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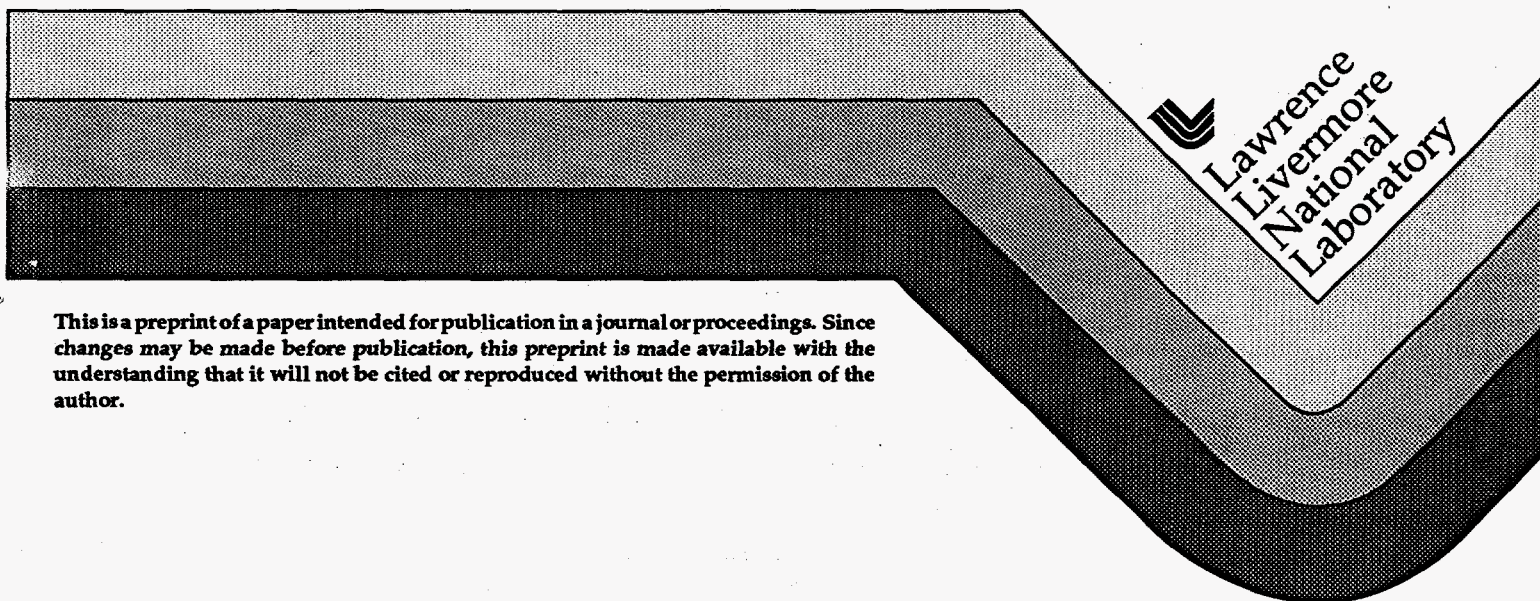
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Useful in Vicarious Nucleophilic Substitution Reactions**

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CONVERSION OF THE ROCKET PROPELLANT UDMH TO A REAGENT USEFUL IN VICARIOUS NUCLEOPHILIC SUBSTITUTION REACTIONS*

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ABSTRACT

The objective of our program is to develop novel, innovative solutions for the disposal of surplus energetic materials resulting from the demilitarization of conventional and nuclear munitions. In this report we describe the use of surplus propellant (UDMH) and explosives (TNT, Explosive D) as chemical precursors for higher value products. The conversion of UDMH to 1,1,1-trimethylhydrazinium iodide (TMHI) provides a new aminating reagent for use in Vicarious Nucleophilic Substitution (VNS) reactions. When TMHI is reacted with various nitroarenes the amino functionality is introduced in good to excellent yields. Thus, 2,4,6-trinitroaniline (picramide) reacts with TMHI to give 1,3,5-triamino-2,4,6-trinitroaniline (TATB) while 2,4,6-trinitrotoluene (TNT) reacts with TMHI to give 3,5-diamino-2,4,6-trinitrotoluene (DATNT). The advantages, scope and limitations of the VNS approach and the use of TMHI are discussed.

