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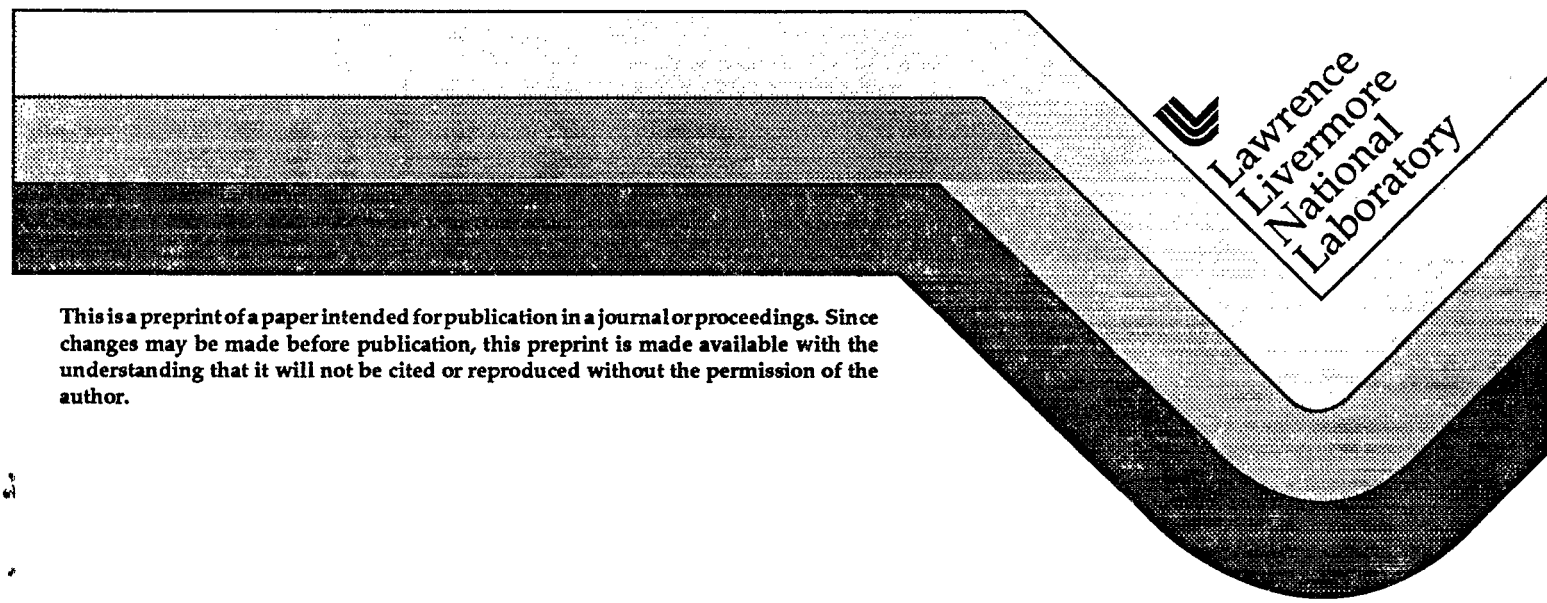

New Aminating Reagents for the Synthesis of 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) and Other Insensitive Energetic Materials.

