~~Functionalized~~ Strained Hydrocarbons as Potential Hypergolic Fuels

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An Overview of Project Goals

We are in search of a storable combination of high-energy hypergolic fuel and oxidizer to increase the efficiency of RLVs

The proposed fuel should:

1) Increase the amount of energy provided per unit volume of fuel
2) Eliminate the need of toxic oxidizers such as nitric acid
3) Eliminate the need of an inorganic catalyst

Why Strained Hydrocarbons (SHCs)?

- Strain is induced in saturated hydrocarbons by altering the C-C bond angle from 109.5°.

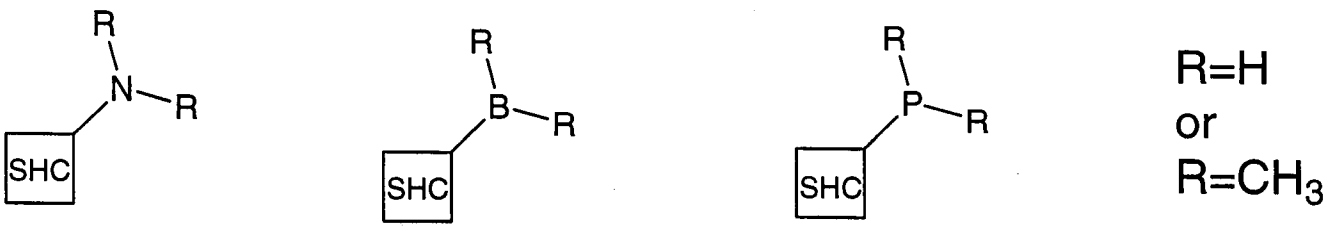
- Increasing the strain energy of a molecule results in a higher heat of combustion per carbon atom

	Bond Angle (°)	Strain Energy per Carbon Atom (kJ/mol)	Heat of Combustion per CH_2 (kJ/mol)	Heat of Combustion per CH_2 (kJ/g)
	108	4	658	47
	90	24	680	49
	60	34	697	50

Lewis, L. et al. *Theo. Chem.* 2002, *592*, 161.
NIST Organic Thermonchemistry Archive. http://www.webbook.nist.org, 2003.

Addition of Functional Groups

- Amines, boranes, and phosphorus functional groups have been found to induce hypergolicity with nitric acid based oxidizers.
- Hydrazine and its simple derivatives are the only known compounds to be hypergolic with H_2O_2 oxidizer.
- A combination of strain and functional groups will perhaps create the desired fuels system.

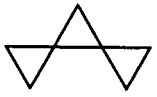
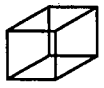


Zletz, A.; Carmody, D. US Patent 2, 892, 305, 1959.

Lewis, B. US Patent 3, 177, 652, 1965.

Broatch, J. *Fuel* **1950**, *24*, 106.

