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**INVESTIGATION OF IGNITION DELAY: NOVEL BETA-SUBSTITUTED ETHYLAZIDE DERIVATIVES
AS POTENTIAL NEW LIQUID PROPELLANT FUELS (PREPRINT)**

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ABSTRACT

Extensive research has been directed at replacing hydrazine and its simple derivatives in liquid propellant fuel applications. While no specific replacement has been discovered, much has been learned about what types of compounds will make good fuels. One compound that has been investigated is 2-dimethylaminoethylazide (DMAZ). DMAZ is simple to prepare, and from a handling perspective is less toxic than hydrazine. Though DMAZ is hypergolic with IRFNA, there is a significant ignition delay. The explanation, based on *ab-initio* calculations is that the onset of ignition involves proton transfer from the acid to the amine nitrogen, and in the lowest energy conformer of DMAZ the azide group inhibits this proton transfer. This offers some insight into how one might design a fuel that overcomes these deficiencies. Either the electron distribution could be altered to allow for an enhanced interaction between the proton and the amine nitrogen, or the molecule could be altered to move the azide group away from the amine group. In either case, the chemistry would have to be done so that the advantages found with the DMAZ molecule (i.e. toxicity and energy) are not lost. While several molecules using either one approach or the other have been identified, this paper focuses on, a molecule that takes advantage of both approaches. The replacement of the tertiary amine nitrogen in DMAZ with 1,1-dimethyl hydrazine results in a molecule, 1,1-dimethyl-2-[2-azidoethyl]hydrazine (DMAEH) with a (calculated) lowest energy conformation in which the tertiary amine nitrogen is free to interact with the acidic proton at ignition. In addition to obvious steric improvements, a group with adjacent unshared electron pairs results in an enhancement of this group's nucleophilicity. Attempts at synthesizing DMAEH have ultimately failed. A description of these attempts and the results of extensive theoretical calculations of the molecule's properties will be presented.

INTRODUCTION

The ongoing effort to replace hydrazine and its simple derivatives is primarily due to the inherent hazards in handling these compounds, which are suspected carcinogens, with high vapor pressures. The attraction of the hydrazine compounds are their high specific impulse and favorable combustion characteristics when used with appropriate oxidants and ignition catalysts. In addition and of considerable importance is the relative low cost of manufacturing these materials.

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The search for viable replacements has not been fruitless. One particular compound that has been thoroughly investigated is 2-dimethylaminoethylazide, or DMAZ¹. While its specific impulse is lower than that of monomethylhydrazine (MMH), its density is high enough to provide a density impulse value comparable to that of MMH. Unfortunately, no adequate catalyst exists for the ignition of DMAZ as a monopropellant, and, though hypergolic with inhibited red fuming nitric acid (IRFNA), there is a significant ignition delay. This delay, based on *ab-initio* calculations, is rationalized by the onset of ignition involving proton transfer from the acid to the amine nitrogen of DMAZ, and the lowest energy conformer of DMAZ places the azide group in a position that inhibits this proton transfer². While no experimental evidence has been produced to support it, the high level calculations backing this theory are convincing, based both on steric and electronic considerations. An understanding of the structure of this molecule, and the proposed theory for the ignition can guide the designing of molecules that will both test the theory and lead to viable candidates for liquid propellant fuel applications.

The most stable conformer of DMAZ (calculated using Hybrid Density Functional Model (B3YLP) with a polarized split valence basis set (6-31G*)) has often been compared to the shape of a scorpion; with the linear azide nitrogens folded over the amine nitrogen like a scorpion's tail. This amusing mental image of the shape of the DMAZ molecule is very instructive. If, as has been proposed, the first step in the ignition of the DMAZ/IRFNA bipropellant involves the transfer of the acidic proton to the nucleophilic amine nitrogen, then the steric interaction between the azide nitrogen could indeed inhibit this transfer. In addition, the azide nitrogen is electrophilic and its interaction with the amine nitrogen could inhibit the transfer of the proton from a strictly electrostatic viewpoint.

