Design and Implementation of a Greener Lab Curriculum

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GREEN CHEMISTRY AND SUSTAINABLE ENERGY

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Golden, Colorado
Evolution of a Green Chemistry Program

- Student empowerment
- Green lessons
- Other lessons …

… including the perils of a chronological presentation – “revisionist history” often leads to a better story.

But important lessons about academic chemistry and its practice, as well as about green chemistry, can arise from hearing the “real” story.
Evolution of Oregon’s Green Laboratory Program

Pre 1992: capacity ~60
Evolution of Oregon’s Green Laboratory Program

Smoke Clearance Test
A “Modern” Chemistry Lab

1992 - 2001: capacity 17
Some Simple Mathematics

\[ \frac{265 \text{ students/week}}{17 \text{ students/lab section}} \rightarrow 17 \text{ lab sections/week} \]

\[ 17 \text{ lab sections/week} \times 3 \text{ hours/lab section} \]

\[ + \ 2 \times 1 \text{ hour/lecture/week} = 53 \text{ contact hours/week} \]
Some Simple Algebra

If $x > 17$, then $z < 53$
An Inconvenient Truth
Green Chemistry Reduces Risk by Addressing Intrinsic Hazard

Risk = \( f(\text{hazard, exposure}) \)

Reducing risk through reduction of intrinsic hazard reduces or eliminates the risk even in the event of exposure.
Green Chemistry Reduces Facility Demands

capacity >>17
The First Offering of the Green Lab

15 students selected on the basis of interest, enthusiasm, and performance in previous classes.

Completely new experiments, sometimes designed only weeks before student exploration.

Recognition by students that …
  things may not always work as planned;
  this is how science works;
  they were pioneers in developing a new approach.
Selecting and Adapting Labs That Teach Green Chemistry

Criteria for selecting experiments:

- Teach **modern reaction chemistry and techniques**
- Illustrate **green chemical concepts**
- Complement the lecture course
- Fit time and material **constraints**
- Use **greener solvents and reagents**
- **Reduce laboratory waste and hazards**
- Be adaptable to both **macroscale and microscale**
- Provides a platform for discussion of **environmental issues** in the classroom

- Allow experimentation on the open bench
# Need for Modernized Organic Laboratory Curriculum

Starting Material Employed in Classic Organic Laboratory Syntheses 1902-1980

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Starting Materials Required (grams)

From *Microscale Organic Laboratory* by D.W. Mayo, R.M. Pike and S.S. Butcher, 1985
Green Experiment Development

Assess existing procedure

Identify hazards or inefficiencies

Find/develop alternative methods

Test efficacy of new procedure

Greener alternative

We teach this simple process to our students as we implement it.
Aromatic Halogenation/Alkynes

Lab Skills

Electrophilic halogenation
Pd-catalyzed coupling
Alkyne chemistry
Natural product synthesis

Green Lessons

Safer reagents
Alternative solvents
Catalysis
Consider the following experiment, from a recent lab manual:

“Consult a chemical catalog to … choose a halophenol and an alkyl tosylate to use for the experiment. Factors to consider are commercial availability of the compounds, costs, and relative reactivities.

Safety First!
Alkyl tosylates should be handled with care as they are cancer suspect agents and toxic irritants. Halogenated phenols are toxic and corrosive.”
Possible Concerns

• Could/should one consider the health and environmental hazards of the starting materials being considered?

  *Health and environmental impacts are as important as melting point, color, and other physical properties.*

• Is it wise to have inexperienced students working with compounds known to present extreme health risks?

  *Let’s talk about this more in a few minutes. But, no.*

• Are all halophenols toxic and corrosive? Maybe some are safer? Maybe others are even worse?

  *Can we avoid teaching that all chemicals are harmful?*
The Second Offering of the Green Lab

**Conscription** is a general term for involuntary labor demanded by some established authority.

From Wikipedia, the free encyclopedia
Laboratory curriculum project implementation

Number of Students

- 97-98
- 98-99
- 99-00
- 00-01
- 01-02
- 04-05

Number of Students

- 250
- 200
- 150
- 100
- 50
- 0
Laboratory curriculum project implementation

**Fall term**
*Synthesis, separations, spectroscopy*

1. Solventless Aldol condensation
2. Bromination of an alkene
3. Preparation/distillation of cyclohexene
4. Synthesis of adipic acid
5. Oxidative coupling of alkynes
6. Gas phase porphyrin synthesis
7. Solvent effects on kinetics
8. Molecular mechanics modeling