Initial Research Focus

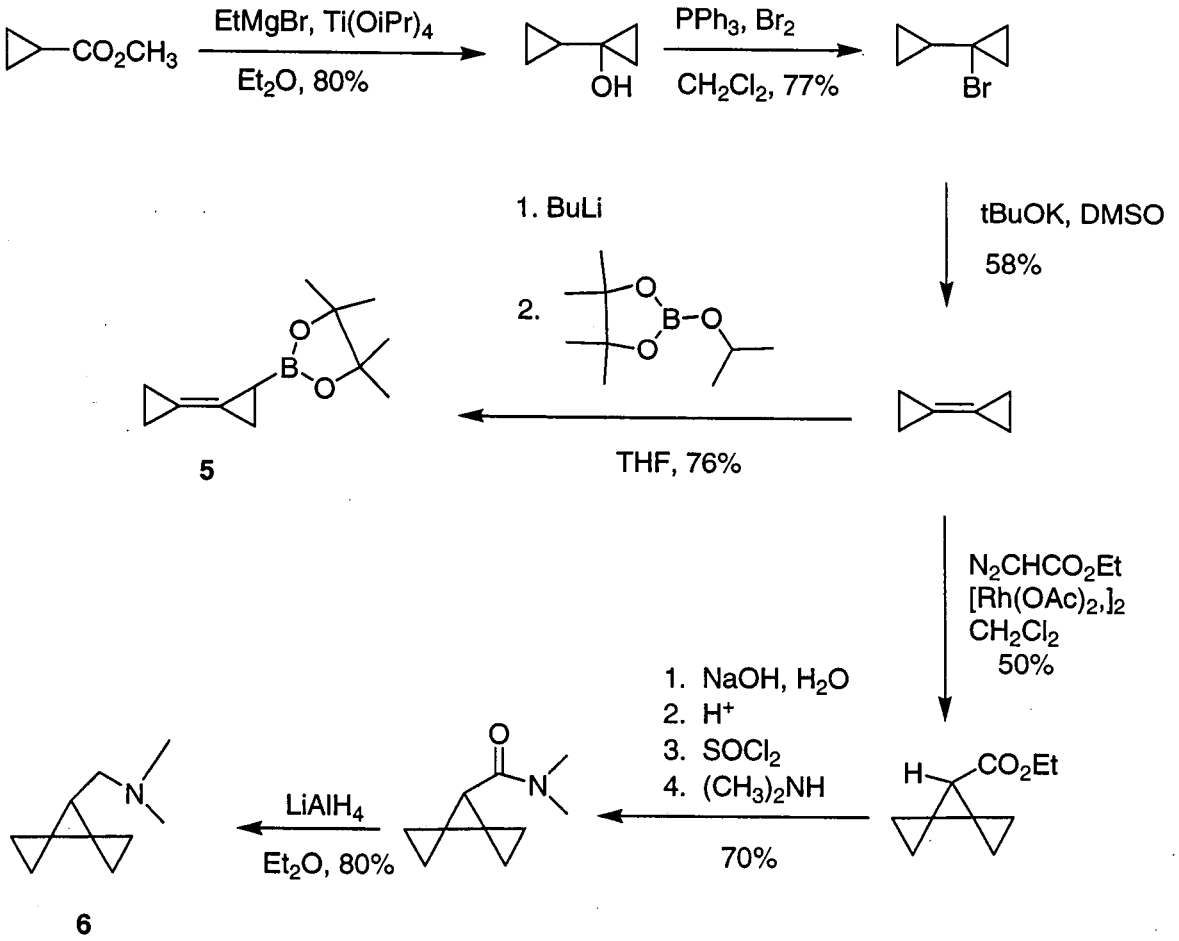
	 1	 2	 3
Strain Energy per Carbon Atom (kJ/mol)	58	79	62

- Despite their strain, triangulanes (**1**) and cubanes (**2**) are remarkably stable and their chemistry is well developed, thus providing a starting point for initial testing compounds.

- The chemistry of **3** requires synthetic development and methodology, but the calculated strain energy is lower than **2**, thus suggesting a realistic goal.

De Meijere, A; Kozhushkov, S.; *Chem. Rev.* **2000**, *100*, 93.
Wiberg, A. *Angew. Chem. Int. Ed. Eng.*, **1986**, *25*, 312

