



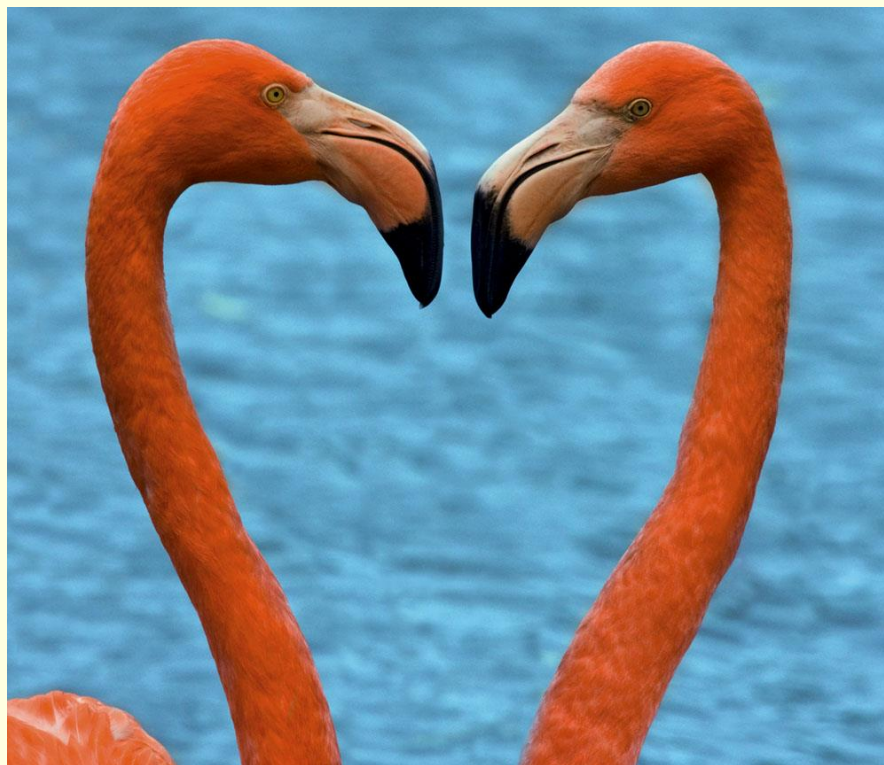
# 3. Alkenes and Alkynes: The Nature of Organic Reactions

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스마트헬스케어학부 의공학전공

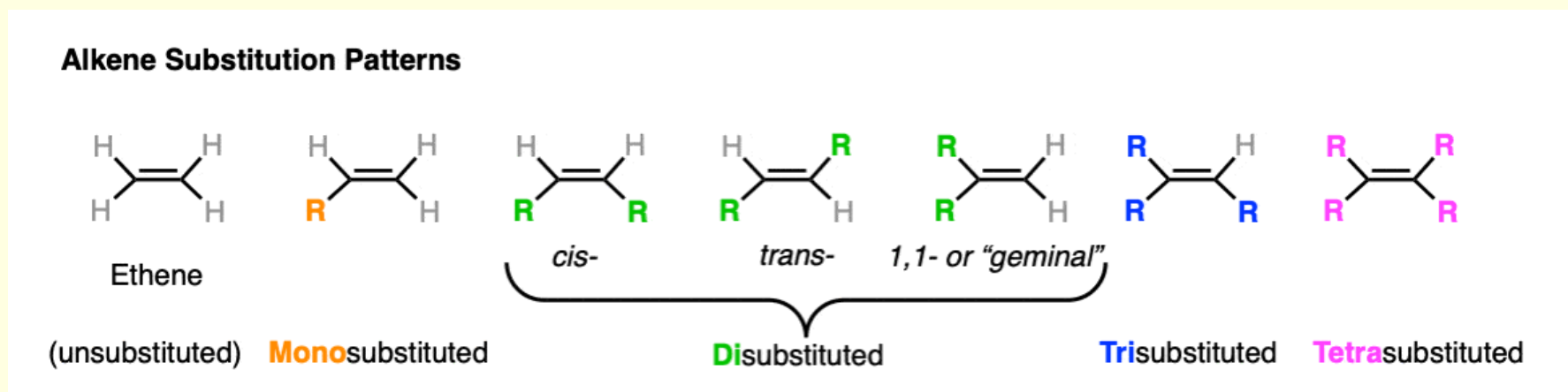
임해균 교수

# 3. Alkenes and Alkynes: The Nature of Organic Reactions



## 3.4 Sequence Rules: The *E,Z* Designation

- Neither compound is clearly “*cis*” or “*trans*”
  - Substituents on C1 are different than those on C2
  - We need to define “similarity” in a precise way to **distinguish** the two stereoisomers
- *Cis, trans* nomenclature **only** works for **disubstituted double bonds**

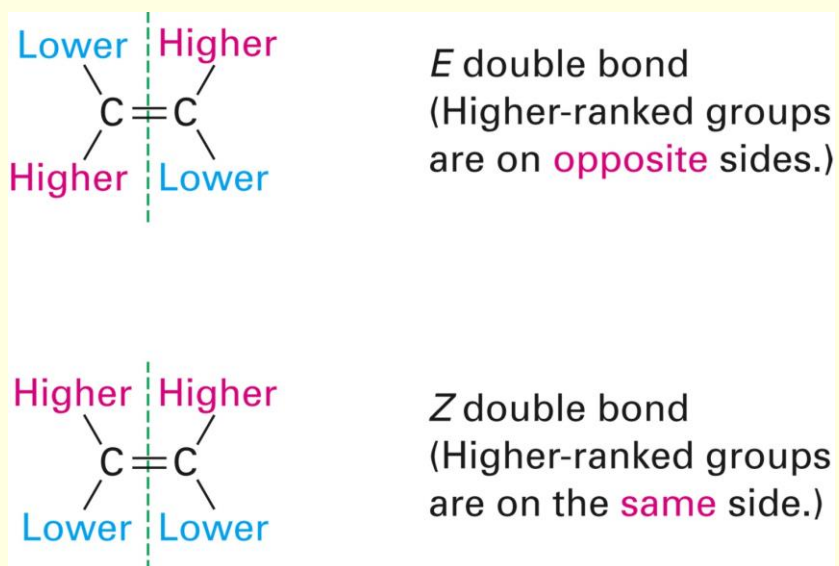


# E,Z Stereochemical Nomenclature

- Priority rules of **Cahn, Ingold, and Prelog**
- Compare where higher priority groups are with respect to bond and designate as prefix

If the higher-ranked groups on each carbon are on **opposite** sides of the double bond, the alkene is said to have **E stereochemistry**, for the German *entgegen*, meaning “opposite.”

If the higher-ranked groups are on the **same** side, the alkene has **Z stereochemistry**, for the German *zusammen*, meaning “together.”

