Adventures in Green Chemistry:

Undergraduate Research in the Development of Environmentally Benign Organic Chemistry

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Overview

- Costs and benefits of Organic Chemistry
- What is Green Chemistry?
- Why is Green Chemistry Important?
- Green Chemistry at Marian College

Benefits of an Organic World

- Organic chemistry and organic molecules play profound roles in our lives.
  - Pharmaceuticals
  - Medical
  - Biochemistry
  - Food and Farming
  - Plastics / polymers
  - Clothing
  - Electronics
  - Transportation
  - Sports and safety equipment
  - Home and consumer products
  - Cosmetic products
  - Office products
- As individuals and as a society, we depend on these products

Benefits at What Cost?

- Global chemical sales totaled 1.5 trillion dollars in 1998.
  - This corresponds to the annual production of millions of tons of chemicals
- The production of chemicals leads to chemical emissions
  - In the United States in 1994, there were 2.26 billion pounds of 300 hazardous substances released into the environment

‘Dilution is the Solution to Pollution’

- Chemical emissions were unregulated from the start of the Industrial Revolution through the mid 1950s
- Chemical release into the air, water, and land did not seem to matter
- Ignorance of:
  - Chronic toxicity
  - Bioaccumulation
  - Carcinogenicity

The Rise of Regulation

- The last 40 years has seen:
  - Public recognition of pollution
  - The creation of the EPA
  - Proliferation of environmental regulation
  - Recognition of the need for environmental stewardship
- However, regulation does not fundamentally address what is needed

New Approach Needed

- When a chemical reaction or process presents a chemical hazard, there are two approaches
  - Minimize human and environmental exposure (short term solution)
  - Reduce or eliminate the hazard (long term solution)

The Need for Green Chemistry

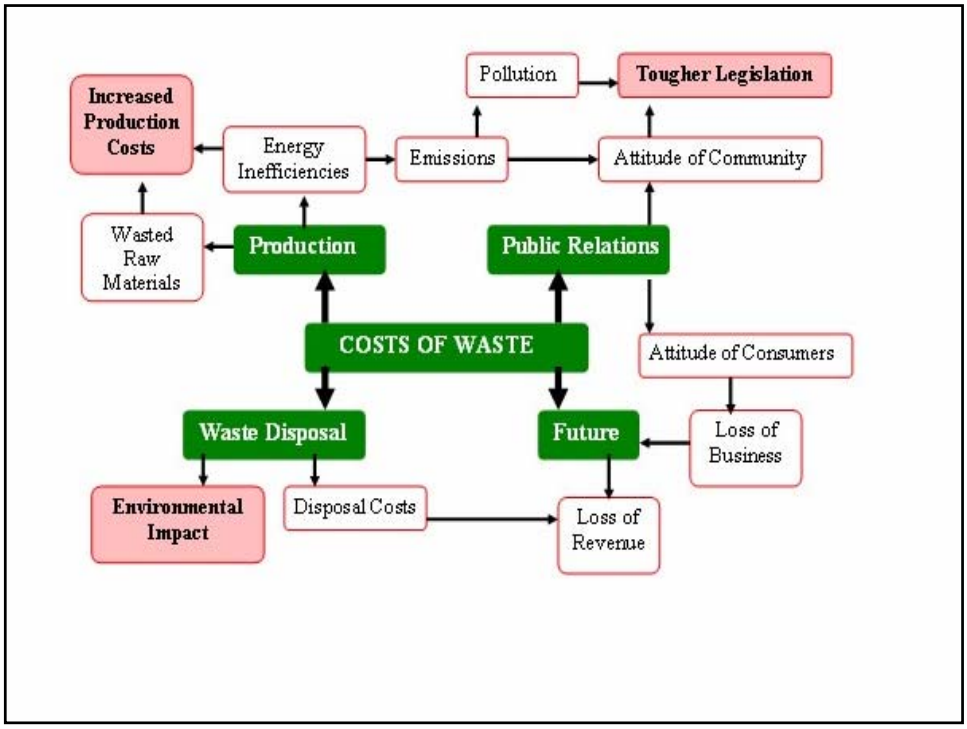
- Green chemistry is the design of chemical products and processes that reduce or eliminate the generation of hazardous substances.
- Green chemistry seeks to reduce the hazards associated with chemical process not just by preventing exposure or release, but by reducing the intrinsic hazards.

What is Green Chemistry?

- It is pollution prevention at the most fundamental level of chemistry: atoms and molecules.

Why is Green Chemistry important?

- Cost of waste
  - Cost of wasted reagents
  - Cost of wasted energy
  - Cost of waste disposal
  - Cost of increased regulation



Impact on Your Life

Green Chemistry can make your community a cleaner, safer place.

- Reducing local pollution.
- Reducing transportation of hazardous materials.
- Reducing production costs leading to more affordable chemical products.

