).

Bellamy and coworkers recently modified the Wolff-Limbach preparation of TATB by replacing the alkylating reagent (diazomethane) used to convert TNP to TMTB with either dimethyl sulfate or a trialkyl orthoformate.[12-14] Also, they discovered that TATB produced by this process is contaminated with small amounts of mono-and bis-aminated products in addition

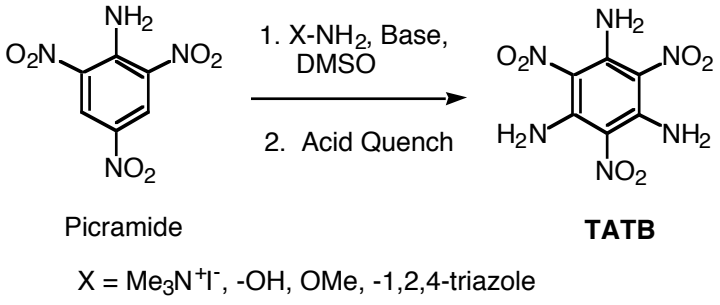


Scheme 3. Conversion of phloroglucinol to ^{15}N-labelled TATB.

to ammonium 3,5-diaminopicrate, an unexpected by-product. Nevertheless, the conversion of phloroglucinol to TATB is noteworthy for efficient synthetic conversions under relatively mild conditions. A major obstacle to this approach is the current cost of starting material (phloroglucinol) at $50/lb (bulk quantities), which precludes a production of TATB in the desired $50 -100/lb range. A cost-effective scale-up of a recently reported microbial conversion of glucose to phloroglucinol may resolve this conundrum.[15]

Synthesis of TATB using VNS Chemistry

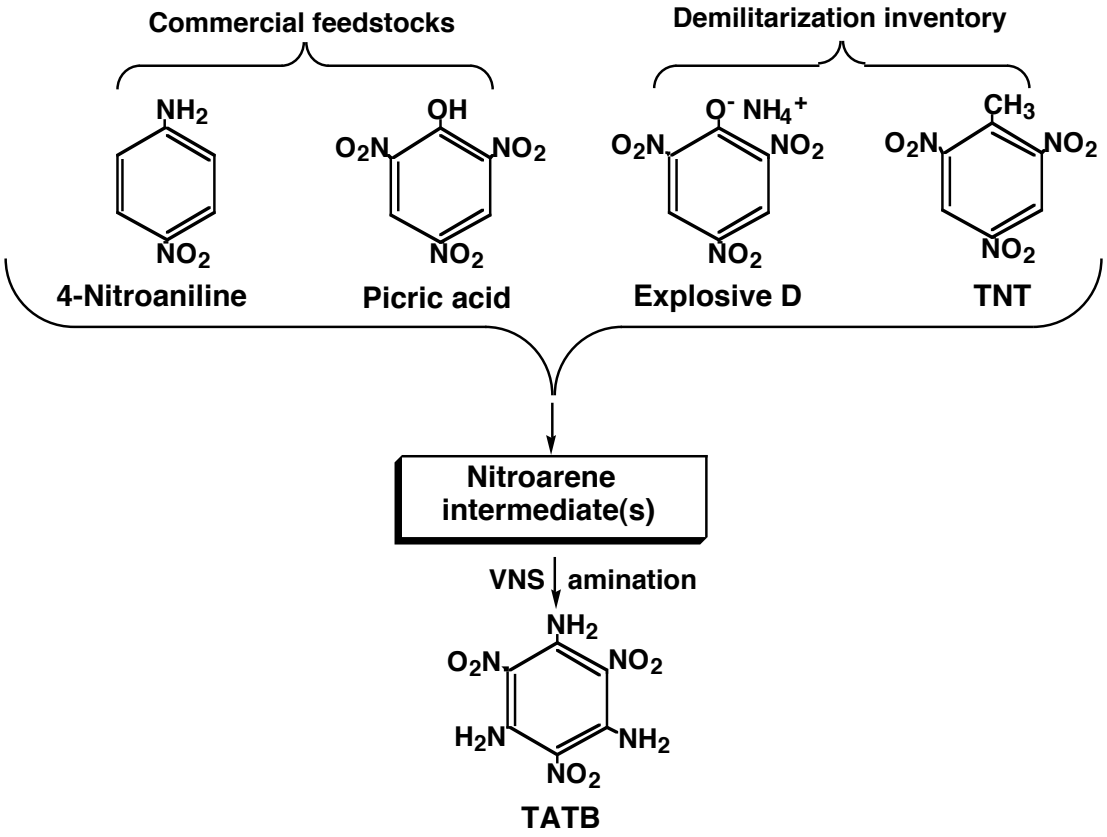
Several years ago, we reported a novel approach to the synthesis of TATB which utilizes relatively inexpensive starting materials and mild reaction conditions (Scheme 4).[16-18]



