CCB DFAs: Tactical Aviation Fuels

Technology Session Area Review:
Catalytic Upgrading

PI: Andrew Sutton

Los Alamos National Laboratory

Quad Chart Overview

Timeline

- Project start date: May 2018
- Project end date: April 2020
- Percent complete: 40 %

	FY 18 Costs	Total Planned Funding (FY 19-Project End Date)
DOE Funded	$333,333	$333,334
Project Cost Share	$100,000	$100,000

•Partner: Gevo Inc.

Barriers addressed

Ct-F: Increasing the yield from catalytic processes

Ct-G: Decreasing time to develop novel industrially relevant catalysts

ADO-A: Process integration

Objective

Diversification of current Gevo product suite to synthesize an energy dense fuel from bio-derived olefins so as to provide a performance advantaged jet fuel.

End of Project Goal

Provide a route to use Gevo intermediates to synthesize an increased energy dense fuel for potential incorporation with Gevo infrastructure by translating the most promising catalyst to a continuous flow reactor, achieving > 24 hours continuous operation and producing > 5 liters of fuel for testing

Project Overview

Goal: Provide a performance advantaged jet fuel with increased energy density

Gevo Process: bio-derived isobutanol to synthetic paraffinic kerosene (ATJ-SPK)

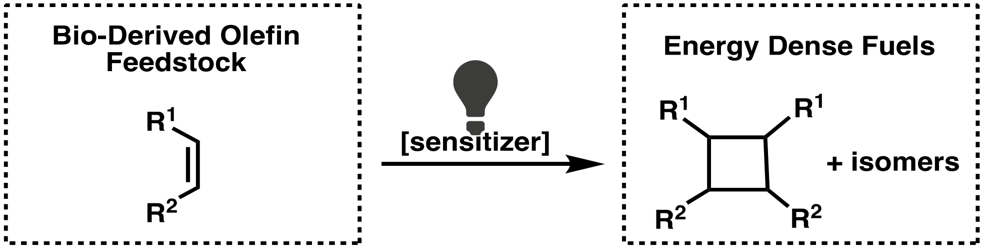
Isobutanol $\xrightarrow{\text{dehydration}}$ **Isobutylene*** $\xrightarrow{\text{oligomerization}}$ **C8-C16 Olefins** $\xrightarrow{\text{hydrogenation \& distillation}}$ **ATJ-SPK**

	ATJ-SPK	Jet-A	JP-10
Energy Density (MJ/L)	36.7	34.5	39.4
Freezing Pt. (°C)	< -80	-50	-80
Flash Pt. (°C)	48	48	52

Approach: use Gevo bio-derived olefins from their current ATJ-SPK production stream (*****) to generate cyclobutanes to increase energy density

Cyclobutanes can add **100 kJ/mol (~ 1 MJ/L)** in energy through ring strain

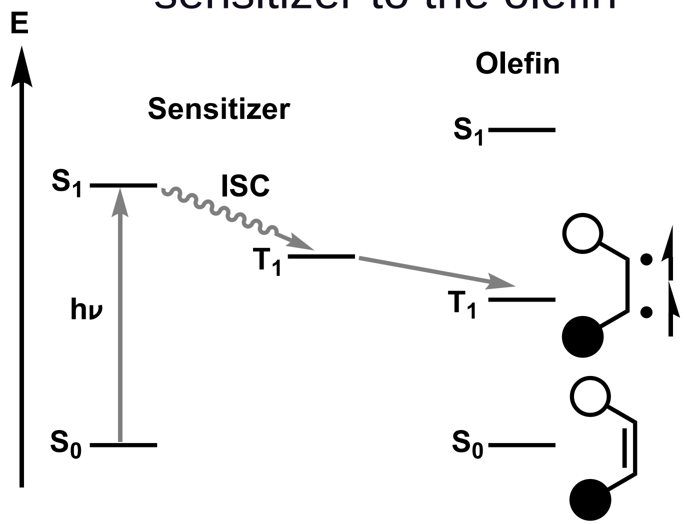
Approach: use photochemical [2+2] cycloaddition to generate cyclobutanes



