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Organic Chemistry

Organic Reactions

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Expected Outcomes

In the end of this chapter, student will have the ability to:

- Write equations for organic reactions
- Identify and classify substitution, elimination, and addition reactions
- Write organic reaction mechanisms

Contents

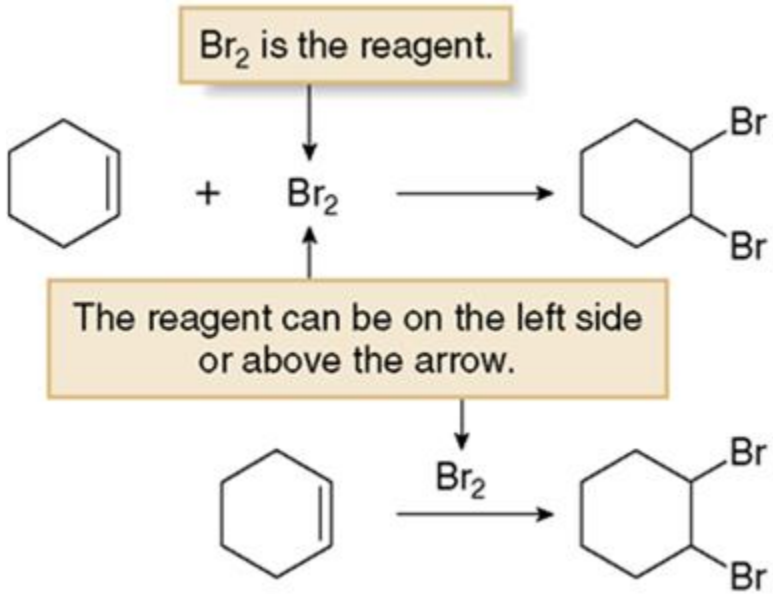
- Organic reaction equation
- Kinds of organic reaction

Understanding Organic Reactions

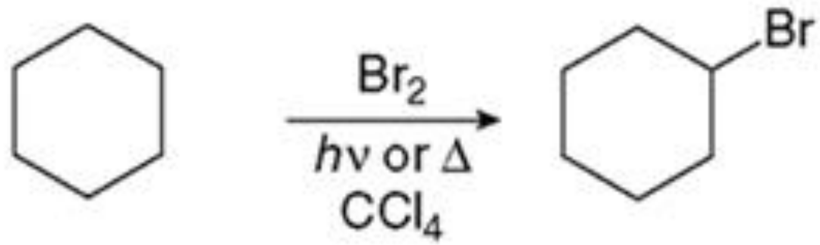
Writing Equations for Organic Reactions

- Equations for organic reactions are usually drawn with a single reaction arrow ($\rightarrow$) between the starting material and product.
- The reagent, the chemical substance with which an organic compound reacts, is sometimes drawn on the left side of the equation with the other reactants. At other times, the reagent is drawn above the arrow itself.
- Although the solvent is often omitted from the equation, most organic reactions take place in liquid solvent.
- The solvent and temperature of the reaction may be added above or below the arrow.
- The symbols "$h\nu$" and "Δ" are used for reactions that require light and heat respectively.

A Single step Chemical Equation



Example of a Single Step Chemical Eqn.

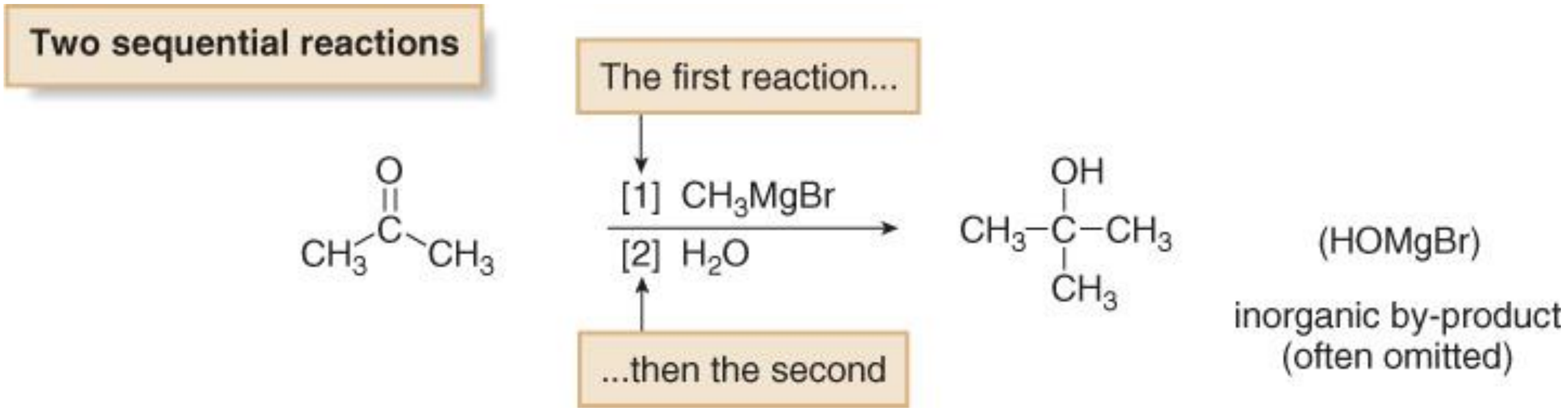


CCl_4 is the solvent.