Scheme 4. VNS Synthesis of TATB from Picramide.

This new process relies on amination of nitroaromatic starting materials using a reaction known

as Vicarious Nucleophilic Substitution (VNS) of hydrogen.[19] Our goal, which has remained unchanged, is to produce TATB using environmentally acceptable processes that use inexpensive feedstocks ($0.50 to $5/lb) obtained from surplus explosives or commodity chemicals. (Scheme 5). This project has focused on three areas of investigation, which are



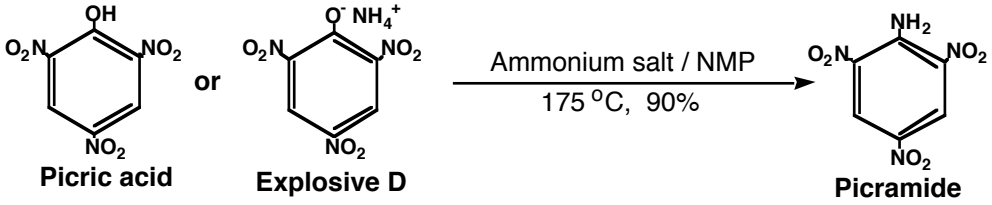
Scheme 5. Production of TATB utilizing surplus explosives or commodity chemicals.

(1) conversion of nitroarene feedstocks to VNS substrates, (2) conversion of VNS substrates to TATB using the appropriate chemistries, and (3) purification of TATB product. The first area requires development of the chemistry necessary for the conversion of Explosive D (ammonium picrate) and TNT feedstocks from demilitarization inventories to VNS substrates (picramide, trinitrobenzene). The second area involves process development studies to optimize the production of TATB from picramide or trinitrobenzene using VNS chemistry. The third area is

concerned with the development of efficient purification processes to produce TATB meeting DOE specifications.[2,20]

CONVERSION OF EXPLOSIVE D AND PICRIC ACID TO PICRAMIDE

There is only one report in the chemical literature that describes the direct conversion of picric acid to picramide.[21] Molten picric acid and urea were heated at 173^{0}C for 36 hours to produce a mixture of picramide, urea and cyanuric acid as a solid glass product. The reaction of molten picric acid with urea and subsequent workup of picramide from a solid product mixture, while tenable on a laboratory scale, presents unnecessary hazards on an industrial scale. We have developed conditions for the safe and direct conversion of Explosive D and picric acid to picramide (Scheme 6).



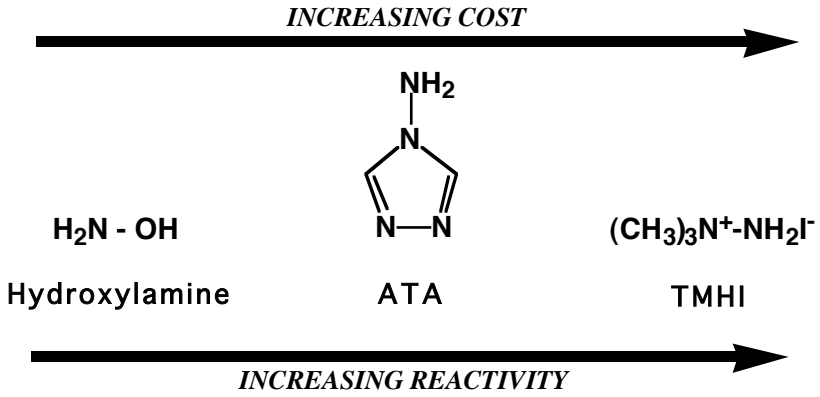
Scheme 6. Conversion of Explosive D and picric acid to picramide.