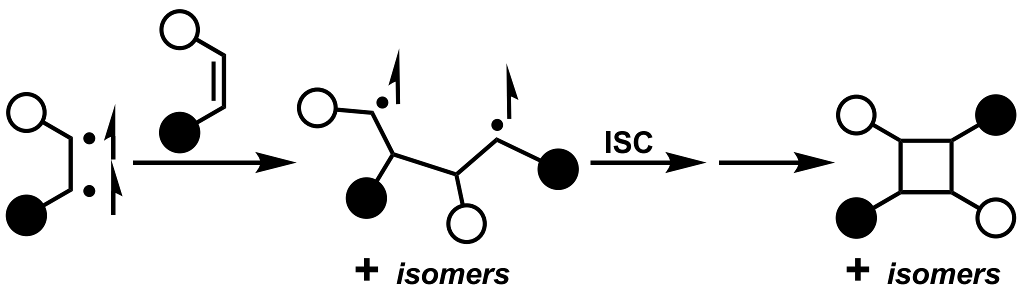
Potential Sensitizers: copper(I) complexes, arenes, or enones

Mechanism of Photochemical [2+2] Cycloaddition:

Step 1: Transfer of energy from sensitizer to the olefin

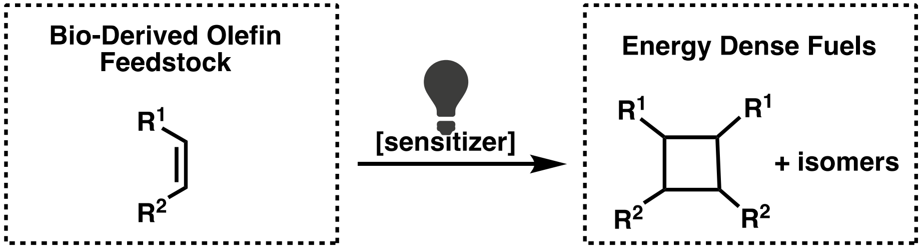


Step 2: Photogenerated diradical undergoes [2+2] addition



Approach and Relevance

Cyclobutanes will be generated through photochemical [2+2] cycloaddition



Gevo will diversify their fuel portfolio using current production streams:

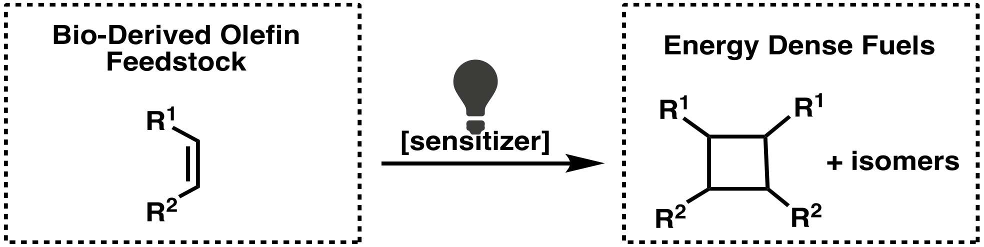
- Low additional plant and infrastructure cost
- Initial target market: Department of Defense tactical fuels – high value and low volume (revenue will be generated while new fuels are going through ASTM testing for other commercial usage)

Necessary expertise from Los Alamos National Lab:

- Development of non-precious metal catalysts for the upgrading and conversion of bio-derived feedstocks for fuel applications and
- Characterization and analysis of the energy density and physical properties of fuels

"Converting a mixed C_4 or C_5 stream to a higher value fuel would diversify our fuel portfolio and give us a competitive advantage in the aviation fuel market" – *Jonathan Smith, Gevo Director of Chemical Development*

Technical Accomplishments



Goal #1:
Synthesize cyclobutanes to be used as fuels

- **Laboratory setup for photochemical synthesis**
- **Optimizing cyclobutane synthesis using a model reaction**