**Winter term**
*Synthesis, spectroscopy, applications*

1. Electrophilic iodination with KI/NaOCl
2. Palladium-catalyzed aryl halide/alkyne coupling
3. Polymer-supported oxidation chemistry
4. Friedel-Crafts acylation of ferrocene
5. Thiamine-mediated benzoin condensation
6. Self-assembled monolayers/patterning
7. Combinatorial synthesis of antibiotics
The Green Chemistry Lab
Students Play a Key Role

• Experiment development

• Openness to new discoveries

• Recognition of the richness of green chemistry

• Participation in Green Workshops
Design Challenges


Reality in the Teaching Lab

Universidad Autónoma de Yucatán

Synthesis of 7-Hydroxy-4-Methylcoumarin by a Solid-Catalyzed Pechmann Reaction
Cost is a Real Issue
Cost is a Real Issue

… and consideration of cost can lead to enhancement of the greenness of a procedure.

50 mL of toluene + 10 mL of methanol

vs.

10 mL of ethanol

Green Synthesis of a Fluorescent Natural Product
(Is Cost a Real Issue?)

The Situation of Senior-High School Chemistry Education in Tohoku District of Japan – From the Results of a Questionnaire to Chemistry Teachers in 1995


Reasons for the Scarcity of Experiments

- a. Shortage of teaching hours: 176, 51.6%
- b. Insufficient money (Financial reason): 32, 9.4%
- c. Not to retard the progress of study: 156, 45.7%
- d. Potential danger of experiments: 22, 6.5%
- e. Insufficient time to prepare experiments: 140, 41.1%
- f. Others: 9, 2.6%
“We” and “They”

- We discuss what type of equipment provides the best experience for our students.

Which of these …

… looks more like this?
“We” and “They”

- They wait two years to receive chemicals and supplies.
“We” and “They”

• And they have no electricity.
Cheap is Good

Marie du Toit (South Africa)
Peter Schwarz (Germany)
Free is Better


Two Consecutive Reactions in Microscaled Electrolysis Cells

Sobhi Basheer† and Muhamad Hugerat‡,*
Experimental Science in Developing Countries

• Recognize and embrace local “limitations”
• Exploit locally available materials
• Develop locally relevant content
• Engage local teachers and students
Locally Relevant Content

Discussion – Possible topics for Middle-East labs
Locally Relevant Content

- Dead Sea – brine, high $P_{\text{atm}}$
- Olive oil
- Textiles and pigments (modern, ancient)
- Natural products (terrestrial, marine)
- Ceramics, glass
- Minerals, sand
- Myrtle wood
- Coins
- Fermentation
Perceptual Challenges

- Some of our tacit assumptions are easy to recognize and (relatively) easy to dismiss.
  - Chemistry is dangerous.
  - Good chemistry is dangerous.
Chemistry has to be Dangerous
The Skeptic Speaks

But Ron Newton, instructional lab supervisor in Washington State University’s chemistry department, said WSU is doing the opposite.

In addition to more fume hoods, Newton said, WSU hopes to also equip its organic labs with steel, glass and rubber “glove boxes.” Stationed inside wider, deeper fume hoods, the glove boxes, up to $75,000 each, would let students handle chemicals so volatile they ignite upon touching air.

Only such experiments, he said, can prepare chemistry students for dangerous jobs in industry.

“We haven’t even heard of (green chemistry) out this way. I don’t think we’d even be interested in it. Yes, it may save money, but you’re not doing any favors for students with it,” Newton said. “We’re trying to get students really interested in chemistry. This gives them a chance to perform processes that will really train them for when they go out into the world.”

Discussion – What do YOU think?
Who are our Clientele?

Most students will not work with hazardous substances. Proper technique can be learned with safe substances.
“Dr. ______ has 44 years of experience in the synthesis of novel high energy oxidizers and rocket propellants. He has achieved the first syntheses of many spectacular compounds, such as ClF$_3$O, ClF$_3$O$_2$, halogen perchlorates, OIF$_4$OF, OsF$_4$O$_2$, ...”
Chemistry has to be Dangerous?

- Safer reagents
- Cheaper reagents
- Better product
- Less hazardous waste
- Higher profits
Challenging Assumptions

• Other assumptions are so deeply ingrained in the chemist’s psyche as to be not just hard to change, but unrecognized.