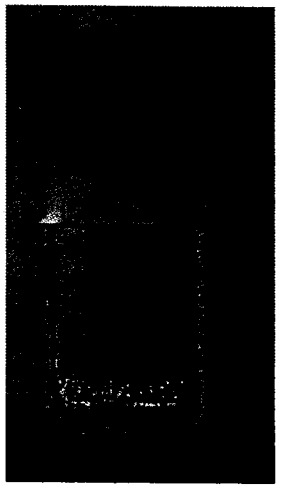
Initial Synthesis of Potential Fuels

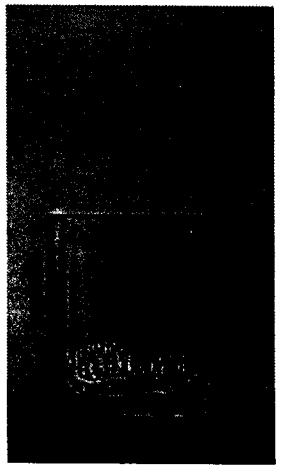


Meijere, A. d.; Kozhushkov, S.; Späth, T. *Org. Synth.* **2003**, *78*, 142-151.
Lohr, S.; de Meijere, A. *Synlett.* **2001**, 489-492.
Demeijere, A.; Kozhushkov, S. I.; Spaeth, T.; Zefirov, N. S. *J. Org. Chem.* **1993**, *58*, 502-505.

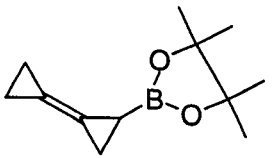
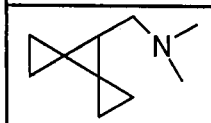
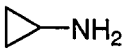
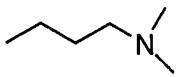
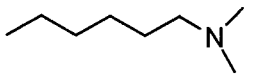
Testing of Potential Fuels

- Compounds are tested using drop test experiments utilizing schlieren high speed video imaging.
- 98% H_2O_2 was used as the oxidizer for all drop tests.
- The potential fuels were tested neat and with 10% of a cobalt (II) 2-ethylhexanoate catalyst





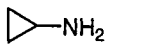
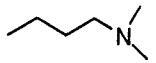
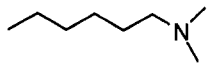
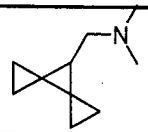
A Summary of Decomposition and Ignition Delay Time

	Neat H_2O_2 decomp. time (msec)	Neat Ignition delay (msec)	Catalyst H_2O_2 decomp. time (msec)	Catalyst Ignition delay (msec)
	ND	NI	ND	NI
	ND	NI	10.0	NI
	ND	NI	6.5	12.0
** 			5.2	9.8
** 			6.1	12.7

ND= No Decomposition
NI= No Ignition

** Blevins, J.; Gostowski, R. *AIAA* 2004-1335.

Summary of Amine Data and Possible Explanations

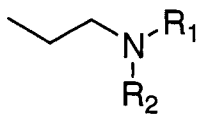
	MW (g/mol)	BP deg. C	Catalyst H_2O_2 decomp. time (msec)	Catalyst Ignition delay (msec)
	57.1	50	6.5	12.0
	101.2	93	5.2	9.8
	129.2	146	6.1	12.7
	137.2	NA	10.0	NI

1) Compounds may have too low vapor pressure to allow ignition

2) Reactions of primary amine hydrogens may cause a delay in ignition time

3) Insufficient miscibility of fuel with H_2O_2 may prevent ignition

Proposal for Future Research



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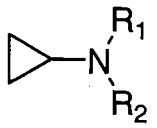

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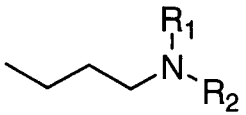

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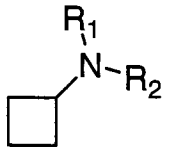


10

a R_1, R_2 = H

b R_1 = H, R_2 = CH_3

c R_1, R_2 = CH_3

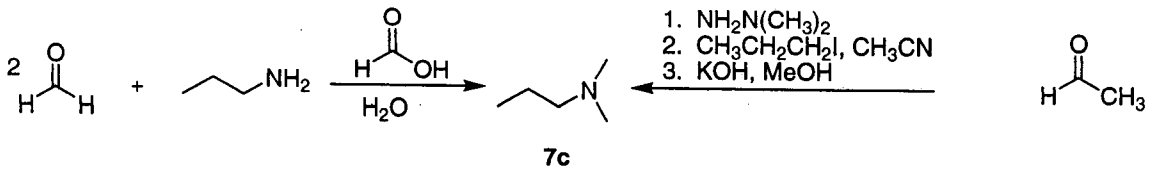
1) Choose lower molecular weight amines with higher vapor pressures

