Chapter 1

Introduction

The study of **organic chemistry** focuses on the chemistry of materials essential for life. Specifically, organic chemistry defines the science surrounding the chemistry of elements essential for life to exist. In addition to carbon, the most common elements present in organic molecules are hydrogen, oxygen, nitrogen, sulfur, and various halogens. Through the study of organic chemistry, our understanding of the forces binding these elements to one another and how these bonds can be manipulated are explored. In general, our ability to manipulate organic molecules is influenced by several factors that include the nature of functional groups near sites of reaction, the nature of reagents utilized in reactions, and the nature of potential leaving groups. Additionally, these three factors impart further variables that influence the course of organic reactions. For example, the nature of the reagents used in given reactions can influence the reaction mechanisms and ultimately the reaction products. By recognizing the interplay between these factors and by applying principles of arrow pushing, which really represents bookkeeping of electrons, reasonable predictions of organic mechanisms and products can be realized without the burden of committing to memory the wealth of organic reactions studied in introductory courses. In this chapter, the concept of arrow pushing is defined in context with various reaction types, functional groups, mechanism types, reagents/nucleophiles, and leaving groups.

1.1 DEFINITION OF ARROW PUSHING

Organic chemistry is generally presented through a treatment of how organic chemicals are converted from starting materials to products. For example, the **Wittig reaction** (Scheme 1.1) is used for the conversion of **aldehydes** and **ketones** to **olefins**, the

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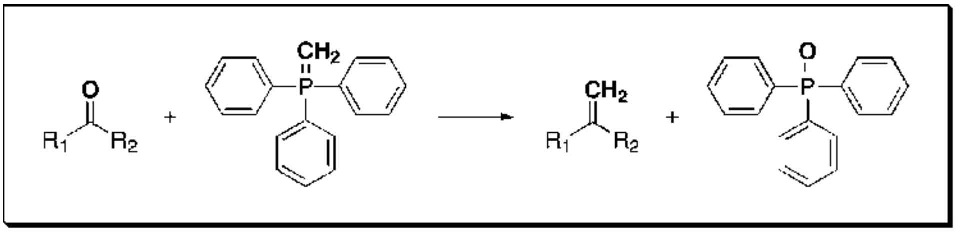
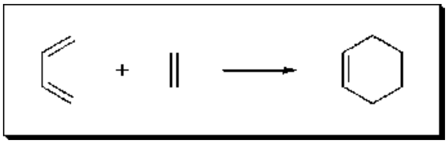
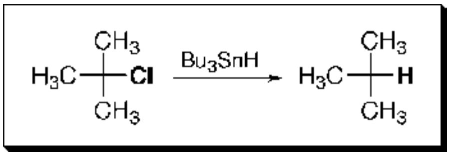
Arrow Pushing in Organic Chemistry: An Easy Approach to Understanding Reaction Mechanisms.
By Daniel E. Levy



Scheme 1.1 *Example of the Wittig reaction.*



Scheme 1.2 *Example of the Diels–Alder reaction.*



Scheme 1.3 *Example of a tin hydride dehalogenation.*

Diels–Alder reaction (Scheme 1.2) is used for the formation of six-membered ring systems, and treatment of alkyl halides with reagents such as tributyltin hydride (Scheme 1.3) results in removal of the associated halides. However, by presenting these reactions as illustrated in Schemes 1.1, 1.2, and 1.3, no explanation is provided as to how the starting materials end up as their respective products.

By definition, the outcome of any chemical reaction is the result of a process resulting in the breaking and formation of chemical bonds. Referring to material covered in most general chemistry courses, bonds between atoms are defined by sets of two electrons. Specifically, a single bond between two atoms is made of two electrons, a double bond between atoms is made of two sets of two electrons, and a triple bond between atoms is made of three sets of two electrons. These types of bonds can generally be represented by **Lewis structures** using pairs of dots to illustrate the presence of an electron pair. In organic chemistry, these dots are most commonly replaced with lines. Figure 1.1 illustrates several types of chemical bonds in both electron dot notation and line notation. The list of bond types shown in Figure 1.1 is not intended to be inclusive with respect to functional groups or potential combinations of atoms.

