Conversion of the Rocket Propellant UDMH to a Reagent Useful in Vicarious Nucleophilic Substitution Reactions

A. R. Mitchell
P. F. Pagoria
R. D. Schmidt

This paper was prepared for submittal to the
Proceedings of the
1995 JANNAF Safety & Environmental Protection Subcommittee Meeting
Tampa, Florida
December 5-8, 1995

November 10, 1995

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.
DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
CONVERSION OF THE ROCKET PROPELLANT UDMH TO A REAGENT USEFUL IN VICARIOUS NUCLEOPHILIC SUBSTITUTION REACTIONS*

Alexander R. Mitchell, Philip F. Pagoria, and Robert D. Schmidt
Energetic Materials Center
Lawrence Livermore National Laboratory
Livermore, California 94550

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). 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. 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.

* Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. Approved for public release; distribution is unlimited.
nitroarenes and nitro-substituted heterocycles.\textsuperscript{3} Katritzky and Laurenzo\textsuperscript{4} 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 Bialecki\textsuperscript{5} 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 \(\sigma\)-adduct during rearomatization of the ring.

This approach prompted us to investigate the use of 1,1,1-trimethylhydrazinium iodide (TMHI)\textsuperscript{6} \([(CH_3)_3N^+\cdash NH_2 (I^-)]\) 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 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, \([(CH_3)_3N^+\cdash NH^-]\), 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.
Scheme 2. Synthesis of TATB and DATB using the VNS approach.

The use of TMHl as the aminating agent also addresses a demilitarization problem currently being investigated in the U.S. *uns*-Dimethylhydrazine [(CH₃)₂N-NH₂] (UDMH) is a surplus propellant in the former Soviet Union that will be demilitarized (Thiokol/Allied Signal) by reduction to give ammonia and dimethylamine. TMHl is produced by the reaction of UDMH with methyl iodide in THF, providing an alternative demilitarization procedure for UDMH. TMHl 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 DATB from picramide or 1,3,5-trinitrobenzene (scheme 4). The use of 4-amino-[1,2,4]-triazole (ATZ)⁴ allowed the synthesis of TATB and DATB under conditions used for TMHl.

Scheme 4. Synthesis of TATB from picramide using ATZ.

aminations. The use of methoxylamine hydrochloride as a VNS aminating agent 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 (Scheme 5) (Table 1). The results of our study were compared to the

\[
\begin{align*}
\text{NO}_2 & \quad \xrightarrow{\text{TMHI}} \quad \text{NH}_2 \\
\end{align*}
\]

Scheme 5. Amination of 3-substituted nitroaromatics.

results using ATZ. 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.

<table>
<thead>
<tr>
<th>R</th>
<th>Total Yield (%)</th>
<th>position of NH\textsubscript{2}\textsuperscript{a}</th>
<th>% isomer</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>85</td>
<td>2</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>39</td>
</tr>
<tr>
<td>CH\textsubscript{3}</td>
<td>84</td>
<td>2</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>35</td>
</tr>
<tr>
<td>Cl</td>
<td>82</td>
<td>2</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>19</td>
</tr>
<tr>
<td>COOH</td>
<td>95</td>
<td>4</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>29</td>
</tr>
<tr>
<td>OCH\textsubscript{3}</td>
<td>66</td>
<td>2</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>F</td>
<td>84</td>
<td>2</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>I</td>
<td>76</td>
<td>2</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>17</td>
</tr>
<tr>
<td>CN</td>
<td>41</td>
<td>2</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>36</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Relative to NO\textsubscript{2}

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.


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
TMHl provides a new synthesis of TATB that has significant advantages over the current preparation of TATB. The use of TMHl to aminate 3,5-dinitropyrazole and TNT to the corresponding 4-amin0-3,5-dinitropyrazole and DATNT in single step reactions further illustrates the utility of TMHl in VNS reactions. The preparation of new energetic materials from TMHl and other quaternary hydrazinium compounds derived from UDMH is under investigation.

REFERENCES