$h\nu$—Indicates light is needed.
Δ—Indicates heat is added.

Example of Multiple Step Chemical Eqn.

- When two sequential reactions are carried out without drawing any intermediate compound, the steps are usually numbered above or below the reaction arrow. This convention signifies that the first step occurs before the second step, and the reagents are added in sequence, not at the same time.



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Types of Reactions

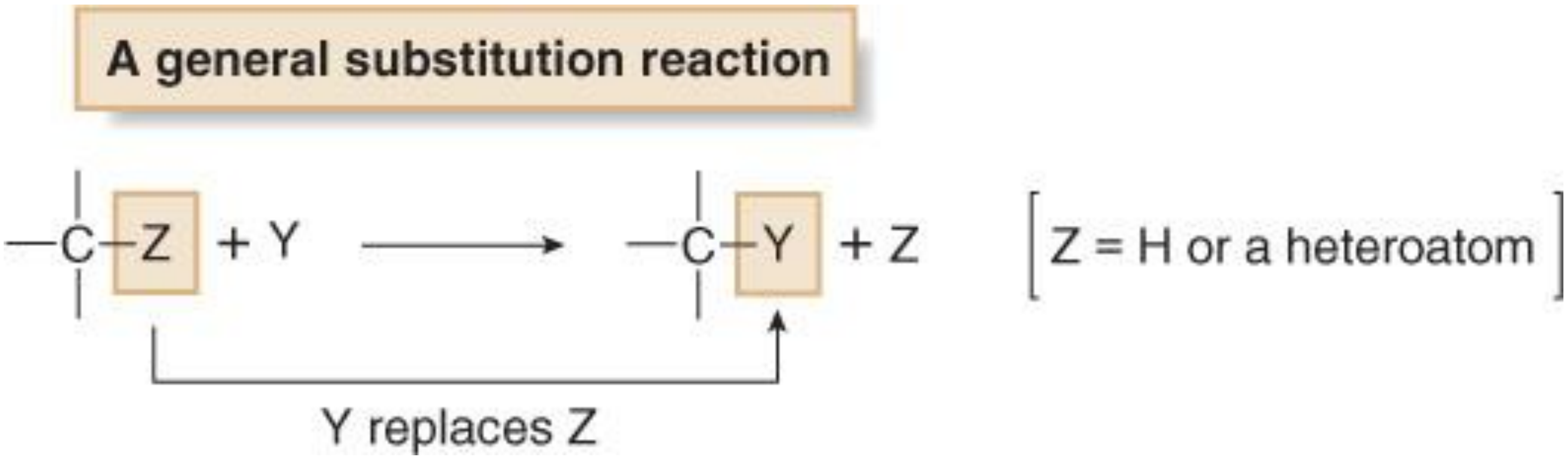
(S, E, and A = SEA)

Substitution Reactions

(Y will replace Z at a carbon atom)

Kinds of Organic Reactions

- A **substitution** is a reaction in which an atom or a group of atoms is replaced by another atom or group of atoms.
- In a general substitution, Y replaces Z on a carbon atom.

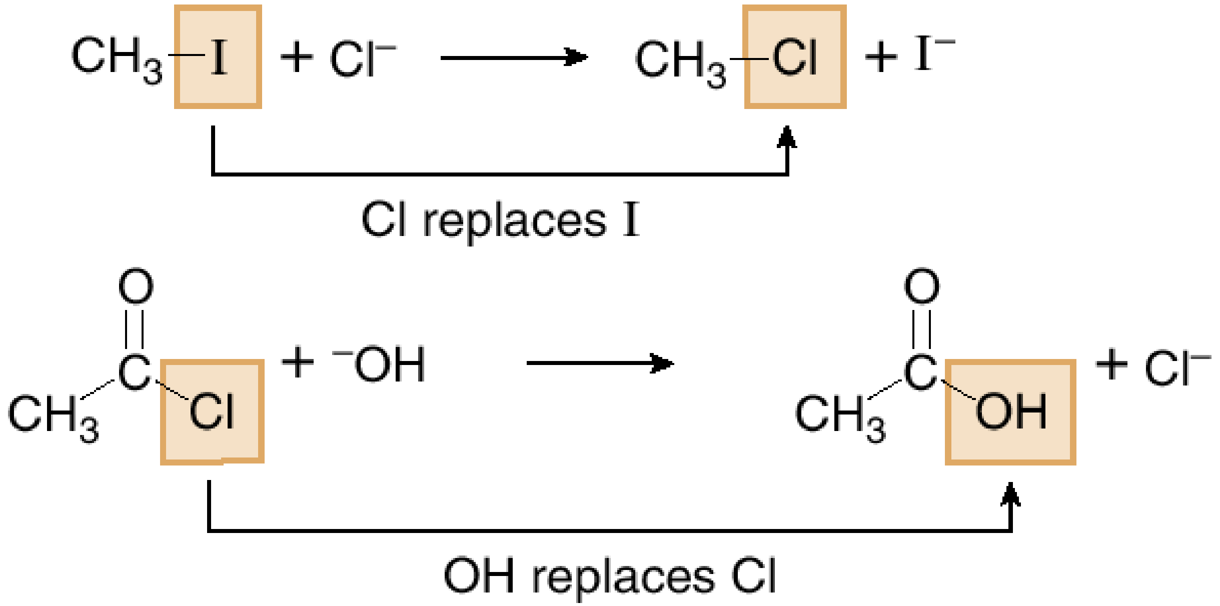


- Substitution reactions involve **σ bonds**: one σ bond breaks and another forms at the same carbon atom.