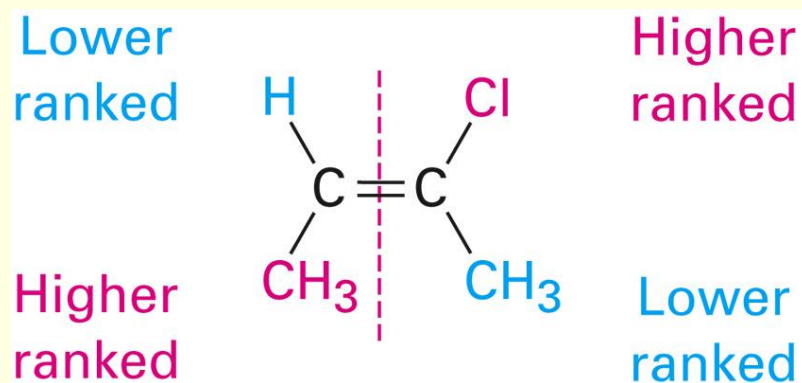


# Ranking Priorities: Cahn-Ingold-Prelog Rules

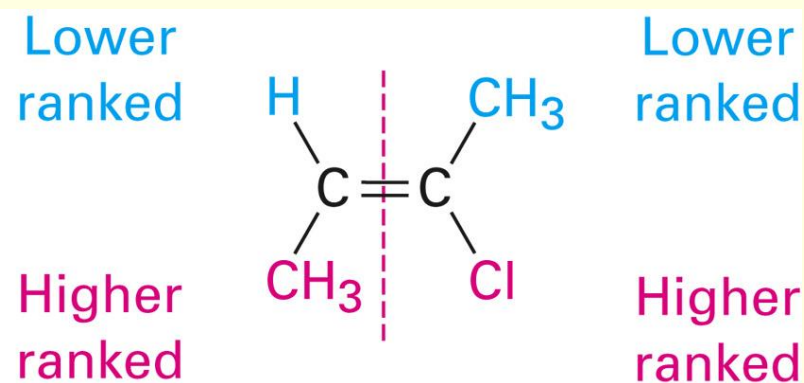
## RULE 1

- Must rank atoms that are connected at comparison point
- Higher atomic number gets higher priority

Atomic number	35		17		16		15		8		7		6		(2)		(1)	
Higher ranking	Br	>	Cl	>	S	>	P	>	O	>	N	>	C	>	<sup>2</sup> H	>	<sup>1</sup> H	Lower ranking