Green Chemistry at Marian

- Green Organic Chemistry in the teaching laboratory
- Green Organic Chemistry in the undergraduate research laboratory

Challenges in the Organic Teaching Laboratory

- Provide a modern organic experience
- Reduce lab costs
- Reduce waste generated
- Make labs safer for students (and instructors)

Traditional Approaches

- Perform work in fume hoods
  - Minimize exposure
- Microscale techniques
  - Minimize costs
  - Minimize waste
  - Minimize exposure

Disadvantages to Traditional Approaches

- Cost of fume hoods
- Inadequate preparation
- Lower student satisfaction

Practical Solutions: Green Organic Chemistry in the Teaching Laboratory

- Reduction of laboratory waste and hazards
- Use of safer, inexpensive solvents
- Use of more benign reagents and conditions
- Adaptable to both macroscale and microscale
- Illustrates green chemical concepts
- Teaches modern chemistry and techniques

Further Benefits

- Students learn:
  - how green method compares to traditional method
  - to recognize and implement green methods
  - to assess conditions for hazards
  - to identify methods that allow reduction of hazards
  - to assess the broader impact of the overall procedure on safety and the environment

Implementation

- Fundamentally different approach
- Development of scenario based labs
- New student experiments are being developed
- More work to be done

Green Organic Chemistry in the Undergraduate Research Laboratory

- Development of new procedures and green techniques for implementation in CHE 305 /CHE 306
- Development of new synthetic methodology

Marian College's First Annual Green Chemistry Undergraduate Research Symposium

Tuesday, April 19th 2:30

Marian Hall, Room 355

Development of CHE 305 /306 Labs

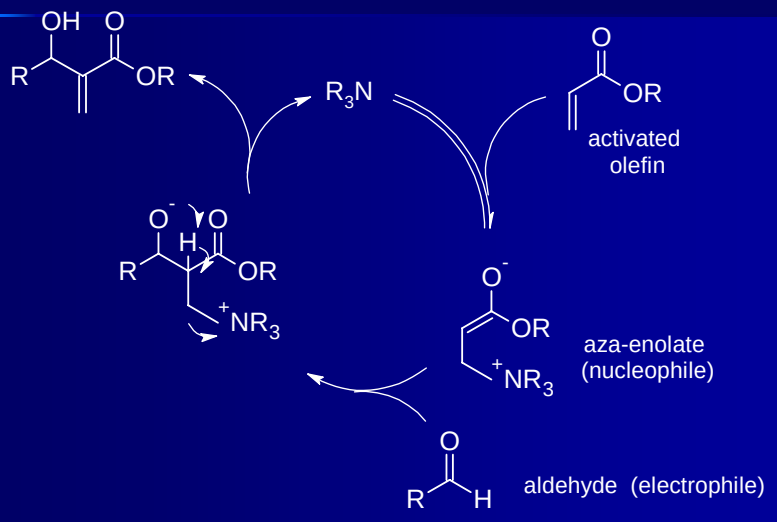
- Perform a traditional functional group modification
- Assessment / development / implementation of a new procedure which emphasizes green concepts and techniques
- Planning and evaluation of the concepts and techniques that their new procedure will demonstrate

Current Projects

- Safer S_N1 reaction
- NaOCl oxidation of a 2^o alcohol to a ketone
- A more environmentally benign $NaBH_4$ reduction of an aldehyde
- A more environmentally benign chemoluminescence demonstration

Development of New Synthetic Methodology

The Baylis-Hillman Reaction…



… A Green Reaction!

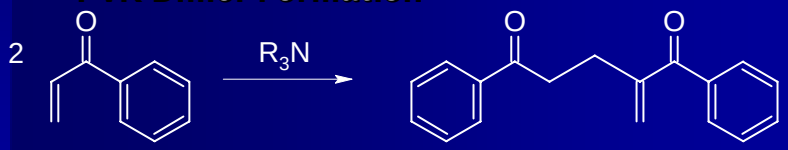
How is the Baylis-Hillman Reaction Green?

- Very atom efficient
- Very little waste formed
- Reaction occurs under mild conditions
- Neat – no solvent used
- Does not need an aqueous quench
- Reagents and products can have low toxicity
- Catalysts can be recovered

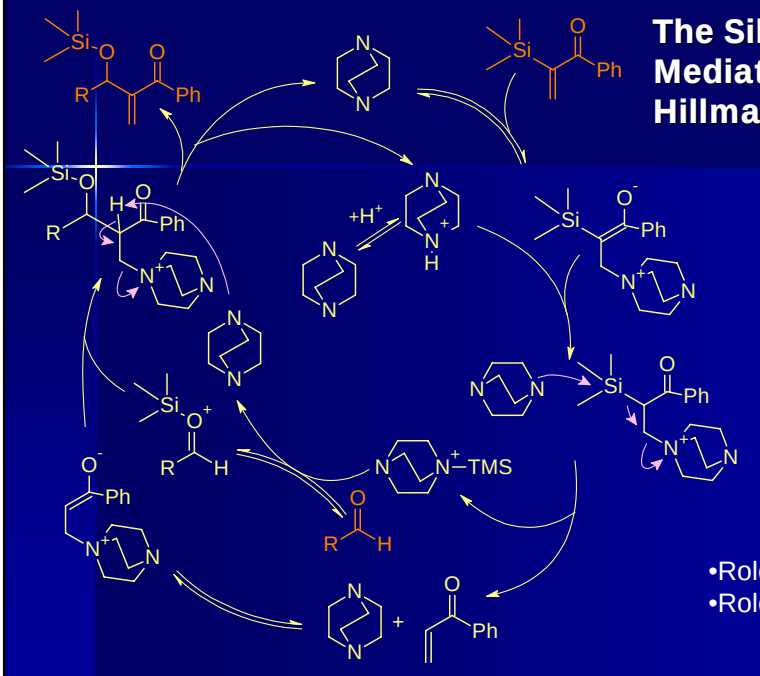
Limitations of the Baylis-Hillman Reaction

