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<th>b. ABSTRACT</th>
<th>c. THIS PAGE</th>
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</thead>
<tbody>
<tr>
<td>Unclassified</td>
<td>Unclassified</td>
<td>Unclassified</td>
</tr>
</tbody>
</table>

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A

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MEMORANDUM FOR PRS (In-House)

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Suri and Tinnirello, "Bicyclopropyliene and 1,5-Hexadiyne from Bench Scale to Pilot Scale: Problems and Solutions"

Presentation HEDM Conference (Statement A)
Bicyclopropylidene and 1,5-Hexadiyne from Bench Scale to Pilot Scale: Problems and Solutions

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DISTRIBUTION STATEMENT A:
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Presentation Outline

- Goal
- Criteria for Fuel Selection
- Structural Requirements and Selection for hydrocarbons
- Synthetic Results and Scale Up Challenges
- Future Efforts
Goal

- To come up with a fuel with 2-5% increase of Isp over LOX/RP-1
  - LOX/RP-1(del.) = 263 sec*
  - LOX/RP-1(calc.) = 300 sec*

* Determined at sea level and 1000 psi chamber pressure
Task Objective

- Survey of energetic hydrocarbons
- Selection of hydrocarbons based on improved theoretical performance
- Synthesis of target hydrocarbons at bench scale
  - Easy preparation, cost effective and safe
- Translate bench-scale synthesis to pilot scale
Criteria for Fuel Selection

- Predicts Better Performance (Isp) Over LOX/RP-1 System
- Most Desirable Physical Properties
  - Lower Vapor Pressure Compared to RP-1
  - Higher Density ($\geq$ RP-1 = 0.801 g/mL)
  - Freezing Point ($\leq$ -10°C; RP-1 = -41.4°C)
  - Boiling Point $\geq$ B. P. of RP-1
- Thermally Stable
- Compatible with the Current System
Structural Requirement for High Energy Contents

- The Energy Contents Can be Increased by Adding Unsaturation in the Molecule
  
  \(-(\text{CH}_2)\)-  CH$_2$=CH$_2$  HC≡CH

$\Delta H_f/C \sim -5 \sim 6.25 \sim 27.1$ Kcal/mole
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\Delta H_f$ (Obs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>CH$_3$CH$_3$</td>
<td>-20.04</td>
</tr>
<tr>
<td>Propane</td>
<td>CH$_3$CH$_2$CH$_3$</td>
<td>-25.02</td>
</tr>
<tr>
<td>Butane</td>
<td>CH$_3$(CH$_2$)$_2$CH$_3$</td>
<td>-30.03</td>
</tr>
<tr>
<td>Pentane</td>
<td>CH$_3$(CH$_2$)$_3$CH$_3$</td>
<td>-35.08</td>
</tr>
</tbody>
</table>

$\Delta H_f/C = \sim -5$ Kcal/mole
Heat of Formation of Unsaturated Hydrocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\Delta H_f$(Obs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>$\text{CH}_2=\text{CH}_2$</td>
<td>+12.5</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$</td>
<td>+26.11</td>
</tr>
<tr>
<td></td>
<td>$\Delta H_f/C = \sim +6.25 \text{ Kcal/mole}$</td>
<td></td>
</tr>
<tr>
<td>Acetylene</td>
<td>HC≡CH</td>
<td>+54.36</td>
</tr>
<tr>
<td></td>
<td>$\Delta H_f/C = \sim +27.1 \text{ Kcal/mole}$</td>
<td></td>
</tr>
</tbody>
</table>
Structural Requirement for High Energy Contents (Cont....)

- The Energy Contents is Also Increased by Incorporating Strain in the Molecule
  - Ring Compound $\Delta H_f$ + 12.73 Kcal/mole
  - Cyclopropane + 6.78 Kcal/mole
  - Cyclobutane - 18.44 Kcal/mole
  - Cyclopentane
Survey of Hydrocarbons

Cyclopropane
\[ \Delta H_f = 12.7 \text{ Kcal/mole} \]
\[ = 0.3 \text{ Kcal/g} \]
\[ I_{sp} = 312 \text{ Sec.} \]

[2.2] Spiropentane
\[ \Delta H_f = 44.4 \text{ Kcal/mole} \]
\[ = 0.65 \text{ Kcal/g} \]
\[ I_{sp} = 311 \text{ Sec.} \]

Bicyclopropylidene
\[ \Delta H_f = 76.1 \text{ Kcal/mole} \]
\[ = 0.95 \text{ Kcal/g} \]
\[ I_{sp} = 312.5 \text{ Sec.} \]

Cyclopropylacetylene
\[ \Delta H_f = 64.0 \text{ Kcal/mole} \]
\[ = 0.97 \text{ Kcal/g} \]
\[ I_{sp} = 311.3 \text{ Sec.} \]