While chemical bonds are represented by lines connecting atoms, electron dot notation is commonly used to represent **lone pairs** (nonbonding pairs) of electrons. Lone pairs are found on **heteroatoms** (atoms other than carbon or hydrogen) that do not require bonds with additional atoms to fill their valence shell of eight electrons. For example, atomic

Single Bonds		Double Bonds		Triple Bonds	
Electron Dots	Lines	Electron Dots	Lines	Electron Dots	Lines
$H_3C:CH_3$	$H_3C{-}CH_3$	$O::O$	$O{-}O$	$N:::N$	$N\equiv N$
$H_3C:Cl$	$H_3C{-}Cl$	$H_2C::CH_2$	$H_2C{=}CH_2$	$HC:::CH$	$HC\equiv CH$
$H_3C:NH_2$	$H_3C{-}NH_2$	$H_2C::NH$	$H_2C{=}NH$	$HC:::N$	$HC\equiv N$
$H_3C:OH$	$H_3C{-}OH$	$H_2C::O$	$H_2C{=}O$		
$H_3C:SH$	$H_3C{-}SH$	$H_2C::S$	$H_2C{=}S$		

Figure 1.1 Examples of chemical bonds.

carbon possesses four valence electrons. In order for carbon to achieve a full complement of eight valence electrons, it must form four chemical bonds leaving no electrons as lone pairs. Atomic **nitrogen**, on the other hand, possesses five valence electrons. In order for nitrogen to achieve a full complement of eight valence electrons, it must form three chemical bonds leaving two electrons as a lone pair. Similarly, atomic **oxygen** possesses six valence electrons. In order for oxygen to achieve a full complement of eight valence electrons, it must form two chemical bonds leaving four electrons as two sets of lone pairs. In the examples of chemical bonds shown in Figure 1.1, lone pairs were not represented in order to focus on the bonds themselves. In Figure 1.2 the missing lone pairs are added where appropriate. Lone pairs are extremely important in understanding organic mechanisms because they frequently provide the sources of **electron density** necessary to drive reactions, as will be discussed later in this book.

As organic reactions proceed through the breaking and subsequent formation of chemical bonds, it is now important to understand the various ways in which atomic

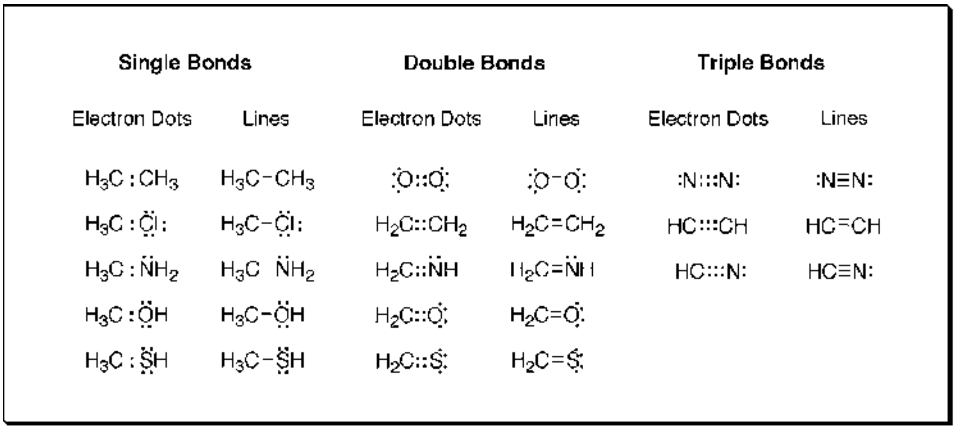
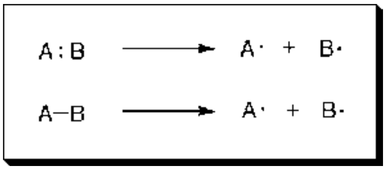
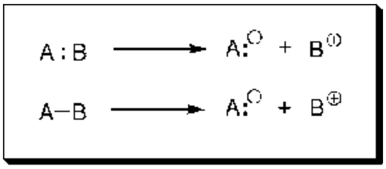


Figure 1.2 Examples of chemical bonds and lone pairs.