The molecular considerations discussed above offer some insight into how one might design a liquid propellant fuel that overcomes the deficiencies in DMAZ, based on the proposed combustion mechanism. Either the electron distribution within the molecule could be altered to allow for an enhanced interaction between the proton and the amine nitrogen, or the conformation of the molecule could be altered to move the azide group away from the amine group, again allowing enhanced interaction between proton and amine nitrogen. In either case, the chemistry would have to be done so that the advantages found with the DMAZ molecule are not lost. While several molecules using either one approach or the other have been identified, for the purposes of this report, a molecule that takes advantage of both approaches has been chosen for further study.

Consider the replacement of the tertiary amine nitrogen in DMAZ with 1,1-dimethyl hydrazine. As shown in Figure 1 the resulting molecule, 1,1-dimethyl-2-[2-azidoethyl]hydrazine (DMAEH) gives the calculated lowest energy conformation where the electrostatic potential map of the molecule indicates that the interaction between the internal hydrazine nitrogen and the azide nitrogen still exists as in DMAZ, however, the terminal dimethylamine nitrogen is now free to interact with the acidic proton at ignition. In addition to the obvious steric improvements, the addition of a group with adjacent unshared electron pairs results in an enhancement of the group's nucleophilicity. This effect is commonly known as the *alpha effect*³. The use of Mulliken charges calculated for each atom in both DMAZ and DMAEH for comparison purposes further support this theory.

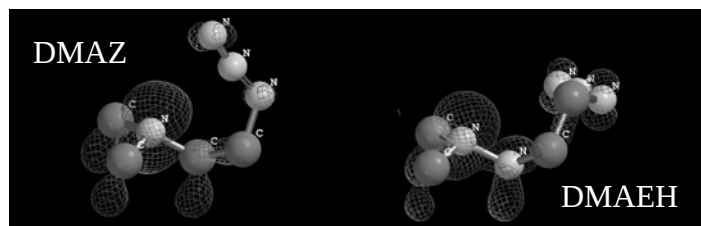


Figure 1: Lowest energy conformation of DMAZ and DMAEH.

Using the calculated lowest energy conformation of DMAEH, thermodynamic properties, in particular the enthalpy of formation of the gas-phase molecule, were calculated. Approximating the heat of vaporization of DMAEH as being equivalent to that of DMAZ, and making the further assumption that

their densities are identical, specific impulse and density impulse values were calculated for DMAEH. The calculations were performed using the NASA Lewis Research Center's Chemical Equilibrium with Applications (CEA) computer program⁴. For comparison, MMH, DMAZ, and DMAEH were all reacted as bipropellants with IRFNA as the oxidant. All variables were identical for the three propellant systems, and the oxygen to fuel ratio (O/F) was varied to find the optimum fuel mixtures. The results can be seen in Figure 2.

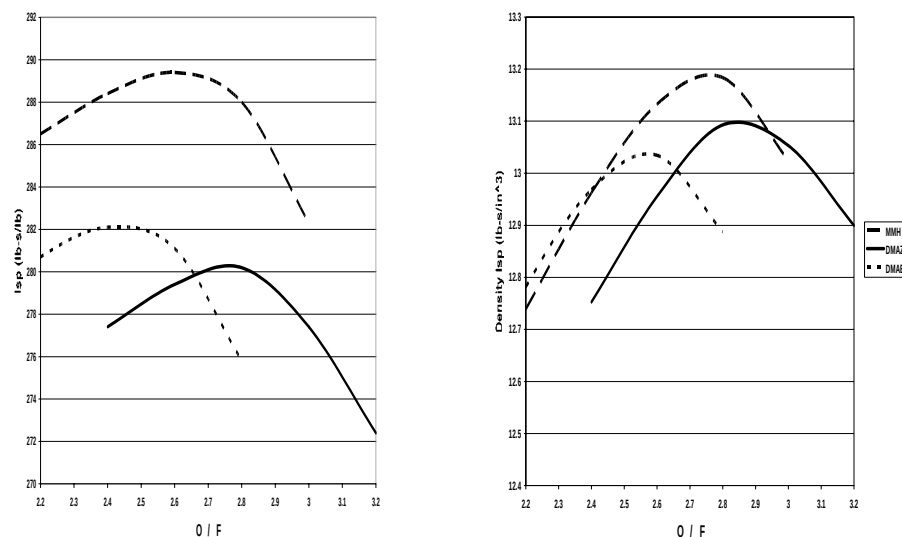


Figure 2: Calculated Isp and Density Isp values for MMH, DMAZ, and DMAEH.