Examples

[1]

[2]



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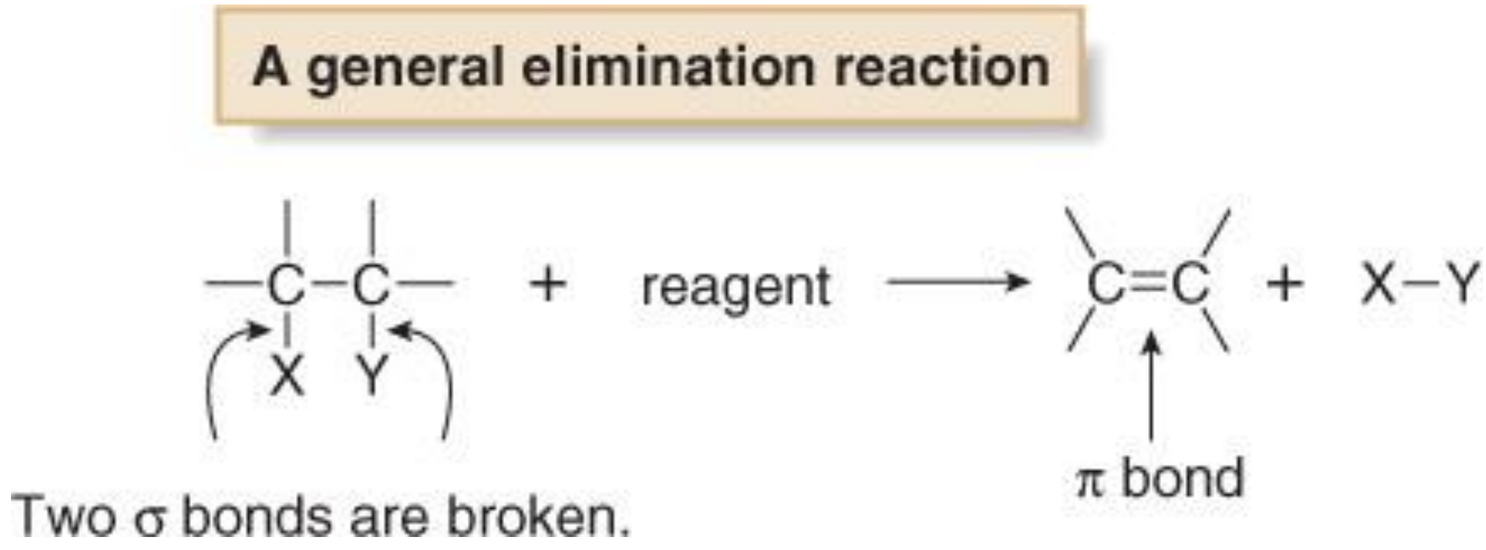
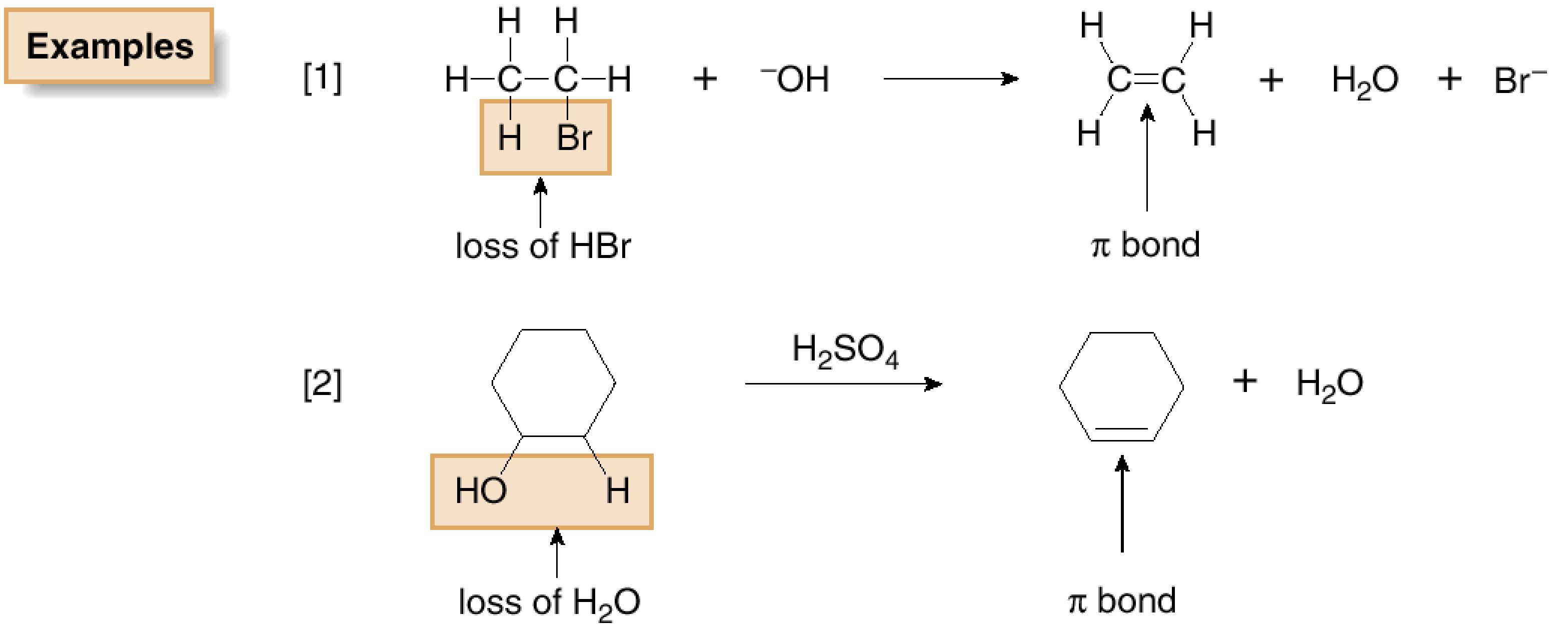
Elimination Reactions