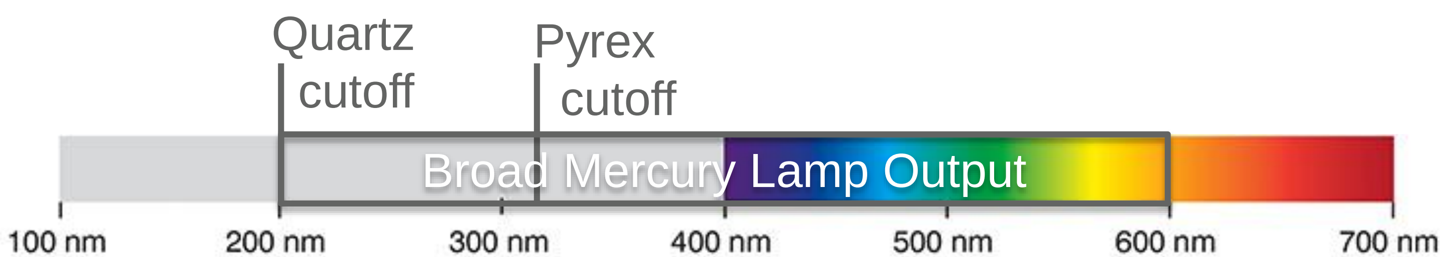
Goal #2:
Incorporate bio-derived feedstocks into fuel synthesis

- **[2+2] cycloaddition using Gevo samples**

Moving forward: determine energy density and analyze fuel properties

Laboratory Setup for Photochemical Synthesis

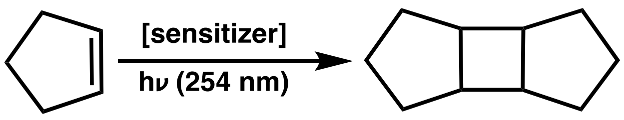
- **Carousel (pictured) allows for screening of small scale reactions**
- **Quartz chiller well can be used with an immersion reactor for large scale synthesis**
- **Light from the mercury vapor lamp can be attenuated with filters – working toward using visible light**



Outcome: Lab is equipped for photochemical synthesis (small scale screening or bulk irradiation – up to 300 mL). Light from the mercury vapor lamp is tunable.

Optimizing Cyclobutane Synthesis Using a Model Reaction

Explored 3 strategies for [2+2] addition, based on literature precedent:

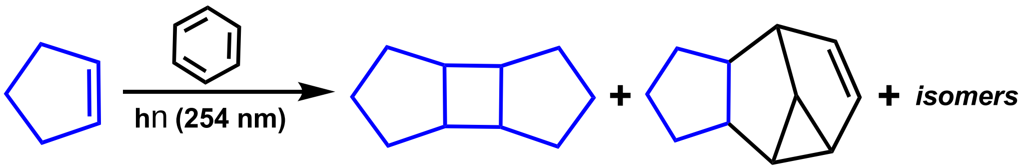


1. Copper(I)-sensitized: screened $(CuOTf)_2$•PhMe, CuCl, CuOAc

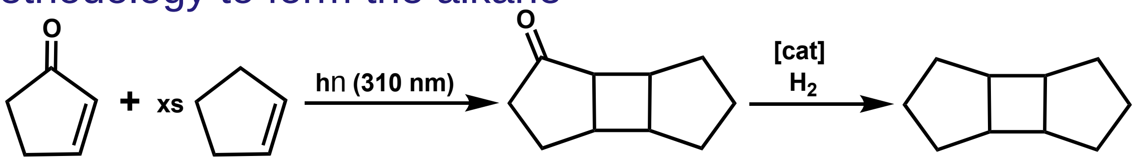
Outcome: Simple copper(I) salts are not suitable sensitizers for [2+2] photoadditions, due to low solubility in organic solvents and low molar absorptivity at 254 nm.

2. Arene-sensitized

Outcome: Arenes form strained ring systems in addition to cyclobutanes.