Scheme 1.4 *Illustration of homolytic cleavage.*

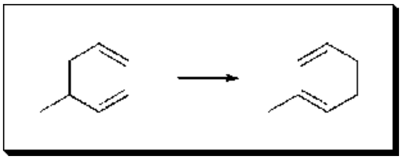


Scheme 1.5 *Illustration of heterolytic cleavage.*

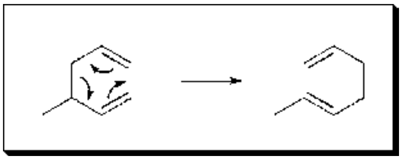
bonds can be broken. In general, there are three ways in which this process can be initiated. As shown in Scheme 1.4, the first is simple separation of a single bond where one electron from the bond resides on one atom and the other electron resides on the other atom. This type of bond cleavage is known as **homolytic cleavage** because the electron density is equally shared between the separate fragments and no charged species are generated. It is this process that leads to **free radical** mediated reactions.

Unlike homolytic cleavage, **heterolytic cleavage** (Scheme 1.5) of a chemical bond results in one species retaining both electrons from the bond and one species retaining no electrons from the bond. Generally, this also results in the formation of **ionic** species where the fragment retaining the electrons from the bond becomes **negatively charged** while the other fragment becomes **positively charged**. These charged species then become available to participate in ion-based transformations governed by the electronic nature of reactants or adjacent functional groups.

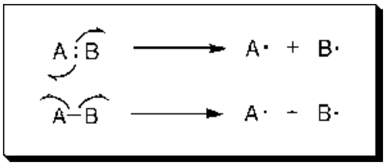
Having introduced homolytic cleavage and heterolytic cleavage as the first two ways in which bonds are broken at the initiation of organic reactions, attention must be drawn to the



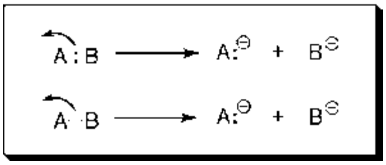
Scheme 1.6 *Illustration of a concerted reaction (Cope rearrangement).*



Scheme 1.7 *Illustration of arrow pushing applied to the Cope rearrangement.*



Scheme 1.8 *Application of arrow pushing to homolytic cleavage using single-barbed arrows.*



Scheme 1.9 *Application of arrow pushing to heterolytic cleavage using double-barbed arrows.*

possibility that bonds can rearrange into lower energy configurations through **concerted** mechanisms where bonds are simultaneously broken and formed. This third process, associated with **pericyclic reactions**, is illustrated in Scheme 1.6 using the **Cope rearrangement** and does not involve free radicals or **ions**. Instead, it relies on the overlap of atomic orbitals, thus allowing the transfer of electron density that drives the conversion from starting material to product. Regardless, whether reactions rely on free radicals, ions, or concerted mechanisms, all can be explained and/or predicted using the principles of arrow pushing.

Arrow pushing is a term used to define the process of using **arrows** to conceptually move **electrons** in order to describe the mechanistic steps involved in the transition of **starting materials** to **products**. An example of arrow pushing is illustrated in Scheme 1.7 as applied to the Cope rearrangement introduced in Scheme 1.6. As the Cope rearrangement proceeds through a concerted mechanism, the movement of electrons is shown in a single step. As will become apparent, arrow pushing is broadly useful to explain even very complex and multistep mechanisms. However, while arrow pushing is useful to explain and describe diverse mechanistic types, it is important to note that different types of arrows are used depending on the type of bond cleavage involved in a given reaction. Specifically, when homolytic cleavage is involved in the reaction mechanism, **single-barbed arrows** are used to signify movement of **single electrons**. Alternatively, when heterolytic cleavage or concerted steps are involved in the reaction mechanism, **double-barbed arrows** are used to signify movement of **electron pairs**. Schemes 1.8 and 1.9 illustrate the use of appropriate arrows applied to homolytic cleavage and heterolytic cleavage.

1.2 FUNCTIONAL GROUPS

Having presented the concept of arrow pushing in context of the steps that initiate chemical reactions, some factors impacting the flow of electrons leading from starting materials to products can now be explored.