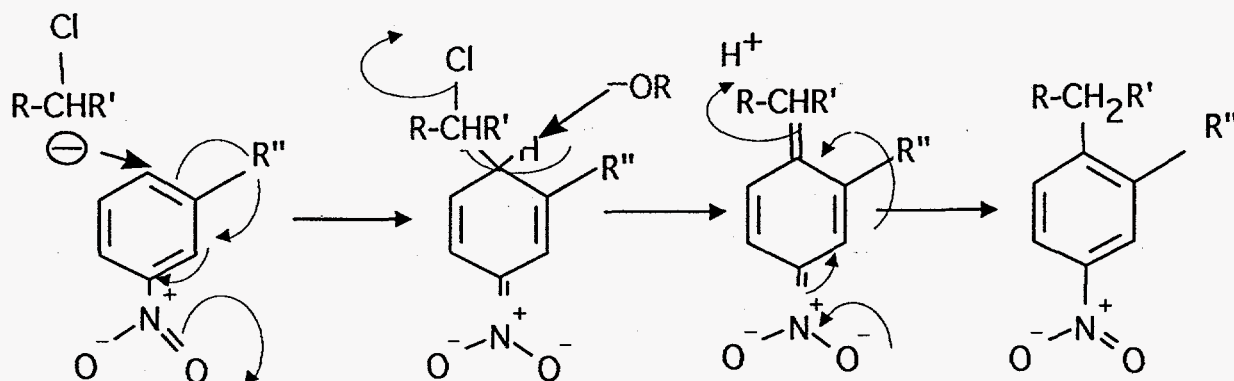
INTRODUCTION

The demilitarization of nuclear and conventional munitions is producing millions of pounds of surplus explosives (energetic materials).¹ Historically, surplus explosives have been disposed of by open burning/open detonation (OB/OD). The disposal of these materials by OB/OD is becoming unacceptable due to public concerns and increasingly stringent environmental regulations. Environmentally sound and cost-effective alternatives to OB/OD are needed. This paper focuses on the use of the rocket propellant UDMH (*uns*-dimethylhydrazine, 1,1-dimethylhydrazine) and surplus explosives (Explosive D, TNT) as chemical precursors to higher value products.

TMHI SYNTHESIS AND DEVELOPMENT

The Vicarious Nucleophilic Substitution (VNS) of hydrogen is a well-established procedure for the introduction of carbon nucleophiles onto electrophilic aromatic rings.² 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

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

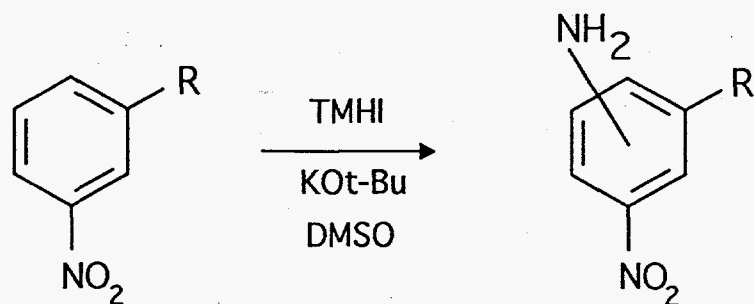
nitroarenes and nitro-substituted heterocycles.³ Katritzky and Laurenzo⁴ extended this approach and reported the use of 4-amino-[1,2,4]-triazole (ATZ) as a VNS reagent to introduce amino groups onto nitro-substituted aromatic rings. Makosza and Bialecki⁵ subsequently reported the use of sulfenamides 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 which is 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)⁶ $[(\text{CH}_3)_3\text{N}^+\text{-NH}_2 (\text{I}^-)]$ 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 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, $[(\text{CH}_3)_3\text{N}^+\text{-NH}^-]$, 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.