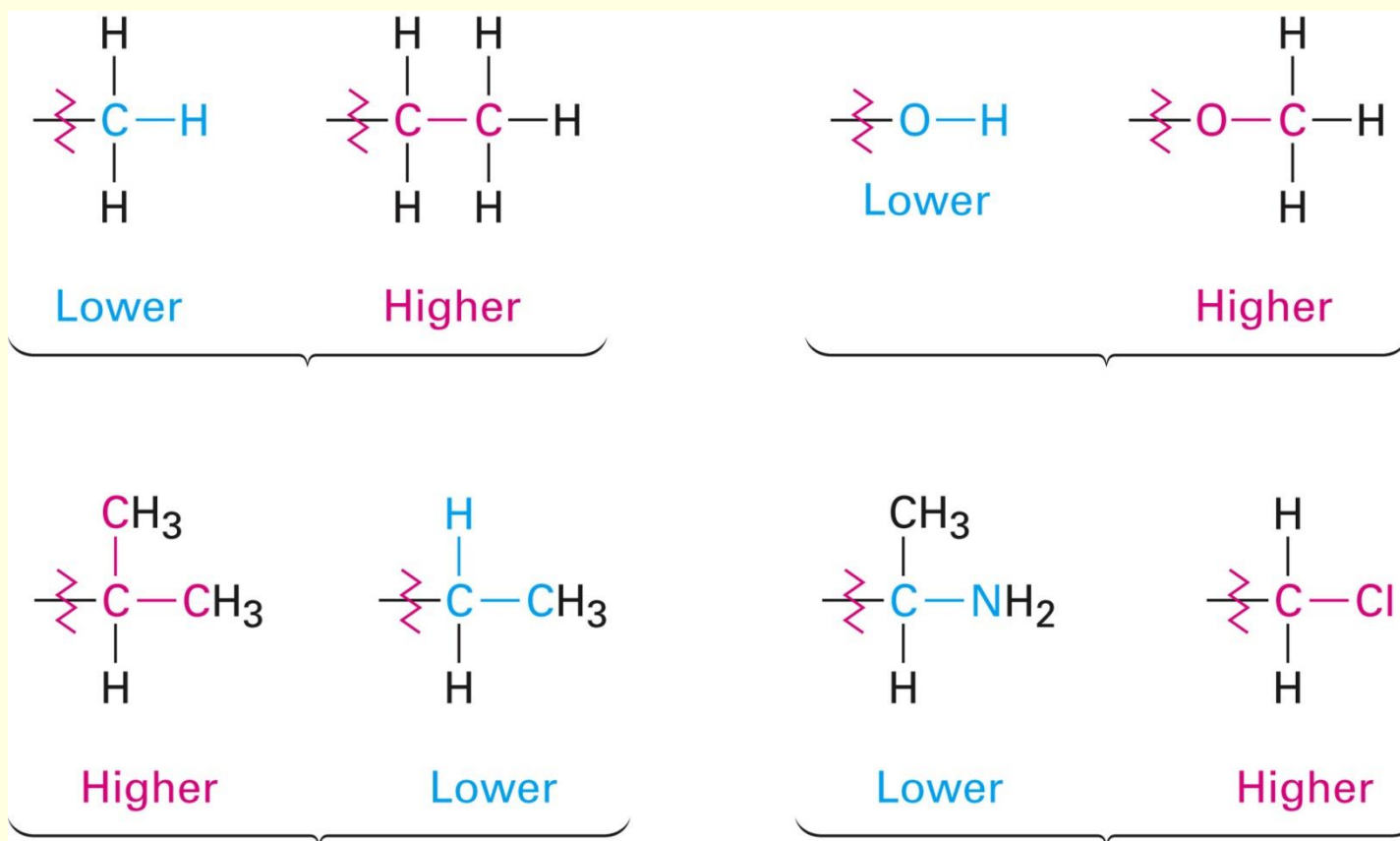
(a) (E)-2-Chlorobut-2-ene



(b) (Z)-2-Chlorobut-2-ene

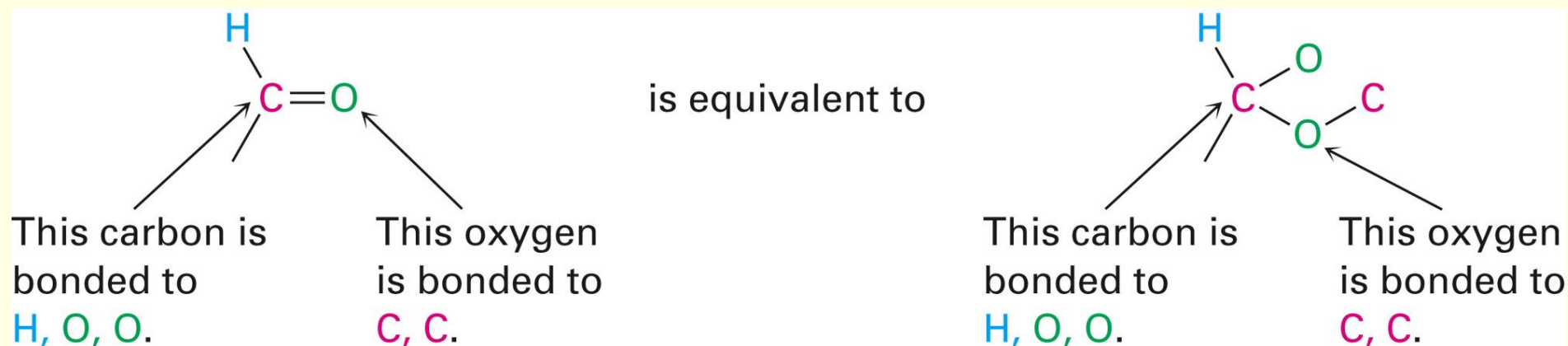
## RULE 2

- If atomic numbers are the same, compare at **next connection point at same distance**
- Compare until something has higher atomic number
- Do not combine – always compare

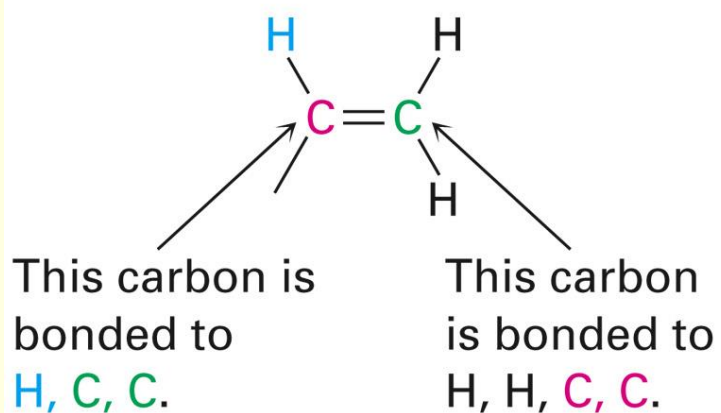


## RULE 3

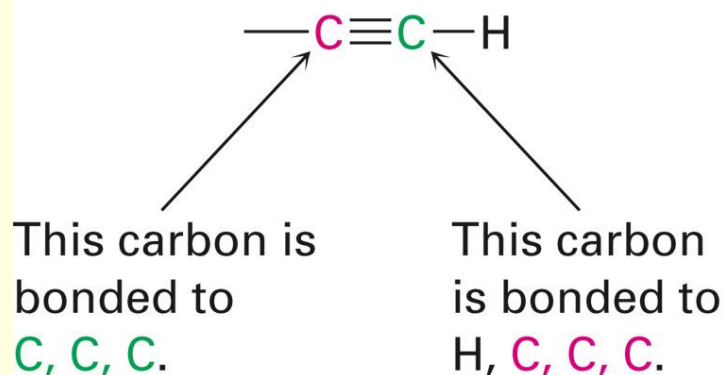
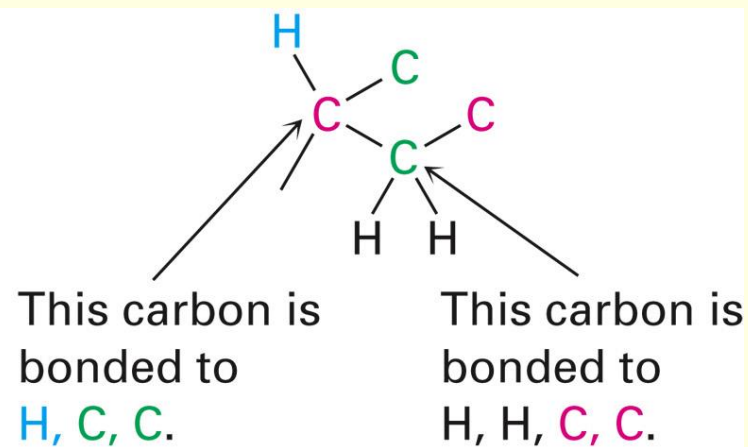
- Multiple-bonded atoms are equivalent to the same number of single-bonded atoms.
- For example, an aldehyde substituent (  $\text{-CH=O}$  ), which has a carbon atom **doubly** bonded to **one oxygen**, is equivalent to a substituent having a carbon atom **singly** bonded to **two oxygens**.
- Substituent is drawn with connections shown and no double or triple bonds
- Added atoms are valued with 0 ligands themselves



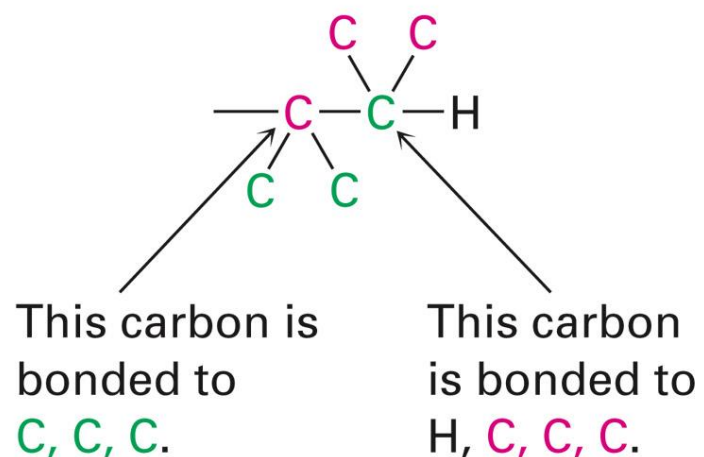
# RULE 3



is equivalent to

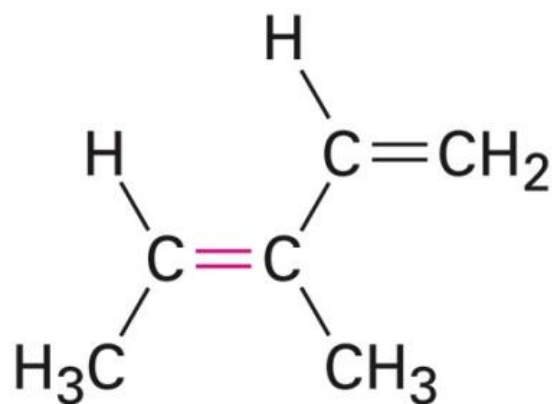


is equivalent to

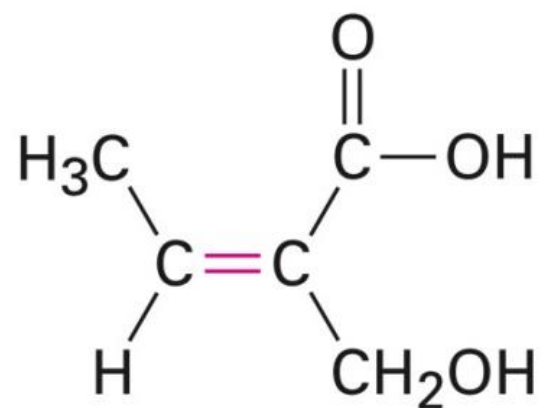




By applying the sequence rules, we can assign the stereochemistry shown in the following examples. Work through each one to convince yourself the assignments are correct.



