

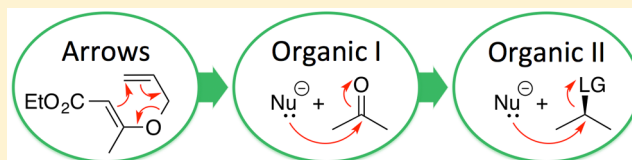
Mechanisms before Reactions: A Mechanistic Approach to the Organic Chemistry Curriculum Based on Patterns of Electron Flow

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ABSTRACT: A significant redesign of the introductory organic chemistry curriculum at the authors' institution is described. There are two aspects that differ greatly from a typical functional group approach. First, organic reaction mechanisms and the electron-pushing formalism are taught before students have learned a single reaction. The conservation of electrons, atoms, and formal charges, how the use of curved arrows helps describe the mechanism, and how to predict reaction mechanisms are emphasized. Second, the reactions taught in the first two semesters of organic chemistry are arranged by their governing mechanism, rather than by functional group. The reactions are taught in order of increasing difficulty, beginning with acid–base reactions, followed by simple additions to π electrophiles, and ending the first semester with addition to π nucleophiles, including aromatic chemistry. The reactions in the second organic semester begin with elimination reactions, then substitutions, and finally more complex π nucleophile mechanisms (e.g., aldol reaction) and π electrophile reactions (e.g., acetals). Ultimately, the goal is for students to learn and interpret reactions based on their patterns of reactivity, allowing them to analyze, predict, and explain new reactions. In principle, a mechanistic method is more general, easier to understand, and provides a better way to achieve a deep understanding of chemical reactivity. Chemical reactions follow patterns, and these patterns can allow a chemist to predict how a chemical will behave, even if they have never seen a particular reaction before. Visualizing reactivity as a collection of patterns in electron movement is a more powerful and systematic way to approach learning in organic chemistry. It still requires some memorization, but because the course organization is directly linked to reaction patterns, deeper learning in the discipline is possible.

KEYWORDS: First-Year Undergraduate/General, Second-Year Undergraduate, Curriculum, Organic Chemistry, Problem Solving/Decision Making, Constructivism, Mechanisms of Reactions, Lewis Structures



INTRODUCTION

Organic chemistry has existed as a distinct science for less than 200 years.¹ In the beginning, chemical tests were used to detect the presence of functional groups, ultimately to identify molecular structures; reaction mechanisms were not yet known. Because of the importance of these chemical tests, it was natural that classroom instruction would also focus on the functional groups detected by the tests. This approach required extensive rote memorization without understanding. Deep understanding of the discipline required a long time and considerable experience to acquire.

Kermack and Robinson first introduced use of the curved arrow to depict bond-forming and bond-breaking processes in 1922.² This was the first method describing chemical reactivity that considered the movement of electrons, rather than just atoms, when describing chemical reactions. This method has proven to be a more general and powerful way to understand chemistry. Using this method, it is possible to describe *why* a reaction occurred, to explain many concepts that had previously been derived from empirical observations, and to predict reactivity.

Today, most textbooks^{3,4} and courses emphasize mechanisms but remain organized around the functional group concept, even though experts rely on reaction mechanisms and the electron-pushing formalism (EPF) in their work.⁵ The

functional group organization frequently results in extensive rote memorization, does not always provide concurrent understanding, presents complex topics before simple concepts are taught, and frequently confuses students by making the subject appear random and difficult.⁶ Common reaction names (e.g., elimination and oxidation) often compound learning difficulties, as they can give the impression of new reaction types or opposite reactivity (e.g., electrophilic and nucleophilic addition).

Research is showing that students can benefit from mechanistic thinking.^{7–9} Despite the emphasis on the EPF, students tend to memorize reactions rather than using the EPF to work through organic reactions. For many students, the EPF is meaningless.^{10–12} Moreover, many students struggle with mechanistic tasks and seem to lack the predictive capacity that should arise from mechanistic competence.^{13,14} A number of suggestions have been published to help students learn mechanisms.^{15–17} Friesen suggested avoiding the overuse of short forms (e.g., R or Ph) and shortcuts (e.g., proton-transfer steps), and instead recommended (a) including key electrons and curved arrows, (b) using balanced reaction equations, and (c) distinguishing between ionic and covalent bonds (e.g., showing Na^+ and OH^- rather than NaOH).¹⁵ When teaching

Table 1. Curriculum Overview for the First Two Organic Chemistry Courses^a

Month	Section	Topic	Mechanism
Organic Chemistry I			
1	1	Lewis & line structures, formal charge, electronegativity, MO theory, etc.	
1	2	Physical properties of organic compounds	
1	3	Conformational analysis: Newman projections, cyclohexane, etc.	
1	4	Stereochemical analysis: isomerism, chirality, etc.	
1	5	Mechanisms, EPF, resonance	
2	6	Acid-base reactions	
2	7	π electrophiles with no LG	
3	8	π nucleophiles: alkenes & alkynes	
3	9	π nucleophiles: aromatics	
Organic Chemistry II			
4	10	σ electrophiles: E1, E2, oxidation	
4	11	σ electrophiles: S _N 1, S _N 2	
5	12	Infrared spectroscopy (IR), NMR spectroscopy	
5	13	π nucleophiles: enols & enolates	
6	14	π electrophiles with a LG: carboxylic acid derivatives	
6	15	π electrophiles with a hidden LG: acetals & derivatives, heterocycles	
6	16	π electrophiles with a LG: S _N Ar	

^aOnly the key components of each mechanism are shown in the table. In the course, the full mechanisms (including each proton transfer) are drawn by students and professor.

mechanisms, students can work through learning activities and be given immediate feedback.^{11,18,19}

Improvements to introductory organic chemistry course curricula have been suggested.^{20–22} For example, Goldish suggested a fundamental change in the organic curriculum including (a) focusing on the use of mechanisms, emphasizing electron flow and electron pair donors and acceptors, (b) not starting with radical reactions, since most reactions taught are ionic in nature, (c) leaving the confusing discussion of S_N1 and

related reactions until later, and (d) covering carbonyl chemistry fairly early.²³

Herein, the fundamental changes to the organic curriculum to a mechanistic approach are described. The goal is to help improve student learning and students' abilities to solve new problems. In this approach: (1) the concept of a mechanism and the electron-pushing formalism is taught before students learn a single reaction, (2) reactions are organized by the pattern of their governing mechanism, and (3) early sections of

an organic chemistry course are structured so that students gain skills needed to interpret, explain, and predict mechanisms. This new curriculum was first implemented in January 2012 (Organic Chemistry I), and the early results have been very encouraging.

OVERALL STRUCTURE OF COURSES

The organic chemistry sequence at the University of Ottawa is divided into four semester-long courses. The first two organic chemistry courses are structured as follows:

- *Organic Chemistry I* is a one-semester, first-year course (CHM 1321/1721) taught in the winter (4 English sections, 1 or 2 French sections)
- *Organic Chemistry II* is a one-semester, second-year course (CHM 2120/2520) taught in the summer and fall (3 English sections, 1 French section)

These two courses encompass the same material taught in most second-year, two-semester courses. They are large-enrollment courses with more than 1000 students per course divided into sections of 200–420 students. The third and fourth organic chemistry courses are a continuation of the second, but they have not been the main focus of the curriculum change and so are not described in detail here. An overview of the new courses' structure is in Table 1, along with an approximate timing of the sections.

Sections 1–4: Organic Structure

The course begins with a section on drawing Lewis structures, line structures, formal charge, and molecular orbital theory (σ , σ^* , π , and π^*).²⁴ Line structures are used extensively in the course because they reduce “clutter” in structural drawing and draw focus to the functional groups. For the same reason, the “R” notation (e.g., see Table 1) is avoided. Although resonance is traditionally taught in conjunction with Lewis structures, it can be a difficult concept to grasp and use without the benefit of electron pushing. Thus, all electron movement, including resonance, is delayed to the first mechanism section of the course (section 5).

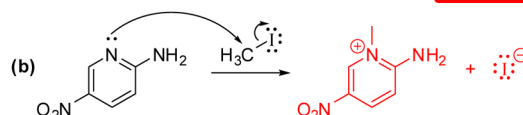
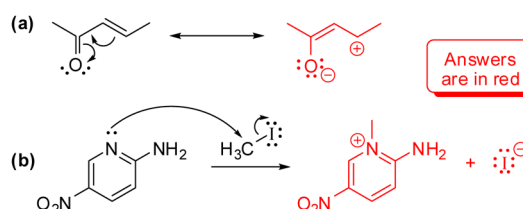
After sections 2–4 on the physical properties of organic compounds, conformational analysis, and stereochemical analysis, the part of the course on reactivity begins. The reactions learned in the rest of the course (sections 6–16) incorporate concepts from the earlier parts of the course.

Section 5: Reaction Mechanisms and the Electron Pushing Formalism

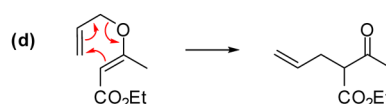
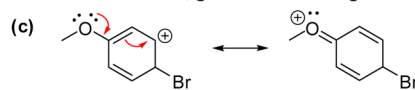
The first section in the reactivity portion of the course (section 5) focuses on the concepts of mechanisms and the EPF. This section is taught before students learn a single reaction. Students need to learn to think mechanistically and use curved arrows before adding the complexity of reactions and before they start trying to memorize mechanisms in an unconnected way. The focus is on **three learning outcomes (LOs)** that students will achieve by the end of this section (Box 1); they will be able to (1) draw the products of a reaction, given the starting materials and curved arrows, (2) add curved arrows, given the starting materials and products, and (3) draw the curved arrows and predict the products of a new reaction, given the starting materials.

When drawing curved arrows, the **arrows must start from electrons and point to an atom or bond**. In the first two organic courses, **arrows are not drawn between charges** because electrons and atoms (not charges) form bonds. The

LO1: Draw the products, given the starting materials and curved arrows



LO2: Add curved arrows, given the starting materials and products



LO3: Add curved arrows and predict the product(s), given the starting materials



Box 1. Three intended learning outcomes for mechanisms with examples using resonance structures (a, c, e) and reactions (b, d, f).

purpose of this section is not for students to memorize the mechanisms; rather, the goal is to achieve the above learning outcomes. On midterms and exams, the questions associated with these learning outcomes include reactions that students have not yet seen (e.g., Box 1d).

Simple resonance structures (Box 1a, c, e) are taught first, so that students need only focus on moving electrons, not both electrons and atoms as they must do in reactions. The principle that electron-rich (negative or δ^-) and electron-deficient (positive or δ^+) centers attract is emphasized.

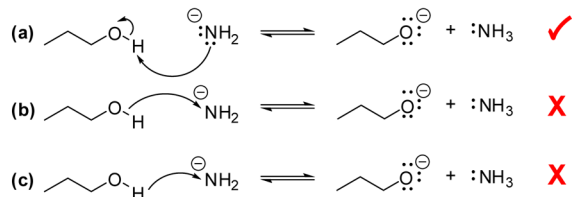
In class, mechanisms are color-coded so that students can see how and where specific electrons have moved (e.g., nucleophile in blue, electrophile in green, curved arrows in red (Table 1)). Drawing all of the lone pairs of electrons and atoms near the reacting center helps in the calculation of formal charges and reinforces the need to keep track of all electrons and atoms. Students can answer resonance and mechanism questions in class using a classroom response system (CRS).^{18,25,26}

Next, the mechanism learning outcomes are addressed using organic reactions—this is still before students have learned a single reaction (Box 1b,d,f). Now, students must track/conserve atoms as well as charges and electrons. Drawing all the nonbonding electrons, the implicit hydrogen atoms, and labeling (e.g., numbering) the atoms at or near the reacting centers are emphasized.

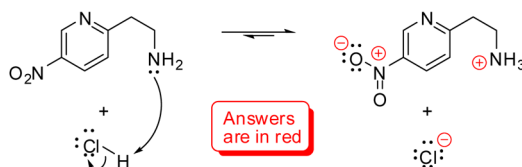
In assignment questions, students are asked questions related to the aforementioned learning outcomes, as well as questions that address common errors (e.g., Box 2). The focus in question 1 is to keep track of electrons. In question 2, students are asked to add the appropriate formal charges to the products.²⁷

Students are quite successful in this section of the course. They have the opportunity to develop basic EPF skills before adding the complexities that accompany chemical reactions. For

1. Decide which of following mechanisms is correct



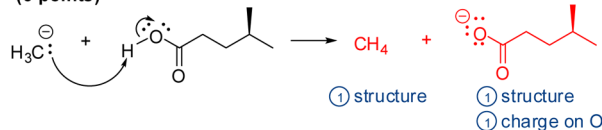
2. Add appropriate formal charges to the final product(s). All atoms have a full octet.



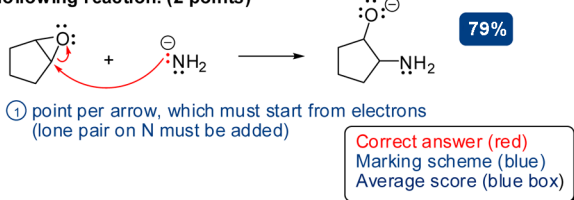
Box 2. Assignment questions that address common errors.

example, the two questions shown in Box 3 were given on a midterm exam before students had learned a single reaction; 90% of students answered question 1 correctly and 79% answered question 2 correctly ($N=354$).

1. Draw the product(s) of the following reaction. (3 points)



2. Draw a mechanism (i.e., add curved arrows) to explain the following reaction. (2 points)



Box 3. Mechanistic questions (in black) given on a midterm exam before students had learned a single reaction ($N = 354$).

Section 6: Brønsted Acid–Base Chemistry

The first organic reaction taught is the proton transfer (section 6). Brønsted acid–base chemistry serves as an introduction to chemical reactions, including the principles of equilibrium and microscopic reversibility.

The mechanism learning outcomes (Box 1) are revisited as they apply to acid–base chemistry, and students are expected to show every proton transfer explicitly using the EPF. That is, students may not use the $-H^+/+H^+$ or PT (proton-transfer) conventions²⁰ or skip proton-transfer steps in any mechanism taught in the first two semesters of organic chemistry. Students are still learning to keep track of electrons and atoms at this point and even a proton transfer can lead to avoidable errors.

REORGANIZATION OF THE REACTIONS IN THE NEW CURRICULUM: SECTIONS 7–16

The next sections (Table 1, sections 7–16) of the course differ most from the functional group approach. The reactions are grouped by similar mechanisms and taught with a gradient of difficulty. All of the reactions taught over two courses can be grouped into four categories: acid–base, π electrophiles, π

nucleophiles, and σ electrophiles. The patterns and similarities between mechanisms are emphasized instead of memorization to promote improved student mastery of the concepts in the course so they can learn new mechanisms independently.

S_N1 , S_N2 , E1, and E2 reactions have been moved to the second semester course. Although these reactions usually make simple products and have traditionally been taught first (after acid–base), the reactions have very complex rules of reactivity. They require an understanding of leaving group abilities, nucleophile and base strengths, analyzing the degree of substitution of the α -carbon (the carbon that bears the leaving group), solvent effects, and more. Students must also consider competing reaction pathways, regiochemistry, and stereochemistry, all when they have only just learned a proton transfer. Teaching those reactions so early forces students to learn a great deal of information in a very short time, and, as a result, many students resort to memorization. Instead, those reactions are taught after students have acquired a stronger mechanistic base.

Section 7: π Electrophiles

After acid–base chemistry, addition reactions to π electrophiles that do not bear a leaving group are taught. The reactions in section 7 involve the addition of nucleophiles to aldehydes, ketones, and imines (Figure 1) under acidic or basic conditions.

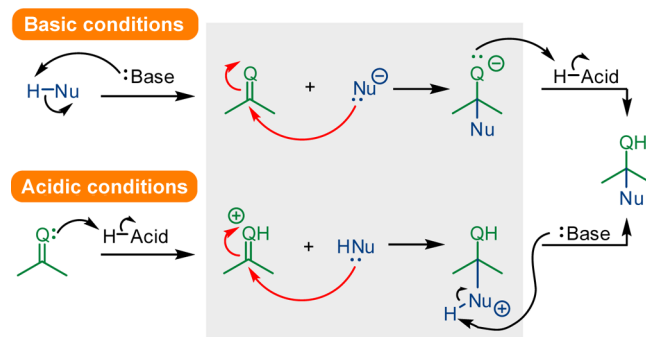


Figure 1. Reactions of nucleophiles with π electrophiles that do not bear a leaving group.

The main step of the mechanism is the same in all these reactions (Figure 1, gray box); only the order of protonation and deprotonation changes. The key step involves only the reaction between the nucleophilic atom with the electrophilic carbonyl carbon and has the “leaving group” (the π bond) pulled toward the more electronegative atom. Acid activates the electrophile (by “pulling” on the π electrons), while base activates or generates a nucleophile (an electron “push”). The fundamental mechanistic pattern is the same (shown in red arrows) regardless of whether the reaction proceeds under acidic or basic conditions. Students only need to consider one pattern of electron movement, rather than memorize two reactions (acid and base catalyzed). By teaching these reactions together, the concepts of acid and base catalysis are introduced in a simple way. The role of the catalyst—activating nucleophile or electrophile—is a pattern that is consistent throughout organic chemistry. Teaching students *why* a catalyst works the way it does (e.g., acid activates electrophiles, base activates nucleophiles) provides them with a foundation to quickly understand reactions they have not seen before.

The specific reactions taught include the Grignard reaction, organolithium reactions, reduction with $NaBH_4$ (aldehydes and

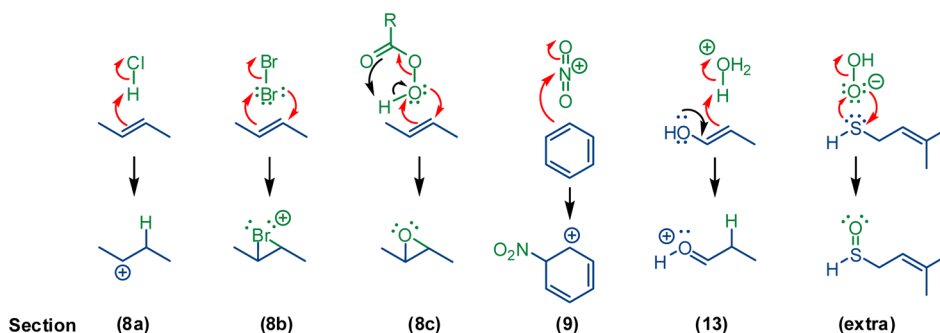


Figure 2. Examples of reactions that fit the category of π nucleophiles. The extra mechanism proceeds by the same electron flow pattern and is used to oxidize thiols, such as the ones found in skunk spray.

ketones) and NaBH_3CN (imines). The electrophiles include aldehydes, ketones, and imines. Those electrophiles do not bear an obvious leaving group (e.g., as does an acid chloride) and the reaction stops at the stage of the tetrahedral intermediate (with the types of nucleophiles that are included at this stage). Reactions to form hydrates and hemiacetals (especially intramolecular variants) are also taught at this stage, because they proceed by the same key steps (Figure 1). Stereochemistry, conformational analysis, and molecular orbital concepts are connected to these reactions.²⁸

Sections 8–9: π Nucleophiles

In section 8, the reactions of π -bond nucleophiles are analyzed as they react with a variety of electrophiles by similar patterns of electron flow (Figure 2). Closely related mechanisms are taught, including the reactions of alkenes with HX (section 8a), X_2 (section 8b), or peroxy acids (section 8c). Stereochemical and regiochemical considerations are addressed, as are the concepts of nucleophilic solvents and intramolecular reactions. When discussing relative carbocation stability, the concept of hyperconjugation and the Hammond postulate are included. Enol ethers are included in the Markovnikov section, reinforcing the role of resonance in reactivity. With each reaction variant, including alkynyl nucleophiles, the repeating patterns of, and the reasons for, reactivity in controlling regiochemistry (Markovnikov addition of nucleophiles) are emphasized. The roles of orbitals in controlling stereochemical outcomes are also discussed.

Two reactions that give anti-Markovnikov addition of nucleophiles are also taught here: hydroboration–oxidation of alkenes and radical-promoted addition of HX to alkenes (including single-headed arrows). Other radical reactions, such as the sodium/ammonia reduction of alkynes, are not taught in the first two semesters but, instead, are taught in the radical sections of more senior courses.

Section 9 includes aromaticity, antiaromaticity, and the reactions of benzene derivatives with activated electrophiles. The electron flow pattern of benzene when it reacts with electrophiles is identical to the first step of reactions of alkenes with electrophiles (Figure 2). The second (deprotonation) step is readily explained by the regeneration of aromaticity driving the reaction; students have already learned the acid–base step required. Nitration, sulfonation, aromatic halogenation, Friedel–Crafts alkylation, and acylation reactions are typically taught.

To explain the effects of directing groups, links are made to inductive effects (sections 1 and 6), resonance (section 5), hyperconjugation (section 8), and the Hammond postulate (section 8). Synthesis is taught from the very first reaction in

section 7. The section on aromaticity in particular provides an opportunity for students to design syntheses in which the order of reactions affects the product isomer.^{29,30} In all of the reactions in Figure 2, the pattern of electron movement is the same in the key step. The curved arrows can be followed in each one to draw the resulting product/intermediate, analyze the intermediate(s), and to deduce what happens next.

Sections 10–11: E1, E2, $\text{S}_\text{N}1$, and $\text{S}_\text{N}2$

The second course in organic chemistry (Organic Chemistry II) begins, after a brief review, with elimination reactions, specifically E1, E2, and oxidations of alcohols and aldehydes (Table 1, section 10). Students have already learned the E1 mechanism, in part, with the analysis of carbocations in section 8 and the E1-type elimination step in the electrophilic aromatic substitution reactions (section 9). Beginning the second course with the E1 reaction provides a link between the two courses. Students must consider electrophilic structure (e.g., degree of substitution of the α -carbon), leaving group ability, solvent effects, regiochemistry, and stereochemistry. The E2 reaction is taught next, linking back to the acid–base section of the first course. Oxidation reactions are taught with E2 because the electron flow patterns of key steps are identical (Figure 3).

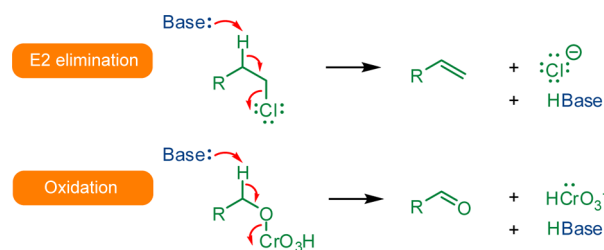


Figure 3. Parallel between the E2 and alcohol oxidation reaction mechanisms.

With the $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ reactions come the analysis of product ratios and how to predict which of the four reactions, E1, E2, $\text{S}_\text{N}1$, or $\text{S}_\text{N}2$, will predominate with given substrates and reaction conditions. The molecular orbitals that dictate the course of these reactions (especially stereochemical aspects) are also analyzed.

Section 13: Enols and Enolates as π Nucleophiles

After section 12 on spectroscopy, nuclear magnetic resonance³¹ and infrared, enols and enolates are the π nucleophiles in the next mechanism (Figure 2). In section 13, sections 8 and 9 (π nucleophiles) are revisited, with some additional complexity in the generation of the π bond (the enol/enolate). The

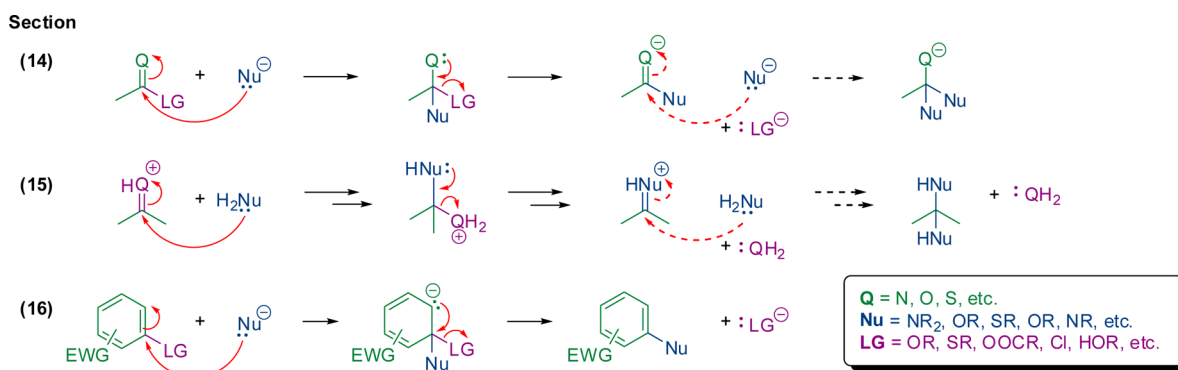


Figure 4. Section: (14) π electrophiles bearing a LG; (15) π electrophiles bearing a nonobvious LG and acid-catalyzed conditions; (16) aromatic (π) electrophiles bearing a LG. Only key steps are shown (not proton transfers).

electrophilic partners have been seen before, i.e., X_2 , alkyl halides, and carbonyls, although this is the first time students learn of a π bond reacting with a carbonyl, providing an opportunity to connect earlier concepts. These reactions are also revisited after sections 14–16 (section 13 has also been taught after sections 14–16).

Sections 14–16: π Electrophiles That Bear a Leaving Group

Sections 14–16 involve π electrophiles that bear a leaving group (Figure 4). Section 14 is the chemistry of carboxylic acid derivatives, which proceeds by two main mechanisms, either under basic or acidic conditions. Students learn the relative reactivity of various electrophiles based on their leaving group ability. They also determine whether these reactions should be conducted under acidic or basic conditions, depending on the reacting partners and desired product.

Section 15 involves the chemistry of acetals and derivatives, which proceeds by the same mechanistic pattern as the derivatives of carboxylic acids, although the leaving group is not apparent until the tetrahedral intermediate forms. Nucleophilic aromatic substitution (section 16) proceeds by the same mechanistic pattern as the two above, although on a benzene ring instead of a carbonyl. The pattern of the mechanism dictates the organization of this curriculum, not the functional group involved.

Students are explicitly shown, and are asked to find, the parallels between the acid- and base-catalyzed mechanisms, which have the same key steps and differ only in the proton transfer steps. Students are taught how to determine whether the reaction will stop after the collapse of the first tetrahedral intermediate or whether a second addition of a nucleophile will occur (dashed curved arrows in Figure 4), depending on the reacting partners. When situations arise in which multiple reaction pathways are possible, the various mechanistic pathways are analyzed in class and students learn to predict the correct products. For example, some decisions related to the site of deprotonation can be made on the basis of pK_a . Students must show every step of a mechanism without taking shortcuts¹⁵ as is done by the instructors when modeling working through mechanisms.

■ IMPLEMENTING THIS APPROACH

This new curriculum was first implemented in January 2012 with Organic Chemistry I and it has been used ever since. All professors who teach these courses, as well as professors of the third-year organic chemistry courses, decided to move forward

with the new curriculum to ensure continuity between each year of instruction.

The instructors found the conversion to the new curriculum to be straightforward. At the simplest level (from an instructional input point of view), the new curriculum required only rearranging sections of the course and modifying some synthesis questions. The associated laboratory experiments were rearranged to stay aligned with the order of the course content. Professors rearrange sections within a course if they wish, and students can still be directed to the relevant sections in a functional group textbook. Continuing discussions help to refine and improve the teaching and learning in the courses. Additionally, students' feedback about the course structure has been very positive.

■ NEXT STEPS

On the basis of the encouraging experiences with this first change in the curriculum, further changes are being considered by moving all carbonyl chemistry into first year, which allows all related reactions to be taught together, keeps complex stereochemical considerations to a minimum in the first course, and helps make connections to biochemical processes earlier. In addition to acetals, the synthesis of simple heterocycles will be introduced, which form by a combination of acetal and enol-type mechanisms. Radical reactions will be omitted from the first two years, so that the focus can be on ionic reactions exclusively.

The second semester will start with aromatic nucleophiles, followed by the π nucleophiles (alkenes and alkynes); the former has fewer reaction variants and can be taught with a minimum of stereochemistry. Next will be elimination reactions, the reverse of addition to alkenes, hence revisiting the principle of microscopic reversibility (first learned with acid–base chemistry). After that comes substitution reactions and identifying reaction conditions that will favor one reaction ($E1$, $E2$, S_N1 , S_N2) over another. The second semester will finish with π nucleophiles: enols and enolates. The reaction of those nucleophiles with carbonyls will provide a link back to the first semester course and into the third organic course. The third year course deals with advanced enolate chemistry, such as the Evans aldol reaction.³² In that course, pericyclic and cycloaddition reactions, rearrangements, advanced heterocyclic chemistry, radical reactions, and cross-coupling reactions are also taught.

CONCLUSIONS

The standard organic curriculum for the first two semesters of organic chemistry was modified in two major ways. First, a section dedicated purely to the electron-pushing formalism and the principles of reaction mechanisms was added to the first-semester course. This section is taught before students have learned a single reaction. The goal is to enable students to master the mechanism learning outcomes without the complexity of later reactions and, importantly, without memorizing the processes and simply decorating with arrows. Assessment is aligned with those intended learning outcomes (LOs) by giving midterm and exam questions that address the three key mechanism LOs, using reactions students have never seen.

Second, the portion of the courses dedicated to reactions was redesigned. The reactions were arranged based on the pattern of their governing mechanism, and the mechanisms were taught in a gradient of difficulty by teaching the mechanistically most simple reactions first. The patterns in electron movement were emphasized to promote a systematic approach to learning organic chemistry. The goal is to improve students' abilities using the electron pushing formalism, including predicting and explaining unknown reactions.

In this report, the focus was only on the aspects of the curriculum that related to teaching reactions and mechanisms, although there remain many other curricular and pedagogical aspects included in course planning. Because of the early indicators of success (the ease of implementation, student and instructor satisfaction in particular), a learning evaluation of this new curriculum will be conducted, which will be reported in due course.

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Notes

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DEDICATION

We dedicate this article to Tony Durst and to the memory of Keith Fagnou. Their insights into teaching and learning will always influence our work.

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