While at this time no attempt has been made to optimize the operating conditions or oxidant for these calculations, these should be instructive for comparison purposes since calculations on each fuel have been done the same way. It is noteworthy from these curves that DMAEH provides an Isp somewhat superior to that of DMAZ, but this advantage is lost in the density calculation since the optimum oxidant level for DMAEH is less than that for DMAZ, and the oxidant provides a significant density boost. It should be emphasized again that the density value for DMAEH has been taken as equal to that of DMAZ. The actual value has yet to be determined. For the purposes of this report, it is enough to note that the three compounds have similar density impulse values and that this certainly encourages the continued study of the DMAEH molecule.

RESULTS AND DISCUSSION

PRIMARY SYNTHETIC STRATEGY

Since DMAEH is novel, methods for its synthesis and characterization need to be investigated. A simple yet efficient two-step retro-synthetic strategy has been designed and is shown in Figure 3.

This particular strategy shown in Figure 3 would serve as our primary strategy. Under a general scenario, intermediate I would have Y and R₂ both be hydrogens while the red X on intermediate II would be a good leaving group like *p*-toluenesulfonate or a halide. More specifically, this scenario would result in intermediate I being 1,1-dimethylhydrazine or unsymmetrical dimethylhydrazine (UDMH), which is commercially available. Intermediate II would then be synthesized from a starting material containing two different leaving groups, X and X₁, where reaction with azide would preferentially result in intermediate II. An example of this type of material would be 2-chloroethyl-*p*-toluenesulfonate. This material is particularly attractive because it is commercially available, relatively inexpensive, and possesses two

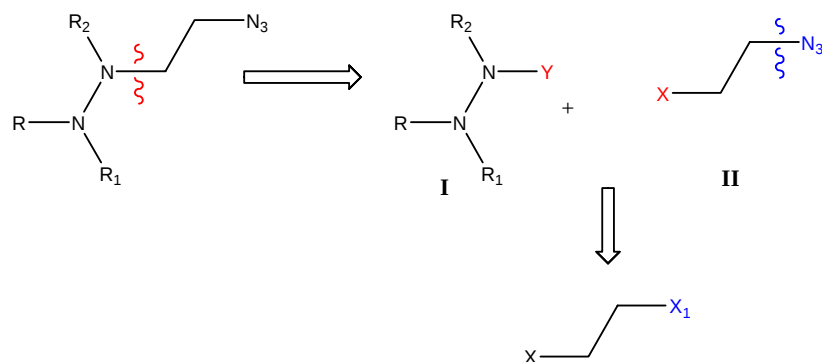


Figure 3: Proposed primary retro-synthetic strategy to DMAEH

attractive leaving groups. Both the chloro and the tosyl groups can be substituted by a nucleophile (e.g. a hydrazine derivative); but the tosyl group is known to be a significantly better leaving group which may permit a preferential substitution. One could envision other potential synthetic routes to intermediate II as well. Several additional retro-synthetic strategies were developed in the event the proposed primary strategy did not result in the successful synthesis of DMAEH. However, those strategies are beyond the scope of this paper.

One additional strategy will however be discussed in this paper which was developed as difficulties arose throughout this project. This strategy uses hydrazine in place of UDMH given the structural and electronic symmetry of hydrazine. Furthermore, hydrazine as a reactant in synthesis has been more widely reported in the literature.

SYNTHETIC INVESTIGATION

The initial goal was to develop and execute the retro-synthetic strategy to prepare enough of the desired material, 1,1-dimethyl-2-[azidoethyl]hydrazine, to perform standard chemical property testing and combustion experiments. Following the retro-synthetic strategy means the preparation of intermediate II from Figure 3. This can be accomplished through one of two methods shown in Figure 4. The top reaction shows the preparation of 2-azidoethyl *p*-toluenesulfonate was accomplished in a two step sequence. The first step involves the substitution of azide on 2-chloroethanol to provide 2-azidoethanol⁵. This material is known to be explosive⁶ therefore it was never isolated or purified. Instead, the 2-azidoethanol was extracted into chloroform and used directly in step 2⁷ where the solution was mixed with pyridine and *p*-toluenesulfonyl chloride. The resulting crude product was column chromatographed (25% ethyl acetate/petroleum ether) on silica gel to provide an overall yield for 2-azidoethyl *p*-toluenesulfonate, substrate 1, of approximately 50%.