**(E)-3-Methylpenta-1,3-diene**

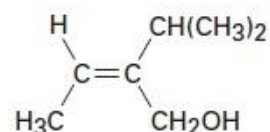


**(Z)-2-Hydroxymethyl-  
but-2-enoic acid**

### Worked Example 3.3

#### Assigning *E,Z* Stereochemistry to an Alkene

Assign *E* or *Z* stereochemistry to the double bond in the following compound:

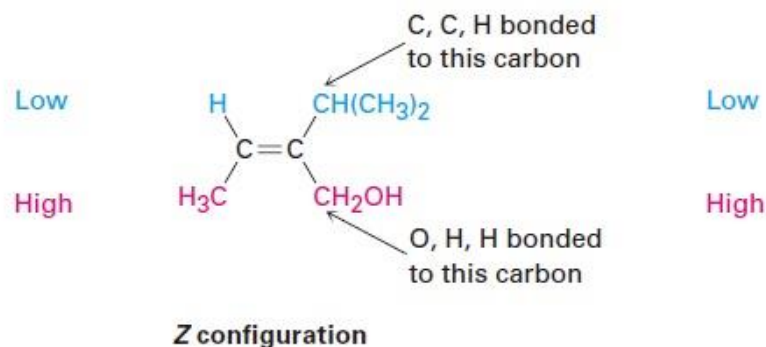


#### Strategy

Look at each double-bond carbon individually, and assign rankings. Then see whether the two higher-ranked groups are on the same or opposite sides of the double bond.

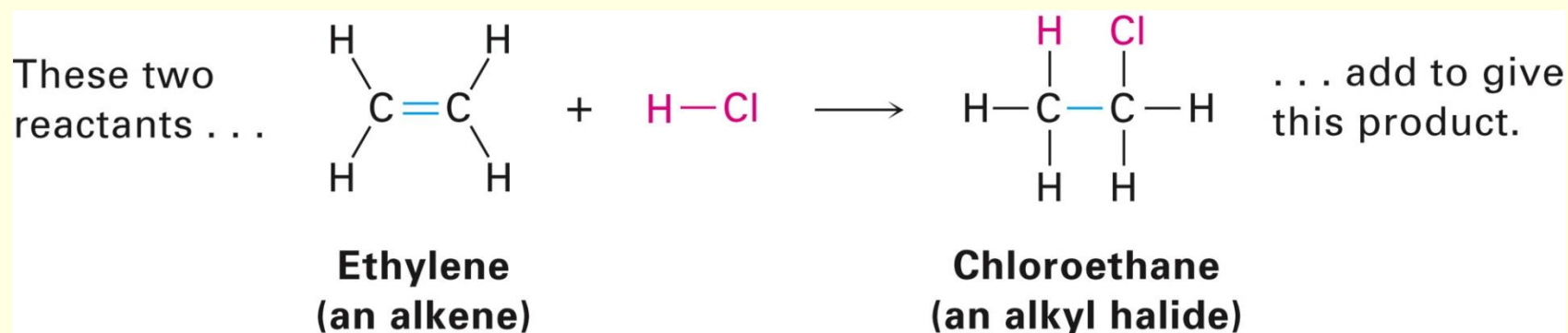
#### Solution

The left-hand carbon has two substituents,  $\text{-H}$  and  $\text{-CH}_3$ , of which  $\text{-CH}_3$  ranks higher by rule 1. The right-hand carbon also has two substituents,  $\text{-CH(CH}_3)_2$  and  $\text{-CH}_2\text{OH}$ , which are equivalent by rule 1. By rule 2, however,  $\text{-CH}_2\text{OH}$  ranks higher than  $\text{-CH(CH}_3)_2$  because  $\text{-CH}_2\text{OH}$  has an *oxygen* as its highest second atom, whereas  $\text{-CH(CH}_3)_2$  has *carbon* as its highest second atom. The two higher-ranked groups are on the same side of the double bond, so the compound has *Z* stereochemistry.