Bicyclopropylacetylene
\[ \Delta H_f = 73.4 \text{ Kcal/mole} \]
\[ = 0.69 \text{ Kcal/g} \]
\[ I_{sp} = 307.2 \text{ Sec.} \]

Dicyclopropylidenemethane
\[ \Delta H_f = 104.6 \text{ Kcal/mole} \]
\[ = 1.13 \text{ Kcal/g} \]
\[ I_{sp} = 313.4 \text{ Sec.} \]
Survey of Hydrocarbons

1,5-Hexadiyne
\[ \Delta H_f = 91.8 \text{ Kcal/mole} \]
\[ = 1.18 \text{ Kcal/g} \]
\[ I_{sp} = 311.8 \text{ sec} \]

1,7-Octadiyne
\[ \Delta H_f = 79.9 \text{ Kcal/mole} \]
\[ = 0.75 \text{ Kcal/g} \]
\[ I_{sp} = 308.2 \text{ sec} \]

Quadricyclane
\[ \Delta H_f = 72.2 \text{ Kcal/mole} \]
\[ = 0.78 \text{ Kcal/g} \]
\[ I_{sp} = 307 \text{ sec} \]

[3]-Triangulane
\[ \Delta H_f = 72.3 \text{ Kcal/mole} \]
\[ = 0.77 \text{ Kcal/g} \]
\[ I_{sp} = 311.4 \text{ sec} \]
Survey of Hydrocarbons

[1.1.1] Propellane and its Derivatives

\[
\begin{align*}
\Delta H_f &= 83.0 \text{ Kcal/mole} \\
&= 1.25 \text{ Kcal/g} \\
I_{sp} &= 316.6 \text{ sec}
\end{align*}
\]

\[
\begin{align*}
\Delta H_f &= 51.0 \text{ Kcal/mole} \\
&= 0.75 \text{ Kcal/g} \\
I_{sp} &= 313.9 \text{ sec}
\end{align*}
\]

\[
\begin{align*}
\Delta H_f &= 45.0 \text{ Kcal/mole} \\
&= 0.54 \text{ Kcal/g} \\
I_{sp} &= 311.2 \text{ sec}
\end{align*}
\]

\[
\begin{align*}
\Delta H_f &= 26.0 \text{ Kcal/mole} \\
&= 0.21 \text{ Kcal/g} \\
I_{sp} &= 308.0 \text{ sec}
\end{align*}
\]

\[
\begin{align*}
\Delta H_f &= 95.0 \text{ Kcal/mole} \\
&= 0.70 \text{ Kcal/g} \\
I_{sp} &= 309.9 \text{ sec}
\end{align*}
\]
Selection of Target Molecules

1,5-Hexadiyne
I_sp = 311.8 \text{scc}

1,7-Octadiyne
I_sp = 308.2 \text{scc}

Bicyclopropyldiene
I_sp = 312.5 \text{scc}

Cyclopropylacetylene
I_sp = 311.3 \text{scc}
Literature Methodology


Literature Methodology

Kulinkovich Reaction

R—CO₂CH₃ \xrightarrow{1.\text{EtMgBr/Ti(OPr-i)₄/Ether}} R\text{OH}
\xrightarrow{2.\text{10\% Aq. H₂SO₄}}

O. G. Kulinkovich, S. V. Sviridov, D. A. Vasilevskii; *Synthesis* 1991, 234

\[\text{CO₂CH₃} \xrightarrow{1.\text{EtMgBr/cat.Ti(OPr-i)₄/Ether}} \xrightarrow{2.\text{10\% Aq. H₂SO₄}} \text{OH}\]

\[\text{Ph₃P/Br₂} \quad \text{t-BuOK/DMSO}\]

Literature Methodology for 1,5-Hexadiyne
AFRL/PRS Methodology

- Eliminated Use of Free Halogen
- Eliminated Use of Methylene Chloride
- Eliminated Use of Liquid Ammonia/Sodium
4,1-Hexadiyne Methadology for 1,5-Hexadiyne

1,5-hexadiene

\[ \text{NaBr/NaBO}_3/\text{glac. AcOH} \rightarrow \text{rt, 90\%} \]

\[ \text{Br} \quad \text{Br} \]

\[ \text{Br} \quad \text{Br} \]

Powd. KOH/(n-Oct)4NBr(2 mol %)/
2,5-Dimethyl-2,5-hexanediol (4 mol %)
Isopar V, rt