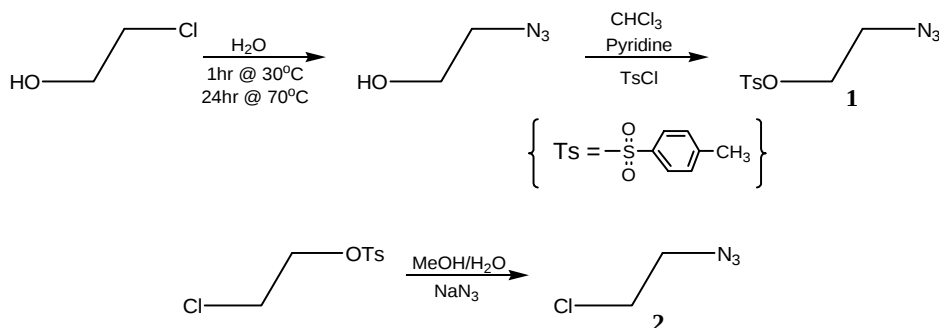


Figure 4: Proposed synthetic scheme to prepare intermediate II of Figure 3

The bottom reaction in Figure 4 shows the preparation of the 2-chloroethyl azide, substrate 2, was achieved in one step from 2-chloroethyl *p*-toluenesulfonate and sodium azide in a water/methanol mixture⁸. After 24 to 48 hr at reflux, the product was extracted with ether then isolated in moderate yields (40-60 %). The water/methanol ratio was critical and had to be systematically adjusted to achieve optimal yields.

Substrate 1 or 2 should react with UDMH to produce the desired DMAEH product as shown in Figure 5. However, regardless of the conditions, UDMH and 2-chloroethyl azide did not react in

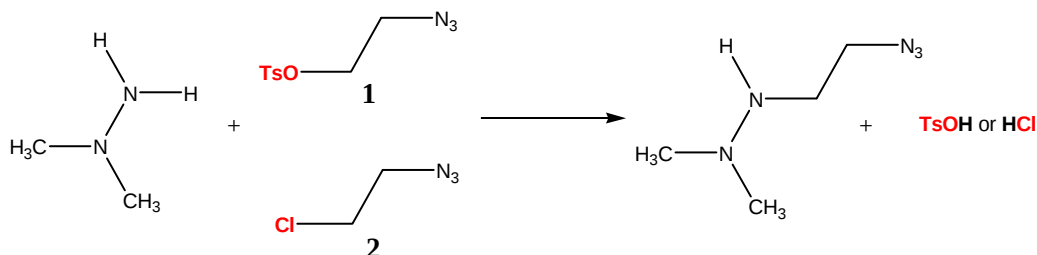


Figure 5: Synthetic scheme between UDMH and substrate 1 or 2

solvents like tetrahydrofuran (THF), toluene, or ether. An article published in *Organometallics*⁹ claimed butylhydrazine as the major product from the reaction of hydrazine and chlorobutane. The preparation was reported as simple and was carried out in neat hydrazine. Therefore, the same procedure was repeated with 2-chloroethyl azide and UDMH, yielding a white precipitate. The precipitate was isolated and characterized by ¹³C and ¹H Nuclear Magnetic Resonance (NMR) Spectroscopy and Liquid Chromatography (LC). Surprisingly the NMR shifts of the characteristic ethyl peaks were not pronounced (only 0.2 ppm), unlike what one might expect from replacing a strong withdrawing group with a donating group like an amine. In contrast, the peaks attributed to the two N-methyl groups on the hydrazine appeared about 1 part per million (ppm) shift downfield, which would be an unexpectedly large shift for these methyl groups as we expect their environment to change little from the transformation. However, this significant 1 ppm shift downfield does indicate an electron withdrawing affect on the N-methyl groups. This affect would be seen if the tertiary nitrogen performed the substitution reaction resulting in a quaternary nitrogen with a positive charge.