(X and Y are detached from two different carbon atoms that are vicinal to each other)

- **Elimination** is a reaction in which elements of the starting material are "lost" and a π bond is formed.



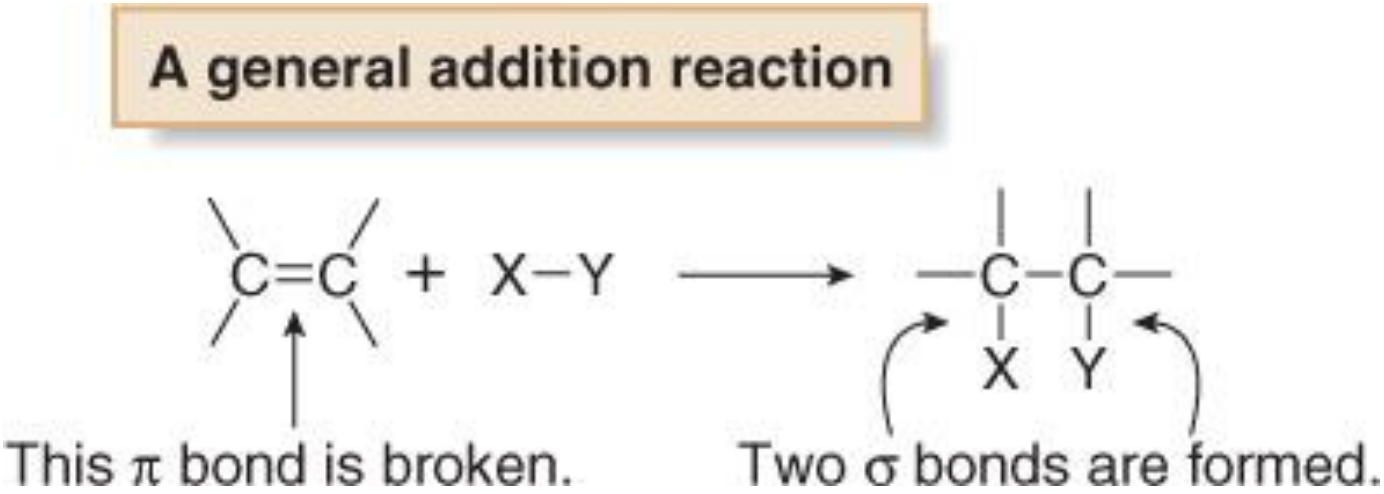
- In an elimination reaction, two groups X and Y are removed from a starting material.
- Two σ bonds are broken, and a π bond is formed between adjacent atoms.
- The most common examples of elimination occur when X = H and Y is a hetero atom more electronegative than carbon.



Addition Reactions

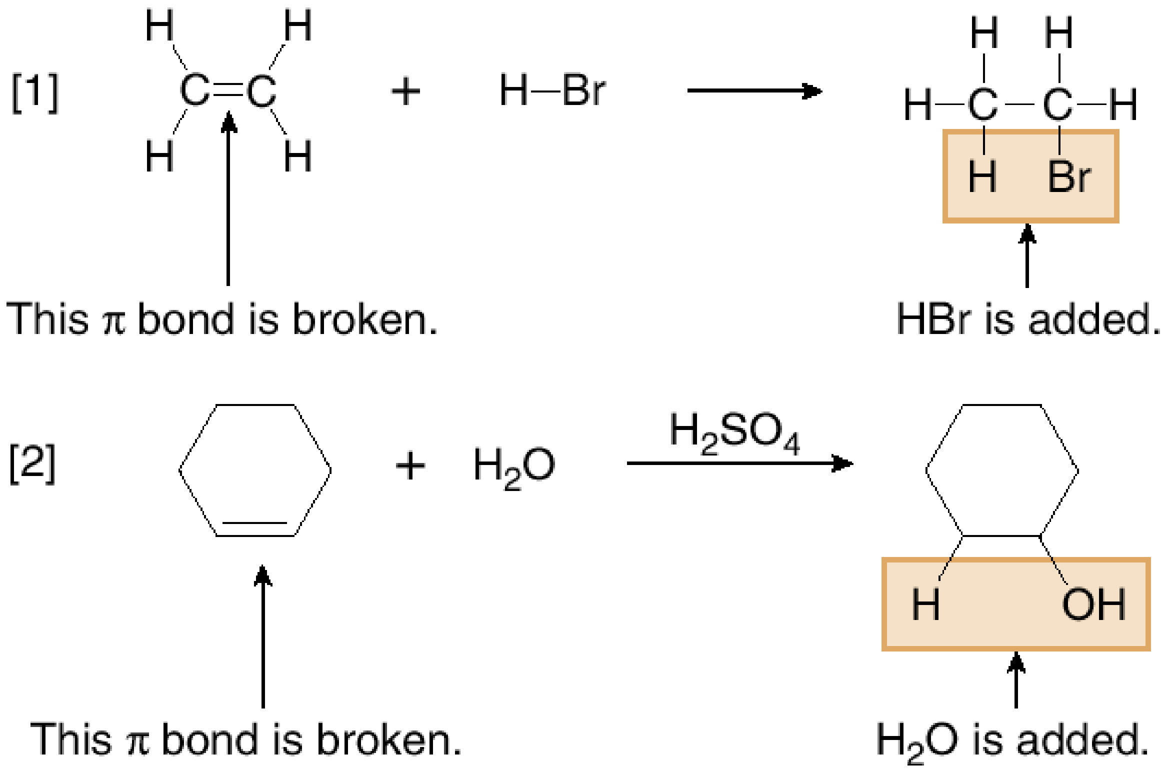
(X and Y add to two different atoms in a molecule that has one or more π bonds)