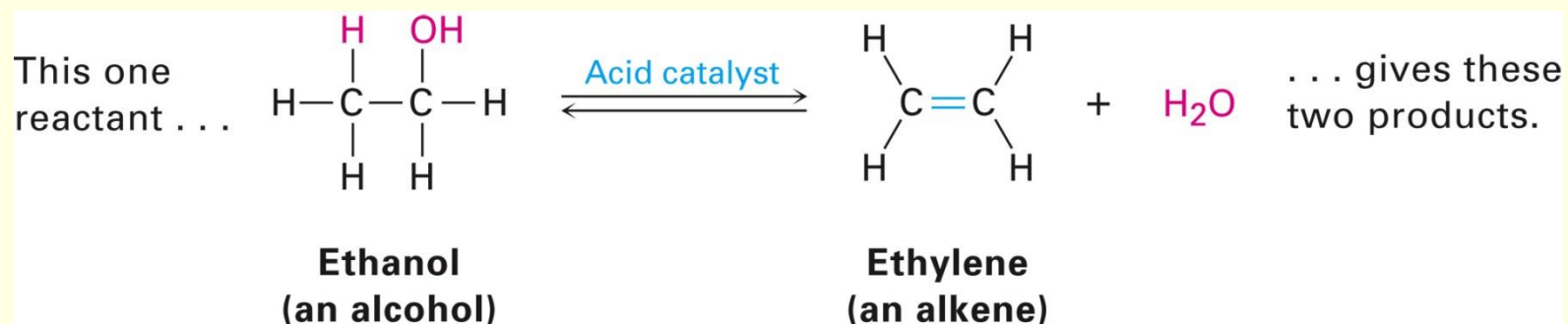


## 3.5 Kinds of Organic Reactions

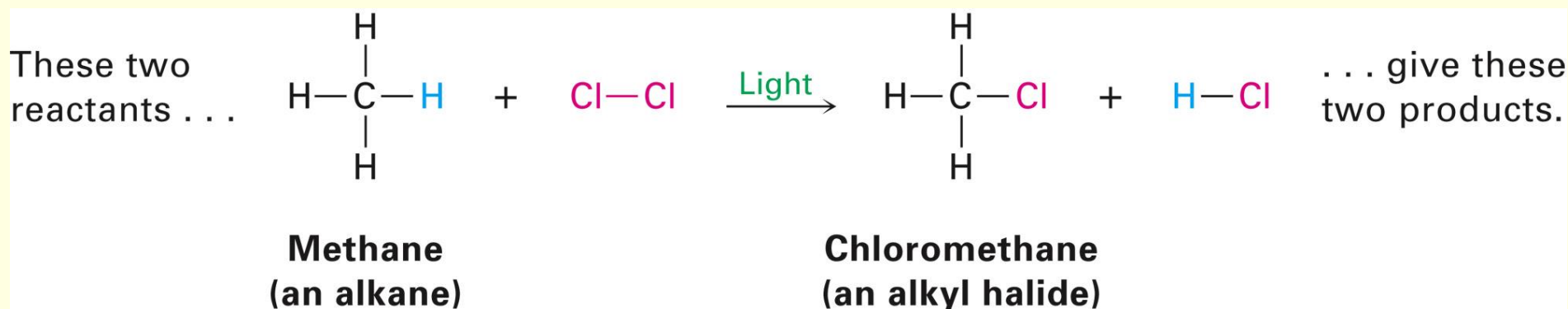
- In general, we look at what occurs and try to learn how it happens
- Common patterns describe the changes
  - **Addition** reactions – two molecules combine



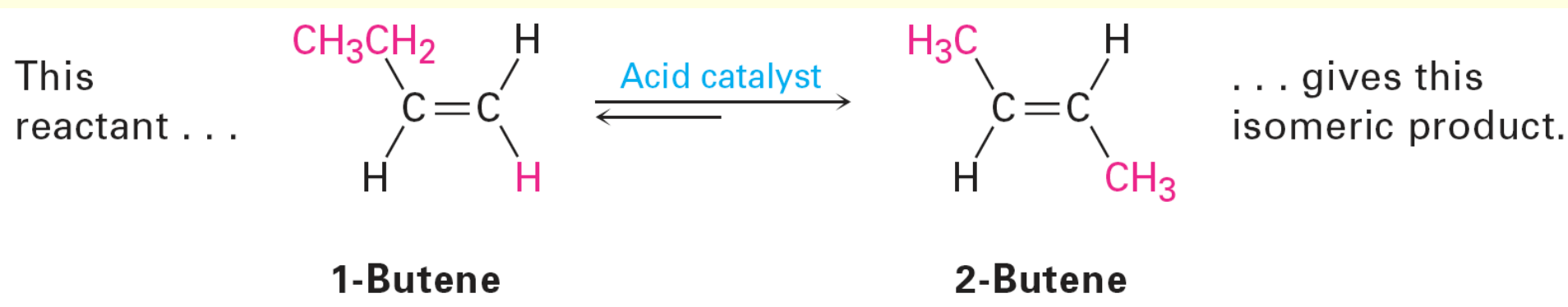
- **Elimination** reactions – one molecule splits into two



- **Substitution** – parts from two molecules exchange



- **Rearrangement** reactions – a molecule undergoes changes in the way its atoms are connected



# 3.6 How Reactions Occur: Mechanisms

## Types of Reaction Mechanisms

- Bond formation or breakage can be symmetrical or unsymmetrical
- **Symmetrical-** homolytic : radical reactions
- **Unsymmetrical-** heterolytic : polar reactions



Symmetrical bond-breaking (radical):  
one bonding electron stays with each product.



Unsymmetrical bond-breaking (polar):  
two bonding electrons stay with one product.

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Symmetrical bond-making (radical):  
one bonding electron is donated by each reactant.

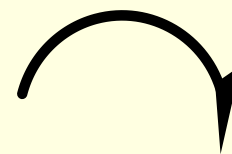


Unsymmetrical bond-making (polar):  
two bonding electrons are donated by one reactant.

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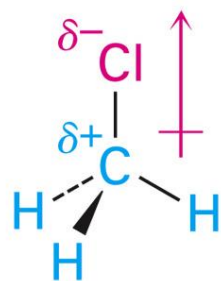
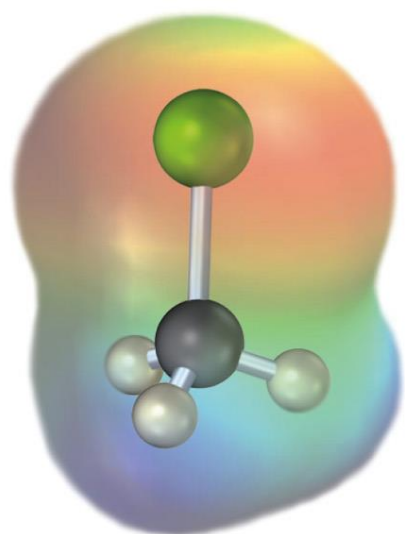
# Indicating Steps in Mechanisms

- Curved arrows **indicate breaking and forming of bonds**
- Arrowheads with a “half” head (“fish-hook”) indicate **homolytic and homogenic steps** (called ‘radical processes’)
- Arrowheads with a complete head indicate **heterolytic and heterogenic steps** (called ‘polar processes’)

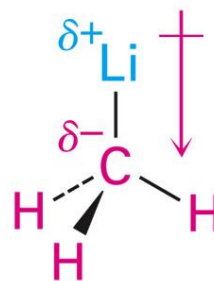


# Polar Reactions

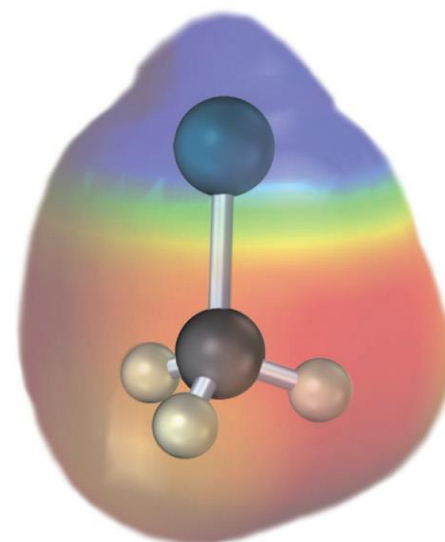
- Molecules can contain local **unsymmetrical electron** distributions due to differences in **electronegativities**
- This causes a partial negative charge on an atom and a compensating partial positive charge on an adjacent atom
- **The more electronegative atom has the greater electron density**
- Elements such as O, F, N, Cl more electronegative than carbon