With the exception of a European patent¹⁰ reporting the displacement of a tosylate group by the UDMH in quite mediocre yields (36%), this substitution reaction is not well documented. It appears as though the displacement of a leaving group by the primary amine of UDMH is sterically favored while electronically disfavored. Literature reports have shown that in the case of hydrazines the most nucleophilic nitrogen is generally the one that bears the alkyl-substituents¹¹. Thus, the substituted nitrogen of UDMH would be considered the most nucleophilic. Depending on whether steric or electronic factors dominate, the reaction between UDMH and substrate 1 (or similarly substrate 2) can result in two isomeric products as shown in Figure 6.

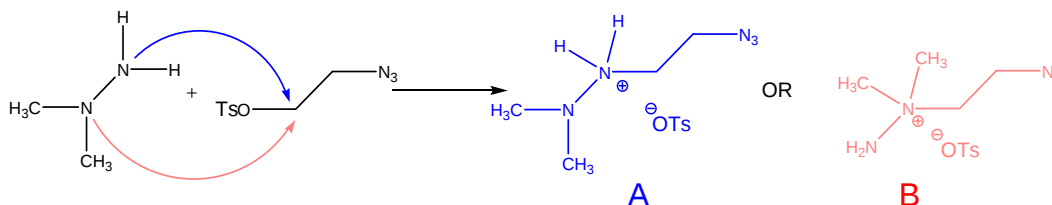


Figure 6: Reaction of UDMH with substrate 1 and the two potential resulting products

The resulting material in Figure 6 produced a white solid that was isolated by filtering and washing with ethyl ether. This precipitate produced similar ^1H and ^{13}C NMR shifts as those discussed previously for the reaction of UDMH and substrate 2. The structural characterization of the material produced from the reaction in Figure 6 was inconclusive as to whether product A or product B was formed. Therefore a more detailed study was needed and this material was characterized using 2-dimensional ^1H NMR and x-ray crystallography.

Two-Dimensional Nuclear Magnetic Resonance Spectroscopy (2-D NMR) has been used to study the long range coupling of the white solid discussed above. In the desired product, isomer A, the protons of the two methyl groups on the hydrazine are farther away (five bonds) from the CH_2 of the ethylazide functionality than in the quaternary ammonium species, isomer B. HSQC (heteronuclear single quantum coherence) and HMBC (heteronuclear multiple bond coherence) are long-range coupling NMR experiments that are specifically designed to provide coupling information through several bonds. The white solid obtained after reaction of UDMH with substrate 1 has been subjected to both experiments and shows coupling between the methyl protons of the hydrazine moiety and the protons on the carbon adjacent to the quaternary nitrogen.

These results provide strong evidence for the formation of the quaternary ammonium salt, isomer B, which is the undesired isomer. While unlikely, this coupling could have occurred through 5 bonds, consistent with Isomer A. To be absolutely certain, other structural evidence is needed and can likely be ascertained through x-ray crystallography.

The product from the reaction in Figure 6 is a white solid from which a single crystal could be grown. Using the classical methods of slow crystallization an ether/methanol mixture provided a single crystal of high quality for X-ray analysis. As suggested by the long-range NMR experiments, the white crystal was identified by x-ray crystallography as isomer B. Clearly, the electronic nature of UDMH is dominating its reactivity.

One way to manipulate the electronic properties governing the reactivity of UDMH is to shift this electronic density from the substituted nitrogen to the unsubstituted nitrogen. This can be performed by removing one of the protons on the primary nitrogen of UDMH using a strong base as shown in Figure 7.

This deprotonated UDMH can then be reacted with substrate 1 or 2. In addition to these two substrates, 2-iodoethyl azide (IETAz) whose use would be desirable in some specific reactions discussed later in this report, was used for some of these preliminary reactions as well.

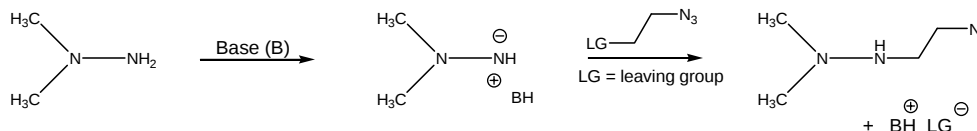


Figure 7: Deprotonation of UDMH followed by reaction with an azidoethyl intermediate

These types of undesirable electronic factors can be overcome synthetically as shown by Robinson et al. who demonstrated that unsymmetrical hydrazines can undergo acid-base reactions regioselectively¹¹. For example, 1,4-diazabicyclo[2.2.2]octane (DABCO) appears to deprotonate only the primary amine of 1-phenylhydrazine. In contrast, stronger but less bulky bases like sodium hydride (NaH) deprotonate the secondary amine, i.e. the nitrogen bearing the phenyl group. However, in the particular case of UDMH there is only one type of acidic proton. In an attempt to “force” the nucleophilic substitution at the primary amine site, the following bases, DABCO, triethylamine, sodium hydride, butyllithium, sodium methylate, and magnesium t-butoxide were tested under a myriad of conditions.