- **Addition** is a reaction in which elements are added to the starting material.



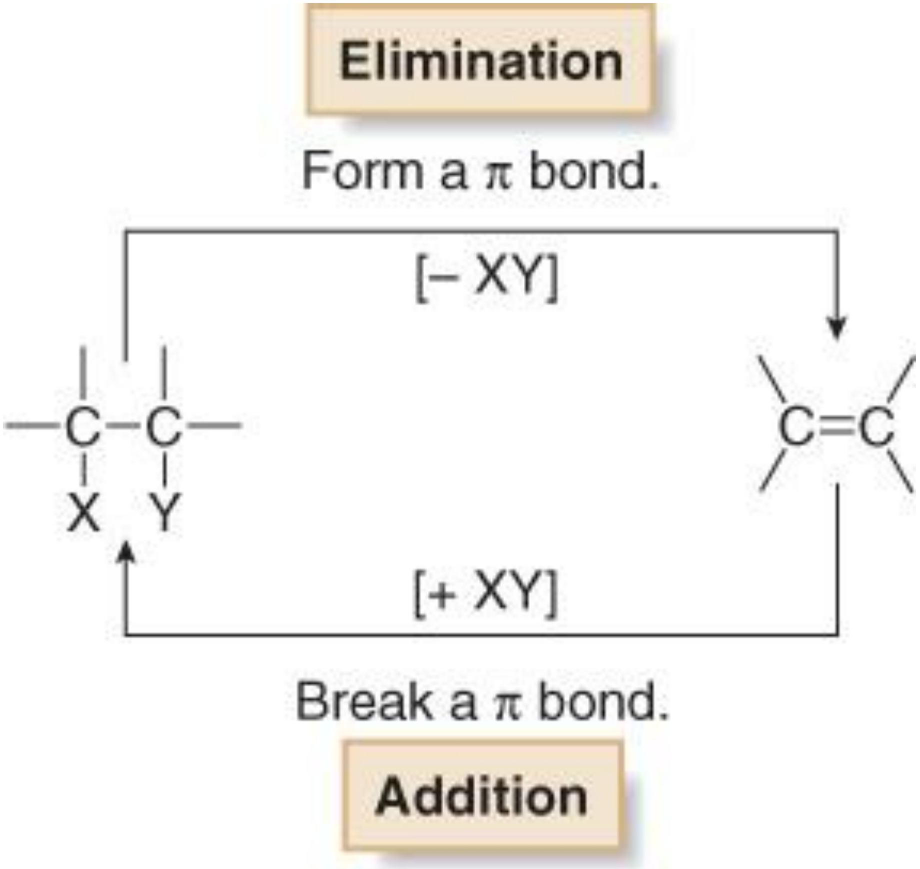
- In an addition reaction, new groups X and Y are added to the starting material. A π bond is broken and two σ bonds are formed.

Examples



- **Addition and elimination reactions are exactly opposite.**

A π bond is formed in elimination reactions, whereas a π bond is broken in addition reactions.



Reaction mechanisms

- A reaction mechanism is a <u>detailed description of how bonds are **broken** and **formed** as starting material is converted into product</u>.

- A reaction can occur either in one step or a series of steps.

- **A one-step reaction is called a *concerted reaction*.** No matter how many bonds are broken or formed, a starting material is converted *directly* to a product.

- **A stepwise reaction** involves more than one step. A starting material is first converted to an unstable intermediate, called a **reactive intermediate,** which then goes on to form the product.