As a rule, electrons will flow from atomic centers **high in electron density** to atomic centers **low in electron density**. This dependence on **polarity** is similar to the way that electricity flows in an electrical circuit. If there is no difference in **electrical potential** between the ends of a wire, electricity will not flow. However, if a **charge** is applied to one end of the wire, then the wire becomes **polarized** and electricity flows. If we imagine a simple **hydrocarbon** such as ethane, we can analogously relate this system to a **nonpolarized wire**. Both carbon atoms possess the same density of electrons and thus ethane has no polarity. However, if functionality is added to ethane through introduction of groups bearing heteroatoms, the polarity changes and electron flow can be used to induce chemical reactions. These heteroatom-bearing groups are known as **functional groups** and serve to donate or withdraw electron density.

While functional groups can be either **electron donating** or **electron withdrawing**, these properties rely upon the specific heteroatoms the functional group is composed of as well as the configuration of these heteroatoms relative to one another. With respect to

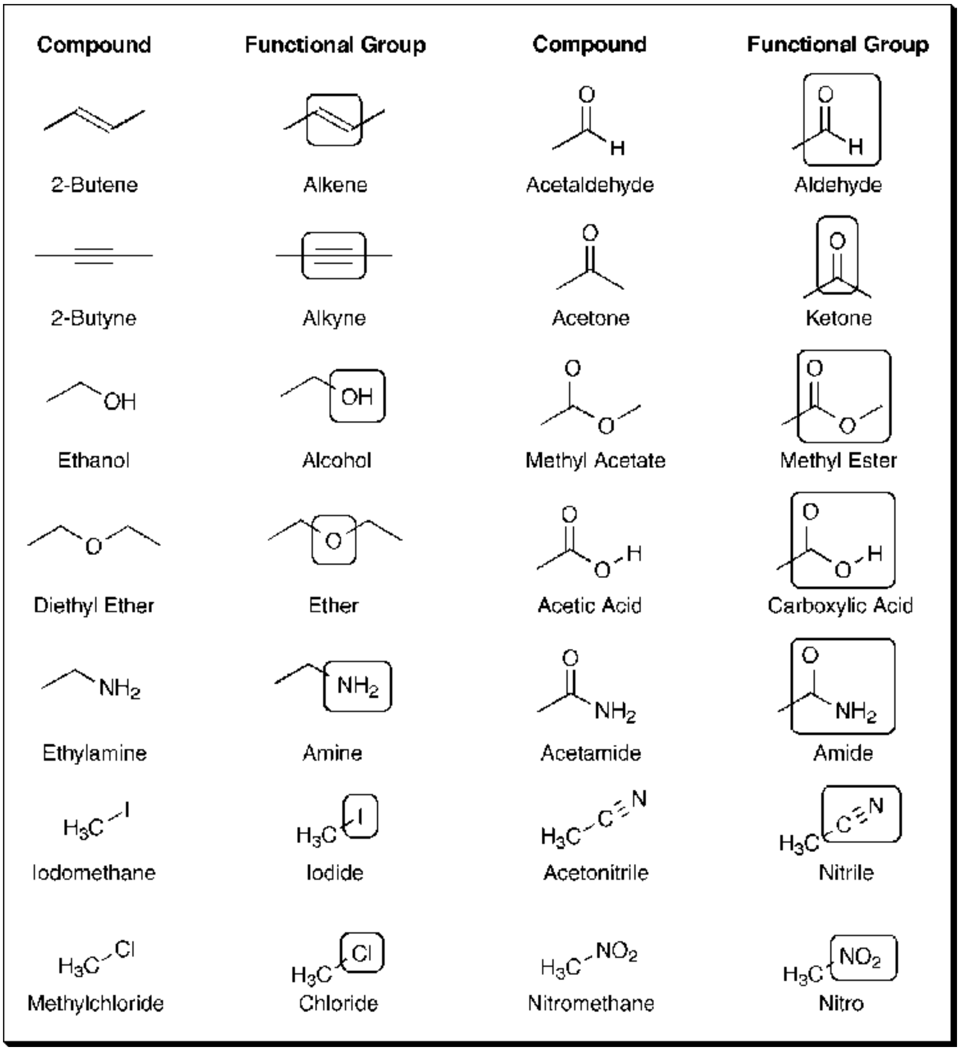


Figure 1.3 *Common organic functional groups.*

the specific heteroatoms, **electronegativity** of the heteroatoms is the driving force influencing polarity. Thus, the more electronegative the atom, the greater the affinity of electrons for this atom. As a calibration for electronegativity, the **periodic table of the elements** serves as an excellent resource. Specifically, moving from left to right and from bottom to top, electronegativity increases. For example, nitrogen is more electronegative than carbon, and oxygen is more electronegative than nitrogen. Likewise, fluorine is more electronegative than chlorine, and chlorine is more electronegative than