SYNTHESIS OF TATB AND DATB USING TMHI

This chemistry described above 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.

A study of product yields and distribution of various 3-substituted nitrobenzene derivatives was performed using TMHI (Scheme 5) (Table 1). The results of our study were compared to the



Scheme 5. Amination of 3-substituted nitroaromatics.

results using ATZ.⁴ ATZ 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 derived from UDMH in an attempt to influence the regio-selectivity of the aminating reagent.

R	Total Yield (%)	position of NH ₂ ^a	% isomer
H	85	2	61
		4	39
		6	0
CH ₃	84	2	38
		4	35
		6	27
Cl	82	2	32
		4	49
		6	19
COOH	95	4	71
		6	29
		2	0
OCH ₃	66	2	90
		4	10
		6	0
F	84	2	45
		4	47
		6	8
I	76	2	45
		4	38
		6	17
CN	41	2	20
		4	44
		6	36

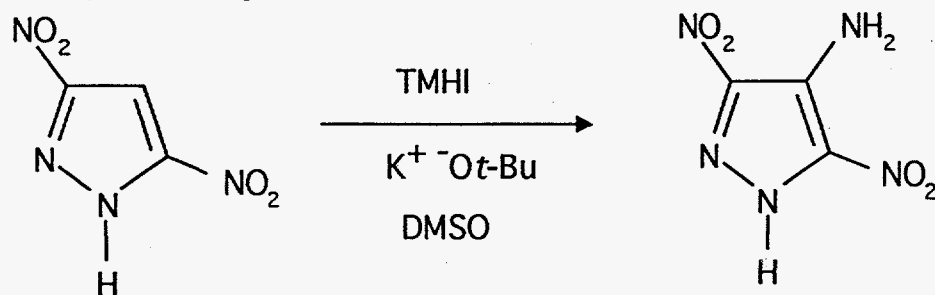
^a Relative to NO₂

Table I. Amination of 3-Substituted Nitrobenzenes

4-AMINO-3,5-DINITROPYRAZOLE (ADNP)

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-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 82% yield (Scheme 6). 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.⁷



Scheme 6. Synthesis of 4-amino-3,5-dinitropyrazole.

3,5-DIAMINO-2,4,6-TRINITROTOLUENE (DATNT)

Iyer has shown that the TNT molecule is significantly desensitized by substitution of ring hydrogens by -NH₂ groups.⁸ 3,5-Diamino-2,4,6-trinitrotoluene (DATNT) is less impact-sensitive than TNT. The CJ pressure and detonation velocity calculated for DATNT indicates that it should be a more powerful explosive than TNT. The general utility of the VNS approach is illustrated in the synthesis of 3,5-diamino-2,4,6-trinitrotoluene (DATNT) in one step from 2,4,6-trinitrotoluene (TNT) using TMHI (Scheme 7). This method is superior to previously reported syntheses of DATNT which involved 3-4 steps from the expensive starting materials, 3,5-dichlorotoluene and 3,5-dihydroxytoluene.^{8,9}



Scheme 7. Synthesis of DATNT using TMHI.

SUMMARY AND CONCLUSIONS

We have converted the rocket propellant UDMH to TMHI. The use of TMHI as a new reagent for the amination of nitroaromatics in VNS reactions is described. The reaction of picramide with

TMHI provides a new synthesis of TATB that has significant advantages over the current preparation of TATB. The use of TMHI to aminate 3,5-dinitropyrazole and TNT to the corresponding 4-amino-3,5-dinitropyrazole and DATNT in single step reactions further illustrates the utility of TMHI in VNS reactions. The preparation of new energetic materials from TMHI and other quaternary hydrazinium compounds derived from UDMH is under investigation.

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