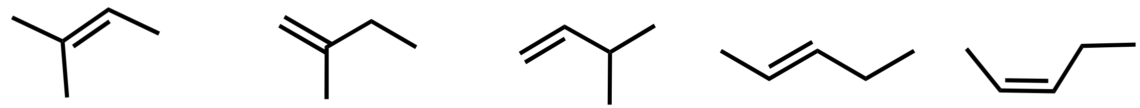
3. Enone-ene coupling: generate a ketone intermediate and use previously developed hydrodeoxygenation methodology to form the alkane



Outcome: Enones provide a route to access cyclobutanes in high yields without a sensitizer. Ketone products can be converted to alkanes.

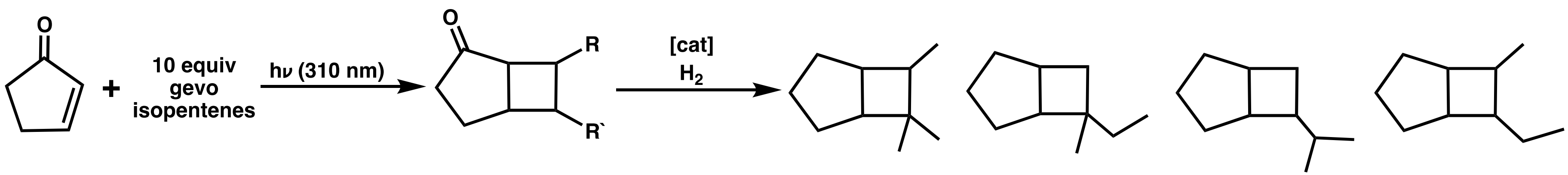
[2+2] Cycloaddition Using Gevo Samples

Analysis of isopentenes mixture provided by Gevo and confirmed by ^{13}C NMR spectroscopy:



2-methyl-2-butene	2-methyl-1-butene	3-methyl-1-butene	trans-2-pentene	cis-2-pentene
59.85%	26.18%	3.70%	2.78%	1.27%

Energy Density (Higher Heating Value): 31.2 MJ/L
(Lower Heating Value): 29.2 MJ/L
Boiling Point: 38 °C



Energy Density: 42.0 MJ/kg
****initial measurement of a crude sample**

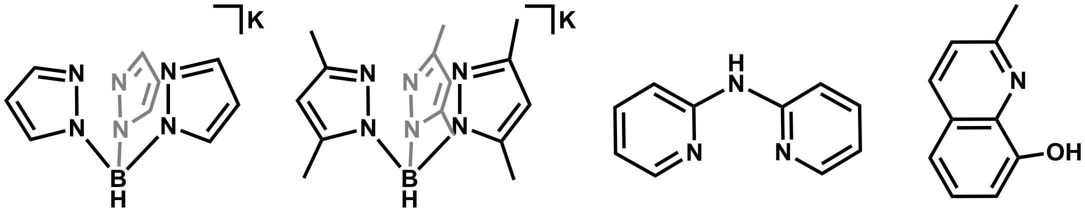
Use optimized conditions from the model cyclopentene reaction to generate a mixture of alkanes

Outcome: A mixture of bio-derived cyclobutanes was generated from photoaddition of olefins to an enone. The ketone intermediate was converted to the alkanes.

Future Work

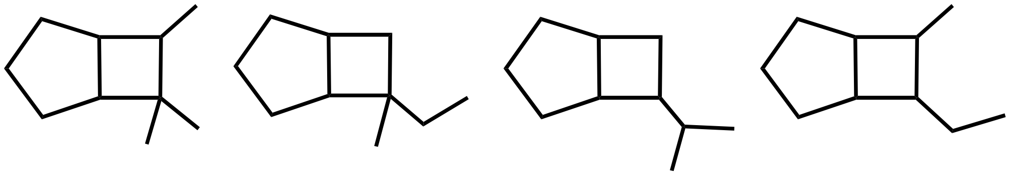
Improve copper(I)-sensitized photoadditions:

