

# Overview of Types of Organic Reactions and Basic Concepts of Organic Reaction Mechanisms

A chemical reaction is the transformation of one chemical or collection of chemicals into another chemical or collection of chemicals.

A chemical reaction involves making new chemical bonds and breaking old chemical bonds.

Reactions of organic compounds can be organized broadly in two ways by:

- I. What types of reactions and
- II. How these reactions occur.

# Overview of Types of Organic Reactions

The types of reactions organic compounds undergo is divided into four categories, these are:

I. Additions reactions

II. Substitutions reactions

III. Elimination reactions

IV. Rearrangement reactions

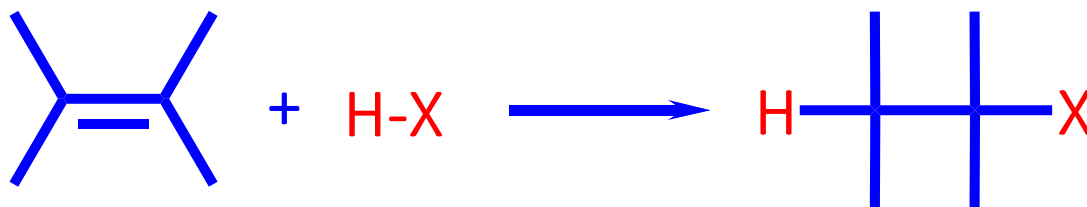
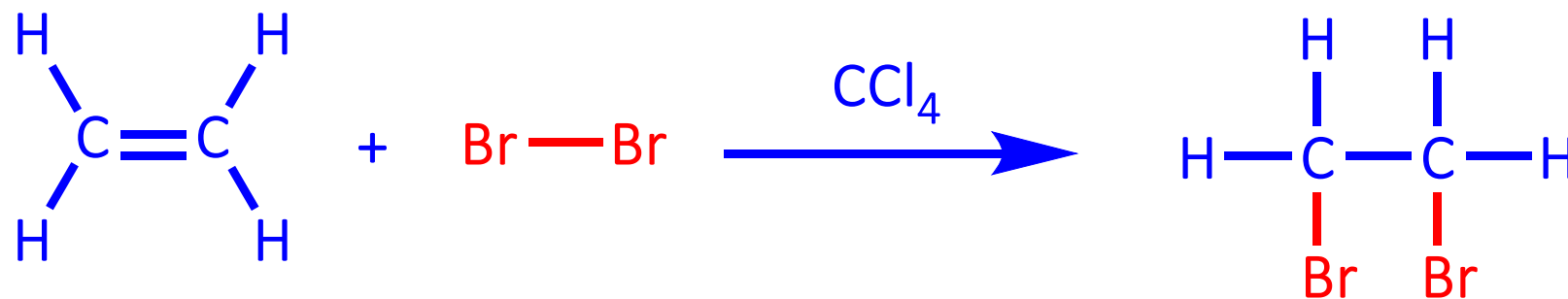
# I. Addition Reactions

Addition reactions occur when two starting materials add together to form only one product with no atoms left over.

$$A + B \longrightarrow A-B$$

In an addition all parts of the adding reagent appear in the product; two molecules become one.

Examples



X = I, Br, Cl

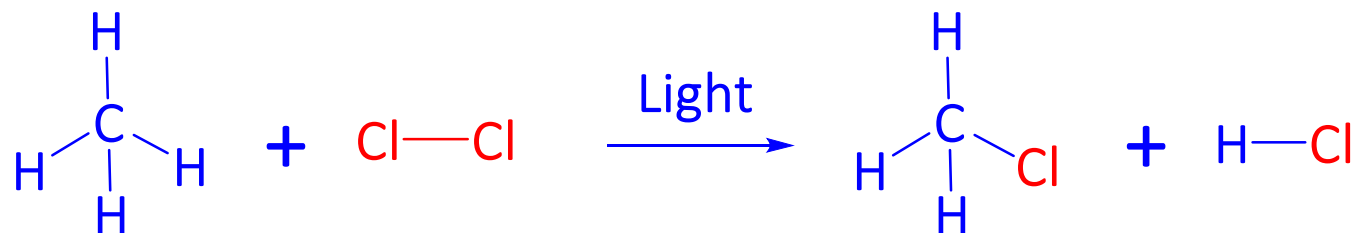
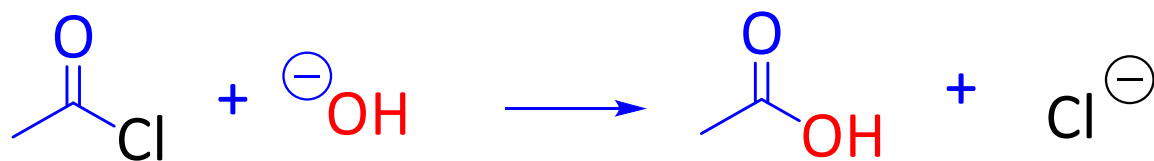
# II. Substitution Reactions

Substitution reactions occur when two starting materials exchange groups to form two new products.



In a substitution, one group replaces another.

## Examples

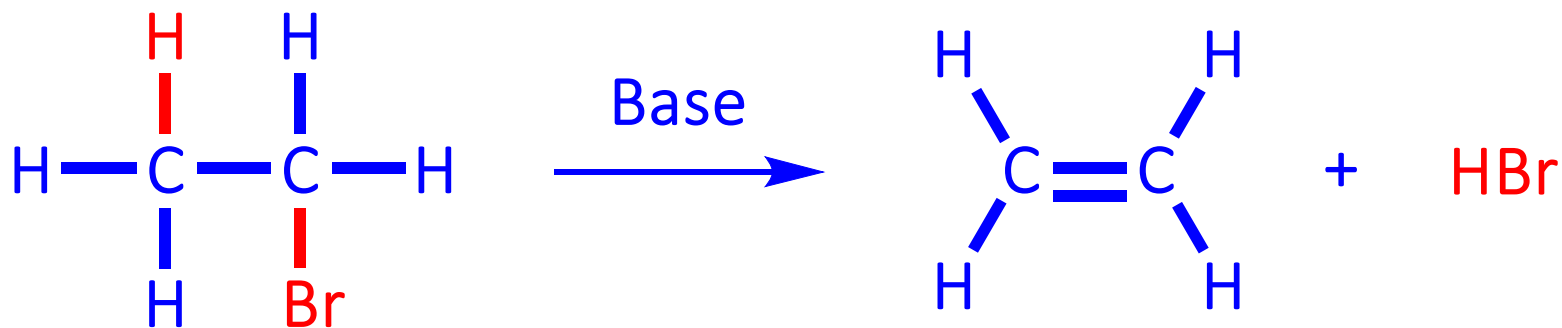


# III. Elimination Reactions

Elimination reactions are the opposite of addition reactions.



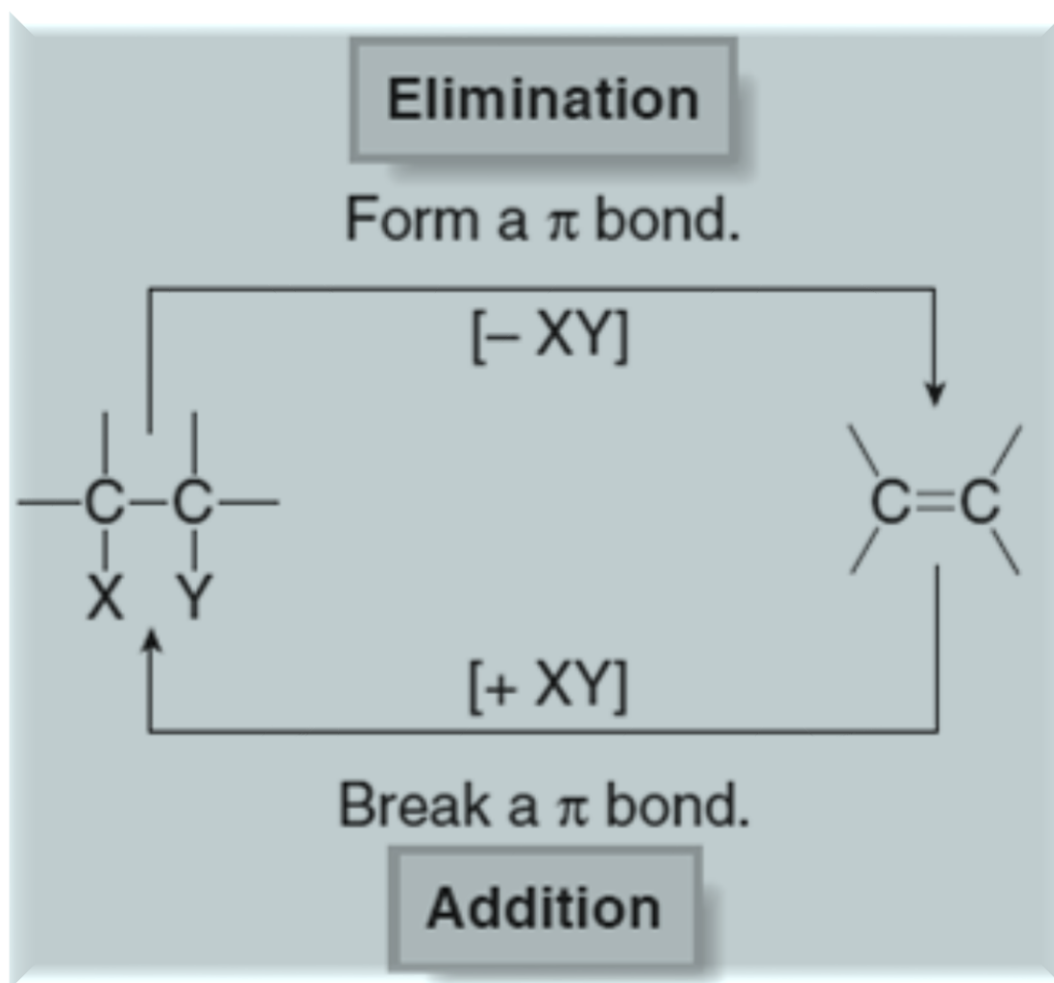
A single reactant is split into two two products.