**Chloromethane**



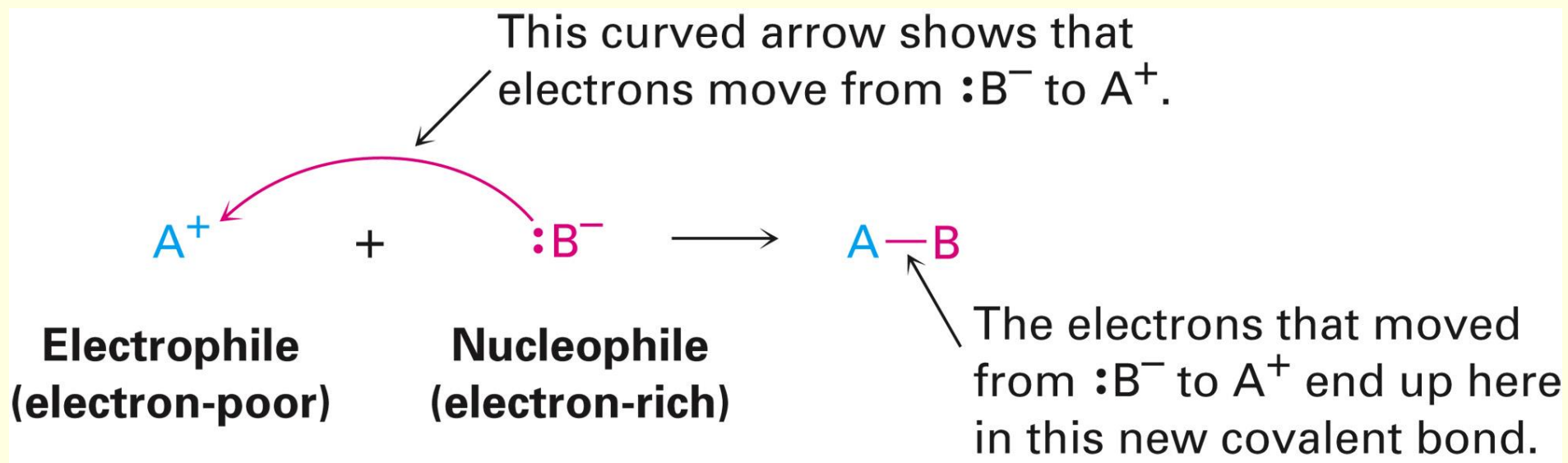
**Methyllithium**



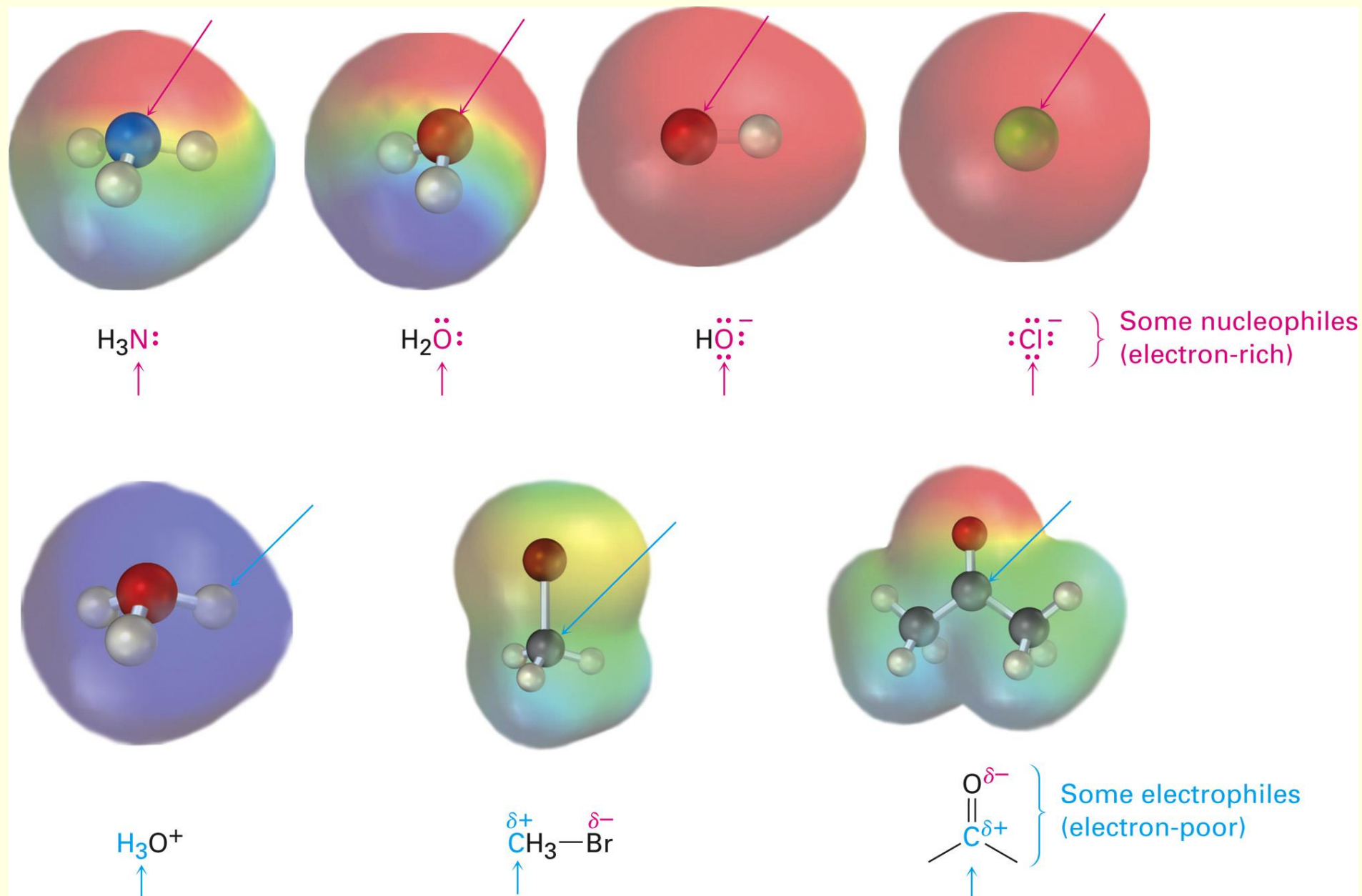


# Generalized Polar Reactions

- An **electrophile**, an electron-poor species, combines with a **nucleophile**, an electron-rich species
- The combination is indicated with a curved arrow from nucleophile to electrophile







Electrostatic potential maps identify the nucleophilic (red; negative) and electrophilic (blue; positive) atoms.

### Worked Example 3.4

#### Predicting the Polarity of a Bond

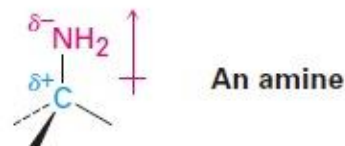
What is the direction of bond polarity in the amine functional group, C—NH<sub>2</sub>?

#### Strategy

Look at the electronegativity values in Figure 1.14 on page 16 to see which atoms withdraw electrons more strongly.

#### Solution

Nitrogen (EN = 3.0) is more electronegative than carbon (EN = 2.5) according to Figure 1.14, so an amine is polarized with carbon  $\delta+$  and nitrogen  $\delta-$ .



