Implantation of the Principles of Green Chemistry in the Teaching of Sophomore Organic Chemistry

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Introduction

• At National Taiwan University there are three different introductory organic chemistry courses, mostly given in sophomore year. In general, an American textbook is chosen for individual section according to the lecturer’s preference.
• “Organic Chemistry B” is a two-semester course consists of three hours of lecture and one hour of recitation per week.

To choose a textbook for my class of students major in agricultural chemistry the latest edition of several popular ones were browsed.

In most books little attention was paid to the topics related to sustainable development, except ozone depletion and greenhouse gases.

The one by Solomons and Fryhle has discussion on the prohibition of using benzene and on green Baeyer-Villiger oxidation in main text, with alkene oxidation, adipic acid from glucose, and PET recycling in the box of “The Chemistry of…”.

The future chemists should be taught to have sufficient knowledge in green chemistry, and to think “green” when dealing with real world problems.

Students in general would not catch the significance of a new concept unless it is mentioned repeatedly over the semester or the school year.
Consequently, supplemental materials about green chemistry have been incorporated in my lectures scattered through the year.

Topics concerning basic principles and practices of green chemistry given to the students in my class are shown as follows:

(A) Introduction to organic chemistry

1. The global carbon cycle and the disruption due to human activities.
3. Challenges to sustainable development and the role of chemistry in solving problems.
4. The definition of sustainable chemistry or green chemistry. (OCED Workshop on Sustainable Chemistry, 1998)
5. The key concepts of green chemistry, based on the 12 principles by Anastas and Warner, and the 12 more principles by Winterton.

(B) Introduction to organic reactions

1. Microwave and ultrasound methods as alternative means to promote reactions.
2. Supercritical fluid carbon dioxide and water as useful and “greener” reaction media than volatile organic solvents.
3. Solvent-free reactions.
(C) Haloalkanes

• 1. The effects of many “useful” haloalkanes to global warming and ozone depletion.
• 2. Efforts to find environmentally benign substitute, such as aerosols and solvents used in dry-cleaning, as opportunities for chemists.

(D) Principles of organic synthesis

• In addition to those traditionally mentioned subjects, environmentally benign procedure and “atom economy” were emphasized. Examples of various reactions were given.
• 2. Students were asked to calculate Experimental atom efficiency (experimental atom economy °— percentage yield) for the preparations they performed in the organic laboratory.

(E) Oxidations

• Principles of “green oxidations”
• Oxidations using H$_2$O$_2$ catalyzed by Ti-molecular sieves
• Epoxidation using H$_2$O$_2$ with various catalysts
• Dihydroxylation of alkenes with H$_2$O$_2$ and resin-supported sulfonic acid catalyst
• Cleavage of C=C using H$_2$O$_2$ with tungstate catalysts and “green synthesis” of adipic acid
• Microwave-assisted oxidation with supported oxidizing agents
• Catalytic air oxidation of alcohols in aqueous media

(F) Diels-Alder reactions

• 1. Comparison of traditional reaction and microwave-assisted reaction (reaction of MVK with 2,3-dimethyl-1,3-butadiene)
• 2. Advantages of reaction in aqueous media, such as higher endo-selectivity and faster rates (reaction fo MVK with cyclopentadiene)
(G) Electrophilic aromatic substitutions

1. Friedel-Crafts acylation using no-chlorine catalysts (e.g., HF and Ac₂O in Ibuprofen synthesis)
2. Solvent-free nitration over zeolite H⁺beta.
3. Microwave assisted bromination and nitration, comparison of ordinary synthesis and green synthesis.

(H) Carbonyl compounds

1. Green oxidation for preparations.
2. Green reductions to alcohols.
4. “Grignard-like” reactions in aqueous media.
5. Microwave assisted condensation reactions, e.g., Knoevenagel reaction and formation of imines.

(I) Carboxylic acid derivatives

1. The greener acetic trifluoroacetic anhydride with similar reactivity as acetyl chloride.
2. Microwave-assisted esterifications.
3. DuPont method for recycling scrap PET as an example of transesterifications.
4. Greener route to ε-caprolactam.
5. Polymers having both CO₂-phobic and CO₂-philic segments as new surfactants used for cleaning in supercritical fluid CO₂.

(J) Biomolecules

1. The transformation of fats and oils to biodiesels.
2. Glucose as the starting material for environmentally benign synthesis using microbes.
3. From aspartic acid to polyaspartate, a biodegradable polymer.
Discussion

- It will take about 8-10 hours for lecturing the above-mentioned topics. So the lecture time for the traditional and basic organic chemistry will be significantly reduced at the expense for teaching “green” organic chemistry.
- Supplemental reading materials should be provided to the students.
- An organic chemistry textbook containing relevant topics of green chemistry in the main text and problems of various chapters is needed.