Elimination reactions give us a method for preparing compounds with double and triple bonds.

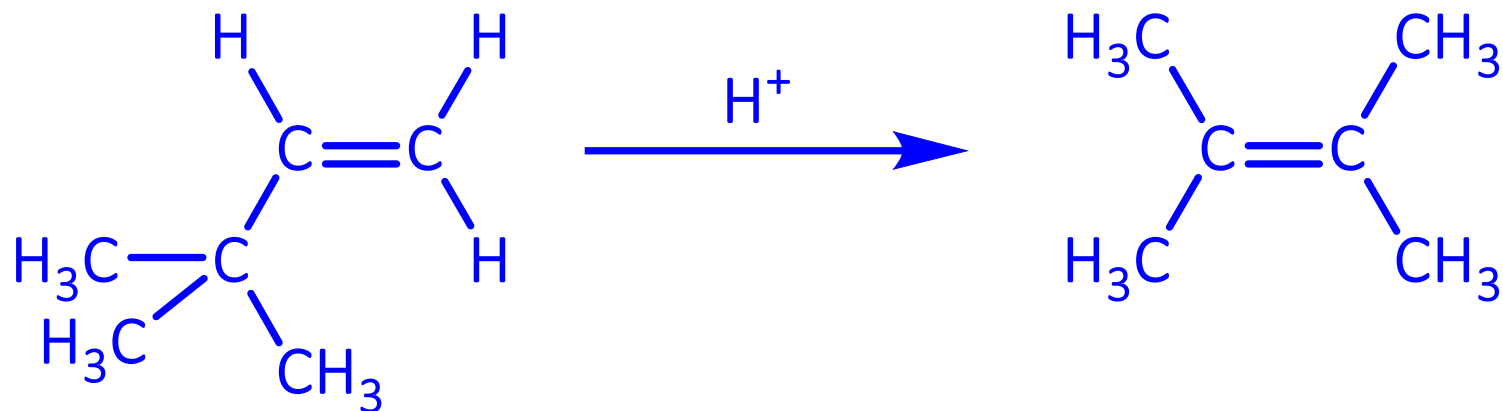
Two  $\sigma$  bonds are broken, and a  $\pi$  bond is formed between adjacent atoms.

Addition and elimination reactions are exactly opposite. A  $\pi$  bond is formed in elimination reactions, whereas a  $\pi$  bond is broken in addition reactions.



## IV. Rearrangement Reactions

Rearrangement reactions occur when one starting material forms one product with a different arrangement of atoms and bonds.



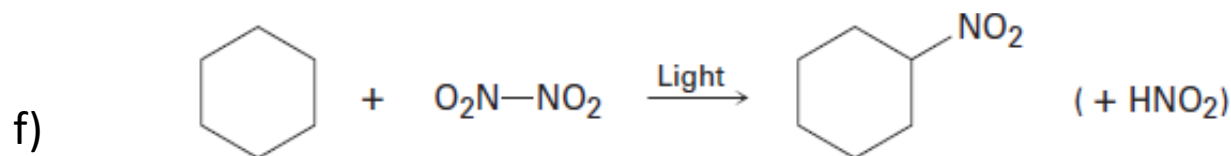
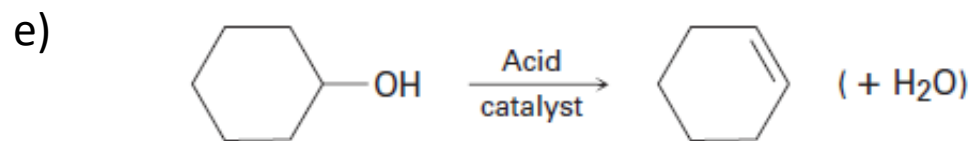
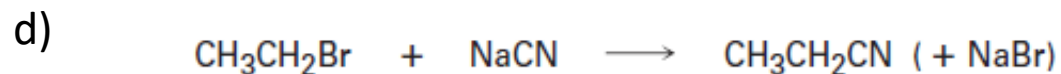
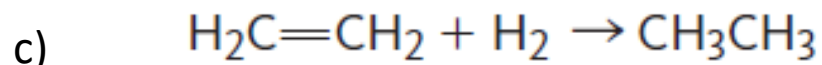
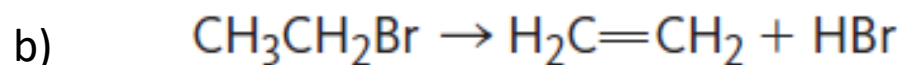
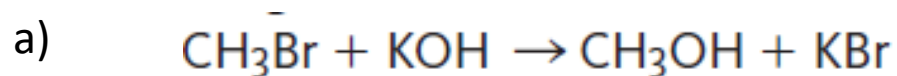
The product is an isomer of the starting material.

We have so far seen the different types of organic reactions, let's now see how reactions occur.



# Assignment 22

Classify each of the following reactions as addition, elimination, substitution or rearrangement



# Basic Concepts of Organic Reactions Mechanisms

An overall description of how a reaction occurs is called a reaction mechanism.

A mechanism describes in detail exactly what takes place at each stage of a chemical transformation—which bonds are broken and in what order, which bonds are formed and in what order.

It is detailed explanation of the electron movement in the course of chemical reactions.

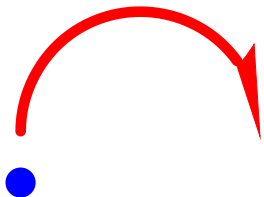
A reaction mechanism must account for all reactants used and all products formed.

A reaction mechanism is a reasonable, stepwise illustration of how the electrons in the bonds of the reactants of a reaction are reorganized into its products under a given set of reaction conditions.

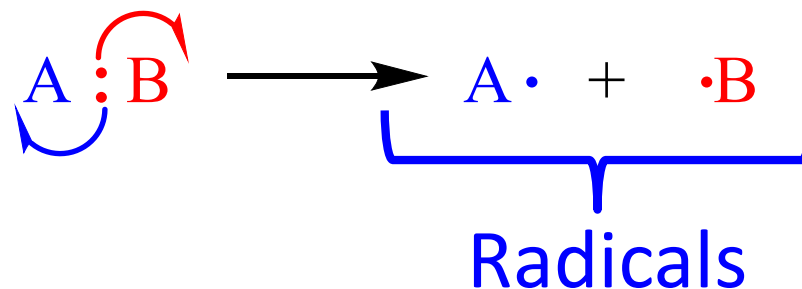
During a course of a chemical reaction chemical bonds in the reactants are broken and bonds in the products are formed, bonds can be broken **symmetrically** (one electron remains with each product fragment) or **unsymmetrically** (bonding electrons remain with one product fragment).

The symmetrical cleavage is **homolytic cleavage**, and the unsymmetrical cleavage is **heterolytic**.

# Homolytic bond cleavage

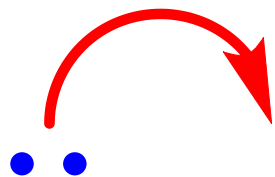


Fish hook arrow

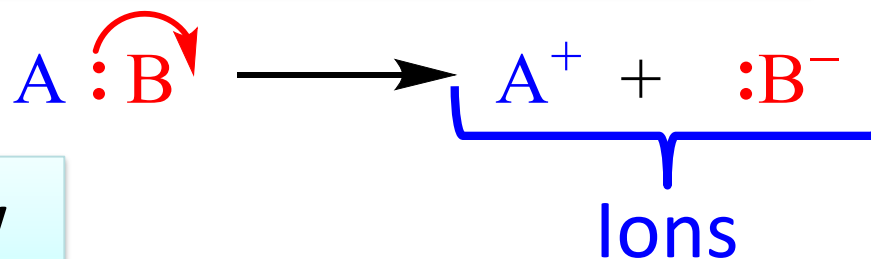


Symmetrical bond-breaking: bonding electrons shared between the two atoms.