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Changes in Bonding During a Chemical Rxn

(Homolysis and Heterolysis)

Two possible ways a bond can break:

Homolysis: an <u>equal</u> division of a bonding electron pair

$$A{-}B \longrightarrow A\cdot + \cdot B$$

Heterolysis: an <u>unequal</u> division of a bonding electron pair

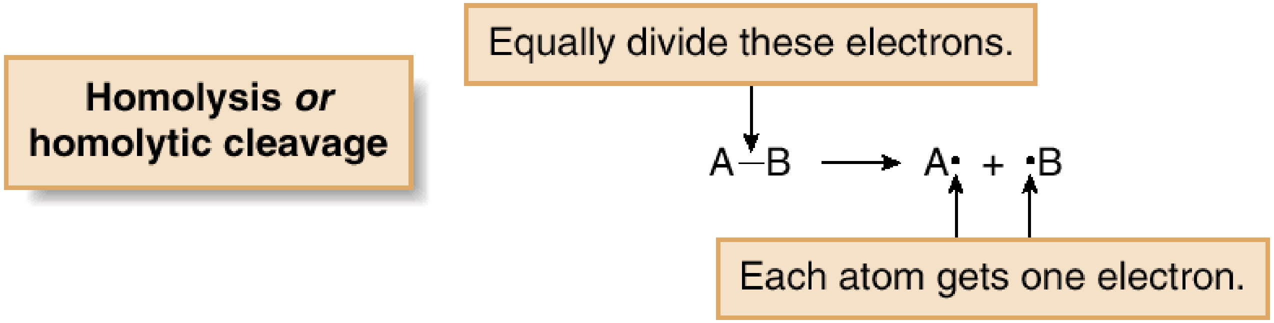
$$A{-}B \longrightarrow A^{+} + B\!:^{-}$$

or

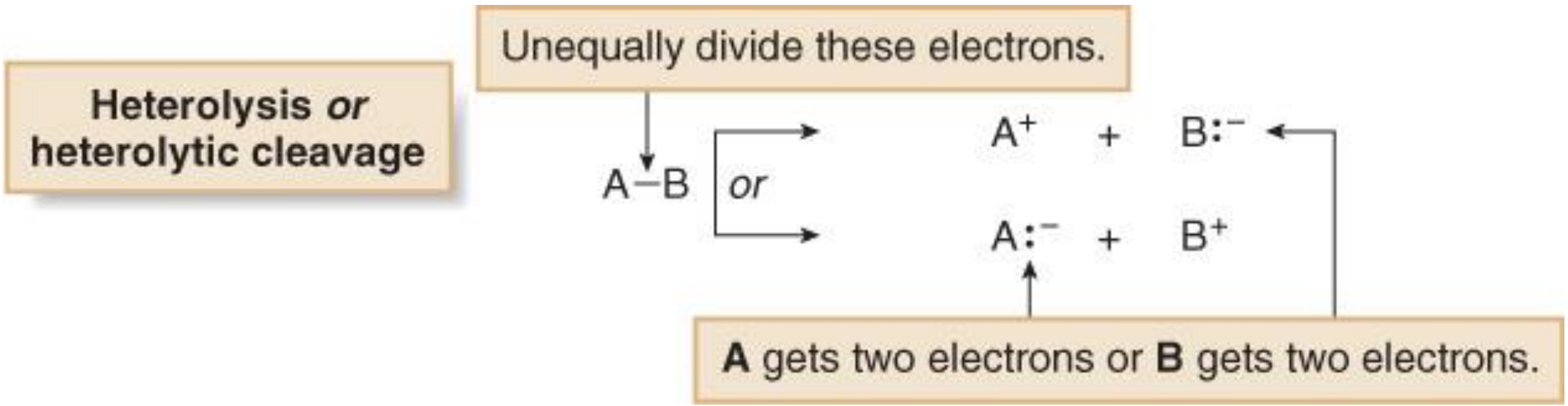
$$A{-}B \longrightarrow A\!:^{-} + B^{+}$$

- Regardless of how many steps there are in a reaction, there are only two ways to **break** (cleave) a bond: the electrons in the bond can be divided equally or unequally between the two atoms of the bond.

- Breaking a bond by **equally dividing the electrons** between the two atoms in the bond is called **homolysis** or **homolytic cleavage.**



- Breaking a bond by **unequally dividing the electrons** between the two atoms in the bond is called **heterolysis** or **heterolytic cleavage.** Heterolysis of a bond between **A** and **B** can give either **A** or **B** the two electrons in the bond. When **A** and **B** have different electronegativities, the ***electrons end up on the more electronegative atom.***



- **Bond breakage through homolysis or heterolysis requires energy.**
- Homolysis generates uncharged reactive intermediates with unpaired electrons.
- Heterolysis generates charged intermediates.

- To illustrate the movement of a **single electron**, use a half-headed curved arrow, sometimes called a fishhook.
- A full headed curved arrow shows the movement of an **electron pair**.