### Worked Example 3.5

#### Identifying Electrophiles and Nucleophiles

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

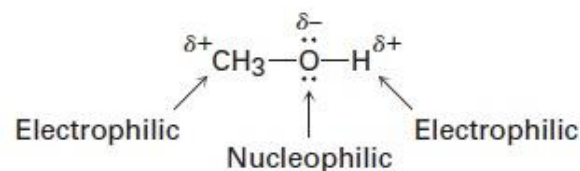
- (a)  $\text{NO}_2^+$     (b)  $\text{CH}_3\text{O}^-$     (c)  $\text{CH}_3\text{OH}$

#### Strategy

A nucleophile has an electron-rich site, either because it is negatively charged or because it has a functional group containing an atom that has a lone pair of electrons. An electrophile has an electron-poor site, either because it is positively charged or because it has a functional group containing an atom that is positively polarized.

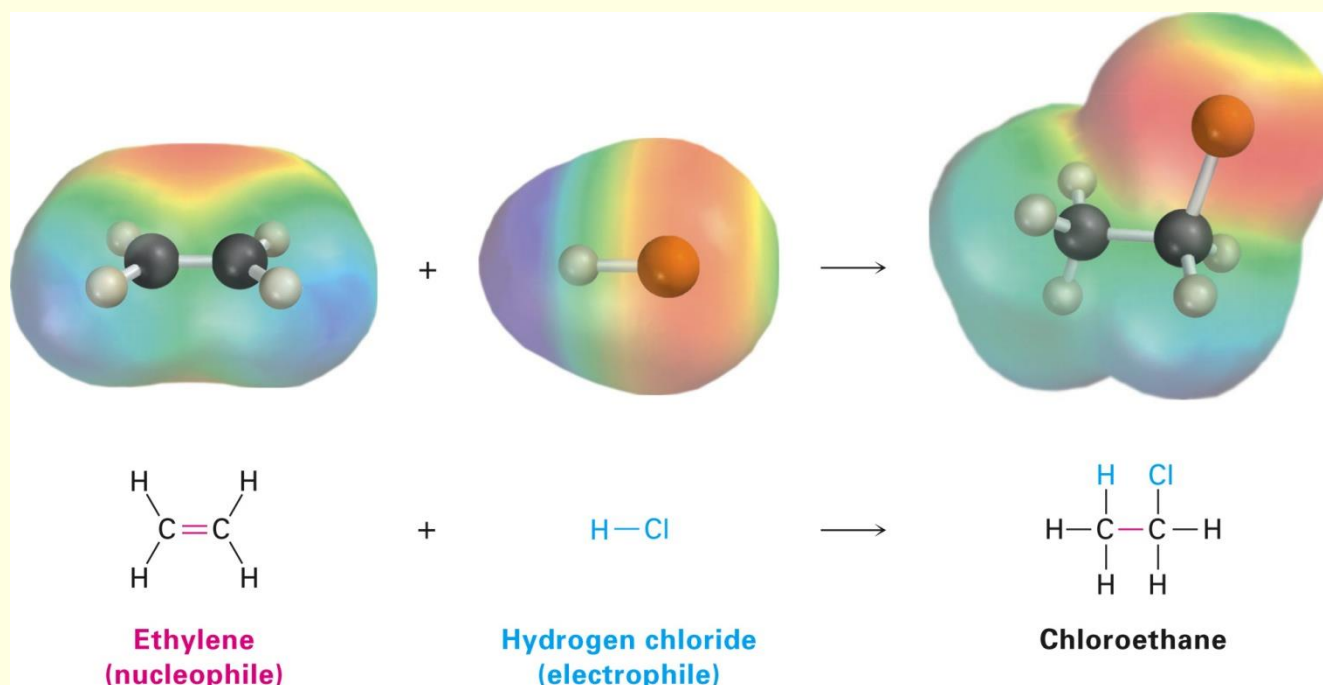
#### Solution

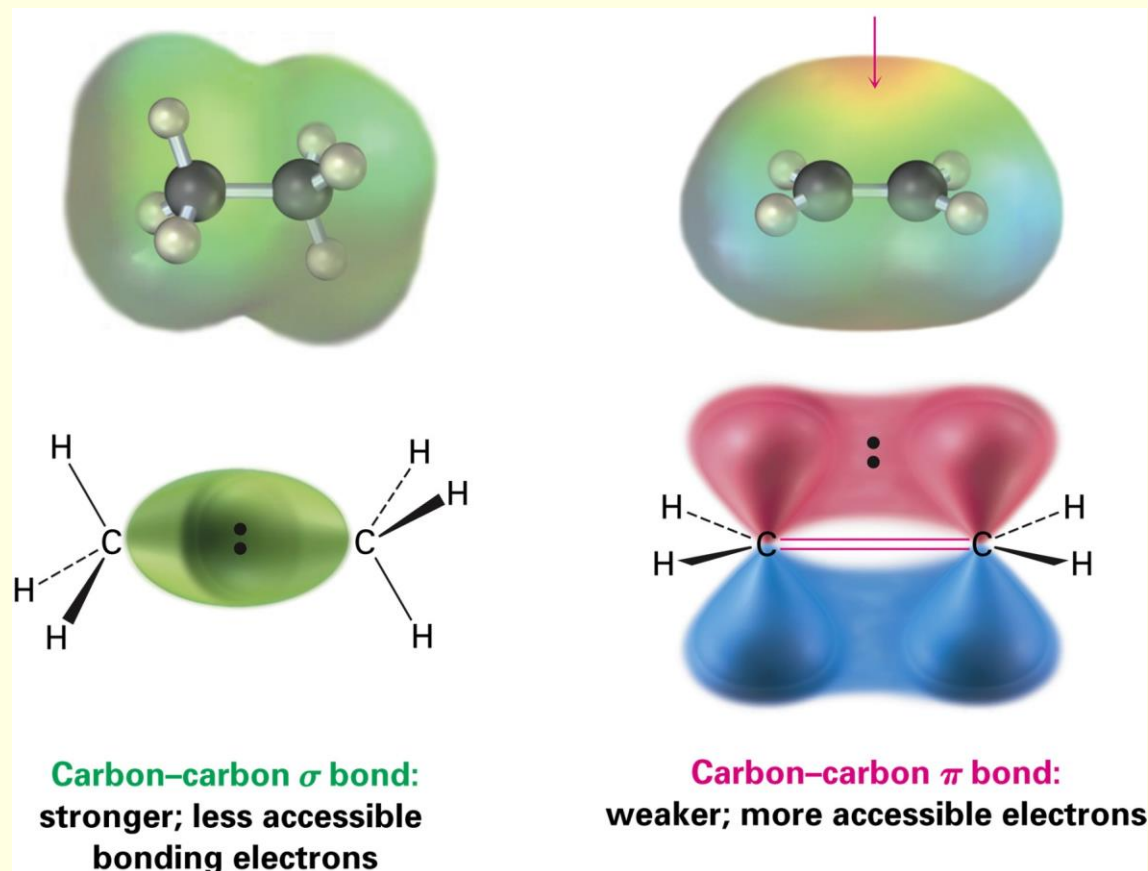
- (a)  $\text{NO}_2^+$  (nitronium ion) is likely to be an electrophile because it is positively charged.
- (b)  $\text{CH}_3\text{O}^-$  (methoxide ion) is likely to be a nucleophile because it is negatively charged.
- (c)  $\text{CH}_3\text{OH}$  (methyl alcohol) can be either a nucleophile, because it has two lone pairs of electrons on oxygen, or an electrophile, because it has polar C–O and O–H bonds.



