Chapter 5

Understanding How to Select Reactants and How to Draw Mechanism Arrows for Any Step of a Reaction

Key Concepts

Atoms react when they are electron-rich, electron-deficient, and/or have some level of instability. If you note these features in molecules, you can predict organic reactions. Labeling is important. Here are the seven key features of molecules you should notice and label:

Highly Reactive

1. An atom that requires a valence octet but doesn't have one. An incomplete valence shell (IVS!) is generally the most unstable, electron-deficient, and reactive situation you might see in an organic chemistry reaction. The most likely cases you will encounter are carbocations and radicals. Radicals are often created by peroxides.
2. Because bonds in a 3- or 4-membered ring are too close together, they are very reactive and especially easy to break (▽!). Although a strained ring is generally less reactive than an atom with an incomplete valence shell, it is usually more reactive than other features.

Moderately Reactive

3. As compared to unstrained sigma bonds, pi bonds (pi) are more likely to react. One reason is that, unlike sigma bonds, they are not directly in-between the nuclei, so they are not held as tightly. Another reason is that since a pi bond represents two additional electrons in a domain, the region is especially electron-rich. When the pi bond of an alkene or alkyne is involved in a reaction, also label the pi bond carbons 1°, 2°, or 3°, as applicable, to determine which carbon is more likely to start to develop a carbocation or carbon radical. (This will be discussed in more detail in Chapter 6.)

Somewhat Reactive

4. Because reactions generally occur between electron-rich and electron-deficient atoms, it's also important to label formal charges (+, –) and partial charges (δ+,

δ–). Formal charges often tell you when the number of bonds isn't optimal. Partial charges tell you when an atom is electron-deficient or electron-rich due to electronegativity differences.

Important if Other Molecule is Very Reactive

5. If there's a relatively high concentration (↑) of a particular reactant, it may be more likely to be involved in a reaction since molecules have to find each other to react. A particularly important case where concentration may play a big role is when an electrophile is highly reactive and the solvent is reactive. Potentially reactive solvents include water and alcohols.

Generally Unreactive

6. Carbon-oxygen, carbon-nitrogen, hydrogen-oxygen, and hydrogen-nitrogen bonds are too strong to break under normal conditions. That's because when small atoms (ones that have only 1 or 2 shells) are bonded together, the bond is short. One way to weaken these types of bonds is by giving the oxygen or nitrogen a positive formal charge. The other is to add an electron-withdrawing and/or resonance group (discussed in Chapter 12.) When bonds are too strong to break during a reaction, cross off the electron-deficient atoms directly attached to the oxygen or nitrogen as a reminder of that fact.

Also Important

7. Watch for resonance or for the opportunity to create a resonance system. (This characteristic will be discussed in Chapter 8.)

Remember that THE MORE REACTIVE AN ATOM IS, THE LESS SELECTIVE IT IS. That rule tells you something about what you need to look for in the other reactant. If an atom is crazy reactive (IVS! or ▽!), it's so desperate that it's more likely to react with whatever possible solution it runs into first. In other words, relative CONCENTRATIONS of appropriate reactants is the important factor. However, if an atom is less reactive, relative REACTIVITIES of the other reactants is usually the most important consideration.

Next, show how the reaction occurs.

Because a reaction involves electrons, mechanism arrows SHOW WHERE ELECTRONS GO…NOT WHERE ATOMS GO. When drawing mechanism arrows: FORM POSITIVE, BREAK NEGATIVE. In other words, when FORMING a bond, draw the mechanism arrow showing the electrons GOING TO a POSITIVE or otherwise ELECTRON-DEFICIENT ATOM. When BREAKING a bond, draw the arrow going from the electrons in the bond TOWARD the MORE ELECTRONEGATIVE (and therefore more negative) ATOM in the bond. (That's because an electronegative atom pulls bond electrons

towards itself.) Note that arrows always go FROM the ELECTRON SOURCE (bonds or non-bonded electron pairs) TO ATOMS.

What You Need to Learn, Understand, and Apply

1. **A working knowledge of the terms electrophile and nucleophile.**
2. **How to label reactants and determine which atoms are most likely to react during each step of a reaction.**
3. **Why peroxide creates radical intermediates.**
4. **One of the methods for weakening an oxygen-hydrogen, oxygen-carbon, or nitrogen-carbon bond so that a reaction can occur.**
5. **What $NaBH_4$ and $LiAlH_4$ are used for in organic reactions.**
6. **How to interpret a variety of reaction symbols used in organic chemistry.**
7. **How to correctly use and interpret reaction mechanism arrows.**
8. **The skills needed to apply the material and to avoid common errors.**