We replaced urea with ammonium salts that are obtained from ammonia and weak acids (acetic, carbonic acid, phosphoric acid). The reaction of ammonium salts with either picric acid or Explosive D in a dipolar aprotic solvents such as N-methylpyrrolidinone (NMP) or sulfolane for several hours at 175^{o}C produces picramide, free of cyanuric acid, in high yields. Our results have been detailed in a recent patent application.[22]

CONVERSION OF PICRAMIDE TO TATB

VNS Amination Reagents

We have studied the use of three reagents for the conversion of picramide to TATB by Vicarious Nucleophilic Substitution (VNS) of hydrogen.[17,18,23,24] The reagents in order of increasing reactivity, as well as increasing cost, are hydroxylamine, 4-amino-1,2,4-triazole (ATA) and 1,1,1-trimethylhydrazinium iodide (TMHI) (Scheme 7). Hydroxylamine



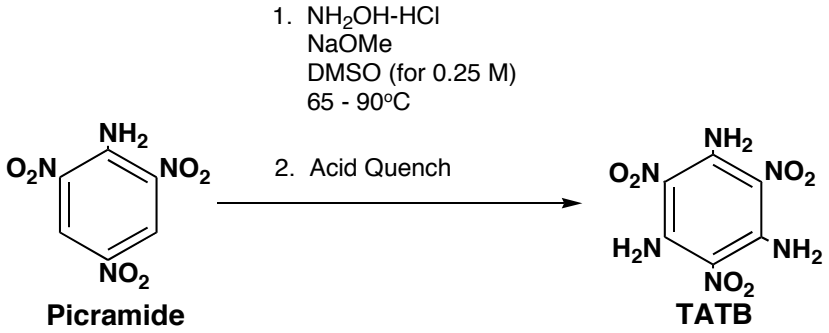
Scheme 7. VNS amination reagents.

is an inexpensive chemical obtained in bulk quantities as the hydrochloride or sulfate salt. ATA is obtained from formylhydrazide, which is prepared from relatively inexpensive hydrazine and ethyl formate (or formic acid).[25,26] TMHI is prepared from reaction of the more expensive 1,1-dimethylhydrazine and methyl iodide.[23] We have demonstrated the *in situ* production of TMHI by allowing 1,1-dimethylhydrazine and methyl iodide to react in DMSO. Subsequent addition of picramide and base produces TATB in yields comparable to VNS syntheses of TATB employing isolated TMHI.[24] We realized at the outset of our work with TMHI[23] that methyl iodide, a relatively expensive halocarbon, would ultimately have to be replaced with a less expensive alkylating agent that is also halogen-free. We have demonstrated that dimethyl sulfate reacts with 1,1-dimethylhydrazine (UDMH) to produce 1,1,1-trimethylhydrazinium methosulfate (TMHM) *in situ* which reacts with picramide in the presence of base to produce TATB.[24] The *in situ* production and use of TMHM in place of TMHI represents a significant cost reduction. The production and use of TMHM in VNS aminations will be influenced by the fluctuating price of UDMH (circa $5-30/lb) on the world market.

Process Development Studies

Our new production of TATB has been the subject of intensive process development studies with the goal of producing a clean, less expensive product in an environmentally acceptable fashion. We have extensively studied VNS amination reactions on nitroarenes and examined the effect of variations in VNS reagents, solvents, temperature, quenching and other parameters on the conversion of picramide to TATB.[16,24,27,28] Hydroxylamine, the least expensive VNS reagent, in combination with strong base, aprotic dipolar solvent (DMSO) and

elevated temperature (65 - 90^{0}C), reacts with picramide to yield TATB in 70-80% yield with about 97% purity (Scheme 8). It is known that prolonged treatment of yellow TATB with hydroxylamine and strong base at elevated temperature will produce a TATB-derived



Scheme 8. VNS synthesis of TATB using hydroxylamine hydrochloride.

