

Saying What You Mean: Teaching Mechanisms in Organic Chemistry

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Learning chemical reactions and their use in synthesis is one of the main objectives of organic chemistry courses. Developing an understanding of reaction mechanisms employing the curved arrow to represent the movement of a pair of electrons is the current approach to learning organic reactions. Virtually every textbook in publication as well as a host of specialized books feature curved arrow reaction mechanisms (1–9). Reasons for this mechanism-based approach to learning organic reactions include

- Avoiding “black box” memorization of organic reactions improves overall retention of acquired organic reactions, even though some memorization is required to learn organic reactions.
- Understanding underlying principles of molecular reactivity that describe reactions increases understanding of how reactions happen and not just what happens in terms of outcomes.
- Being aware of the principles of molecular reactivity helps students understand why reactions happen and allows that knowledge to be transferred to new situations.
- Drawing representational molecular structures and the curved arrow to represent the movement of a pair of electrons leads to appreciation of the three-dimensional inter- and intramolecular interactions that occur on the molecular level.

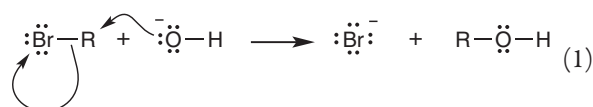
Despite the commitment of instructors and textbooks to teaching reaction mechanisms, there currently exist several common practices that work against a student's clear understanding of molecular reactivity. A recent study shows that there remains significant confusion when applying reaction mechanisms among chemistry students (10). Consistent application of reasonable practices that plainly reveal the basic chemistry involved in reaction equations and mechanisms allows students to better understand the value of the mechanism-based approach to learning reaction mechanisms. The consistent use of balanced reaction equations, avoiding the use of shortcut notations, including key electrons and bonds in structural representations, and distinguishing between covalent and ionic bonds will be discussed in detail below.¹

Writing Chemical Equations and Mechanisms

Avoid the Use of Shortcut Notations

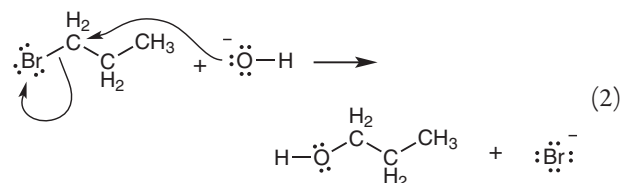
Shortcut notations are part of the language of organic chemistry but can be overused especially in introductory organic chemistry.² One of the worst offenses is the use of R to designate an alkyl group. It is a standard tenet of organic chemistry that alkyl groups are often interchangeable in chemical reactions. However, introduction of a typical S_N2 reaction with an R group obscures the fact that the leaving group is bonded to a carbon

atom as shown in eq 1:

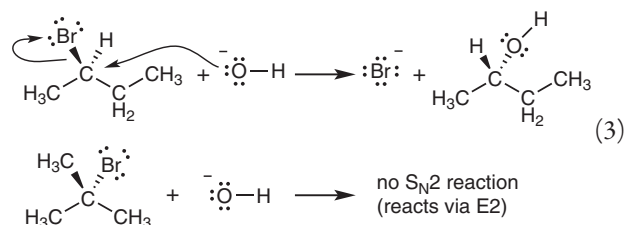


An additional drawback of using the R notation is that the nature of the alkyl group can sometimes have an influence on reactivity depending if the carbon is primary, secondary, or tertiary.

It is more advantageous to use a token alkyl group to represent a multitude of alkyl groups when introducing a reaction. The appreciation of the interchangeableness of alkyl groups may be introduced as part of the further investigation of the particular reaction. A representative 1-bromopropane structure in eq 2 exemplifies a typical reaction S_N2 on which to expand:



Later on, other nuances can be presented, such as those presented in eq 3 that include the inversion of stereochemistry and steric hindrance of a tertiary substrates:

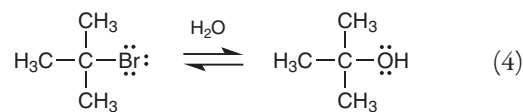


Other shortcuts that are used too liberally are Ph for a phenyl group, Ar for an aryl group, X for a halogen, and M for a metal atom. These abbreviations are sufficient for someone who is familiar with the fine points of chemical reactivity but they are problematic for students who are essentially just learning about the reactivity of chemical bonds.

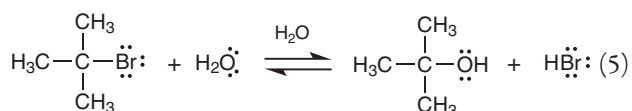
Balance Reaction Equations

Students learn stoichiometry and the importance of balanced reaction equations in introductory chemistry. In introductory organic chemistry courses, all too often, the importance of balanced equations is downplayed or even ignored. Simply stated, every atom of the reactants should be found on the products side and every atom in the products should be present in the reactants. Balancing reactions makes them more comprehensible for students who are being introduced to reactions and reactivity of organic compounds and reagents.

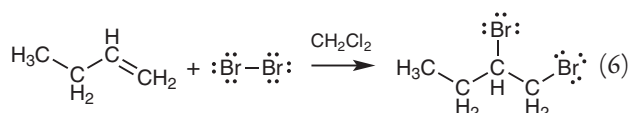
Consider the following representation of an S_N1 hydrolysis of 2-bromo-2-methylpropane to 2-methyl-2-propanol in eq 4:



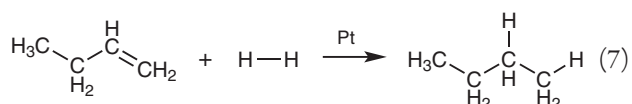
The role of the water molecule and the fate of the bromine leaving group are not clearly represented. Balancing the S_N1 reaction helps students see what is happening even without the aid of a detailed mechanism. In eq 5, the water in the balanced equation and on the arrow clearly shows that the water is both the nucleophile and the solvent for the solvolysis reaction:



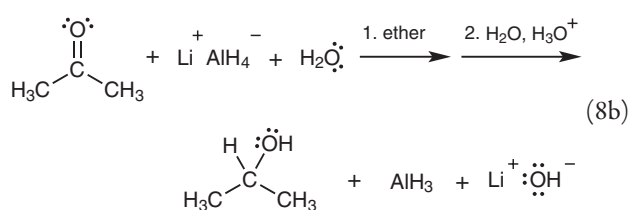
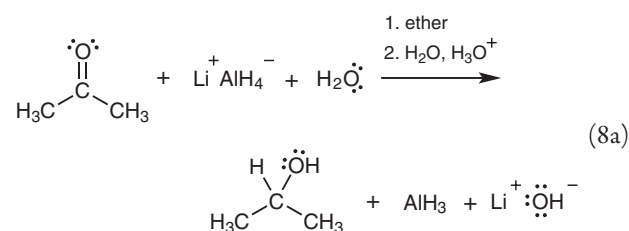
The arrow is the ideal place to include reaction conditions such as an appropriate solvent that is important for the reaction but does not participate in the balanced reaction equation such as the solvent dichloromethane in the electrophilic addition of bromine to an alkene illustrated in eq 6:



Catalysts should also be included on the arrows since they are essential species that do not show up in the balanced reaction equation as reactants or products, such as the role of a metal catalyst in the hydrogenation of an alkene shown in eq 7:

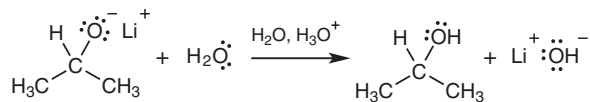
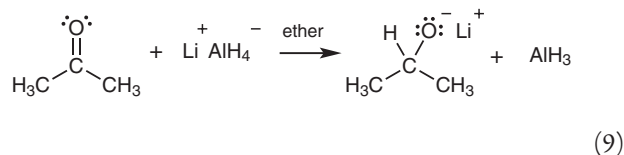


Difficulties arise when a two-step one-pot reaction is being represented. The arrow may be used to show the distinct steps of a one-pot reaction such as lithium aluminum hydride reduction of a ketone shown in eqs 8a or 8b:



The equation is balanced, however, the proximity of lithium aluminum hydride and water in the reaction gives the wrong

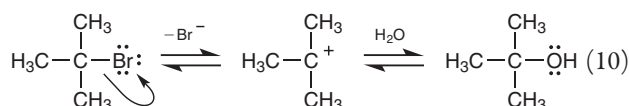
impression that they are added together to the reaction mixture. The only way out of the predicament is to show each step individually such as is shown in eq 9:



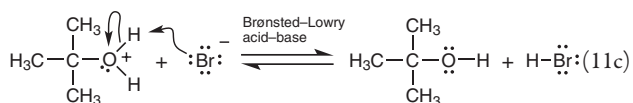
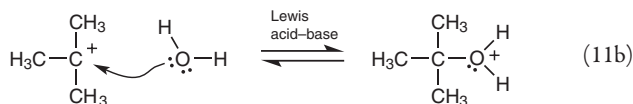
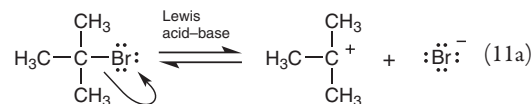
This is an example where clarity must have priority over efficiency of space in the education of chemistry students. The necessity of a dry reaction to form the alkoxide will be reinforced when this reaction, or a similar reaction, is performed in the accompanying laboratory section. The addition of an aqueous acid to the reaction mixture is then consigned to a separate step of the experiment.

Balance Detailed Reaction Mechanisms

In keeping with the commitment to full disclosure of organic reactions, a reaction should be introduced with a detailed reaction mechanism where each step is a distinct balanced reaction. This is another case where shortcuts often obstruct a careful exposure of the mechanistic details that fully describe the reaction. The “sequential arrow” approach is often used in mechanistic explanations of molecular reactivity. However, the sequential arrow approach does not adequately represent the origin and fate of all chemical species. Arrows indicating movement of electrons are incompletely represented as well. Consider the mechanism of the preceding S_N1 hydrolysis of 2-bromo-2-methylpropane:



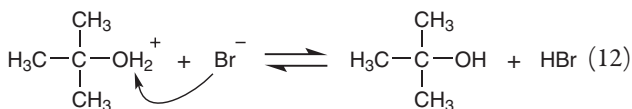
The advantage of detailed reaction mechanisms is that most reactions can be broken down into simple steps that give an overall cohesiveness to organic chemistry reactions. For example, Brønsted–Lowry acid–base and Lewis acid–base mechanistic steps are clearly relevant to the hydrolysis reaction mechanism of 2-bromo-2-methylpropane as shown in eqs 11a–c:



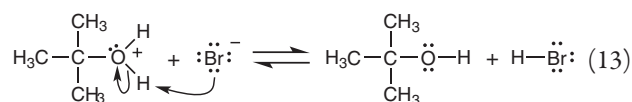
The overall reaction can be easily deduced from the detailed mechanism.

Write Structural Representations That Reveal Key Electrons and Bonds

Since electron movement is the basis of mechanism-based organic chemistry, valence electrons and reactive bonds should be clearly shown. In the reaction shown in eq 12, it is not clear what is happening to the electrons associated with the oxygen–hydrogen bond:

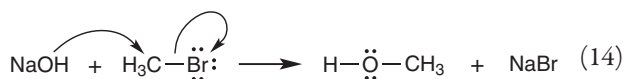


Drawing the oxygen–hydrogen bond and adding appropriate valence electrons reveals the fate of the bonding electrons as well as the source of the electrons for the new bromine–hydrogen bond:



Distinguish between Covalent and Ionic Bonds

Even though the difference between covalent and ionic bonds is included in first-year chemistry and in the introduction to organic chemistry, it is still important to distinguish between the two when writing reactions. The $\text{S}_{\text{N}}2$ substitution reaction shown in eq 14 does not give a clear indication that the sodium does not form covalent bonds with oxygen or bromine:



In eq 15 the ionic bonds are shown clearly:



The inclusion of spectator ions in chemical equations is a matter of personal taste. In the laboratory, the student will add sodium hydroxide to a reaction mixture. However, in the classroom the student may add either sodium hydroxide or hydroxide ion to his or her representation of a chemical reaction. Some instructors may feel that spectator ions add unneeded clutter to a reaction equation, while others may feel that the inclusion of spectator ions is a necessary representation of reality.

Challenges in Writing Clear Chemical Equations and Mechanisms

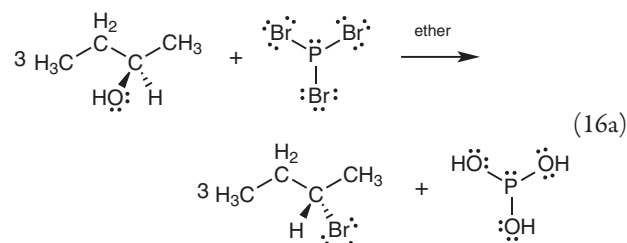
An Inductive Approach Must Lead to Generalizations

One of the admonishments of this article is that generalizations should not be introduced too soon in the learning process. The inductive method of teaching that is popular in the inquiry-based instruction models used in chemistry courses today proposes that the students be introduced to a specific reaction that is representative of a general reaction type. Other specific examples of the general reaction are subsequently presented to the student along with explanations of the particular nuances they signify such as stereochemical outcomes or interchangeability of halo-

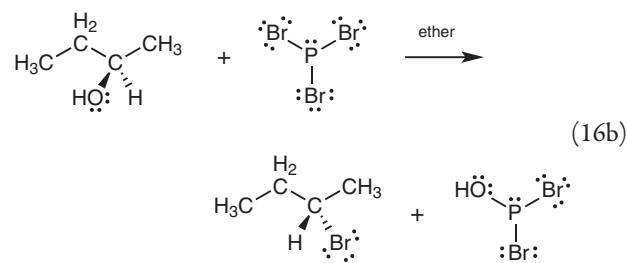
gen nucleophiles. Along the way students will form their own generalizations that link these particular reactions. Moreover, these generalizations should be enlightened and informed by a mechanistic understanding of the reaction type. However, the number of specific examples that are needed to convey the idea of a general reaction type that encompasses a wide variety of reagents varies significantly from student to student.

Oversimplification of Chemical Equations and Reaction Mechanisms Prevents a Complete Appreciation of Mechanistic Complexity

As previously mentioned, in order to write a balanced chemical equation, simplifications may be required. Accompanying the introduction of a chemical reaction with explanations of all possible outcomes of that reaction is often a case of too much information too soon in the learning process. On the other hand, mechanistic integrity does require that students be given the whole story at some point in their education. In practice, some reactions such as the phosphorus tribromide reaction with a secondary alcohol shown in eq 16a,



may need to be simplified in order to balance them as in eq 16b:



This is another case of where the nuances of chemical reactivity are not allowed to obscure the basic understanding of a particular reaction but can be presented once the reaction has been introduced.

Balanced Chemical Reactions and Complete Reaction Mechanisms Are Tedious

Writing complete reaction mechanisms can be tedious for both instructor and student. Repeated demonstration of a concept that is already understood by everyone is handily avoided by use of shortcuts. For example, the reason that bond-line molecular representations quickly replace Lewis, Kekulé, and even condensed molecular representations in organic chemistry is that they are easier and quicker to draw once the concept of four-bonds-to-carbon is well understood. There always seems to be a trade-off between giving proper emphasis to a basic concept and using shortcuts to facilitate the movement to higher levels of understanding.

Summary

An enlightening experiment that will reinforce the proposals contained in this article may be performed by choosing a well-known chemical reaction, such as a Fischer esterification, and comparing how several textbooks illustrate its mechanism. It will quickly become apparent that not only are generalizations and shortcuts used liberally, but that there is no accepted universal format for representing reaction mechanisms. One purpose of this article is to provide guidance of how reaction mechanisms can be clearly and definitively represented in introductory organic chemistry.

As highlighted by a recent book title, *Organic Chemistry as a Second Language*, introductory organic chemistry entails the extensive use representational terminology (11). A consistent effort needs to be made to properly emphasize basic concepts of introductory organic chemistry by adopting practices that clearly reveal the mechanistic nature of chemical reactivity. The objectives of a mechanistic approach to learning organic reactions are (i) to build on what students know from high school and first-year chemistry courses, (ii) to provide tools to understand chemical reactivity, (iii) to offer skills to build upon in subsequent chemistry courses, and (iv) to supply skills for other applications of chemical principles. The abstract language of chemical reactions should not be an obstacle to the consistent understanding of chemical reactivity.

Notes

1. The observations and examples in this article apply to every textbook currently in publication. This article should not be considered an endorsement or condemnation of any particular published work. I am not comparing the merits of any popular textbooks. The examples represented are typical and not intentionally copied from any particular text on the market.

2. The "introductory organic chemistry" course refers the course for chemistry or science majors, not to a one-semester class offered to nonscience majors (nursing and nutrition majors, for example) in some institutions.

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