Green Organic Chemistry @ Mt. SAC

Mt. San Antonio College
Walnut, California

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210th 2YC3 Conference
Chemistry for a Sustainable Future
Kaneohe, Hawaii

May 22-23, 2015
Mt. San Antonio College

- The largest single campus of the CA 112 Comm. College system-Located in the suburb of Los Angeles
- 40,000+ students, rich in diversity
- Chemistry Department
  - 11 Full-Time Faculty (15-18 Adjunct Faculty)
  - 45-50 Introductory Chemistry sections (CHEM 10, 20, 40)
  - 22-25 General Chemistry sections (CHEM 50 & 51)
  - 9-10 Organic Chemistry sections (CHEM 80 & 81)
  - 2300 - 2400 students per year

Almost all students going through our program transfer to Universities
Chemistry Department
Instrumentation & IT Facility

- 60 MHz Anasazi FT-NMR
- HP 5890 GC/MS (*not being utilized currently*)
- Perkin Elmer FT-IR (4, 2 brand new, equipped with the ATR accessory for solid samples)
- Varian AA
- Gas Chromatographs (2)
- *Spartan* Molecular Modeling Software (100 student License)
- *IT Facility* (30 networked facility w/instructor station) plus ~ 60 Additional computers/laptops for students use
- MeasureNet Data Collection System in Gen. Chem. Labs
Green Chemistry at Mt. SAC

- Completing our fifth year of full Implementation in Organic Laboratory I & II
- **Start?** At the cCWCS Green Chemistry Workshop at the University of Oregon-Summer 2008
- Hendrix College, w/Tom Goodwin Summer 2009
- Result of my sabbatical project: 2009 –2010
Green Chemistry at Mt. SAC

- **Goal:** Improve our Organic Lab Curriculum
  - Reduce waste
  - Save on the cost of lab textbook for students
  - Incorporate more Instrumentation & Computation in the Labs

- **Proposed:** Test, Adapt and Implement 8-10 Green Labs in Organic Lab Curriculum

- **Final Product:** Two Green Chemistry Lab manuals (Resources: UO Workshop, GEMs, J. Chem. Ed., Hendrix College Labs)
Green Chemistry at Mt. SAC

- Introduction to Green Chemistry
  - Why green chemistry
  - What is green chemistry
  - Twelve Principles of green chemistry
  - Measures of Efficiency of a Reaction

- Introduction to IR Spectroscopy

- Introduction to NMR Spectroscopy (1D/2D)

- Introduction to Molecular Modeling (w/Spartan)
Green Experiments (CHEM 80)

1. Biosynthesis of Ethanol from Molasses
2. Trimyristin: A Fat from Nutmeg
3. Isolation of Chlorophyll and Carotenoid Pigments from Spinach
4. Identification of an Unknown Organic Compound
5. Structure and Nuclear Magnetic Resonance
6. Chemical Kinetics: Evidence for the $S_{N1}$ Mechanism
7. Which Structural Isomer? (DEPT NMR)
8. The Nucleophilic Substitution Reaction ($S_{N2}$)
1. A Green Solventless Diels – Alder Reaction
2. Diels – Alder Reaction in Water
3. Iodination of Salicylamide
4. Electrophilic Aromatic Substitution: Friedel-Crafts Alkylation
5. Oxidation of Aromatic Aldehydes Using Oxone
6. A Solventless Aldol Condensation Reaction
7. Complete Assignment of Ibuprofen Structure (1D/DEPT/HETCOR NMR)
8. Reductive Amination: Three Easy Pieces
9. Identification & Complete Assignment of an Unknown Organic Structure (2D NMR - COSY)
Computational Experiments

**Organic Chemistry I (CHEM 80)**
1. Conformational Analysis (Open Chain Alkanes)
2. Conformational Analysis (Substituted Cyclohexanes)
3. Ring Strain in Cycloalkanes
4. Carbocation Stability
5. Regioselectivity of Electrophilic Addition to C = C Bond

**Organic Chemistry II (CHEM 81)**
1. Aromatic Compounds
2. Heterocyclic Aromaticity
3. Electrophilic Aromatic Substitution (*Reactivity* Effect)
4. Electrophilic Aromatic Substitution (*Directing* Effect)
Which Structural ($C_6$ or $C_7$) Isomer
Introduction to $^{13}$C & DEPT NMR

Adapted from: Reeves and Chaney, JCE, 1998

**DEPT** $^{13}$C NMR (Distortionless Enhancement by Polarization Transfer)

- distinguishes among carbon signals due to CH$_3$, CH$_2$, CH, and quaternary carbons

<table>
<thead>
<tr>
<th></th>
<th>(C)</th>
<th>(CH)</th>
<th>(CH$_2$)</th>
<th>(CH$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dept 135</td>
<td>0</td>
<td>up</td>
<td>down</td>
<td>up</td>
</tr>
<tr>
<td>Dept 90</td>
<td>0</td>
<td>up</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Dept 45</td>
<td>0</td>
<td>up</td>
<td>up</td>
<td>up</td>
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$^{13}$C NMR of 2-Butanone
DEPT NMR of 2-Butanone
Pre-DEPT Quiz

Read and respond to the problem below.
An AP high school student is studying NMR. The student is given the following PDC and DEPT-NMR spectra of a molecule. The student is asked to identify the structure of the molecule, and asks you for help. On the space below, describe how you would teach the student to identify the structure of the molecule from the NMR spectra. Continue your answer on the back. Propose a structure for the compound at the end of your description.