bromine. It is important to note that the influence of electronegativity on polarity is so strong that simply replacing a carbon atom with a heteroatom is enough to impart strong changes in polarity compared to the parent structure. Figure 1.3 illustrates common organic functional groups as components of common organic molecules.

Polarity in organic molecules is generally represented as **partial positive** (δ^{+}) **charges** and **partial negative** (δ^{-}) **charges**. These **partial charges** are induced based upon the presence of heteroatoms either by themselves or in groups. These heteroatoms, as described in the previous paragraph and in Figure 1.3, define the various functional groups. Returning to the example of ethane as a nonpolar parent, Figure 1.4 illustrates how polarity changes are influenced by the introduction of heteroatoms and functional groups. As shown, heteroatoms such as nitrogen, oxygen, and halogens, due to their increased electronegativities compared to carbon, adopt partial negative charges. This causes **adjacent carbon atoms** to take on partial positive characteristics.

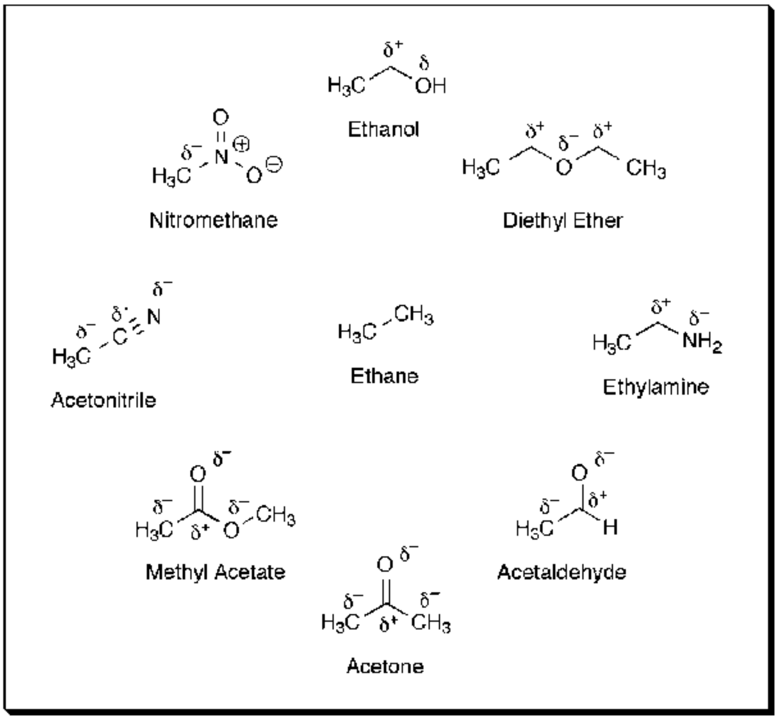


Figure 1.4 *How functional groups influence polarity.*

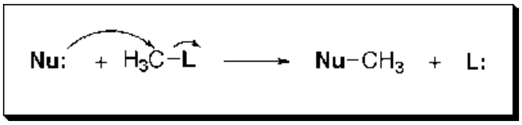
As illustrated in Figure 1.4, charges on carbon atoms are not limited to positive. In fact, when a carbon atom is adjacent to a positive or partial positive center, it can adopt partial negative characteristics. As will be discussed in later chapters, this ability to control the charge characteristics of carbon atoms leads to the ability to create reactive centers with a diverse array of properties. By taking advantage of this phenomenon of **induced polarity**, we are able to employ a multitude of chemical transformations allowing for the creation of exotic and useful substances relevant to fields ranging from material science to food science to agriculture to pharmaceuticals.