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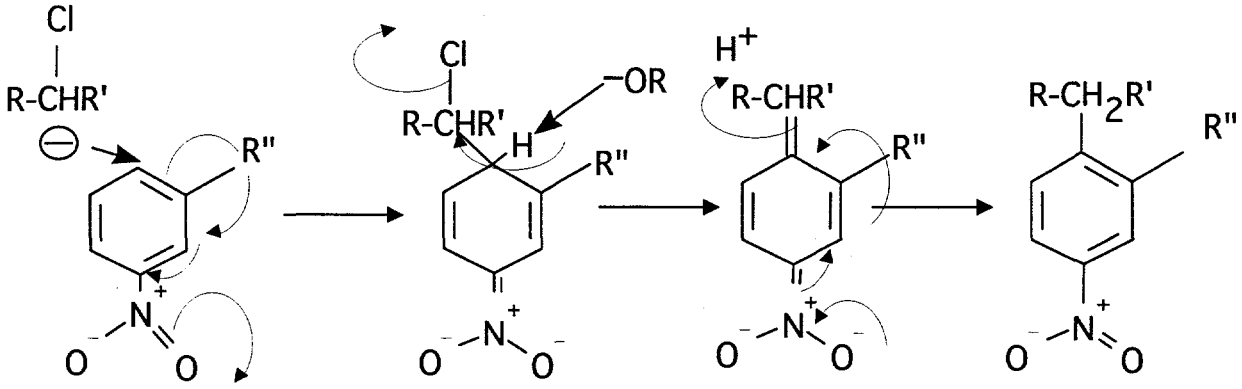
Abstract: We are investigating the amination of electrophilic aromatic systems through the use of Vicarious Nucleophilic Substitution (VNS) chemistry. This research has led to a new synthesis of 1,3,5-Triamino-2,4,6-trinitrobenzene (TATB) and 1,3-diamino-2,4,6-trinitrobenzene (DATB) which uses 2,4,6-trinitroaniline (picramide) or 1,3,5-trinitrobenzene as starting materials. We also describe the development of a new class of VNS aminating reagents based on quarternary hydrazinium halides. 1,1,1-Trimethylhydrazinium iodide (TMHI), available from the methylation of the surplus propellant *uns*-dimethylhydrazine (UDMH), was used in a new synthesis of TATB. The advantages, scope and limitations of the VNS approach to the synthesis of TATB and other amino-substituted nitroarenes are discussed.

The Vicarious Nucleophilic Substitution (VNS) of hydrogen is a well-established procedure for the introduction of carbon nucleophiles onto electrophilic aromatic rings.[1] The reaction involves the addition of a carbanion bearing a leaving group (X) to an electrophilic aromatic ring and subsequent rearomatization by loss of the leaving group through elimination as HX. (Scheme 1) This reaction has found application in the synthesis of a wide variety of nitroarenes and nitro-substituted heterocycles.[2] Katritzky and Laurenzo[3] extended this approach and reported the use of 4-amino-[1,2,4]-triazole (ATA) as a VNS reagent to introduce amino groups onto nitro-substituted aromatic rings. Makosza and Bialecki[4] subsequently reported the use of sulfenamides as VNS aminating reagents. They designed these reagents to be both good nucleophiles to easily add to the electrophilic aromatic ring and also possess a leaving group that forms a stable anionic species to be easily eliminated from the σ-adduct during rearomatization of the ring.

This approach prompted us to investigate the use of 1,1,1-trimethylhydrazinium iodide (TMHI)[5] [$(CH_3)_3N^+$-NH_2 (I^-)] as a VNS reagent for the introduction of amino

groups. We reasoned that TMHI would be sufficiently nucleophilic to substitute onto nitro-substituted aromatic rings but would be superior to the previous examples because

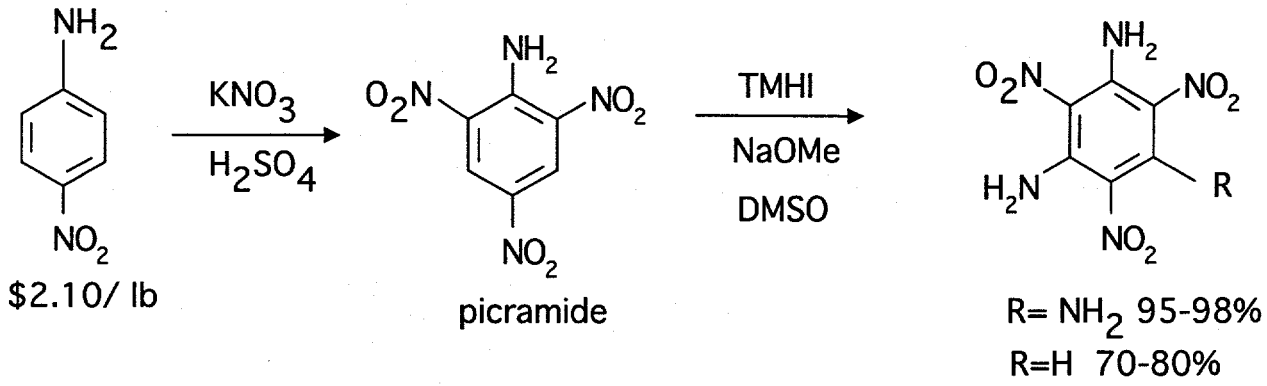


Scheme 1. Introduction of carbon nucleophiles by Vicarious Nucleophilic Substitution.