# Heterolytic bond cleavage



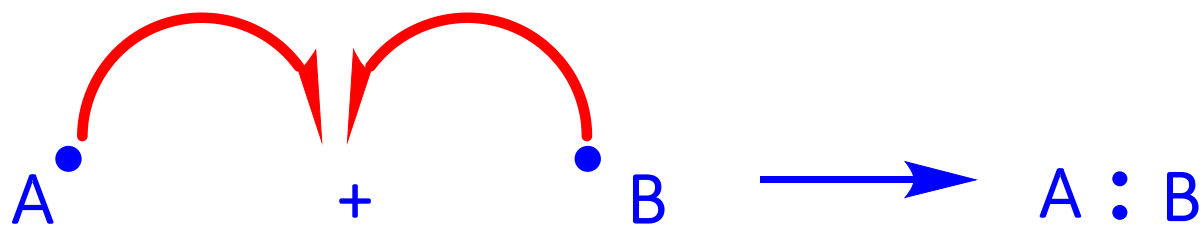
Double sided arrow



Unsymmetrical bond-breaking: One of the elements taking both bonding electrons.

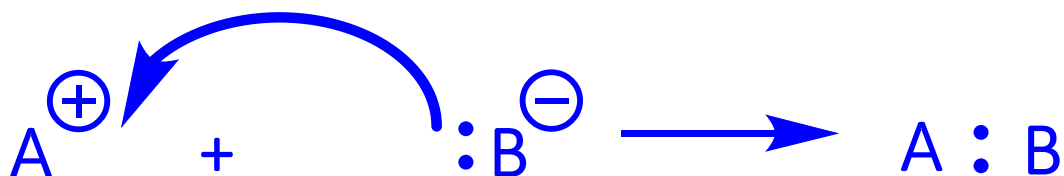
Just as there are two ways in which a bond can break, there are two ways in which a covalent two-electron bond can form.

### Symmetrical bond-making (Homogenic)



One bonding electron is donated by each reactant.

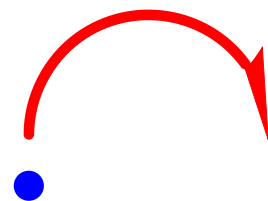
### Unsymmetrical bond-making (Heterogenic)



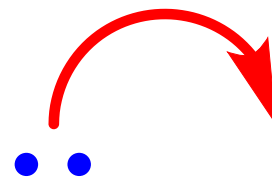
Two bonding electrons are donated by one reactant.

Curved/Curly/Pushing arrows indicate breaking and forming of bonds.

- Arrowheads with a “half” head (“fish-hook”) indicate homolytic and homogenic steps (called ‘radical processes’)—the motion of one electron



- Arrowheads with a complete head indicate heterolytic and heterogenic steps (called ‘polar processes’)—the motion of an electron pair.



Reactions that involve symmetrical bond-breaking and bond-making are called radical reactions. A radical, often called a “*free radical*,” is a neutral reactive chemical species that contains an odd number of electrons and thus has a single, unpaired electron in one of its orbitals.

Reactions that involve unsymmetrical bond-breaking and bond-making are called polar reactions. Polar reactions occur between negatively charged (anions) and positively charged (cations) ions.

Polar reactions are by far the most common reaction type in organic compounds.

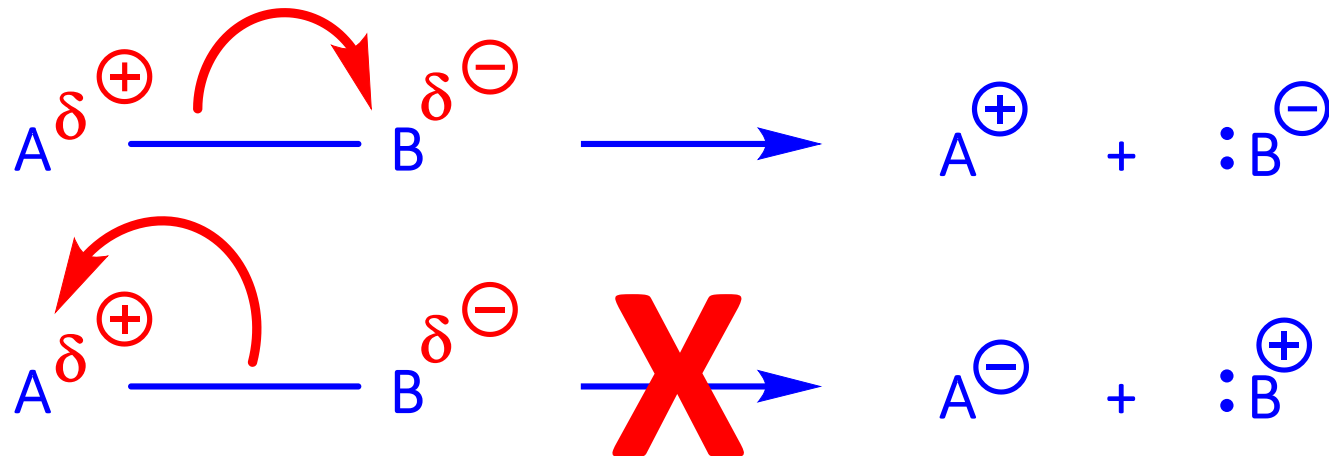
Radical species are mostly generated in nonpolar bonds, while ions are generated during reactions of polar molecules.

Heterolysis is more likely if the two atoms in the bond have different electronegativities (polar covalent molecules).

A polar covalent bond between two elements with differing electronegativities is polarized in the direction  $\delta^+A-B\delta^-$ , where B is the more electronegative element.

In a heterolysis, the bond will almost always break in the direction which will leave both bonding electrons on the more electronegative atom, B.





The less electronegative element, A, will have positive charge while the more electronegative element, B, will have negative charge.

Polar reactions proceed by the movement of pairs of electrons from areas of high electron density (nucleophiles) to areas of low electron density (electrophiles), or from filled orbitals to empty orbitals.

# Free Radical Reactions

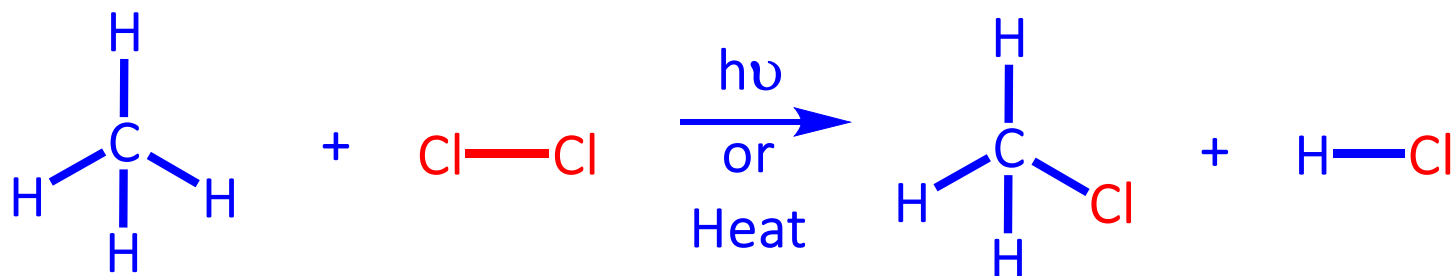
The term free radical refers to any atom or group of atoms with an odd number of electrons. As a result the electrons in a free radical cannot all be paired.

Even though a free radical does not have a +ve or -ve charge, such a species is highly reactive.

A classical example a reaction that involve a free radical is halogenation of alkanes in the presence of ultraviolet (UV,  $h\nu$ ) light.

As an example of a free radical reaction let's look at the mechanism of monochlorination of methane.

# Mechanism of chlorination of methane



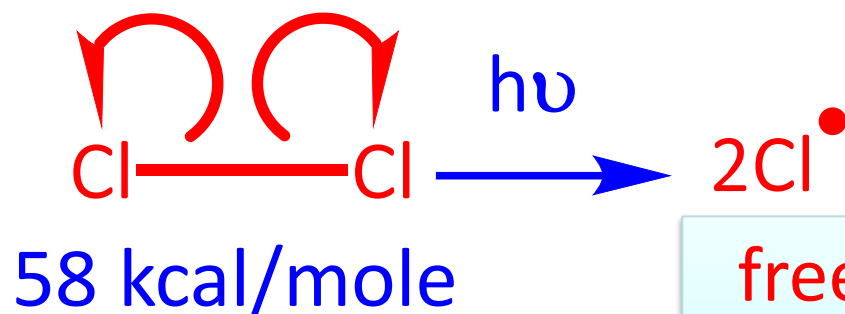
For the reaction to occur a C-H and Cl-Cl bond must be broken and a C-Cl and H-Cl bond must be formed.

The Cl-Cl bond (bond energy = 58 kcal/mole) is weaker than C-H bond (bond energy = 104 kcal/mole) and it is the weaker Cl-Cl bond that will break first to initiate the reaction.

The above reaction involves three steps, **initiation**, **propagation**, and **termination**.

## Step I: Initiation

The initiation step in the chlorination of methane is the homolytic cleavage of  $\text{Cl}_2$  into two chlorine free radicals.