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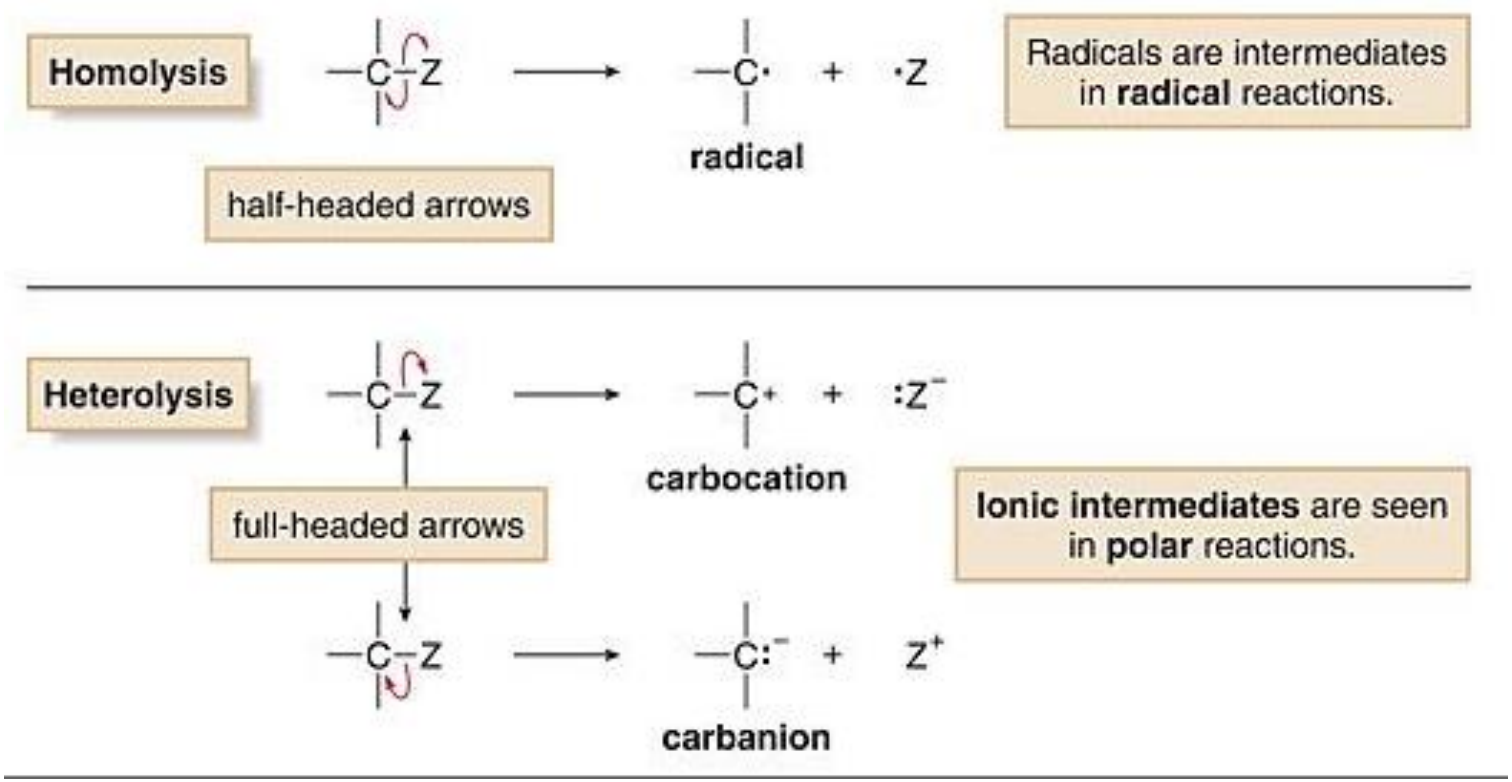
- Homolysis generates two uncharged species with unpaired electrons.
- A reactive intermediate with a single unpaired electron is called a radical.
- Radicals are highly unstable because they contain an atom that does not have an octet of electrons.

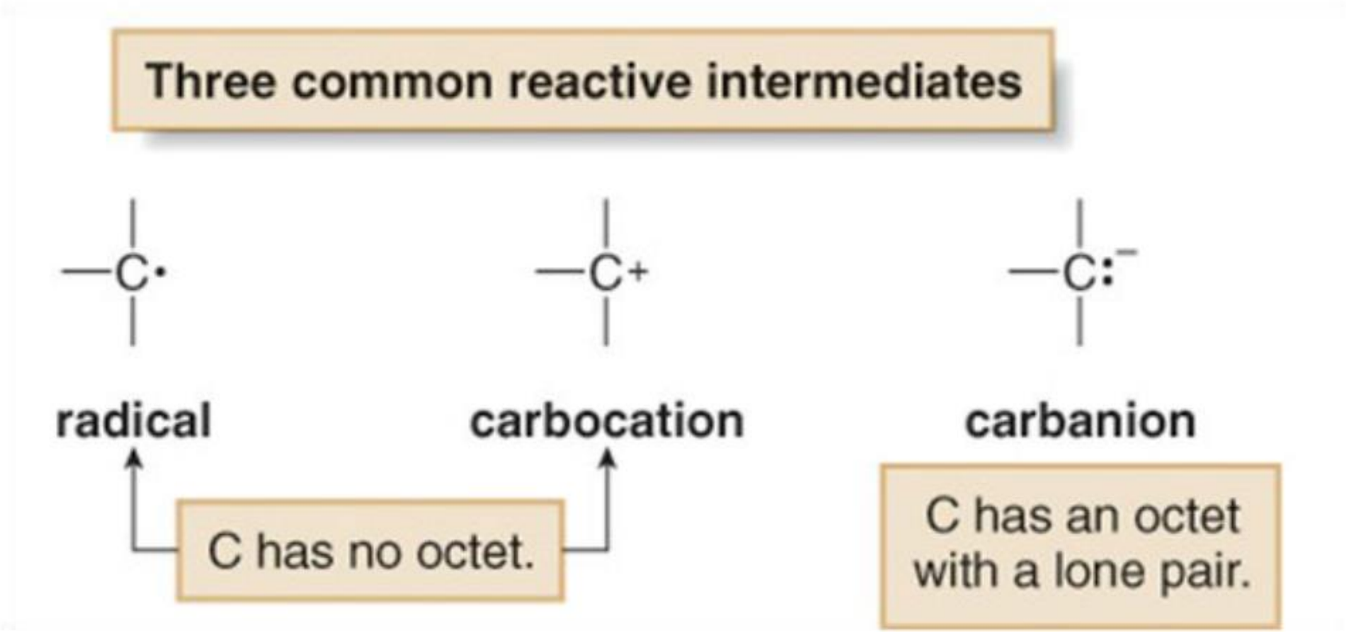
- Heterolysis generates a carbocation and a carbanion.
- Both carbocations and carbanions are unstable intermediates. A carbocation contains a carbon surrounded by only six electrons, and a carbanion has a negative charge on carbon, which is not a very electronegative atom.