the leaving group would be the neutral trimethylamine instead of a stabilized anionic species. In addition, there is a possibility that the hydrazinium halide would react with base to form the neutral ylide species, $[(CH_3)_3N^+\text{-}NH^-]$, which may be the reactive species in the amination process. Indeed, when TMHI was reacted with various nitro-substituted aromatics the amino functionality was introduced in good to excellent yields. We found that the number of amino- groups which may be added to the electrophilic aromatic ring is equal to the number of nitro groups present on the ring. The reactivity of TMHI has led to an investigation a series of 1,1,1-trialkyl- and 1,1,1,2-tetraalkylhydrazinium halides as reagents for the introduction of amino- and substituted amino- groups onto electrophilic aromatic rings. 1,1,1,2-Tetramethylhydrazinium iodide and 1,1,1-trimethyl-2-phenylhydrazinium iodide are currently being investigated as reagents to allow the addition of -NHMe and -NHPh groups, respectively.

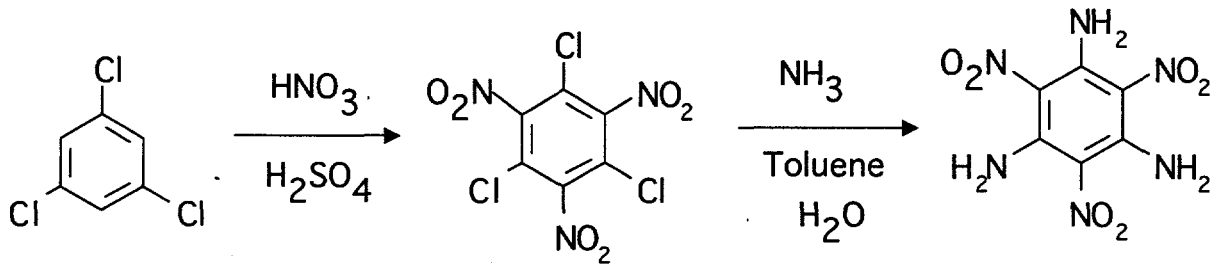
This chemistry has led us to investigate the synthesis of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) and 1,3-diamino-2,4,6-trinitrobenzene (DATB) from picramide using TMHI (Scheme 2). Both TATB and DATB are insensitive energetic materials with total energy approximately equal to TNT. TATB, however, is superior to TNT in metal

acceleration experiments with 20% more kinetic energy. The synthesis involves the treatment of picramide at room temperature for 3-24h with an appropriate amount of TMHI in dimethylsulfoxide in the presence of a two-fold excess of a strong base (NaOMe or KO*t*-Bu). Quenching the reaction in aqueous acid gives TATB or DATB in 95% and 75% yields, respectively. This synthesis has many advantages over the current synthesis of TATB (Scheme 3): 1) a significantly shorter two-step reaction sequence from an inexpensive starting material (4-nitroaniline); 2) the elimination of entrained ammonium chloride; and 3) the elimination of the expensive starting material, 1,3,5-trichlorobenzene, which is not currently available from domestic sources.



Scheme 2. Synthesis of TATB and DATB using the VNS approach.

The use of TMHI as the aminating agent also addresses a demilitarization problem currently being investigated in the U.S. *uns*-Dimethylhydrazine [$(CH_3)_2N$-NH_2] (UDMH) is a surplus propellant in the former Soviet Union currently being demilitarized (Thiokol/Allied Signal) by reduction to give ammonia and dimethylamine. TMHI is produced by the reaction of UDMH with methyl iodide in THF, providing an alternative demilitarization procedure for UDMH. TMHI is also synthesized directly from inexpensive hydrazine in 70-80% yield by alkylation with methyl iodide in the presence of aqueous base.



Scheme 3. Current synthesis of TATB.

We have also investigated other VNS aminating reagents for the synthesis of TATB and 1,3-Diamino-2,4,6-trinitrobenzene (DATB) from picramide or 1,3,5-trinitrobenzene. The use of 4-amino-[1,2,4]-triazole (ATA)[3] allowed the synthesis of TATB and DATB under conditions used for TMHI aminations. The use of methoxylamine hydrochloride gave exclusively DATB in 80% yield while the use of hydroxylamine yielded only 16% of DATB.