2) Compare 1°, 2°, 3° amines to determine the effect of amine substitution

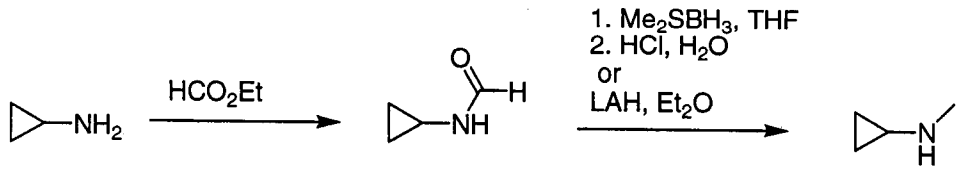
3) A lower Carbon:Nitrogen ratio may provide higher fuel/oxidizer miscibility and provide faster ignition

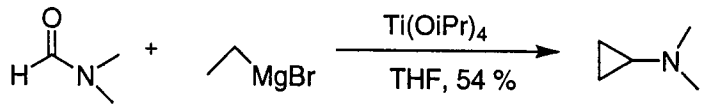
Synthesis of Amines

While most of the compounds commercially available, the synthesis of **7c**, **8b**, **8c**, **10b**, and **10c** is required.

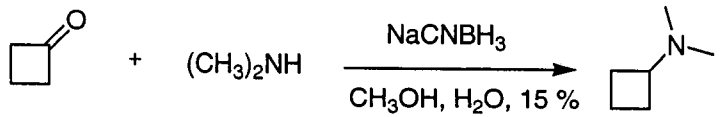


7c





8c



10c

Smith, R. F.; Marcucci, J. L.; Tingue, P. S. *Synth. Commun.* **1992**, *22*, 381-389.

Giardina, G.; Clarke, G. D.; Dondio, G.; Petrone, G.; Sbacchi, M.; Vecchietti, V. *J. Med. Chem.* **1994**, *37*, 3482-3491.

Chaplinski, V.; deMeijere, A. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 413-414.

Borch, R. F.; Bernstei.Md; Durst, H. D. *J. Am. Chem. Soc.* **1971**, *93*, 2897-2904.

Final Conclusions

Testing of the proposed amines will allow us to determine:

1) The effect of vapor pressure upon ignition of amines
2) The effect of 1°, 2°, or 3° amines on ignition
3) If miscibility is a factor in the ignition of fuels

Providing these initial compounds show an increase in H_2O_2 decomposition time and ignition delay, systems containing higher strain energy that require a more arduous synthesis. Commercial cyclobutyl and cyclopropyl bromines can undergo halogen- metal exchange to result in boron and phosphine derivatives to allow a complete analysis of strained potentially hypergolic systems.

Acknowledgements

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Strained Hydrocarbons as Potential Hypergolic Fuels

A storable combination of high-energy hypergolic fuel and oxidizer is advantageous to the future of reusable launch vehicles (RLVs). The combination will allow an increase in energy per unit volume of fuel and eliminate the need for an external ignition system. Strained systems have been studied as potential high-density fuels. Adding hypergolic functional groups, such as amino groups, to these hydrocarbons will potentially allow auto ignition of strained systems with hydrogen peroxide.

Several straight chain amines and their strained counterparts containing an equivalent number of carbon atoms have been purchased and synthesized. These amines provide initial studies to determine the effects of fuel vapor pressure, strain energy, fuel miscibility, and amine substitution upon fuel ignition time and hypergolicity with hydrogen peroxide as an oxidizer.