- Increase solubility and molar absorptivity with synthesis of copper(I) catalysts



- Using commercially available ligands will allow for faster screening of new complexes
- Shift maximum absorption of catalysts into the visible region

Analyze Energy Density and Fuel Properties of Gevo-derived cyclobutanes:



- Physical properties to be measured: density, lower heating value, yield sooting index, freezing point, boiling point, flash point, viscosity, derived cetane number
- Focus on homo-coupling of Gevo materials to avoid external material sourcing

Summary

Overview:
- Synthesize bio-derived cyclobutanes to serve as energy dense aviation fuels

Approach
- Photosensitized [2+2] cycloaddition of Gevo's bio-derived olefin feedstocks will generate cyclobutanes

Technical Accomplishments
- 3 methods of sensitizing [2+2] cycloadditions were examined on model substrates (copper(I) and arene sensitizers; enone-ene coupling)
- High yields of cyclobutane ketone products were isolated from enone-ene couplings and hydrodeoxygenated to form the desired alkanes
- The cyclobutanes were synthesized from the Gevo bio-derived olefins

Future Work
- Improvements to copper(I) sensitizers to allow for the use of visible light
- Fuel property analysis of the synthesized cyclobutanes
- Focus on homo-coupling of Gevo materials to avoid external material sourcing

Acknowledgements

BETO

Andrea Bailey

Nichole Fitzgerald

Contributors (LANL)

Cameron Moore

Courtney Ford

Juan Leal

Troy Semelsberger

Gevo Collaborators

Jonathan Smith

U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

Additional Slides

Presentations & Publications

Presentations:

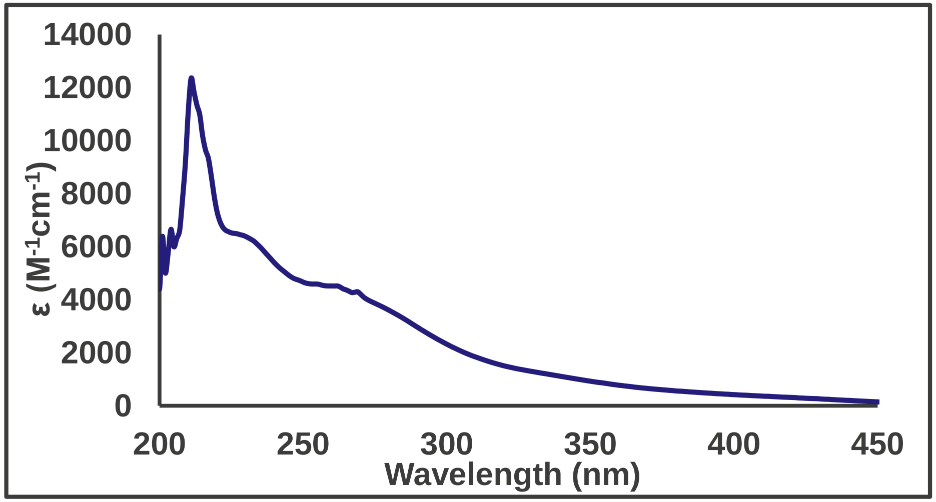
A Photochemical Approach to generate Energy Dense Fuels from Biomass. C. Ford, Frontiers in Biorefining, 5-7th November 2018, St Simons, GA.