  – Percent yield is a good measure of reaction efficiency.
  – Fume hoods, gloves, and other “environmental controls” protect us.
  – Chemical reactions require solvents.
  – Intrinsic chemical hazards are unavoidable.
Deeply Ingrained Assumptions

• Percent yield is a good measure of reaction efficiency.
Reaction Efficiency

Cisplatin

Experimental Procedure

Prepare a solution of 63 mg (0.202 mmol) of silver sulfate in 10 mL of water in a 25-mL beaker containing a magnetic stirring bar. Add 100 mg (0.207 mmol) of the cis-diiodo derivative prepared in Part 48.A, in small portions, to this Ag⁺ solution.

Heat the suspension, with stirring, on a sand bath (70-80 °C) for 10-12 min. Filter the mixture to separate the precipitate of AgI.

Isolation of Product

Concentrate the filtrate to a volume of about 2.0 mL. Treat this solution with 330 mg (4.43 mmol, a large excess) of KCl. Heat the mixture on a sand bath at 70-80 °C for 2-3 min. Bright yellow crystals of cis-diammine dichloroplatinum(II) should precipitate out. The heating is continued for an additional 5-8 min. Cool the mixture to 0 °C in an ice-water bath. Filter the product using a Hirsch funnel. Wash the crystals with 500 µL of ethanol followed by 1 mL of ether and dry them under suction in air. Determine the percentage yield.
Is This a Good Experiment?

Yes

• Balancing Equations
• Mole Ratios
• Stoichiometry
• Coordination Chemistry
• Chemotherapy
• Laboratory Techniques
  • Filtration, Elevated Temperatures
Measures of Reaction Efficiency

- Chemical yield (82%)
- Atom economy (32%)
- Experimental atom economy (12%) (theoretical yield vs. mass of reactants)
- Actual atom economy (10%)
- Waste generation (8.9 g / 1.0 g product)
- Solvent usage (11.1 g)
- Yield based on all inputs (0.4%)

(No chromatography or recrystallization)
Cisplatin in Action

Dosage: 2-3 mg/kg every 3-4 weeks

• May cause severe allergic reaction … … which may get worse with continuing exposure.

• Very toxic if inhaled, swallowed, or absorbed through the skin.

• Experimental carcinogen, teratogen; IARC probable human carcinogen.

• May cause reproductive damage.

• Most effects of overdosage are not usually seen immediately, but occur several days to months after the event.
Is This a Good Experiment?

No

- Physiologically active product!!
- 232 g waste per 1 g product
- Requires heating (energy usage)
Always Ask Questions

• Why are we making this compound?
• What are its properties – particularly in terms of health and environmental impact?
• Can we accomplish the same goals by making a different and safer compound?
• Can we make the compound from safer starting materials, or using safer solvents, or using less energy input (either heating or cooling)?
• Can we reduce the amount of waste that is generated, or eliminate it entirely?
Deeply Ingrained Assumptions

- Fume hoods, gloves, and other “environmental controls” protect us.
Environmental Controls

Does avoidance of exposure make us safe?

“working in a fume hood.”

Karen Wetterhahn
Dartmouth College, 1996
Deeply Ingrained Assumptions

- Chemical reactions require solvents.
Solvent is a Given

Synthesis of 7-Hydroxy-4-Methylcoumarin by a Solid-Catalyzed Pechmann Reaction
Warner, John C.; in Greener Approaches to Undergraduate Chemistry Experiments, p. 25, Kirchhoff, Mary; Ryan, Mary Ann, Eds., American Chemical Society, 2002.
Deeply Ingrained Assumptions

• Intrinsic chemical hazards are unavoidable.
Intrinsic Chemical Hazards

“LiAlH₄ is flammable and reacts violently with water. … (CF₃)₃COH is toxic by inhalation, in contact with skin, and if swallowed. … Petroleum ether is extremely flammable, harmful and dangerous for the environment, toxic to aquatic organisms, and may cause long-term adverse effects in the aquatic environment or lung damage if inhaled.”

“Diisopropylcarbodiimide (DPC): flammable, very toxic by inhalation, irritating to skin, and can cause serious eye damage.”

“Barium perchlorate is explosive and a strong oxidizing agent. Inhalation or contact with eyes or skin causes irritation. Prolonged exposure to fire or heat may result in an explosion.”
Academic Barriers to a Green Curriculum
Exercise

What (else) might a skeptical person say about a Green Chemistry curriculum?
Pedagogical Concerns

“The curriculum will not teach students what they need to know for admission to graduate school or for standardized examinations.”
# Academic Preparation

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<th>Traditional</th>
<th>Green</th>
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<tr>
<td>Fundamentals of chemistry</td>
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<tr>
<td>Practical lab procedures</td>
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<td>Green chemical concepts</td>
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<tr>
<td>Process chemical concepts</td>
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<td>Waste generation/disposal</td>
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<td>Realistic scale and apparatus</td>
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<tr>
<td>State-of-the-art curriculum</td>
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Skepticism

“Green is political, not scientific.”