In the current system, the strong bases NaH, butyllithium (BuLi) and magnesium tert-butoxide seem to only yield decomposition and/or no reaction. The use of DABCO, sodium methylate or triethylamine produced a white precipitate from reactions involving both substrates 1 & 2. Regardless of the conditions, the NMR spectra of the resulting white precipitate were identical to the NMR spectra discussed previously, indicating the material was the undesirable quaternary ammonium salt isomer.

However, the liquid phases for a few of the reactions were analyzed via Gas Chromatography-Mass Spectroscopy (GCMS) resulting in a peak which provided a molecular ion peak in the mass spectra of $m/z = 129$. Not only does this mass happen to correspond to the mass of our desired product DMAEH, but the fragmentation pattern is consistent with DMAEH thus providing evidence we are forming the desired product. All efforts at isolation of the identified DMAEH proved unfruitful.

In another effort to manipulate the reactivity of UDMH, it was assumed that if the electronically favored properties of the tertiary nitrogen could be minimized, the primary nitrogen would be favored for reaction. Therefore, UDMH was reacted with a series of different electrophiles, shown in Figure 8, with the expectation that the tertiary nitrogen of UDMH would form an adduct and become less reactive. This strategy appeared attractive since removal of these adducts after reaction would be trivial.

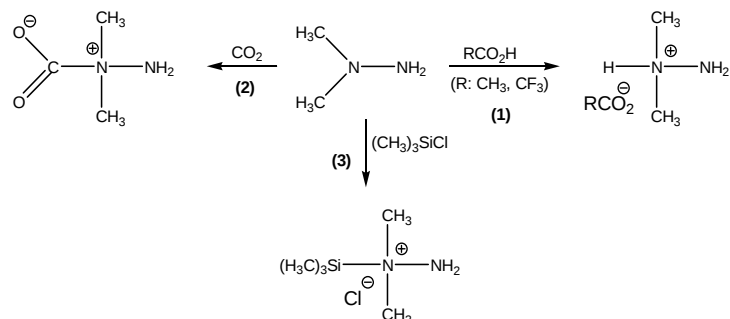


Figure 8: Proposed schemes for preparing four different UDMH adducts

The four electrophiles shown in Figure 8 are acetic acid, trifluoroacetic acid, carbon dioxide and trimethylsilyl chloride. Acetic acid and trifluoroacetic acid (TFA) reacted strongly with UDMH to form a white solid and viscous liquid, respectively. The reaction was very exothermic and was therefore performed under cold dilute conditions (THF was used as solvent). After removal of the solvent, the ammonium analogs were isolated and characterized.

Another acidic compound but of milder strength is carbon dioxide. As shown in reaction 2 above, UDMH forms a white solid very quickly upon exposure to CO_2 . Characterization supports the complete regioselective reaction at the tertiary nitrogen.

Finally, reaction 3 with trimethylsilyl chloride, a very widely used electrophilic protecting group, forms a white precipitate after a few hours. This solid precipitate was filtered, washed with ether, and immediately used in a subsequent step where it was reacted with either AzEtOTs or IEtAz. The mother liquor from this reaction was analyzed to find all of the starting material had disappeared. Given this disappearance of starting materials and the quick formation of a white precipitate combined with the nature of this reaction, we anticipated the desired intermediate was formed. Due to this system being investigated near the very end of the project deadline, time was not devoted to fully characterize this material. Instead, we moved on to performing reactions with these adducts with the anticipation that any success would result in a full characterization.