Internal LANL Invention Disclosures (pre provisional filings):

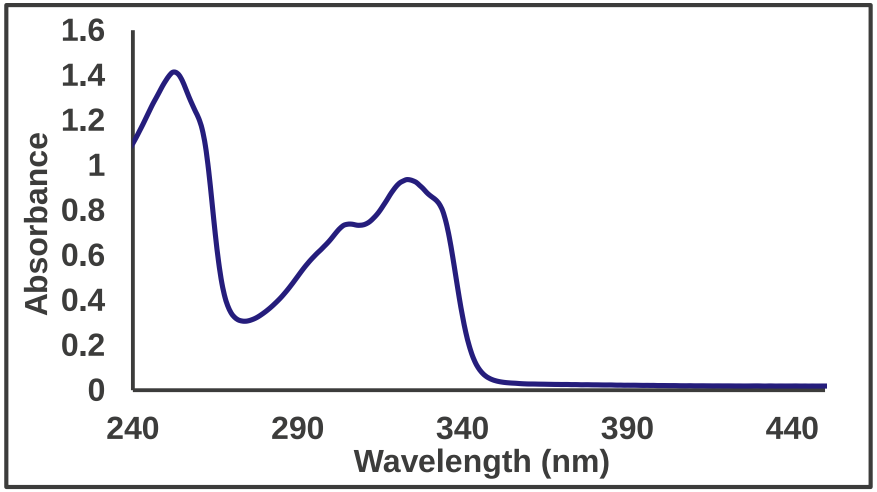
Synthesis of High Energy Density Fuels from Bioderived Olefins. C. Ford, A. Sutton, C. Moore,

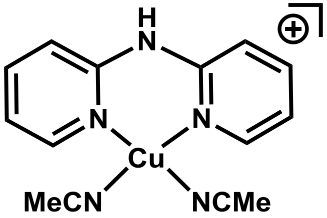
Copper(I)-Sensitized Photoaddition

Electronic absorption spectrum of $(CuOTf)_2PhMe$ in THF:



Electronic absorption spectrum of $[HdpaCu(MeCN)_2]OTf$ in DCM:

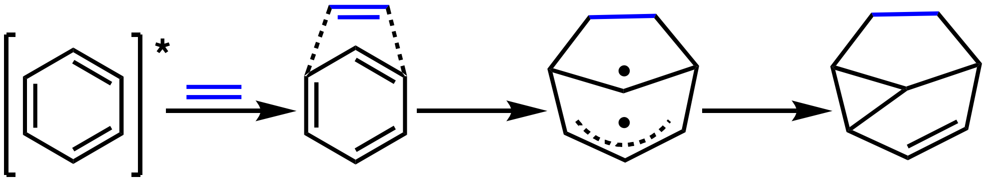




Makes use of a commercially available ligand
Shifts absorbance closer to the visible region

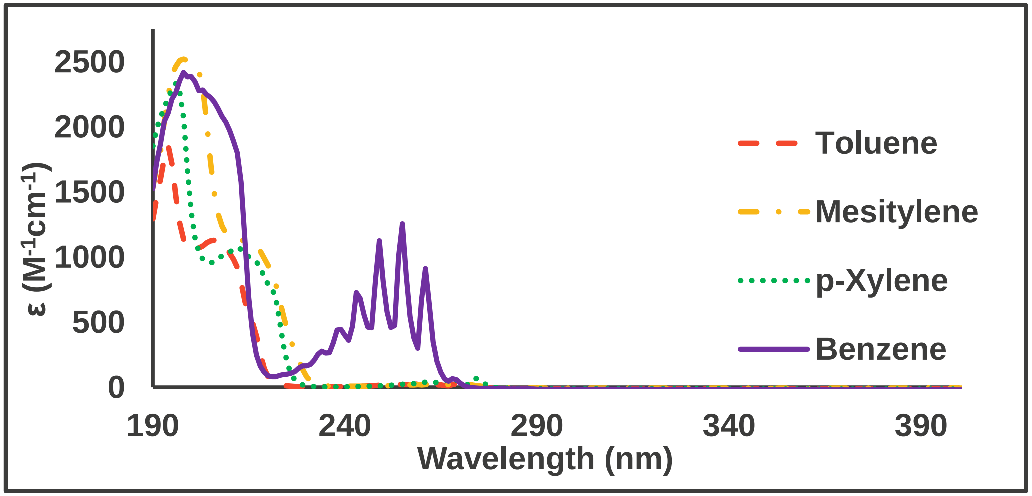
Arene-Sensitized Photoaddition

At 254 nm arenes undergo addition to olefins:

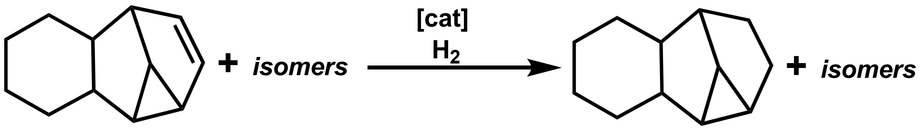


Beilstein J. Org. Chem. **2011**, *7*, 525-542.

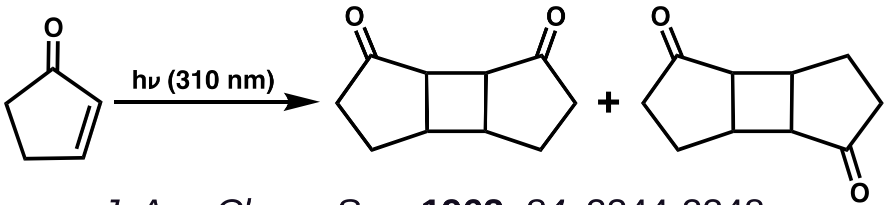
Electronic absorption spectra of arene solvents in hexanes:



Future plans: synthesize a range of strained ring systems from various olefins and arenes to hydrogenate and test as fuels (example below is product of cyclohexene + benzene)

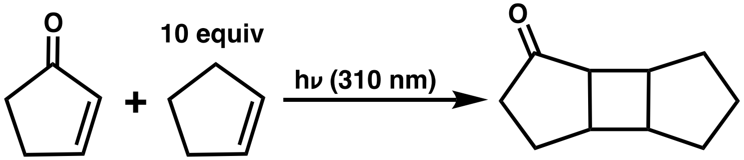


Enone-Ene Coupling



J. Am. Chem. Soc. **1962**, *84*, 2344-2348.

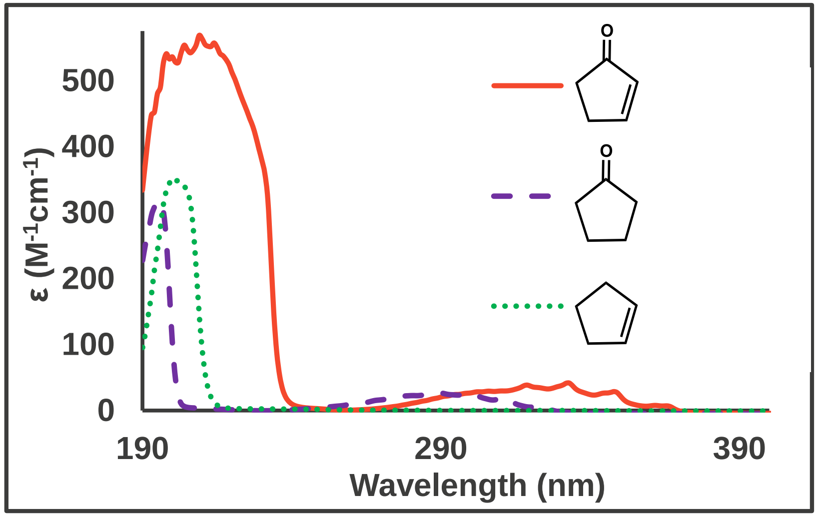
25% isolated yield



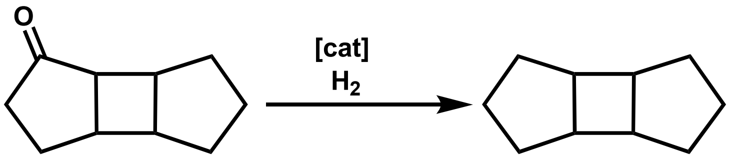
J. Am. Chem. Soc. **1962**, *84*, 2454-2455.