1.3 NUCLEOPHILES AND LEAVING GROUPS

As discussed in the previous section, polarity is key to the ability to initiate most **chemical reactions**. However, this is not the only factor influencing the ability to initiate reactions. In fact, the type of reaction on a given molecule is often dependent upon the nature of the **solvent** and the **reagents** used. For example, solvent polarity can influence the **reaction rate** and the **reaction mechanism**. Furthermore, the nature of the chemical **reagents** used can affect the **reaction mechanism** and the identity of the final product. The following definitions will be key to understanding the terminology used in the following chapters.

Nucleophiles are reagents that have an affinity for **positively charged species** or **electrophiles**. In organic reactions, **nucleophiles** form **chemical bonds** at sites of partial positive charge through donation of their electrons. This generally results in the need for the starting compound to release a leaving group. An example of a nucleophilic reaction is shown in Scheme 1.10 where Nu: represents the nucleophile and L: represents the leaving group. Arrow pushing is used to illustrate the movement of the electron pairs.

Leaving groups are the components of chemical reactions that detach from the starting material. Referring to Scheme 1.10, the leaving group, L:, ends up separate from the product while the nucleophile, Nu:, becomes incorporated into the product. Furthermore, while an initial evaluation of the material covered in an introductory organic chemistry course may seem overwhelming, the majority of the material covered can be reduced to the principles illustrated in the single reaction shown in Scheme 1.10.



Scheme 1.10 Example of a nucleophilic reaction.

1.4 SUMMARY

In this chapter, the basic principle of arrow pushing was introduced in the context of organic reactions driven by homolytic cleavage, heterolytic cleavage, or concerted mechanisms. Furthermore, the concept of polarity was introduced using heteroatoms and common organic functional groups. This discussion led to the definitions of nucleophiles and leaving groups in the context of simple nucleophilic reactions. Finally, by pulling these ideas together, the concept of approaching the study of mechanistic organic chemistry from a simplified perspective of understanding the principles of arrow pushing was introduced.

While characteristics such as homolytic cleavage, heterolytic cleavage, and concerted mechanisms were discussed, the principles of arrow pushing apply equally to all. However, with respect to heterolytic cleavage, an understanding of the properties of organic acids and bases is essential in order to understand underlying organic mechanisms. Therefore, moving forward, this book primarily focuses on arrow pushing as applied to heterolytic reaction mechanisms.

PROBLEMS

1. Use arrow pushing to explain the following reactions:

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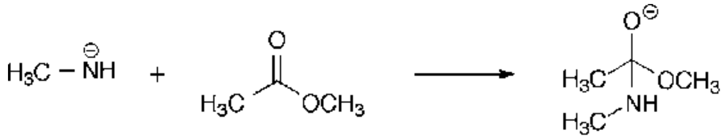
b.



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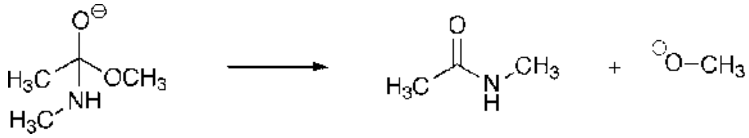

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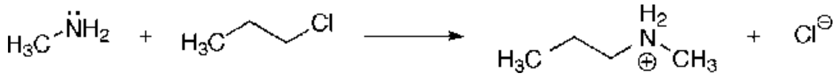

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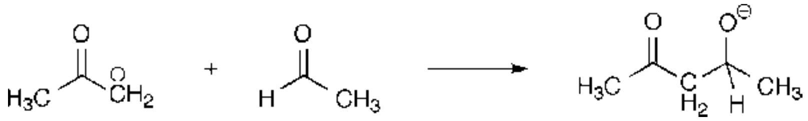

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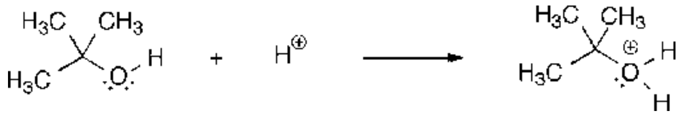