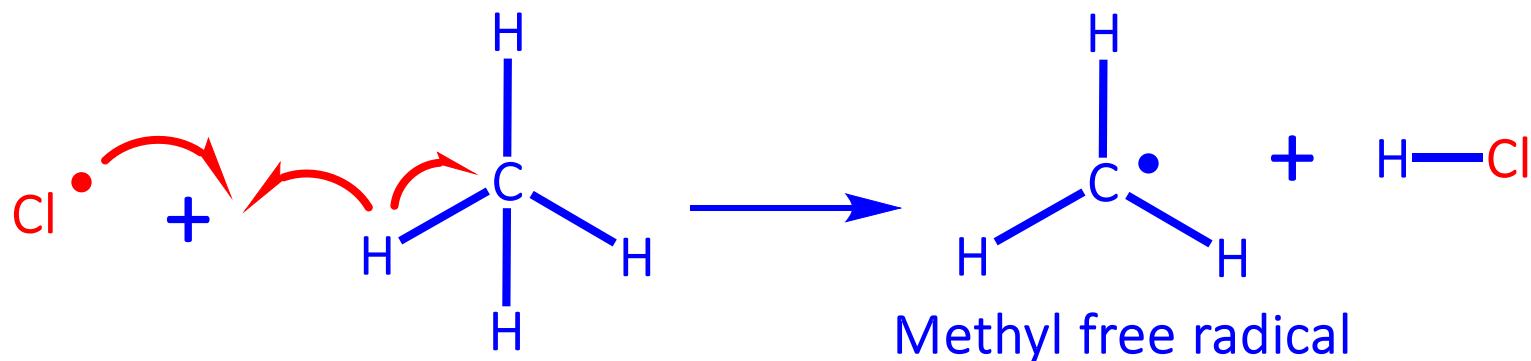


free radical (highly reactive, unstable, initiates a reaction)

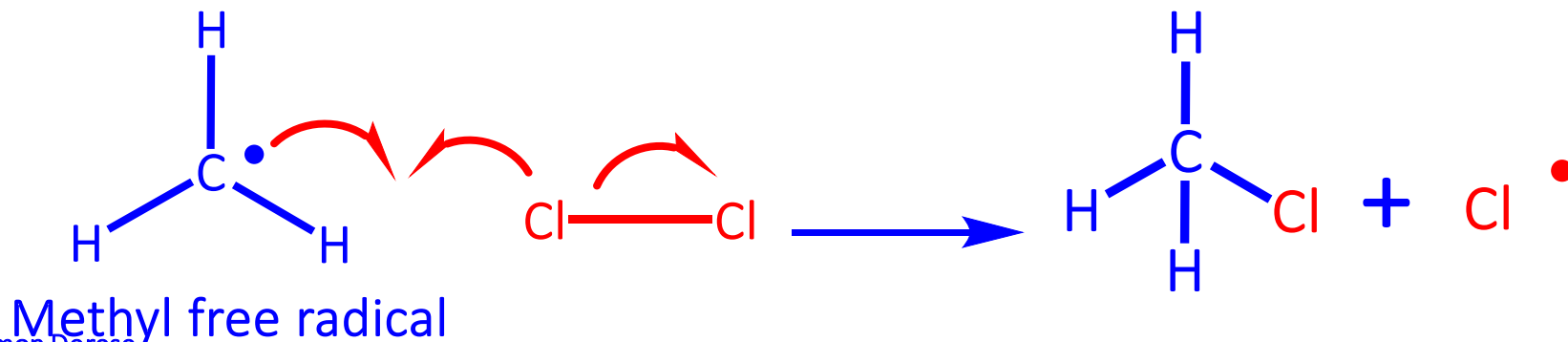
The energy required for the heterolytic cleavage of  $\text{Cl}_2$ , 58 kcal/mole, is provided by UV light or heat. Halogenation of alkanes does not take place in the dark.

## Step II: Propagation

The unstable chlorine free radical forces, the strong C-H to break homolytically in the propagation step (formation of new free radicals).



The reactive chlorine free radical abstract a hydrogen from methane to yield a methyl free radical and HCl.



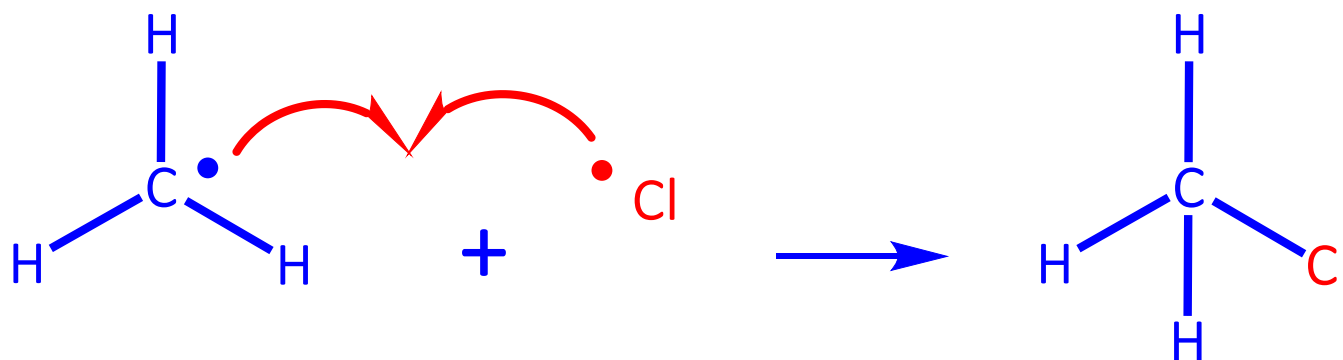
The methyl free radical is also reactive. In the second propagation, it abstracts a chlorine from  $\text{Cl}_2$  to form another chlorine free radical, **one radical generates another.**

This step yields one of the products of the overall reaction, chloromethane. This step also generates a new chlorine free radical that can abstract a hydrogen from atom from another methane molecule and starts the propagation step all over again.

Thus, once the sequence has been initiated, it becomes a self-sustaining cycle of repeating steps (I) and (II), making the overall process a **chain reaction.**

## Step III: Termination

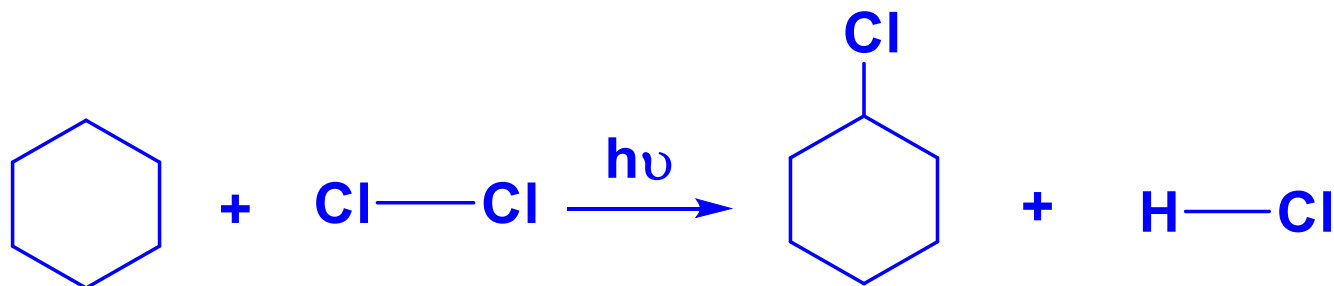
The propagation cycle is broken by termination reaction. Occasionally, two radicals might collide and combine to form a stable product. When that happens, the reaction cycle is broken and the chain is ended, terminated. Removing radicals from the reaction mixture without generating any new radicals stops the reaction.



Coupling of free radicals to form a stable product.

## Assignment 23

- a) Write equations and mechanism for the initiation, propagation and termination reactions leading to the formation of chlorocyclohexane from cyclohexane and chlorine.



- b) When methane is chlorinated, among the products found are traces of chloroethane. How is it formed?



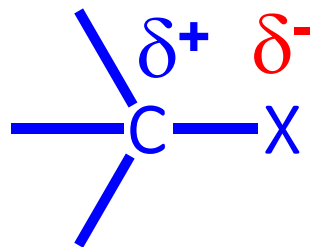
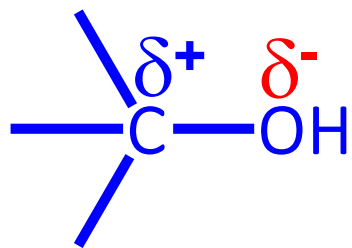
# Polar Reactions

Polar reactions occur between oppositely charged species, cations and anions, or between an electron deficient and an electron rich species.