Once the three adducts resulting from reactions 1 and 2 in Figure 8 were isolated, they were reacted neat in AzEtOTs. For all three of these reactions, only the quaternary ammonium salt, isomer B, was formed and only in yields less than 20%. Unfortunately, this approach did not meet our expectations. The adduct formed in reaction 3 was reacted with both AzEtOTs and IEtAz under a number of differing conditions while neat, or dissolved in acetonitrile or methanol. Unfortunately, only the quaternary ammonium salt resulted.

While investigating the literature, only one example of a tosylate displacement by UDMH was identified¹⁰. This displacement reaction was carried out in methanol at reflux for 12 hours to provide a 36% conversion. By analogy, substrate 1 was combined with UDMH in methanol overnight at reflux as shown in Figure 9. All of substrate 1 reacts under these conditions, however to again produce the undesired quaternary ammonium salt.

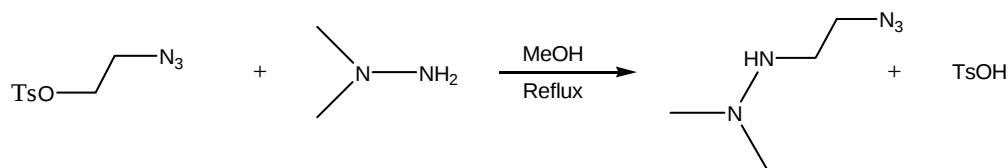


Figure 9: Reaction between AzEtOTs and UDMH in methanol at reflux

Further investigation of the literature led to a patent¹² discussing the reaction between UDMH and a haloacetyl compound. In this patent, UDMH was reacted with a 2-bromoacetyl compound in anhydrous ethyl ether to produce the respective quaternary ammonium salt which was isolated. This salt was then dissolved in methanol and refluxed to cause a rearrangement whereby the first step was the “flip flop” of the UDMH with subsequent loss of hydrobromic acid (HBr). It's believed that the halide attacks the carbon bonded to the quaternary nitrogen releasing UDMH. The primary nitrogen of the released UDMH then attacks that same carbon releasing HBr. This particular system then follows a series of rearrangements to get to the final product. However, the first few steps can be used as evidence for possibly getting our system to rearrange.

By analogy, the anion of our quaternary ammonium salt could attack the carbon alpha to the quaternary nitrogen to displace UDMH and “force” a similar rearrangement as shown in Figure 10.

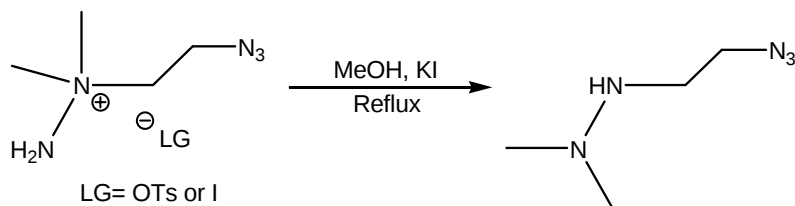


Figure 10: Reaction between the undesired quaternary ammonium salt and KI in methanol at reflux to induce rearrangement to the desired DMAEH product

The undesired quaternary ammonium salt has either the tosylate or iodide anion as the counter ion. The tosylate anion in particular does not make a good nucleophile to initiate this rearrangement. Therefore an excess of KI was added to the reaction mixture to initiate the rearrangement. In cases where the quaternary ammonium iodide substrate was used, an excess of KI was also added. The analysis of these reaction mixtures never identified the formation of any of the desired DMAEH product. Potassium iodide has limited solubility in methanol and therefore some reactions were run with trace amounts of water added to bring KI into the organic phase without success. Quaternary ammonium phase transfer catalysts (i.e. tetrabutylammonium iodide) were also attempted as a means to shuttle the iodide into the organic phase without success.

In the synthetic pursuit of 1,1-dimethyl-2-[2-azidoethyl]hydrazine (DMAEH) the dominant reactivity of the tertiary nitrogen of unsymmetrical dimethylhydrazine (UDMH) has become clear. Regardless of the conditions or even the presence of base, the substituted nitrogen of UDMH dictated its nucleophilic reactivity with all intermediate electrophiles it was reacted with. The result was an undesired quaternary ammonium or hydrazonium salt. Trace amounts of the desired product could be detected via gas chromatography mass spectrometry when reactions were carried out in methanol between UDMH and any one of a number of intermediate electrophiles. However, these reactions were never able to produce sufficient quantities of product for isolation.