“Green is a passing fad. It is hippie chemistry.”

“Green chemistry is not rigorous.”
Designing better products and better processes is what synthetic chemists do. Green chemistry is intrinsically more rigorous than traditional chemistry due to the imposition of significant “boundary conditions.”

\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}, t) \right] \Psi(\vec{r}, t) = i\hbar \frac{\partial \Psi(\vec{r}, t)}{\partial t}
\]
State-of-the-Art Experimentation

Electrophilic halogenation
Pd-catalyzed coupling
Alkyne chemistry
Natural product synthesis

Safer reagents
Alternative solvents
Catalysis
Inertia

“We’ve always done it this way.”

“We just revised our curriculum when we converted to microscale.”
Sustainability is Complicated

... and requires complicated choices and decisions
Complex Problems

“… complexity should not be equated with intractability …”

John S. Dryzek, 2002

“The extent and complexity of the problem does not matter as much as does the willingness to solve it.”

Ralph Marston, 1998

“The difficult I’ll do right now; the impossible will take a little while.”

Linda Ronstadt
Toma de Decisiones Estrategica

How do we make personal choices?

A. Personal impact

Benefit: Increased athletic performance

Risk: Disqualification, heart disease
Toma de Decisiones Estrategica

How do we make personal choices?

B. Impact on others ("inflicted choice")

Benefit: Enjoyment of enhanced athletic exhibitions (observers)

Risk: Decreased chances of winning (competitors)

None? (observers)

"Quantification of Steroid Hormones ... in Municipal Wastewater Effluent"

Androgens (testosterone and androstenedione) were detected at concentrations as high as 6.1 and 4.5 ng/L, respectively ..."

E. P. Kolodziej, J. L. Gray, and D. L. Sedlak
Environ. Toxicology and Chem. 2003, 22, 2622-9
Decisiones Personales Que Pueden Afectar a Otros

Choice: Exceeding the speed limit

<table>
<thead>
<tr>
<th>Personal Impact</th>
<th>Impact on Others</th>
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<tr>
<td>Benefit: Arrive faster</td>
<td>Benefit: ?</td>
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<tr>
<td>Risk: Accident</td>
<td>Risk: (health care costs)</td>
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<td>Citation</td>
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[Image of a highway with cars]
Decisiones Personales Que Pueden Afectar a Otros

Choice: Thalidomide

Personal Impact
Treat erythema nodosum leprosum (leprosy-related)
Benefit: Treat multiple myeloma (plasma cell cancer)
Risk: ?

Impact of Others
Benefit: ?
Risk: Birth defects (health care costs)
Decisiones Grupales Que Pueden Afectar a Otros

Choice: Bioethanol from corn

Benefit: Renewable fuel source

Risk: Loss of food source

Environmental impacts

MEXICAN FARMERS REPLACE TEQUILA PLANT WITH CORN
Ethanol demand has doubled corn prices, making it more profitable than agave.

Christian Science Monitor, June 21, 2007
Hipoxia – “La Zona Muerta”

US corn biofuels will expand Gulf of Mexico 'dead zone'

Mar 10, 2008

http://cas.bellarmine.edu/tietjen/Ec&Ev_Distance_learning/
EcologyIntro/gulf_of_mexico_dead_zone.htm

http://www.smm.org/deadzone/
Decisiones en la Industria Química

Choice: Environmental controls for hazardous chemicals

Benefit: Make desired product
Protect workers

Risk: Failure of controls
Release of hazardous materials
Security

Choice: Intrinsically safer chemicals and products (Sustainable Chemistry)

Benefit: Make desired product
Protect workers
Increase profits
Improve public relations
Comply with regulations
Save the planet

Risk: ?
Decisiones en el Currículo de Química

• Students select their major field of study.
• Students select courses, but must meet faculty-defined requirements.
• Faculty choose what materials to present to students.
  – Lecture – “fair and balanced” coverage.
  – Laboratory – exposure to chemicals.

A Qualitative Organic Analysis That Exploits the Senses of Smell, Touch, and Sound

\[ \text{H}_2\text{C} = \text{C} - \text{C} = \text{N} \]
Agents for Change

An agent of change, is someone who intentionally or indirectly causes or accelerates social, cultural, or behavioral change.

An agent of change is YOU.

From Wikipedia, the free encyclopedia