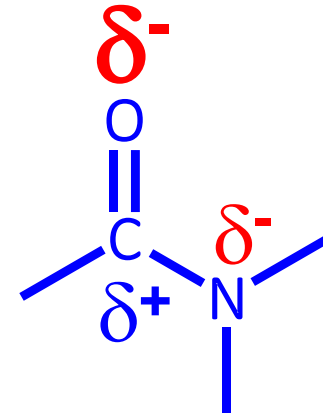
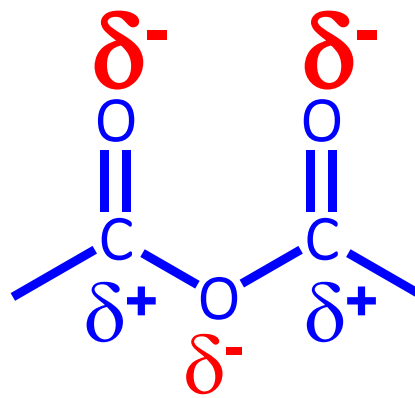
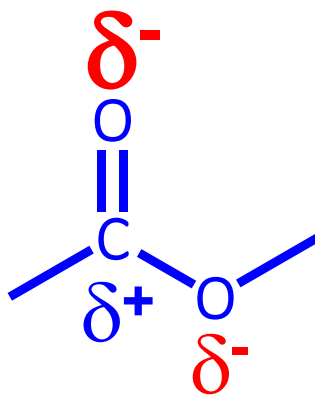
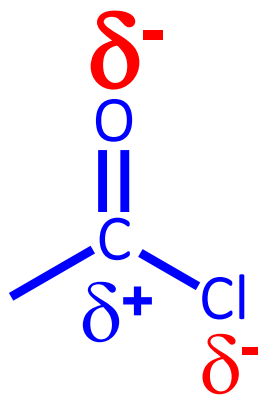
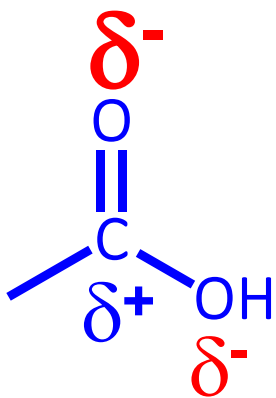
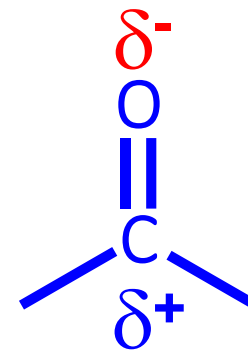
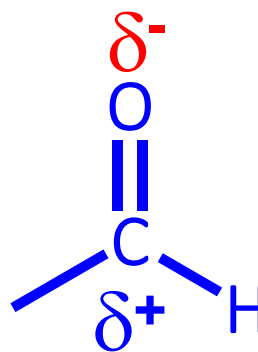
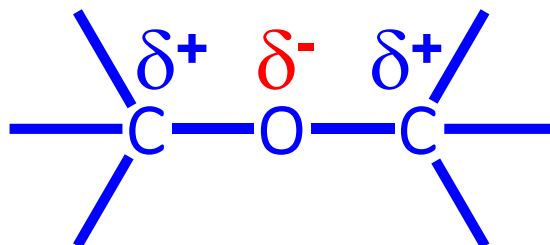
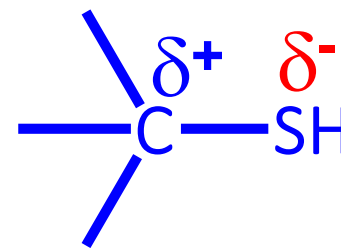
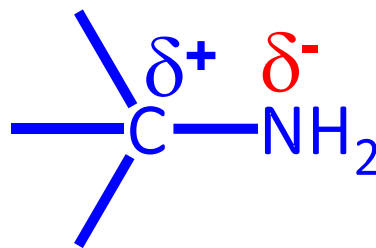
The driving force of the reaction is the Coulombic electrical force of attraction between positively polarized and negatively polarized centers on functional groups in molecules. It is based on the principle “unlike charges attract and like charges repel”.

Bond polarity is a consequence of an unsymmetrical electron distribution in a bond and is due to the difference in electronegativity of the bonded atoms.

# Polarity Patterns in Some Common Functional Groups



X = Halogen



What does functional-group polarity mean with respect to chemical reactivity? Because unlike charges attract, the fundamental characteristic of all polar organic reactions is that electron-rich sites,  $\delta^-$ , react with electron-poor sites,  $\delta^+$ .

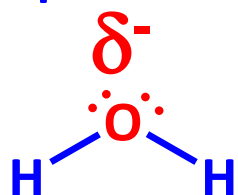
Bonds are made when an electron-rich atom donates a pair of electrons to an electron poor atom, and bonds are broken when one atom leaves with both electrons from the former bond.

In referring to the electron-rich and electron-poor species involved in polar reactions, chemists use the words **nucleophile** and **electrophile**, respectively.

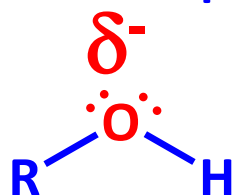
# Nucleophile (nucleus loving)

A nucleophile is a substance that has a negatively polarized, electron-rich, atom and can form a bond by donating a pair of electrons to a positively polarized, electron poor atom. Nucleophiles can be either neutral or negatively charged.

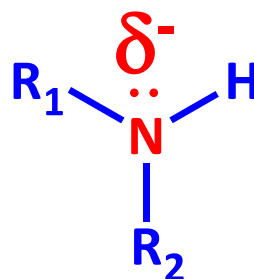
Examples of nucleophiles



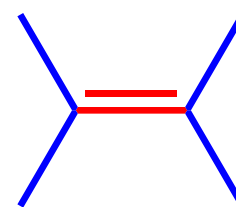
Water



Alcohol

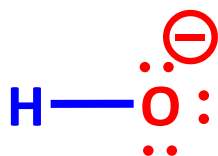


Amines

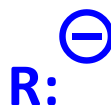


Alkene

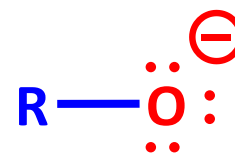
The  $\pi$ -bond  
acts a  
nucleophile



Hydroxide



Carbanion

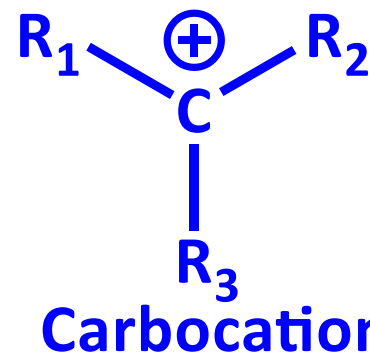
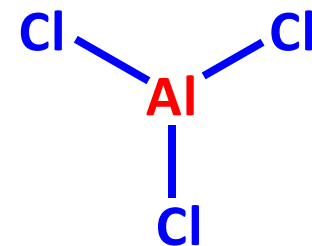
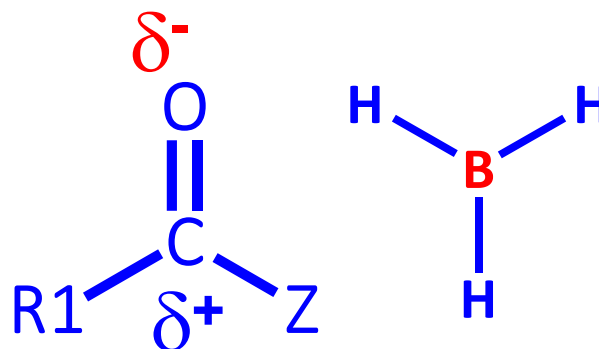
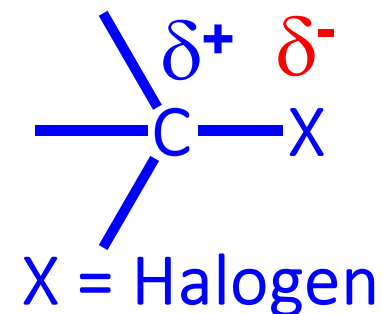


Alkoxide

# Electrophile (electron loving)

An electrophile has a positively polarized, electron poor, atom and can form a bond by accepting a pair of electrons from a nucleophile. Electrophiles can be either neutral or positively charged.

Examples of electrophiles



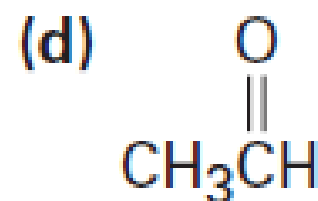
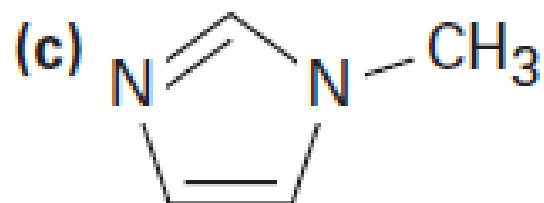
Note that neutral compounds can often react either as nucleophiles or as electrophiles, depending on the circumstances. After all, if a compound is neutral yet has an electron-rich nucleophilic site, it must also have a corresponding electron-poor electrophilic site.

# Assignment 24

a) Which of the following species is likely to behave as a nucleophile and which as an electrophile?

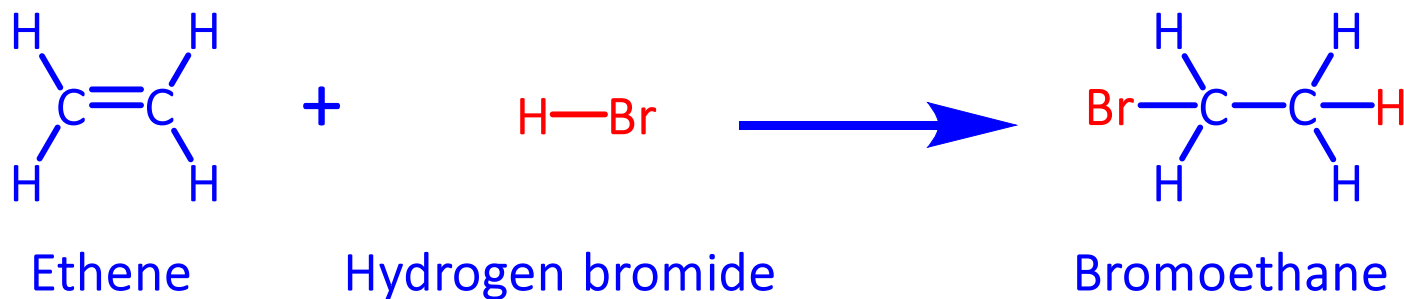


b) Which of the following species are likely to be nucleophiles and which electrophiles? Which might be both?