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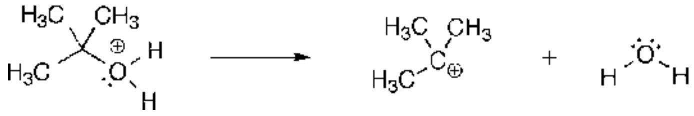
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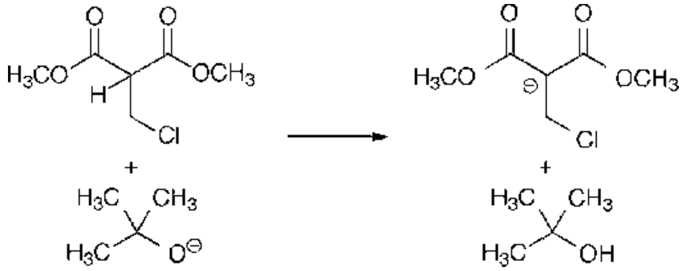
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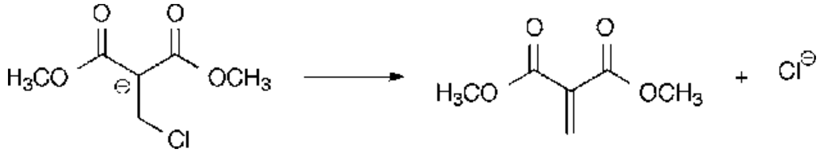
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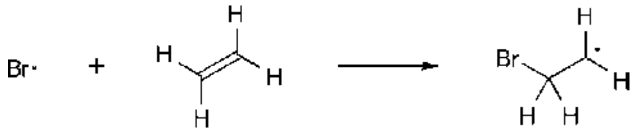

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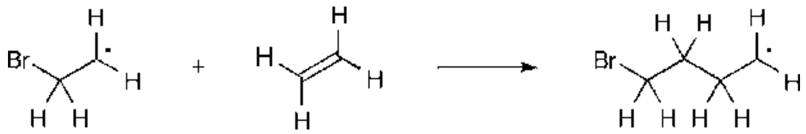

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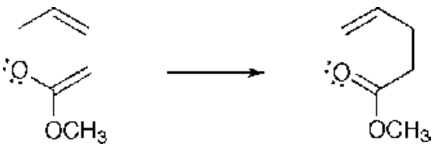

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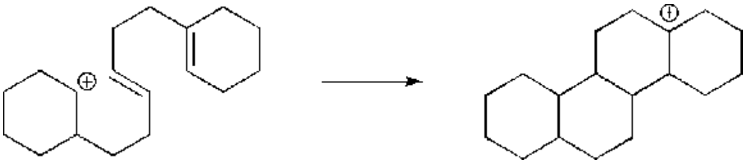

2. Place the partial charges on the following molecules.

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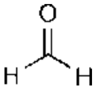

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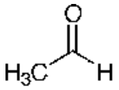

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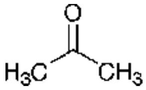

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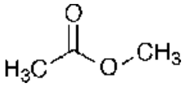

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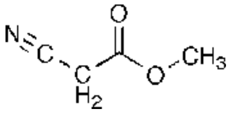

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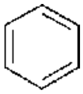

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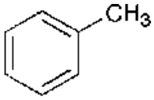

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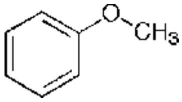

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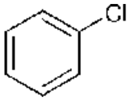

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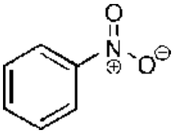

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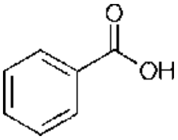

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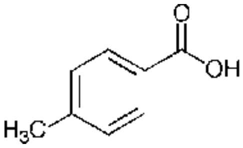

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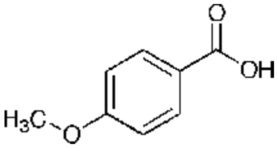

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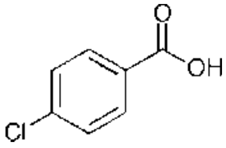

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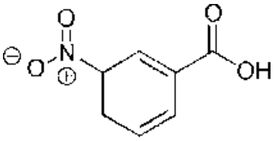

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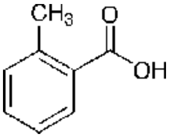

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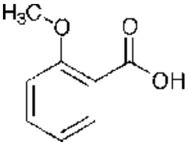

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