A study of product yields and distribution of various 3-substituted nitrobenzene derivatives was performed using TMHI (Figure 1). The results of our study were compared to the results using ATA.[3] ATA was found to be regioselective, giving substitution exclusively in the 4-position relative to the nitro- group, while TMHI showed no selectivity but presumably greater reactivity, giving all possible product isomers. There was a general tendency for TMHI to yield products in which the amine substitution occurs ortho- to the nitro group as the major components but there were exceptions. We are currently investigating the use of more sterically crowded 1,1,1-trialkylhydrazinium halides in an attempt to influence the regio-selectivity of the aminating reagent.

The synthesis of TATB by amination of 1,3,5-trinitrobenzene with TMHI suggested a mechanism in which each nitro group was available to stabilize a negative charge formed by reaction with the TMHI nucleophile, allowing the formation of an intermediate, tri-anionic species. This mechanism led us to investigate the amination of

3,5-dinitropyrazole (DNP), which carries an acidic hydrogen, to give 4-amino-3,5-

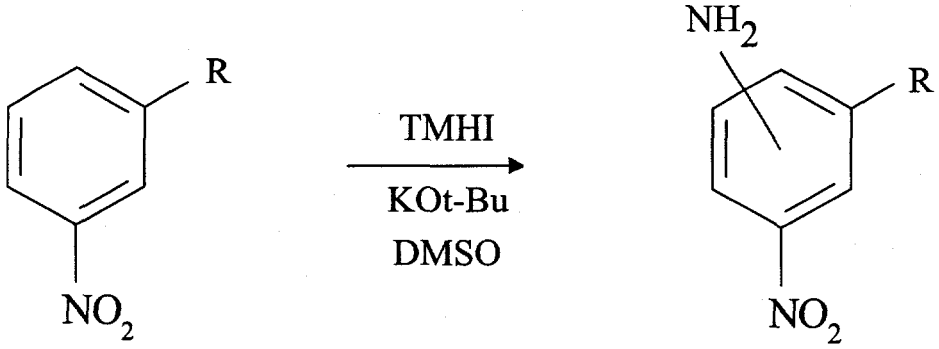


Figure 1. Amination of 3-substituted nitroaromatics.

dinitropyrazole (ADNP). We reasoned that the acidic proton on DNP would initially react with one equivalent of base to form a stable nitronate anion leaving the second nitro-group available to participate in the VNS amination. This would allow the synthesis of ADNP without the need of a protecting group for the pyrazole proton. We found the reaction of DNP with TMHI in the presence of excess potassium *tert*-butoxide gave ADNP in 70% yield (Fig. 2). The structure of ADNP was confirmed by x-ray crystallographic analysis; isolated as a 1:1 complex with dimethylsulfoxide with a crystal density of 1.608 g/cc.[6]

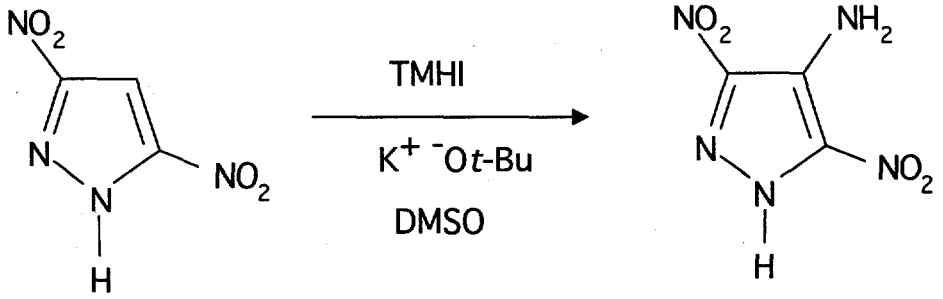


Figure 2. Synthesis of 4-amino-3,5-dinitropyrazole.

Summary: We have introduced the use of TMHI as a "Vicarious Nucleophilic Substitution" (VNS) aminating reagent in the synthesis of amino-substituted nitroaromatics. We demonstrated a new synthesis of TATB and DATB from picramide

using TMHI with significant advantages over the current method of synthesis. We are currently investigating the use of quarternary hydrazinium compounds in the synthesis of new energetic materials. We have synthesized 4-amino-3,5-dinitropyrazole from 3,5-dinitropyrazole in one step using TMHI as the aminating agent.

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