# Using Curved Arrows in Polar Reaction Mechanisms

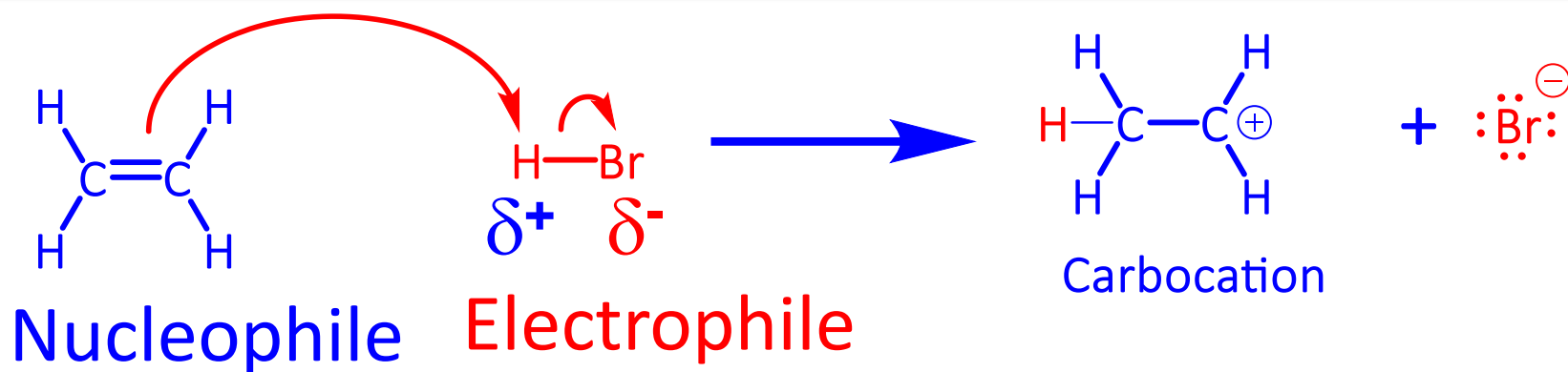
One example polar reaction is the synthesis of bromoethane by electrophilic addition of hydrogen bromide to ethene.



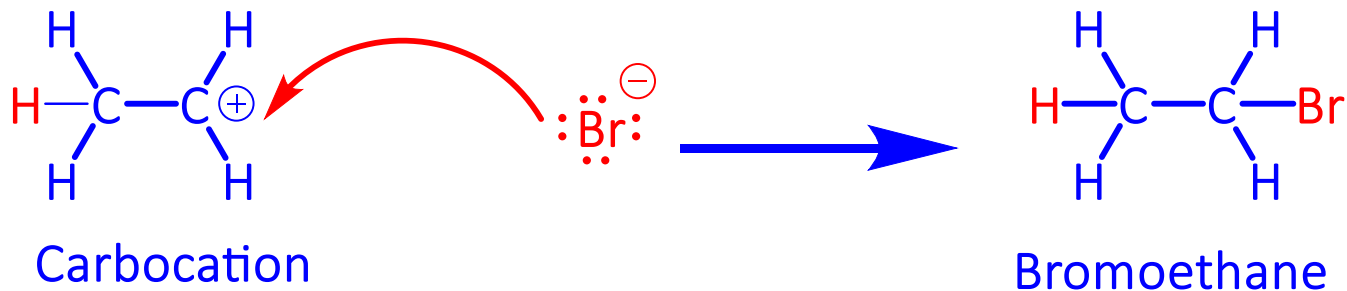
Let us work out the mechanism of this reaction using curved arrows.



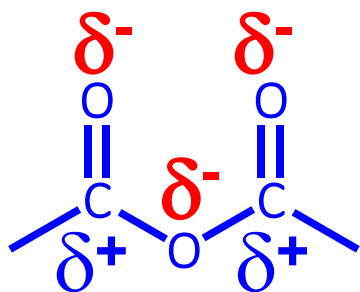
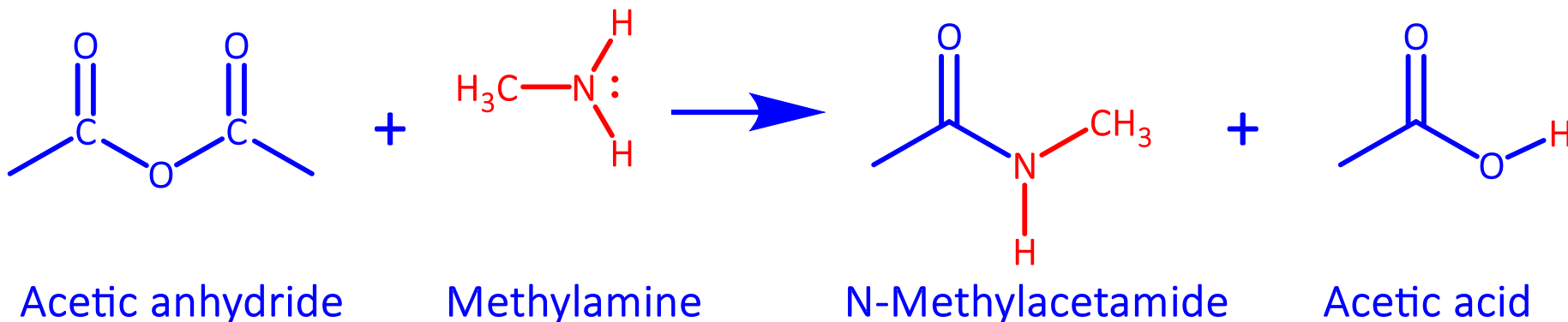
# Mechanism of electrophilic addition reaction to alkenes



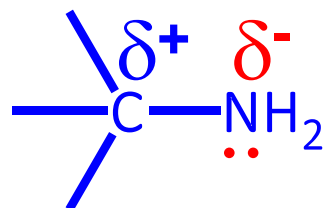
The C = C the double bond is nucleophilic and the chemistry of alkenes is dominated by reactions with electrophiles.



Let us look at another example of polar reaction, a reaction between acetic anhydride and methyl amine to yield N-methylacetamide and acetic acid.

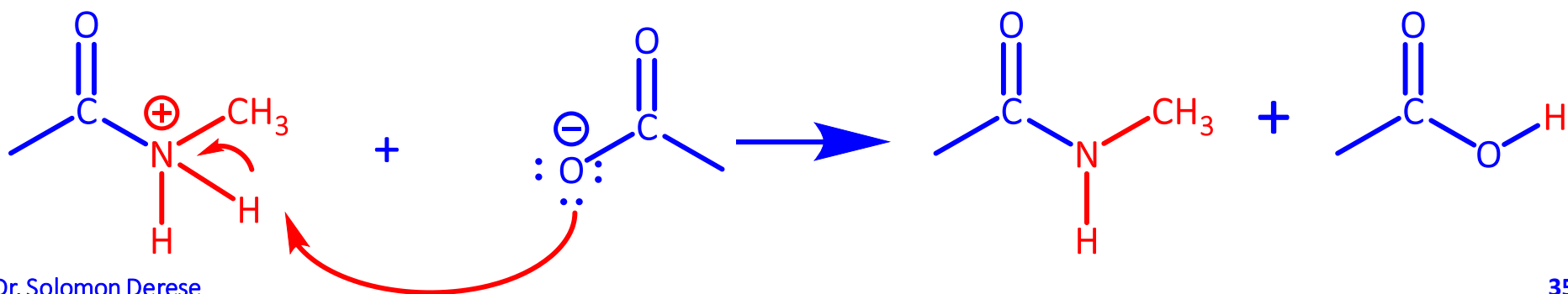
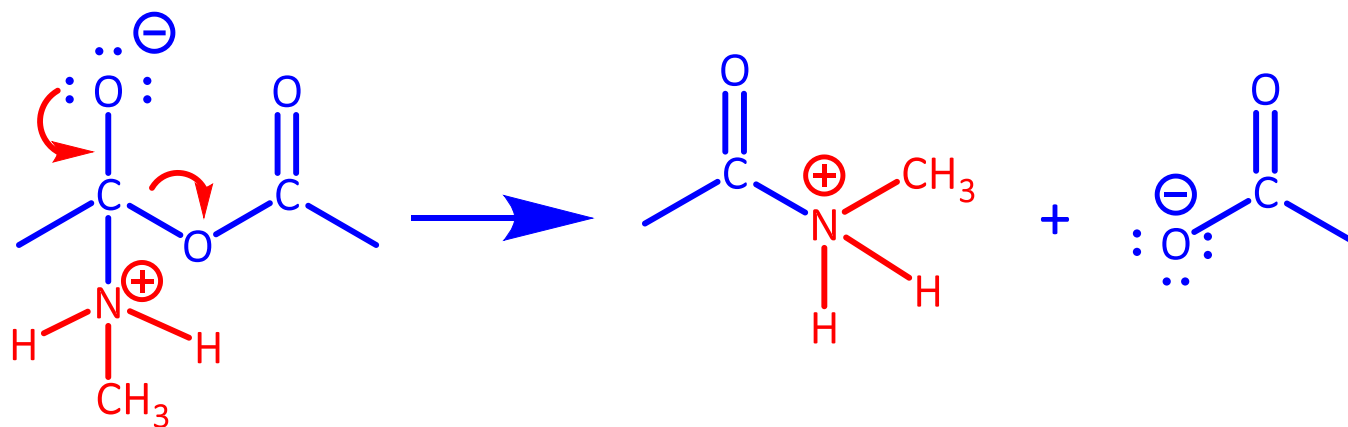
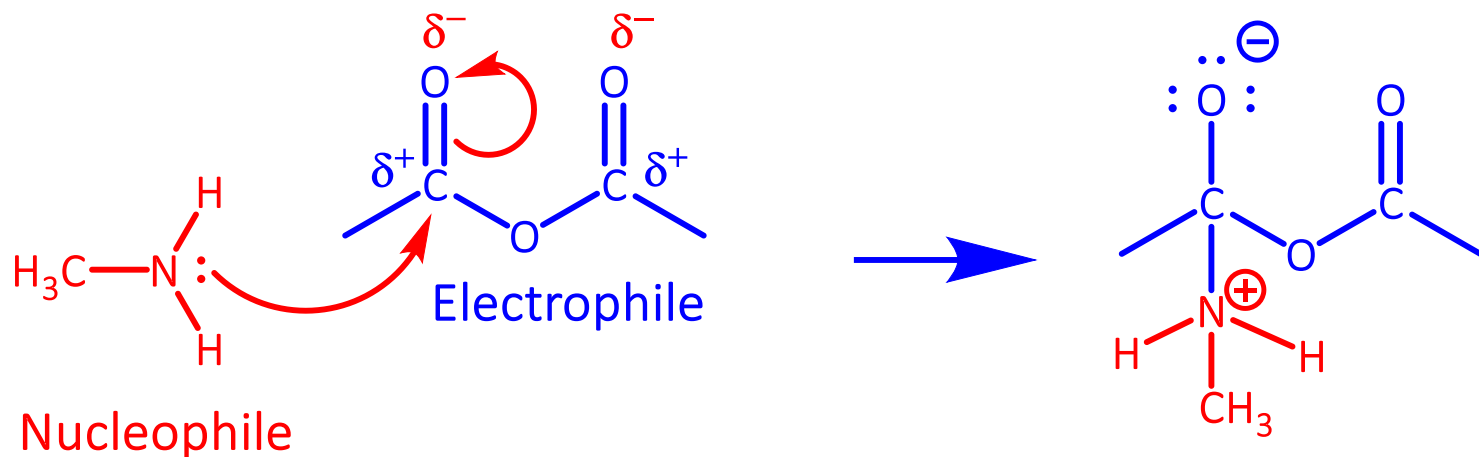


