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# Formation of Diazirine Functionality for Propellant Applications

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## Abstract

Overall, this research focuses on a cost-effective approach which minimizes synthetic overhead when assembling compounds with diazirine functionality. The goals are to prevent the surplus use of ammonia in the formation of the diaziridines and use electrochemistry to perform the oxidation of diaziridines. In addition, this project will evaluate the efficiency of different diazirine molecules as propellants.



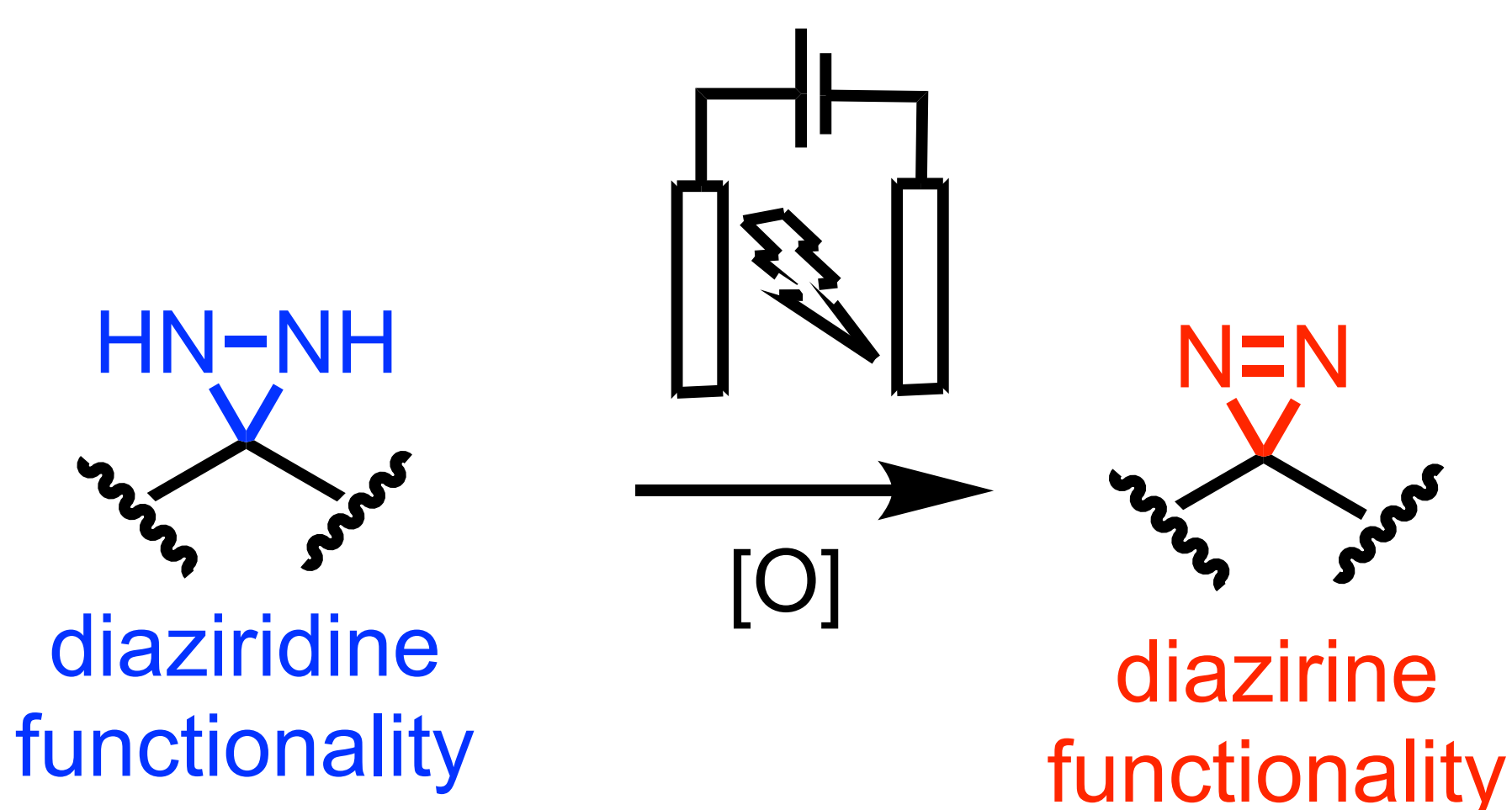
Image of a NASA rocket.

Propellants:

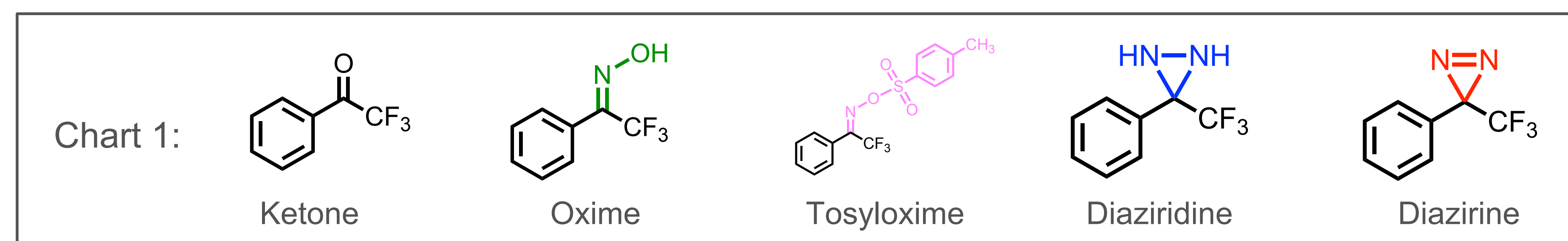
- According to NASA, diazirines have the potential to make up components of propellants, specifically for missiles [1].