HYDRAZINE BASED DERIVATIVE

In contrast to UDMH, nucleophilic displacements using hydrazine as a nucleophile have been more widely reported.¹³ There is no difference in the nitrogen reactivities of hydrazine as they are sterically and electronically equivalent. Substrates 1 and 2 were reacted with hydrazine (Figure 11) to produce no precipitate during the reaction and the crude product remained a liquid after the evaporation of hydrazine. The NMR spectra were different than those discussed earlier. First, the ethylene peaks shifted 1 to 2 ppm upfield. Secondly, a distinct peak at 6.1 ppm appeared which can be attributed to the amine hydrogens.

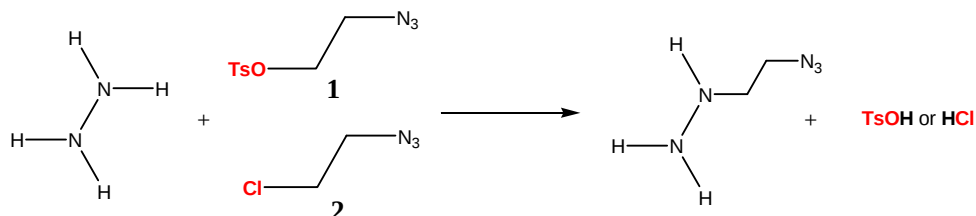


Figure 11: Reaction of hydrazine with substrate 1 or 2

The reaction with AzEtOTs (substrate 1) reached completion after 24 hours at room temperature. *p*-Toluenesulfonic acid (PTSA) is expected to form along with the desired 2-azidoethyl hydrazine. Further evidence was provided by the LC analyses clearly indicating the presence of PTSA in the crude product. Although the 2-chloroethyl azide reacted slower, after 72 hours most of the starting material had disappeared and the resulting crude provided evidence for product formation. Because significant quantities of AzEtOTs had been prepared for future reactions, this material was primarily used in attempts to prepare 2-azidoethylhydrazine by reaction with hydrazine.

Once the reaction was complete it was cooled on an ice bath. Ether was added and the reaction was stirred. The resulting white precipitate was filtered and analyzed. The precipitate was believed to be PTSA. The filtrate was cautiously evaporated by blowing nitrogen over the surface of the liquid to provide an oil whose NMR analysis was found to be consistent with the desired product. However a purity of 95% was insufficient for further characterization and testing. The major impurity was the disubstituted hydrazine. The mass spectrum also detected another high molecular weight impurity that was not seen in the NMR and never identified.

The next purification method attempted was short path liquid column chromatography with silica gel. As expected the hydrazine does not move much on Thin Layer Chromatography, while the product does move slightly. The eluent used was ethyl acetate/hexane (80/20). The spot attributed to the product was successfully separated but was impure (90 %) with a low mass recovery. This technique does not appear to be the most promising; however alumina may prove to be gentle enough while still providing sufficient separation. Unfortunately all of our attempts at isolating and purifying 2-azidoethylhydrazine have been unsuccessful. However, we do believe this material is being produced in significant enough quantities to be isolated if a mild enough system for purification is used.

CONCLUSIONS

Unfortunately, all synthetic attempts to prepare and isolate 1,1-dimethyl-2-[2-azidoethyl]hydrazine were unsuccessful. UDMH or hydrazine was considered the key reactant in all synthetic strategies discussed in this paper. The orientation of DMAEH's reactivity predominantly resulted in the undesired product in every reaction scheme attempted. The electronic properties of UDMH dominate over the steric regardless of the solvent used or system conditions. The reactivity of UDMH as a nucleophile was unaffected by all attempts to modify it. The presence or choice of base does not influence UDMH nucleophilicity. Converting UDMH to a reactive intermediate through its interaction or reaction with an electrophile had no influence on its nucleophilicity. Changing the electrophile used in the final step, that is, using a chloro or iodo alkane, or a tosylate does not alter the nucleophilicity of UDMH. As a nucleophile, UDMH consistently attacks via the most substituted nitrogen to form a quaternary ammonium

or hydrazonium salt. When the reaction conditions utilized MeOH with no base, trace amounts of the desired product were identified via GCMS.

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