Molecular Formula  \( \text{C}_4\text{H}_9\text{Cl} \)

\( ^{13}\text{C}-\text{NMR} \)

\( \text{DEPT} ^{13}\text{C}-\text{NMR} \)
Post-DEPT Quiz

Read and respond to the problem below.
The following $^{13}$C- and DEPT $^{13}$C-NMR spectra belong to one of the structural isomers of the aliphatic C$_6$ or C$_7$ hydrocarbons. On the space below, describe how you would deduce the structure of the molecule from the NMR spectra. Continue your answer on the back. Propose a structure for the compound at the end of your description.
Determination of Correct Structure (pre/post DEPT)
$S_N^2$ Rxn - DMAP w/CH$_3$I

\[
\begin{align*}
\text{DMAP} & \quad \text{N}^+ \quad \text{N(CH}_3\text{)}_2 \\
& \quad \text{N(CH}_3\text{)}_3 \\
& \quad \text{I} \\
\text{Prod A} & \quad \text{N}^+ \quad \text{N(CH}_3\text{)}_2 \\
& \quad \text{I} \\
\text{Prod B} & \quad \text{N}^+ \quad \text{CH}_3 \\
& \quad \text{I}
\end{align*}
\]
DMAP Product $^1$H NMR

DMAP product in D2O

- a
- b
- c
- d
- HOD
DMAP product $^{13}$C NMR
### Computational Results

<table>
<thead>
<tr>
<th>Product</th>
<th>$\Delta H_{\text{rxn}}$ (kJ)</th>
<th>$E_a$ (kJ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prod. A</td>
<td>678</td>
<td>321</td>
</tr>
<tr>
<td>Prod. B</td>
<td>563 (-115 kJ)</td>
<td>258 (-63 kJ)</td>
</tr>
</tbody>
</table>

Product B is the **Thermodynamically** preferred product. Product B is also the **Kinetically** preferred product.
DMAP ELPOT Surface
DMAP Potential Surface
Reductive Amination Experiment

(Touchette, K.M, GEMs site)

ortho-vanillin  para-toluidin  Imine product  Acetylated amine
Imine Product Crystals
Imine Product Crystals
Reductive Amination Experiment

Imine DEPT

CH peak

Image: Spectroscopic chart showing various peaks and labels for chemical analysis.
Reductive Amination Experiment

Acetylated Amine DEPT
Complete Assignment of Ibuprofen Structure

8 Unique Hydrogens
10 Unique Carbons
Complete Assignment of Ibuprofen Structure ($^{1}$H NMR Spectrum)
Complete Assignment of Ibuprofen Structure \( (^{13}\text{C NMR Spectrum}) \)
Complete Assignment of Ibuprofen Structure (DEPT Spectrum)
Complete Assignment of Ibuprofen Structure (HETCOR Spectrum)
Group Work
Spring 2012 waste:

Non-halogenated: Chem 80/81 (7 L/5.5 L)

Overall: ~ 8L/section (non-Green Labs) to ~ 2.8L/section (Green labs)

Halogenated: 2 L total between all three Labs (down from 6 L in Fall 2011)
Green Chemistry at Mt. SAC

- **Challenges**
  - **Time**: Extensive... Search for, analyze, select, pilot and finally implement appropriate labs
  - **Resources**: Instrumentation, Computers and $$$
  - **Colleagues**: buy-in
Green Chemistry at Mt. SAC

Outcome?

- Still teaching organic chemistry but within the context of green chemistry
- Saving to College through waste reduction
- Saving to students
- **Dynamic organic lab curriculum**... new green experiments can be tried and added to the curriculum at any time
Acknowledgements

- Mt. San Antonio College
- Deans Matt Judd & Larry Redinger
- U. of Oregon Green Chemistry Workshop Leaders (Jim Hutchison, Kenneth Doxsee, Julie Haack, all green chemistry Staff)
- Tom Goodwin & his Staff at Hendrix College
- Chemistry faculty at several US institutions who graciously shared their green materials with me
- My Colleagues in the Chemistry Department
- Student assistants Stella Hartono, Vivian Le, Yingqiu Zhang
- CHEM 80/81 students - 2009 & 2010
- National Science Foundation