- Limited number of activated olefins suitable for the reaction due to competitive dimerization.
- Phenyl vinyl ketone (PVK), which dimerizes rapidly under Baylis-Hillman conditions, is essentially unsuitable as a substrate.

PVK Dimer Formation



The Silicon-Mediated Baylis-Hillman Reaction



- Role of Silicon
- Role of H^+

Benefits of the Silicon-Mediated Baylis-Hillman Methodology

- Essentially eliminates head-to-tail dimerization of PVK under reaction conditions
- This methodology is allowing new applications of the Baylis-Hillman reaction to be developed

Current Research

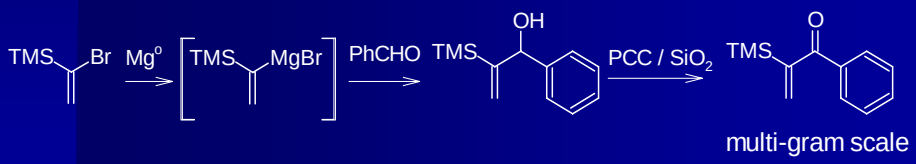
- The development of a tandem Baylis-Hillman condensation / cyclization reaction for the preparation of biologically active aromatic heterocycles.

Proposed Research

- To develop methodology to utilize additional activated olefin substrates in the Baylis-Hillman reaction.
- To develop a stereoselective variant for the silicon-mediated Baylis-Hillman reaction.

Is the Silicon-Mediated Baylis-Hillman Reaction Really Green?

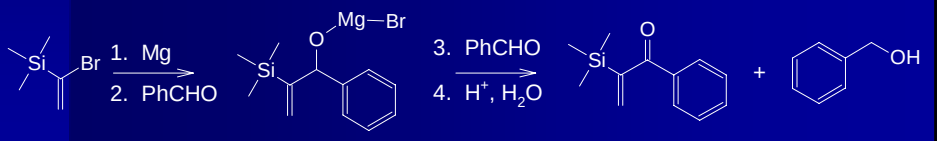
- Green Chemistry calls for an assessment of the big picture!
- Where does trimethylsilyl phenyl vinyl ketone come from?



multi-gram scale

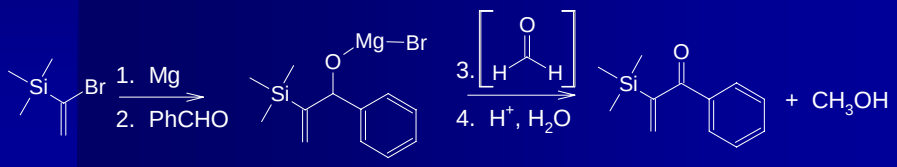
The Tandem Grignard Addition-Oppenauer Oxidation

- This new protocol replaced a multi-step Grignard Addition-pyridinium chlorochromate (PCC) oxidation sequence.
- The carcinogenic PCC has been eliminated, with benzaldehyde now serving as the oxidant.
- Improvements in atom efficiency needed
- Purification can be problematic



Can the Tandem Grignard Addition-Oppenauer Oxidation be Further Improved?

- Other ketones and aldehydes are being explored to determine the most atom efficient oxidant for the reaction.
- The most atom efficient oxidant for this transformation would be paraformaldehyde
- Paraformaldehyde has show promising results in a recent experiment



Why Green Chemistry at Marian College?

- Is this research “at home” at Marian?

Appropriate for an Undergraduate Teaching Institution

- The chemistry is well suited to undergraduates – it is challenging with out being overwhelming.
- Emphasis on learning

Marketability

- Green chemistry is a topic that can be presented to and understood by all (most), including prospective students, current students, faculty, potential donors.
- It is chemistry that is “real”

Distinction

- Our unique research program in Green Chemistry distinguishes the chemistry program at Marian from other small liberal arts colleges.

Fundability

- The growing interest in the value of Green Chemistry should help in obtaining funding.

Marian Values

- Promotes Marian College's mission of advancing Franciscan values, specifically responsible stewardship.

A Good Fit

- Fits with the developing environmental focus of the Chemistry Program and the Department of Natural and Behavioral Sciences.

Conculsions

- Green chemistry is off to a successful start!
- Our undergraduate research program teaches student core concepts in chemistry, while at the same time promoting Marian College's mission as a liberal arts-based Franciscan college.

Acknowledgements

- CHE 498 Spring 2005
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