impurity that results in a discolored or "green" TATB containing 1,3,5-triamino-2,4-dinitro-6-nitrososbenzene (TADNB).[29] Similarly, exposure of TATB to UV irradiation produces green TATB.[30]

VNS reactions normally employ dipolar aprotic solvents (DMSO, DMF and NMP).[19] Our solvent of choice has been DMSO, which is more expensive than most organic solvents used in industrial processes. Our early attempts to convert trinitroarenes to TATB using VNS reagents in less expensive solvents such as alcohols were unsuccessful.[17,18] We have since discovered reaction conditions, depending on the particular VNS reagent employed, that will allow us to partially or fully replace DMSO with less expensive solvents.[22] The results are encouraging and indicate a potentially significant cost reduction for the VNS production of TATB.

PURIFICATION OF TATB

Although TATB has been known for over 100 years ago, no industrial scale purification has been developed due to the low solubility[30,31] and low volatility[32] of TATB. These properties preclude the application of techniques (chromatography, crystallization, sublimation) normally employed in the purification of materials on an industrial scale. Foltz illustrated this in the crystallization of TATB from DMSO.[30] While producing the largest crystals of TATB known (≤

2 mm diameter), she also demonstrated the impracticality of purifying TATB using DMSO due to the large quantities of this high boiling and relatively expensive solvent required. Firsich also evaluated several TATB purification processes that used DMSO.[33] It was found that while all of the processes reduced the chloride impurity in TATB, sulfur content increased due to the occlusion of DMSO in the TATB crystals.

It is economically desirable to have effective purification procedures in place so that TATB can be recovered, rather than discarded, from TATB preparations containing impurities that exceed specifications.[2,20] The major obstacle to TATB purification is the very low solubility of TATB in most solvents (0.047% in DMSO at 21 ^{O}C).[30] This obstacle can be overcome by converting impure TATB preparations to relatively soluble derivatives which, after purification, are converted to purified TATB.

We have developed two procedures to remove impurities that may form during a VNS synthesis of TATB employing hydroxylamine, strong base and elevated temperature (60 – 90 ^{o}C)[22] The preferred procedure entails acetylation of crude, synthetic TATB to Ac_3-TATB which is soluble in dipolar aprotic solvents (DMSO, DMF) as well as NH_4OH (28% NH_3/H_2O). Crude TATB (containing TADNB, DATB and other impurities) is acetylated to provide crude triacetyl-TATB (Ac_3-TATB) which is dissolved in NH_4OH (28% NH_3 in H_2O) and treated with activated carbon (column or batchwise) to produce a solution of purified Ac_3-TATB in NH_4OH. The solution is heated (sealed vessel) to affect ammonolysis of the Ac_3-TATB and yield purified TATB. Ac_3-TATB has good solubility in ammonium hydroxide and solutions containing up to 10% Ac_3-TATB have been prepared. The ammonolysis of Ac_3-TATB has been studied in the temperature range from 20 –130 ^{O}C using NH_4OH (28% NH_3 in water) as well as mixtures of NH_4OH and DMF. Ammonolyses ($\leq$ 2 hr) at temperature $\leq$ 100 ^{O}C produce TATB and unreacted Ac_3-TATB while ammonolyses ($\geq$ 0.5 hr) at $\geq$ 120 ^{O}C yield only TATB. Purified TATB is obtained in 50 to 80% yields depending on the impurity levels in the original TATB and ammonolysis conditions employed.

In a typical run, a sample of impure TATB containing DATB and TADNB was acetylated, treated with activated carbon and ammonolyzed. TATB was obtained with no

detectable DATB or TADNB. The DSC for the purified TATB gave an exotherm peak @ 382.29 ^{o}C compared with an exotherm peak @ 377.26 ^{o}C obtained from production grade TATB prepared by the Benziger procedure.[6]

SUMMARY

A safe and efficient conversion of Explosive D/ picric acid to picramide, a key precursor in the VNS synthesis of TATB, has been accomplished. Extensive process development studies have led to significant improvements in the VNS synthesis of TATB. An efficient and practical purification of TATB is now available.

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