## Introduction

The Haber-Bosch process is a named reaction used in the chemical engineering industry, specifically for fertilizers [2]. The Haber-Bosch process works as written in literature, yet literature for diazirine functionality synthesis is misleading and more complicated than what appears on paper. To counteract this difficulty met with literature, this project explores the use of electrochemistry to move electrons in diaziridine functionality, to form diazirine functionality. This is accomplished through an Electrosyn 2.0.



## Methodology



First, several different aldehydes and ketones are selected as the starting materials. **Chart 1** shows one reagent tested using this synthetic route [3].

Three different experimental routes are being tested from diaziridine to produce diazirine:

1. Electrochemistry
2. Silver (I) Oxide, Ag<sub>2</sub>O
3. Iodine, I<sub>2</sub>

Each step of the process is evaluated using:

- gas chromatography-mass spectroscopy (GC-MS)
- nuclear magnetic resonance (NMR)
- thin-layer chromatography (TLC)

## Results

Ketone to Oxime:

- Table 1** show high conversion and TLC retention factor values

Oxime to Tosyloxime:

- Solidified a prep that stabilizes the compound

Tosyloxime to Diaziridine:

- Small head space in reaction vial it vital for high yields

Diaziridine to Diazirine:

1. Electrochemistry – not a dependable method
2. Tested several electrodes, running times, and current on the Electrosyn 2.0 and still no conversion
3. Lack of conversion is due to fouling of electrodes
4. Ag<sub>2</sub>O and I<sub>2</sub>
5. Currently experimenting with these methods
6. NMR data shows that diazirine functionality is being produced, yet the yield and quality is poor
7. Key <sup>19</sup>F NMR peaks are displayed in **Table 2** for each step in **Chart 1**

TGA-DSC:

- Table 3** displays the melting points determined for key intermediates

Table 1: Data for Oxime Reactions

	Starting Material	Structure	Percent Yield	TLC Data	
				Solvent System	R <sub>f</sub>
Ketone Functionality	acetophenone		81.1%	1:9 EtOAc:Hex	0.18
	2,2,2-trifluoro-1-phenylethanone		72.3%	1:4 EtOAc:Hex	0.60
	4-tert-butylcyclohexanone		83.6%	1:4 EtOAc:Hex	0.31
	levulinic acid		N/A	1:1 EtOAc:Hex	0.07
Aldehyde Functionality	octanal		95.9%	1:4 EtOAc:Hex	0.23, 0.34
	1,4-benzenedicarboxaldehyde		98.2%	1:2 EtOAc:Hex	0.31, 0.41
	4-methoxybenzaldehyde		93.9%	1:4 EtOAc:Hex	0.4
	4-nitrobenzaldehyde		90.9%	1:4 EtOAc:Hex	0.24, 0.35

Table 2: Key <sup>19</sup>F NMR Peaks

Compound	2,2,2-trifluoro-1-phenylethanone	Oxime	Tosylate	Diaziridine	Diazirine
<sup>19</sup> F NMR (ppm)	71.3	66.5	66.6	75.4	75.4

Table 3: Melting Points determined from TGA-DSC

Compound	Melting Point
Oxime	40.2 ± 0.1
Tosylate	103.8 ± 0.1
Diaziridine	18.5 ± 0.1

## Summary and Future Work

An efficient synthesis of diazirine functionality has not been reached. So far, students have established that the prep for producing oxime functionality results in high yields, developed a method that stabilizes tosyloxime functionality, and learned the importance in lessening head space in reaction vials when producing diaziridine functionality. Through repetition and practice, a detailed prep is being developed for **Chart 1**, and our efforts are focused on improving the last synthetic step. After completion of the synthesis process, a thermogravimetric analyzer - digital scanning calorimeter (TGA-DSC) was used to assess the energetic properties for the product of each synthetic step. Further data will need to be collected used to evaluate if diazirines have the potential to serve as propellants components.

## Supportive Documentation

[1] NASA. (n.d.). *PROPELLANTS*. <https://history.nasa.gov/conghand/propelInt.htm#:~:text=Most%20liquid%20chemical%20rockets%20use,liquid%20oxygen%2C%20and%20liquid%20fluorine> (accessed 2023-08-23).

[2] Clark, J. (2023-01-30). The Haber Process. [https://chem.libretexts.org/Bookshelves/Physical\\_and\\_Theoretical\\_Chemistry\\_Textbook\\_Maps/Supplemental\\_Modules\\_\(Physical\\_and\\_Theoretical\\_Chemistry\)/Equilibria/Le\\_Chateliers\\_Principle/The\\_Haber\\_Process](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Equilibria/Le_Chateliers_Principle/The_Haber_Process) (accessed 2024-03-11).

[3] Beebe, A. W. (2015-08-18). *Diastereoselective synthesis of substituted diaziridines from simple ketones and aldehydes*. Chemical Communications (RSC Publishing). <https://pubs.rsc.org/en/content/articlelanding/2015/cc/c5cc04813c#!divAbstract> (accessed 2023-08-23).

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