Bond Breaking forms particles called reaction intermediates.

Three reactive intermediates resulting from homolysis and heterolysis of a C – Z bond

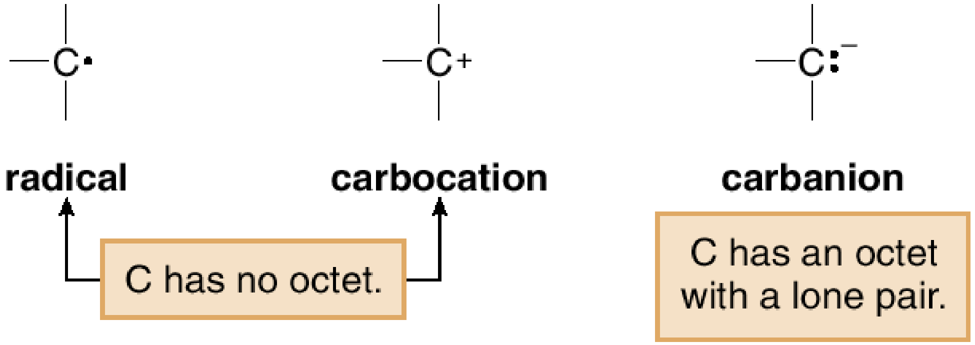


Common Reaction Intermediates Formed by Breaking a Covalent Bond



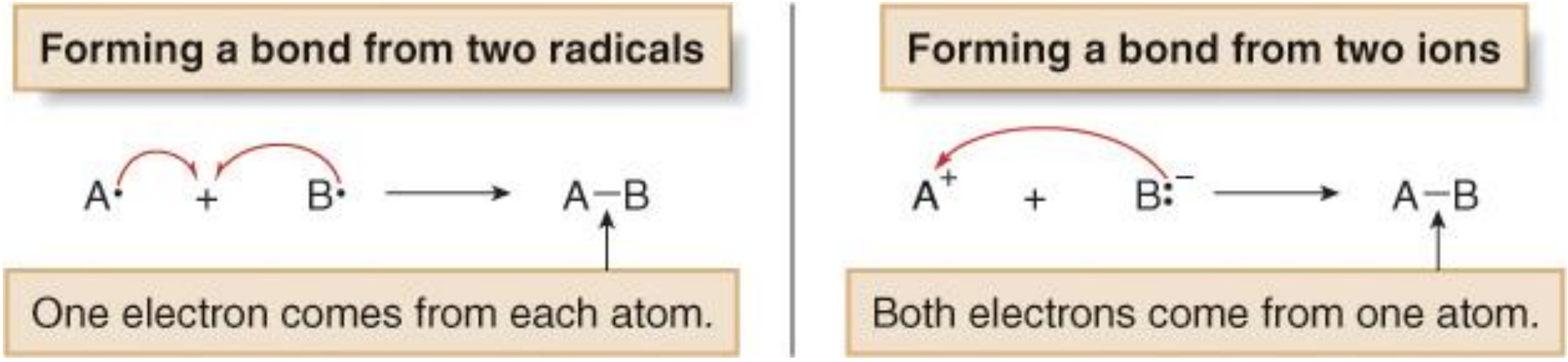
- A carbocation contains a carbon surrounded by only six electrons.
- A carbanion has a negative charge on carbon, which is not a very electronegative atom.

- Radicals and carbocations are electrophiles because they contain an electron deficient carbon.
- Carbanions are nucleophiles because they contain a carbon with a lone pair.



- Radicals and carbocations are electrophiles because they contain an electron-deficient carbon.
- Carbanions are nucleophiles because they contain a carbon with a lone pair.

- **Bond formation** occurs in two different ways.
- Two radicals can each donate one electron to form a two-electron bond.
- Alternatively, two ions with unlike charges can come together, with the negatively charged ion donating both electrons to form the resulting two-electron bond.
- **Bond formation always releases energy**.



- A number of types of arrows are used in describing organic reactions.

A Summary of Arrow Types in Chemical Reactions

Arrow	Name	Use
→	Reaction arrow	Drawn between the starting materials and products
⇌	Double reaction arrows (equilibrium arrows)	Drawn between the starting materials and products
↔	Double-headed arrow	Drawn between resonance structures
	Full-headed curved arrow	Shows movement of an electron pair
	Half-headed curved arrow (fishhook)	Shows movement of a single electron

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$

$$N_{2(g)} + {}_3H_{2(g)} \underset{723K,\ 200atm}{\overset{Fe,\ Mo}{\rightleftharpoons}} 2NH_{3(g)}$$