1,5-hexadiyne
Hazard Characteristics of Hydrocarbons

<table>
<thead>
<tr>
<th>Compound</th>
<th>Olin Matheson Liquid Impact*</th>
<th>Julius Peters Sliding Friction*</th>
<th>NOL Card GAP At Zero Card</th>
</tr>
</thead>
<tbody>
<tr>
<td>RP-1</td>
<td>&gt;200 Kg/cm</td>
<td>&gt;371 N</td>
<td>Negative</td>
</tr>
<tr>
<td>Bicyclopropylidene</td>
<td>&gt;200 Kg/cm</td>
<td>133 N</td>
<td>Negative</td>
</tr>
<tr>
<td>Cyclopropylacetylene</td>
<td>&gt;200 Kg/cm</td>
<td>78 N</td>
<td>Negative</td>
</tr>
<tr>
<td>1,5-Hexadiyne</td>
<td>56 Kg/cm</td>
<td>112 N</td>
<td>Negative</td>
</tr>
<tr>
<td>1,7-Octadiyne</td>
<td>148 Kg/cm</td>
<td>100 N</td>
<td>Negative</td>
</tr>
</tbody>
</table>

* Obtained five negative results
Proposed Mechanism of Kulinkovich Reaction
<table>
<thead>
<tr>
<th>Problems</th>
<th>Consequences</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rise in temperature (Exothermic reaction)</td>
<td>Loss of flammable solvent ($T_p = -45^\circ C$)</td>
<td>Perform addition of Grignard reagent below $0^\circ C$</td>
</tr>
<tr>
<td></td>
<td>Product rearranges to cyclopropyl ethyl ketone</td>
<td>Operation is done below $30^\circ C$</td>
</tr>
<tr>
<td>Water contamination</td>
<td>Decreases the concentration of Grignard reagent</td>
<td>Purge the reactor with nitrogen gas all the time to reduce the condensation of water vapors in the reactor.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Use anhydrous ether</td>
</tr>
<tr>
<td>High acid concentration while quenching</td>
<td>Probability of formation of rearranged product</td>
<td>Use of low concentration of acid</td>
</tr>
<tr>
<td>Gummy deposit on the wall of reactor and around cooling coil</td>
<td>Methylcyclopropyl carboxylate entraps in the gummy material.</td>
<td>Decrease the size of the batch. Try Continuous Process</td>
</tr>
<tr>
<td>By Products (Isopropanol and Methanol)</td>
<td>Reacts with brominating reagent in the second step.</td>
<td>Azetrope removal of Isopropanol &amp; methanol using ethylacetate at $\leq 50^\circ C$</td>
</tr>
<tr>
<td>Problems</td>
<td>Consequences</td>
<td>Solution</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>-----------------------------------</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Contamination of Isopropanol/methanol</td>
<td>Consumption of brominating agent to form 2-bromopropane/bromomethane</td>
<td>Try to minimize IPA/methanol contamination in step 1. After checking GC, compensate for IPA/Methanol by adding excess of reagent</td>
</tr>
<tr>
<td>Contamination of Pyridine</td>
<td>Carried over to next step</td>
<td>Wash the product in p-methylene chloride with aqueous HCl</td>
</tr>
<tr>
<td>Distill off solvent directly from reactor</td>
<td>Resulted in thick solid triphenyl phosphine oxide in the reactor.</td>
<td>Transfer to rotary evaporator directly and remove 2/3 of dichloromethane followed by treatment with pentane to form free flowing solid</td>
</tr>
<tr>
<td>Problems</td>
<td>Consequences</td>
<td>Solution</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>----------------------</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Exothermic Reaction</td>
<td>Loss of Product</td>
<td>Reaction vessel is equipped with condensor hooked to chiller at ≤ -10°C.</td>
</tr>
<tr>
<td>Direct Distillation under high vacuum at room temperature</td>
<td>Loss of Product</td>
<td>Quenching by adding the reaction mixture into ice-water and extracted with pentane, Distilling off pentane under vacuum using water aspirator at dry ice-acetone temperature, Putting multiple cold-traps in series</td>
</tr>
<tr>
<td>Purification</td>
<td></td>
<td>Using packed column, It further removes traces of pentane</td>
</tr>
</tbody>
</table>
Future Target Molecules

Bicyclopentadecane
Isp = 307.2 sec

Bicyclopropylidenemethane
Isp = 313.4
Summary

- The synthesis of 1-cyclopropylcyclopropan-1-ol was developed by generating Grignard reagent in situ, thus avoiding handling of moisture sensitive and flammable preformed ethylmagnesium bromide.
- Three steps synthesis was used to prepare 7-8 lbs of bicyclopropylidene. There is a need to find an alternative synthetic route (maximum 2 steps) for it.
- About 200 g of 1,5-hexadiyne was synthesized using environmentally friendly process that eliminates the use of free bromine, controlled solvent dichloromethane and liquid ammonia, was worked out.
- Collected hazard data on bicyclopropylidene and 1,5-hexadiyne