74% isolated yield

Electronic absorption spectra of an enone, a ketone, and an olefin in hexanes:

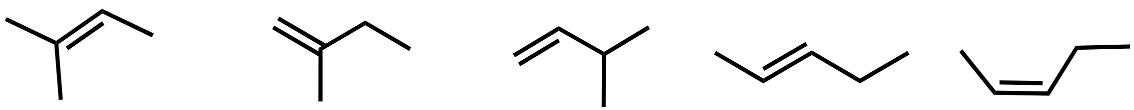


Use previously developed hydrodeoxygenation methodology to generate the alkane:



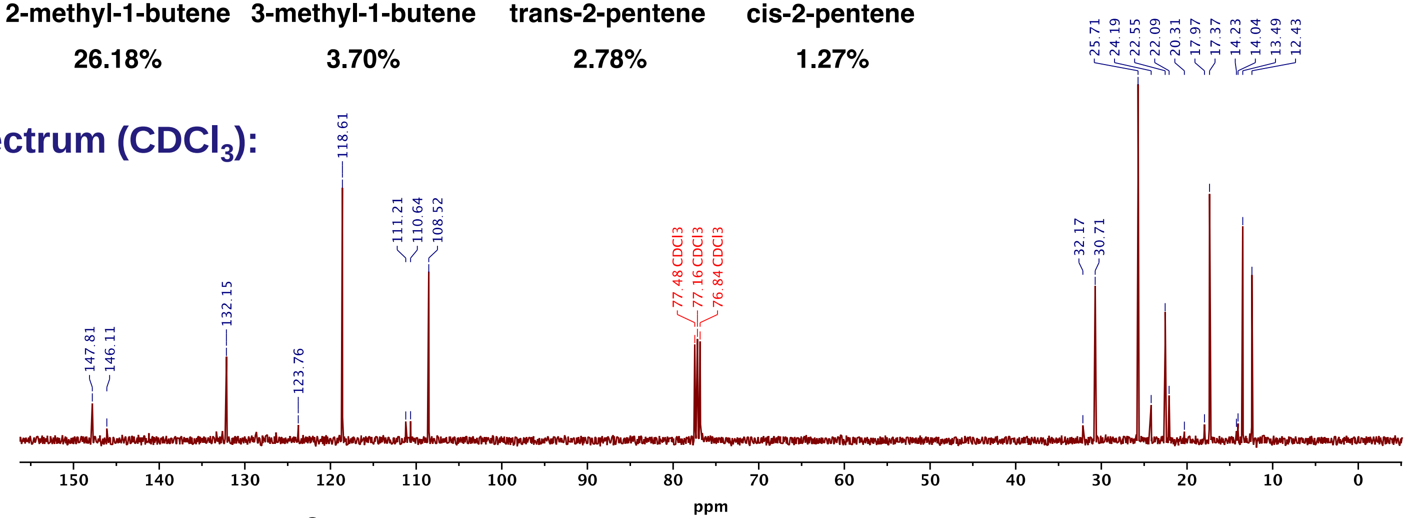
[2+2] Cycloaddition Using Gevo Samples

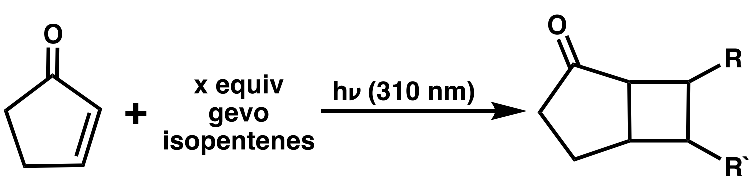
Analysis of isopentenes mixture provided by Gevo and confirmed by ^{13}C NMR spectroscopy:



2-methyl-2-butene	2-methyl-1-butene	3-methyl-1-butene	trans-2-pentene	cis-2-pentene
59.85%	26.18%	3.70%	2.78%	1.27%

^{13}C NMR Spectrum ($CDCl_3$):





GC-MS Spectra: