CHAPTER 7 | An Overview of the Most Common Elementary Steps

This chapter’s material is unique to this textbook and is the foundation of the rest of the textbook. Taking your time reading this chapter and planning how to present the material is worthwhile. That approach will be new to most, but it is well worth the effort. This chapter introduces the following concepts:

- The elementary steps that students will see in practically all mechanisms in later chapters, allowing organic reactions in later chapters to be categorized by what type of elementary steps occur. That introduction also establishes the general framework for discussing reactions.
- Some useful simplifications for students—the tendency of electrons to move from electron-rich to electron-poor sites and to focus on the reactive anions (and ignore the cations) in hydride and organometallic reagents.
- How to use charge stability and bond energy to evaluate a reaction’s driving force, which in later chapters will lead to discussions of reversible and irreversible steps and mechanisms, as well as slow and fast steps.
- The mechanism for keto–enol tautomerization, in acidic or basic conditions, first appears here and is used in many later chapters.

Although “curved arrow notation” for electron flow in mechanisms was introduced in Chapter 6, it is reinforced and applied a great deal in this chapter.

The primary goal for Chapter 7 is to give students vocabulary (e.g., terms that describe different elementary steps) and the ability to visually identify the types of species in an elementary step (e.g., nucleophile, electrophile, leaving group). If students can “read” a mechanism, everything else quickly falls into place.

Students are not expected to predict what elementary steps will occur when simply given reactants; at this stage, the focus is not on predicting products from reactants. The focus is on understanding and using the language of elementary steps; students should learn that mechanisms are powerful tools that will simplify organic chemistry for them. Given the vocabulary of elementary steps, students should be able to:

- Provide products, and curved arrow notation of electron flow, when given both reactants and the name of an elementary step.
- Recognize and name an elementary step, and draw curved arrow notation, when given that step’s products and reactants.
- Recognize what species to expect as reactants and products for elementary steps—for example, that electrophilic addition is expected to have a C–C π bond and an electrophile on the reactant side and a carbocation on the product side.

Although students won’t see some of these elementary steps again until much later in the text, possibly not until the second semester of the sequence, cover all the steps now. Telling students that by the end of this chapter they will have all the tools they need to understand every mechanism for every reaction for the entire course is extremely powerful.

Again, whereas earlier chapters in the text cover material that appears in other textbooks and is familiar to instructors, this chapter contains material that does not appear in other books. I suggest that you read the chapter carefully to formulate your presentation and your expectations for students.

HEADS UP!

Teaching elementary steps without the full reactions to accompany them might seem strange. The method is different, but it works. Approaching this chapter as a process chapter helps me stay focused on driving forces instead of bringing in synthetic nuances right away.

You’ll see that no IUPAC designations or universally accepted descriptions are present for some elementary steps described in this chapter. The single-step reactions such as S_N2 and E2 are, of course, exceptions because they represent complete reactions, but other elementary steps are simply described as neatly as possible after a great deal of struggle and thought. Joel Karty’s goal was to find brief “handles” that students could apply to elementary steps.
Your challenge is to accept the designations (some of which you may not entirely approve of, but trust that keeping to those designations will pay off) and to coach students in applying them. Those designations will be used throughout the book to describe elementary steps and will become active vocabulary for students.

I see two steps to teaching this material:

1. Take students through the steps (either in lecture or through assigned reading), giving them visual clues to help them identify each step. This is also a good opportunity to reinforce analysis of charge stability and discuss the driving forces for steps.

2. Present students with multistep mechanisms and have them identify each elementary step in the mechanism. This chapter gives students practice in recognizing and identifying the different elementary steps. The end-of-chapter problems include 10 multistep mechanisms from later chapters (7.46–7.55); students are asked to, among other tasks, name each elementary step that occurs. Problems 7.56–7.60 are new to the second edition and are problems that Joel Karty has found particularly effective in helping students learn what they need from these elementary steps. I typically either assign all those problems or work through them in class. Doing so may seem like almost too much practice, but there is no such thing as too much practice at this stage. This chapter, when fully covered and understood, removes the barriers to learning when students begin multistep mechanisms (starting in Chapter 8). Everything done during this chapter pays off throughout the rest of the year.

I do not recommend that you show students animations of mechanisms at this point. Even though good animations are helpful, wait until specific reactions are discussed in future chapters. The goal of this chapter is to introduce the steps and teach students to recognize them on paper. When future chapters cover the kinetics, stereochemistry, and other aspects of different reactions, students will be in a better position to appreciate animations.

COMMENTS BY SECTION

7.1. Mechanisms as Predictive Tools: The Proton Transfer Step Revisited

This section shows students how they can use the attraction of opposite charges and the octet rule to predict how electrons will move. The section expands on something students learned in the last chapter, a proton transfer reaction, applying it to definitions of Lewis acids and bases. It concludes with the observation that in coordination, an elementary step, a Lewis base tends to form a bond with a Lewis acid.

A theme introduced in this section is familiar to most teachers: Keep it super simple (KISS). This chapter introduces several simplifications that will be useful to students. One simplification is to use charge stability and “electron rich to electron poor” to understand why an elementary step occurs. That approach leads students away from memorizing the steps in a mechanism and toward understanding why the steps occur—one purpose of this chapter. Section 7.1b shows a simplification that allows students to edit out “noise” in the signal they need to receive: In organometallic reagents and hydride reagents, the negatively charged species is the one that participates in reactions. At this stage, you can encourage students to simply ignore the cations.

As with most KISS actions in teaching, I am withholding some information. Technically, the atoms that are omitted do participate in some reactions. For example, the aluminum in LiAlH₄ has a critical role in the reduction of amides. However, using hydride alone simplifies the reduction of aldehydes, ketones, and esters. After students practice with those reactions, they will be in a better position to understand aluminum’s role in amide reductions.

For students to more readily identify reactive species and eliminate some of the noise in reactions, the discussion here suggests that they omit the spectator ions in bases and organometallic reagents and ignore the central Al or B in hydride sources. Those practices result in the following simplifications:

\[
\begin{align*}
\text{Treat:} & \quad \text{As:} \\
\text{KOH, NaOR} & \quad \text{HO}^-, \text{RO}^- \\
\text{RMgX, RLi, R}_2\text{CuLi} & \quad \text{R}^- \\
\text{LiAlH}_4, \text{NaBH}_4 & \quad \text{H}^-
\end{align*}
\]
7.2. Bimolecular Nucleophilic Substitution (S\textsubscript{N}2) Steps

The section introduces S\textsubscript{N}2 steps. It also defines nucleophile, leaving group, and molecularity and elaborates on each. The section also notes that good leaving groups tend to be conjugate bases of strong acids, that nucleophiles are attracted to atoms with full or partial positive charges, and that nucleophiles generally have lone pairs and full or partial negative charges. It concludes with a discussion of the electron-rich and electron-poor sites in an S\textsubscript{N}2 reaction and compares that step with a proton transfer step.

You may be tempted to teach the entirety of S\textsubscript{N}2 at this point, but stick to working through these basic examples. You’ll have time to cover all the nuances (solvent, type of carbon) later; this chapter is simply about the steps and the big picture. Make sure that your students realize that, for any S\textsubscript{N}2 step, they should expect a nucleophile to react with a substrate. The more care you take with presenting those concepts now, the easier it will be to overlay all the synthetic considerations later.

7.3. Bond-Formation (Coordination) and Bond-Breaking (Heterolysis) Steps

Section 7.3 is the first of several that present two steps that are the reverse of each other. These sections analyze the steps in terms of the flow of electrons from electron-rich sites to electron-poor sites.

In Section 7.3, the examples for coordination show both ions and neutral species reacting. In the examples for heterolysis, both neutral and charged species are also shown as reactants.

Keep reminding students that for coordination, they should expect the reactants to include a species lacking an octet and a species with a lone pair of electrons, and for heterolysis they should expect those species as products. The discussion notes that these elementary steps generally occur as part of a multistep reaction since one of the species (a reactant or product) lacks an octet and is consequently unstable and reactive.

7.4. Nucleophilic Addition and Nucleophile Elimination Steps

The section’s title refers to adding nucleophiles to polar \( \pi \) bonds and losing a leaving group to form a \( \pi \) bond. This section felt strange when I first taught it because it seemed so out of place with a traditional approach. But it actually flows neatly from the discussion of coordination and heterolysis. The examples (Equations 7-9 through 7-13) show charged and neutral nucleophiles as well as charged and neutral leaving groups. The discussion foreshadows the significance of those steps in redox and substitution reactions as well as their use in carbon–carbon bond formation in synthesis.

Again, the section concludes with an analysis of electron-rich and electron-poor sites in each step, representing the step generically by using \( \text{Nu}, \ L, \text{ and } \ X \). Technically, the eliminated species is a leaving group, not a nucleophile. Point out to your students that this elementary step was called “nucleophile elimination” so that the name would clearly reflect that it is the opposite of nucleophilic addition.

Students should leave this chapter knowing that every nucleophilic addition step has a nucleophile and a species with a polar \( \pi \) bond as reactants. Also, they should know that every nucleophile elimination step produces a polar \( \pi \) bond and a species that has the characteristics of a nucleophile.

7.5. Bimolecular Elimination (E2) Steps

The section defines E2 steps and gives three examples, showing double bond and triple bond formation and charged and neutral leaving groups. The discussion explains how the carbon with the leaving group is the electron-poor site in this step. The section concludes with a generic representation of the reaction, using \( B^- \) and \( L \) to represent the base and leaving group, respectively. Again, resist the temptation to introduce stereochemistry or solvents or other synthetic considerations—that will be introduced later (and will be much more satisfying to teach when building on a strong foundation of driving forces). Students should leave this chapter understanding to expect a \( \pi \) bond in the products from an E2 step.

7.6. Electrophilic Addition and Electrophile Elimination Steps

The section illustrates adding electrophiles (Bronsted–Lowry acids and other positively charged species) to nonpolar \( \pi \) bonds, as well as the reverse step, in which a proton is lost to form a nonpolar \( \pi \) bond. The examples of electrophile elimination initially show \( H^+ \) as the species that leaves; the section goes on to discuss the need to incorporate a base in the step to remove the proton. The section, like earlier ones, concludes with generic
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representations of the steps.

To begin emphasizing that the names of elementary steps give clues about the reaction’s driving force (nucleophilic vs. electrophilic) is worthwhile. Students should expect to see an electron-poor species and a nonpolar π bond in the reactants and a carbocation in the products. In-text problems such as Your Turn 7.10 and 7.11, labeling electron-rich and electron-poor sites, might seem too trivial to assign or emphasize, but no amount of practice at this stage is wasted.

### 7.7. Carbocation Rearrangements: 1,2-Hydride Shifts and 1,2-Alkyl Shifts

The section discusses the reactivity of carbocations and other steps that may occur with them (coordination and electrophile elimination). It then introduces rearrangements, explaining the two types and the significance of the notation “1,2.” Again, the section concludes with a generic representation of the step and a discussion of the movement of electrons from electron-rich to electron-poor sites.

*Chapter 6 discussed the relative stability of carbocations. Students will apply that information in several in-chapter and end-of-chapter problems.*

### 7.8. The Driving Force for Chemical Reactions

Just as the previous sections might have initially seemed too trivial to spend a lot of time on, this section might initially seem too advanced at this stage. It isn’t: It is a great balance between general justifications and quantitative data. This section introduces driving force as an explanation for why elementary steps occur: The *driving force* for a reaction reflects the extent to which the reaction favors products over reactants, and that tendency increases with increasing stability of the products in relation to the reactants.

The section then proceeds through examples that show how charge stability and bond energy can explain product-favored steps. The final example shows a reaction in which charge stability favors products, whereas bond energy favors reactants. The large $K_{eq}$ for that reaction leads to an important generalization: When charge stability and bond energy favor opposite sides of a chemical reaction, charge stability usually wins.

The section follows up that guideline with an E2 reaction in which the net loss of a σ bond to form a π bond favors the reactants, but the charge stability of the leaving group favors the products. It concludes with examples in which other factors affect the prediction of the driving force. That discussion cautions students that charge stability and bond energy are not the only considerations but indicates that they are the major considerations to focus on and that other factors will be discussed in the context of specific reactions.

### 7.9. Keto–Enol Tautomerization: An Example of Bond Energies as the Major Driving Force

This final section might seem like a special topic that could be held until later, but including it now is worthwhile. This example brings the entire chapter together. This section introduces the two resonance structures for enolate anions and the corresponding keto and enol forms. The term *tautomerization* is also introduced. Keto–enol tautomerism is presented as an example of a situation in which bond energy alone determines the favored product (because both forms are neutral).

The section also includes a numeric comparison of bond energies for the keto and enol forms (Figure 7-4), a table showing the percentages of the keto and enol forms present in samples of aldehydes and ketones, and a box showing the isomerism of glucose-6-phosphate to fructose-6-phosphate.

This section allows early introduction of enolates and keto–enol tautomerization, especially the mechanisms of tautomerization in both acidic and basic conditions, which students will use repeatedly. Early introduction allows this material to be “old news” when students encounter it in later chapters.

### STUDENTS’ PERSPECTIVES

This chapter allows students to intelligently discuss reactions in an unprecedented way. Students go from being passive receivers of presentations of “This is what occurs” to active participants in discussions that begin with questions such as “How do we describe this step?” “Do we expect this step to occur?” “Why does this step appear unlikely to occur?” “What could occur?” “What is the driving force for this step?” “How is the reaction similar to previous reactions? How is it different? What additional step could occur next?”

Using that approach, my students have been less likely to be intimidated by reagents, less likely to attempt to
blindly memorize, and more likely to participate in active learning. They feel empowered by this chapter and have said things like “Organic chemistry isn’t that bad, since it just makes sense” as they approach problems.

One challenge for me with this chapter is that it seems so easy that sometimes students don’t realize they still need to work hard. This is a chapter for which students simply need to commit to working problems. Some students can fool themselves into thinking that they understand the material simply from understanding what is presented in class. This chapter is so logically set up, and lends itself to such a good “story” for class, that students can easily imagine that they don’t need to practice something so seemingly easy. Taking the time in class to have students attempt (and sometimes initially fail at working) problems is extremely useful to convince students that applying concepts through problems is a necessary part of organic chemistry (no matter how clear the lecture is). Working through arrows and elementary step names for a multistep mechanism for which I have provided the products and reactants is useful. Something about seeing all those steps together intimidates students at first, but they ultimately feel liberated when they can successfully identify each elementary step.

Several testimonials posted on teachtheclass.com have featured student feedback regarding this chapter, including “The Chapter Every Textbook Should Have,” posted October 23, 2012, and “It’s Elementary: First Steps to Active Learning,” posted March 5, 2013.

RESOURCES

Although the end-of-chapter problems offer students many mechanisms to analyze, you may want additional sources. Diving into mechanisms from later chapters of this text, or from other organic textbooks, can be an interesting and useful way to challenge the students while looking ahead in the course. For example, asking students to provide electron-pushing arrows for the reaction (in acid) of an aldehyde with ethylene glycol to the acetal is a great way to help them see how intimidating groups and processes actually are accessible.

If you wish to bring in biochemical mechanisms, The Organic Chemistry of Biological Pathways, 2nd edition, by John E. McMurry and Tadhg P. Begley (W. H. Freeman: United Kingdom, 2015), has examples that seem complex to students until they break them down into simple steps (a great way to build their confidence). Also, I found Organic Reaction Mechanisms: Selected Problems and Solutions, by William C. Groutas (John Wiley & Sons: New York, 2000), particularly useful. That text contains 210 reactions with multistep mechanisms. From it, you can pull several nonconventional mechanisms for students to evaluate. Below, for example, is an exam question adapted from reactions found in that book:

Consider the following elementary steps:

(a)
Describe each step by using the nomenclature from the text:

(a)
(b)
(c)
(d) Which step is most likely to be product favored? Justify your answer.

One unexpected benefit of this chapter is that, once they learn the elementary steps common in organic reactions, students can quickly perform a large variety of experiments in the lab. Because students have examined elementary steps in class, learned to identify the individual steps in multistep mechanisms, and predicted the products of elementary steps, options for laboratory experiments are limitless. See “Liberation in the Laboratory,” posted August 14, 2012, on the Teach the Mechanism blog for complete details.

**Suggested Clicker Questions**

The following clicker questions have been selected from the Chapter 7 Clicker Question PowerPoints available on wwnorton.com/instructors. More questions for each chapter are available at the website.

7.2. **Bimolecular Nucleophilic Substitution (SN2) Steps**

“What is the nucleophile in the following SN2 reaction?”

That question, while seemingly just testing simple definitions, helps students identify reactive groups and gain confidence in recognizing reactive species.

7.7. **Carbocation Rearrangements: 1,2-Hydride Shifts and 1,2-Alkyl Shifts**

“Indicate the cation that would most likely form on rearrangement of the following.”

Students often have difficulty identifying the most stable carbocation and determining which direction rearrangement will occur. That question helps assess their comfort with those concepts.

**Summary Question**

“What is the product of the following sequence of elementary steps?”

That question really shows how far students can go in this chapter; this is a sequence of steps that seems intimidating to students at first, but once they work through the steps (using what they have learned from this chapter), they will be able to predict the product and feel that they are “doing chemistry.”