The carbonyl carbon is very electrophilic



Amines are strong nucleophiles

# Mechanism

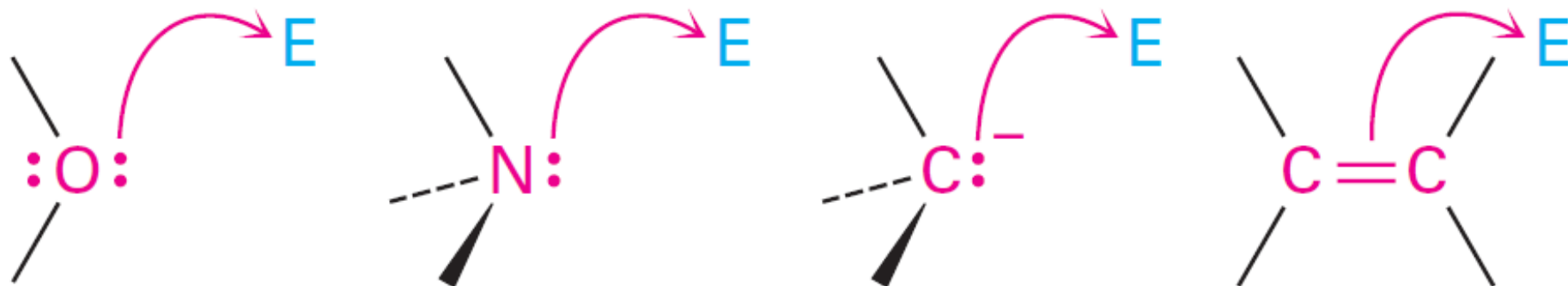


# Rules for Using Curved Arrows in Polar Reaction Mechanisms

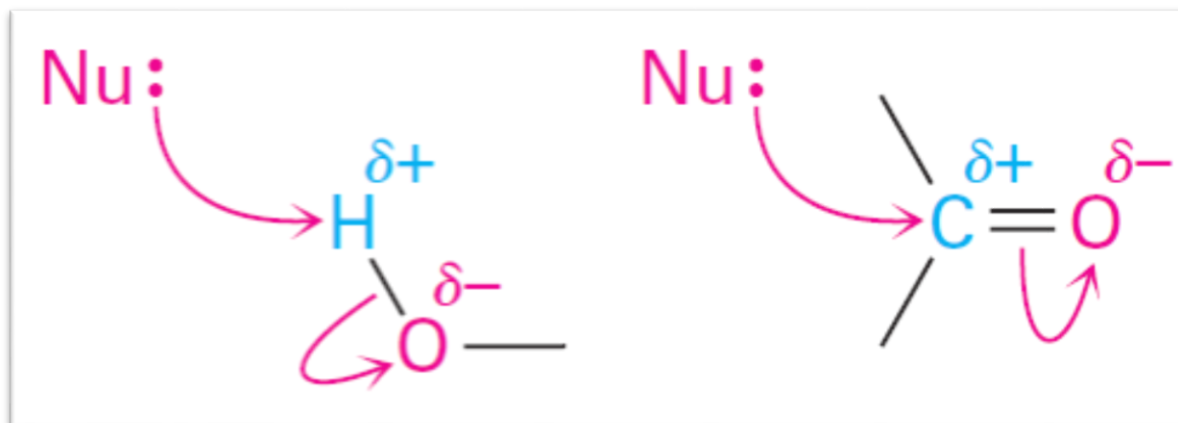
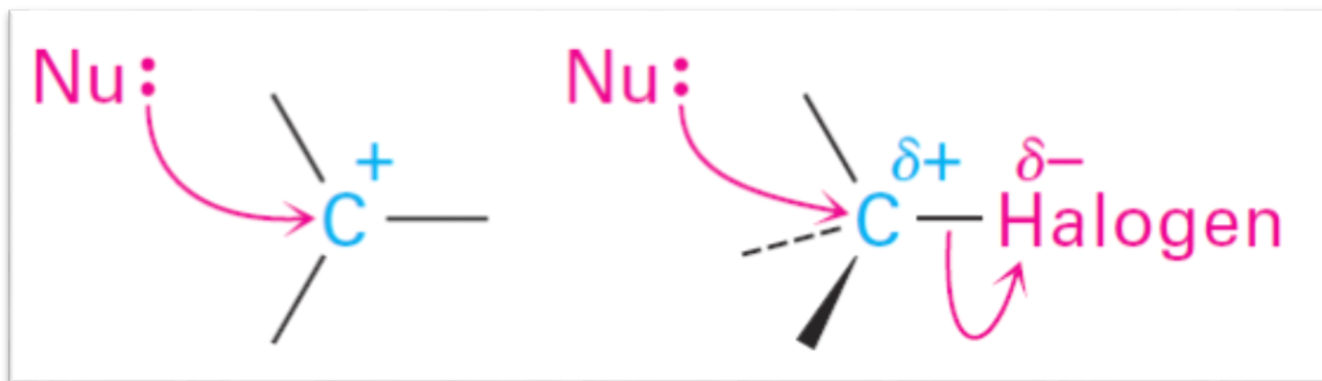
## Rule 1

Electrons move *from* a nucleophilic source (Nu: or Nu:<sup>-</sup>) *to* an electrophilic sink (E or E<sup>+</sup>). The nucleophilic source must have an electron pair available, usually either as a lone pair or in a multiple bond.

Electrons usually flow from one of these nucleophiles.

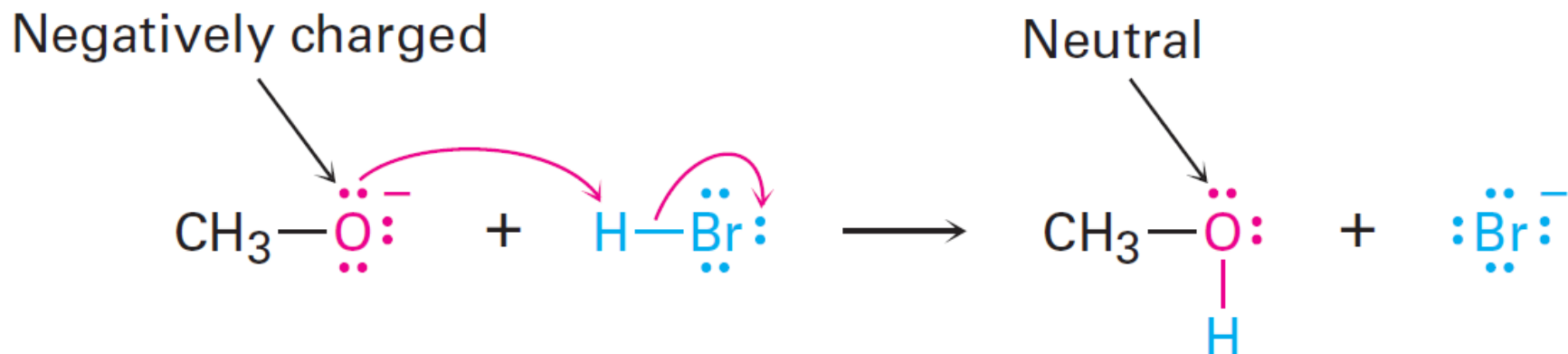


The electrophilic sink must be able to accept an electron pair, usually because it has either a positively charged (+) atom or a positively polarized ( $\delta^+$ ) atom in a functional group.

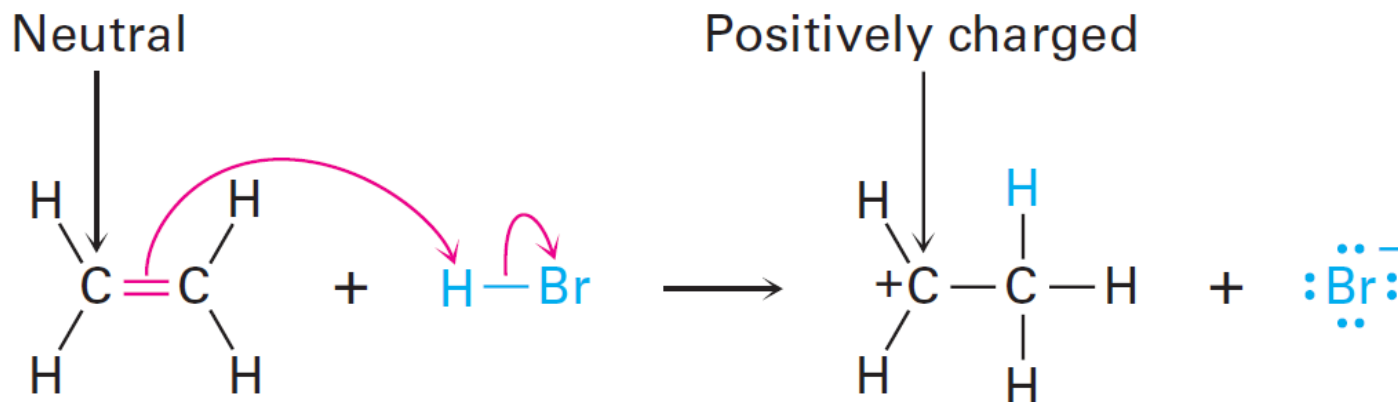


## Rule 2

The nucleophile can be either negatively charged or neutral. If the nucleophile is negatively charged, the atom that donates an electron pair becomes neutral.

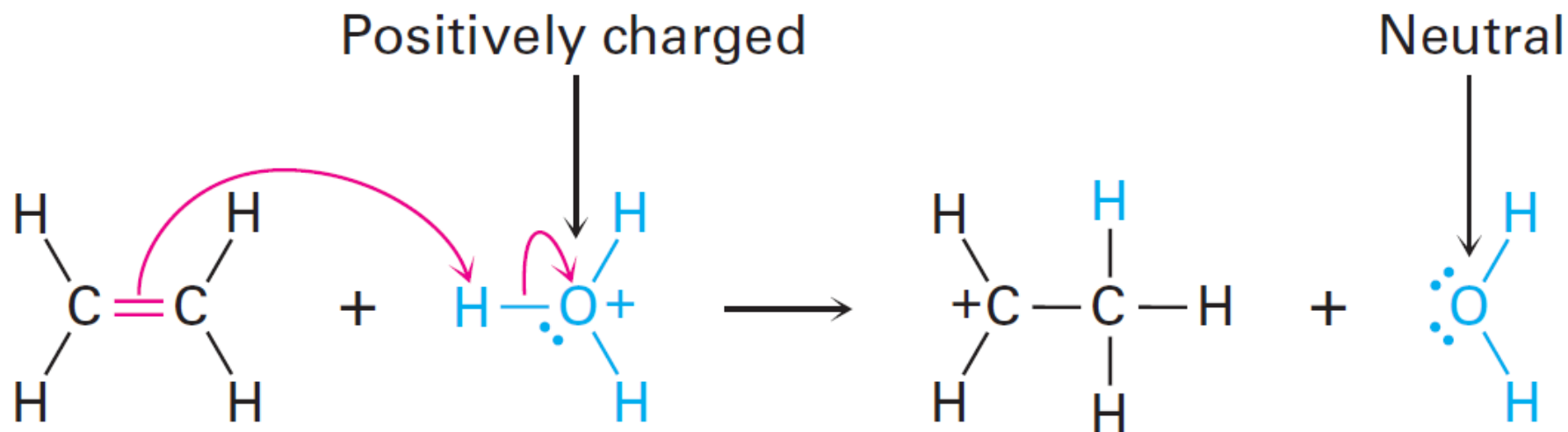


If the nucleophile is neutral, the atom that donates the electron pair acquires a positive charge.

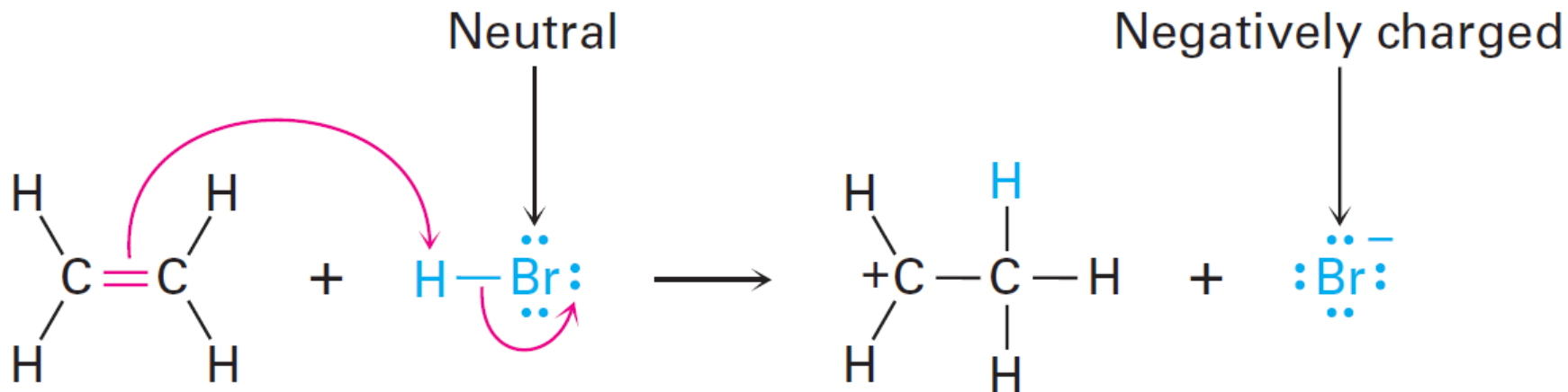


## Rule 3

The electrophile can be either positively charged or neutral. If the electrophile is positively charged, the atom bearing that charge becomes neutral after accepting an electron pair.



If the electrophile is neutral, the atom that ultimately accepts the electron pair acquires a negative charge.



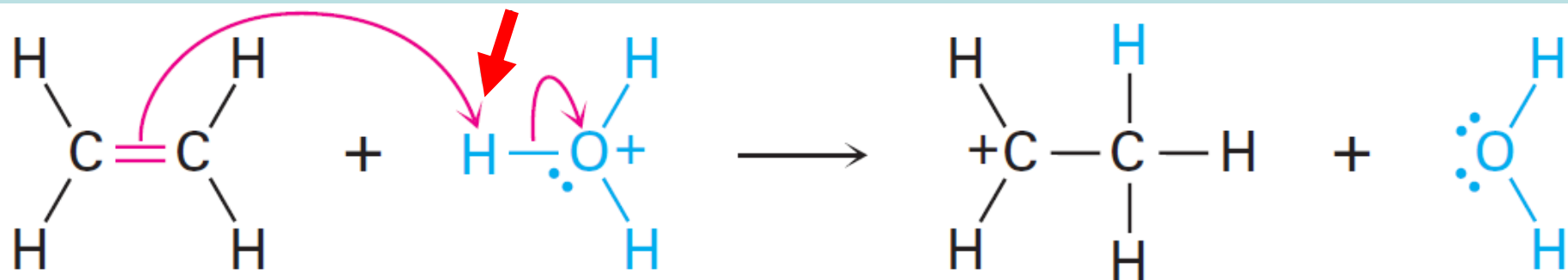
For this to happen, however, the negative charge must be stabilized by being on an electronegative atom such as oxygen, nitrogen, or a halogen. Carbon and hydrogen do not typically stabilize a negative charge.



## Rule 4

The octet rule must be followed. That is, no second-row atom can be left with ten electrons (or four for hydrogen). If an electron pair moves to an atom that already has an octet (or two for hydrogen), another electron pair must simultaneously move from that atom to maintain the octet.

This hydrogen already has two electrons. When another electron pair moves to the hydrogen from the double bond, the electron pair in the H–O bond must leave



## Assignment 25

Identify the nucleophile and electrophile in each of the following reaction. Give a step by step mechanism for the reactions using curved arrows.