## 3.7 The Mechanism of an Organic Reaction: **Addition of HCl to Ethylene**

- HCl adds to the  $\pi$  part of C-C double bond
- The  $\pi$  bond is electron-rich, allowing it to function as a nucleophile
- H-Cl is electron deficient at the H since **Cl is much more electronegative**, making HCl an electrophile





**Figure 3.5** A comparison of carbon–carbon single and double bonds.

A double bond is both more accessible to approaching reactants than a single bond and more electron-rich (more nucleophilic). An electrostatic potential map of ethylene indicates that the double bond is the region of highest negative charge (red).

Furthermore, an alkene  $\pi$  bond is much weaker than an alkane  $\sigma$  bond, so an alkene is more reactive.

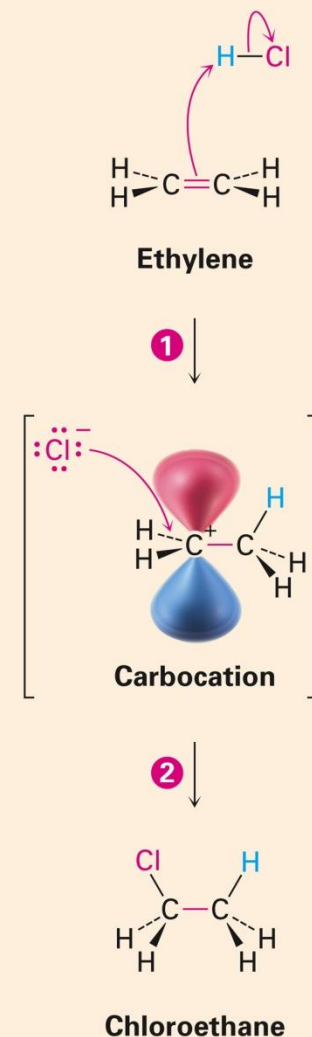


# Mechanism of Addition of HCl to Ethylene

- General reaction mechanism:  
**electrophilic addition**
- Attack of electrophile (such as HCl) on  $\pi$  bond of alkene
- Produces **carbocation** and **chloride ion**
- **Carbocation** is an electrophile, reacting with nucleophilic chloride ion

1 A hydrogen atom on the electrophile HCl is attacked by  $\pi$  electrons from the nucleophilic double bond, forming a new C-H bond. This leaves the other carbon atom with a + charge and a vacant  $p$  orbital. Simultaneously, two electrons from the H-Cl bond move onto chlorine, giving chloride anion.

2 Chloride ion donates an electron pair to the positively charged carbon atom, forming a C-Cl bond and yielding the neutral addition product.



### Worked Example 3.6

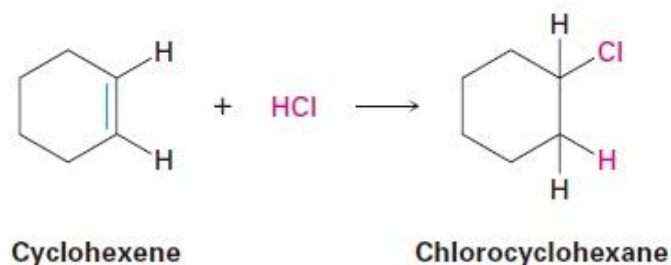
#### Predicting the Product of an Electrophilic Addition Reaction

What product would you expect from reaction of HCl with cyclohexene?

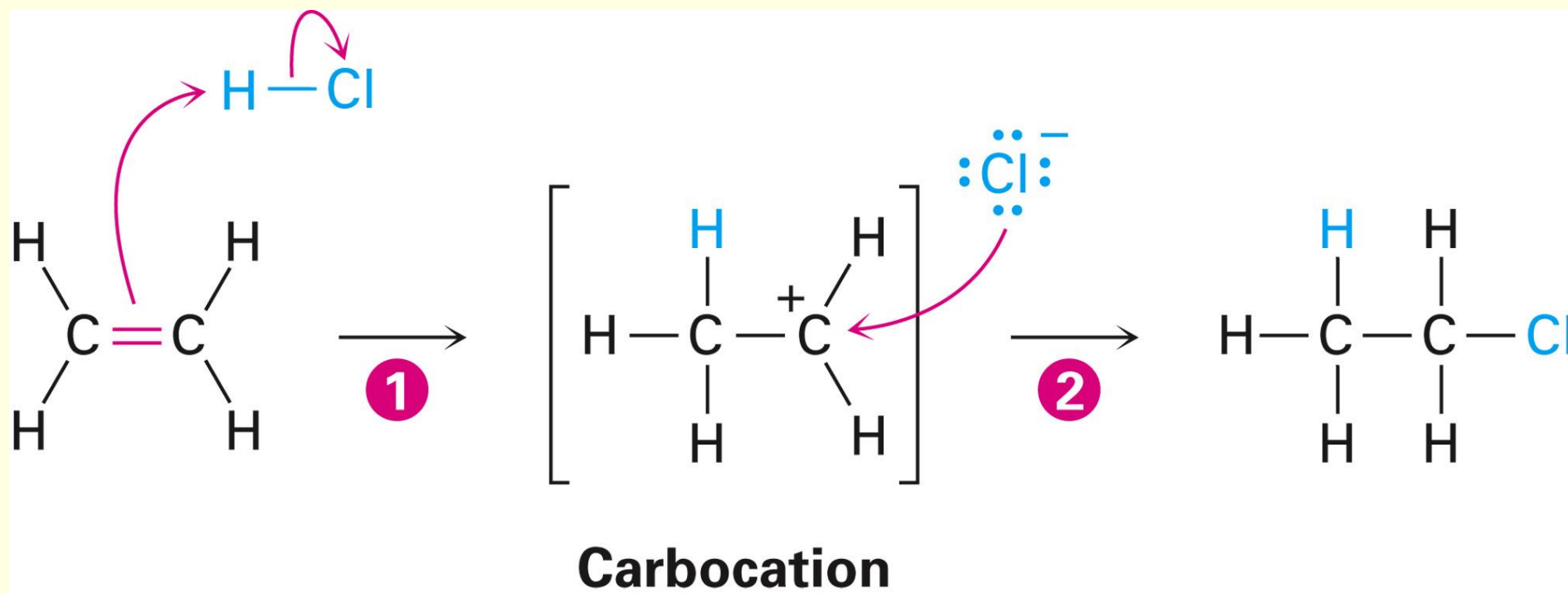
#### Strategy

HCl adds to the double-bond functional group in cyclohexene in exactly the same way it adds to ethylene, yielding an addition product.

#### Solution

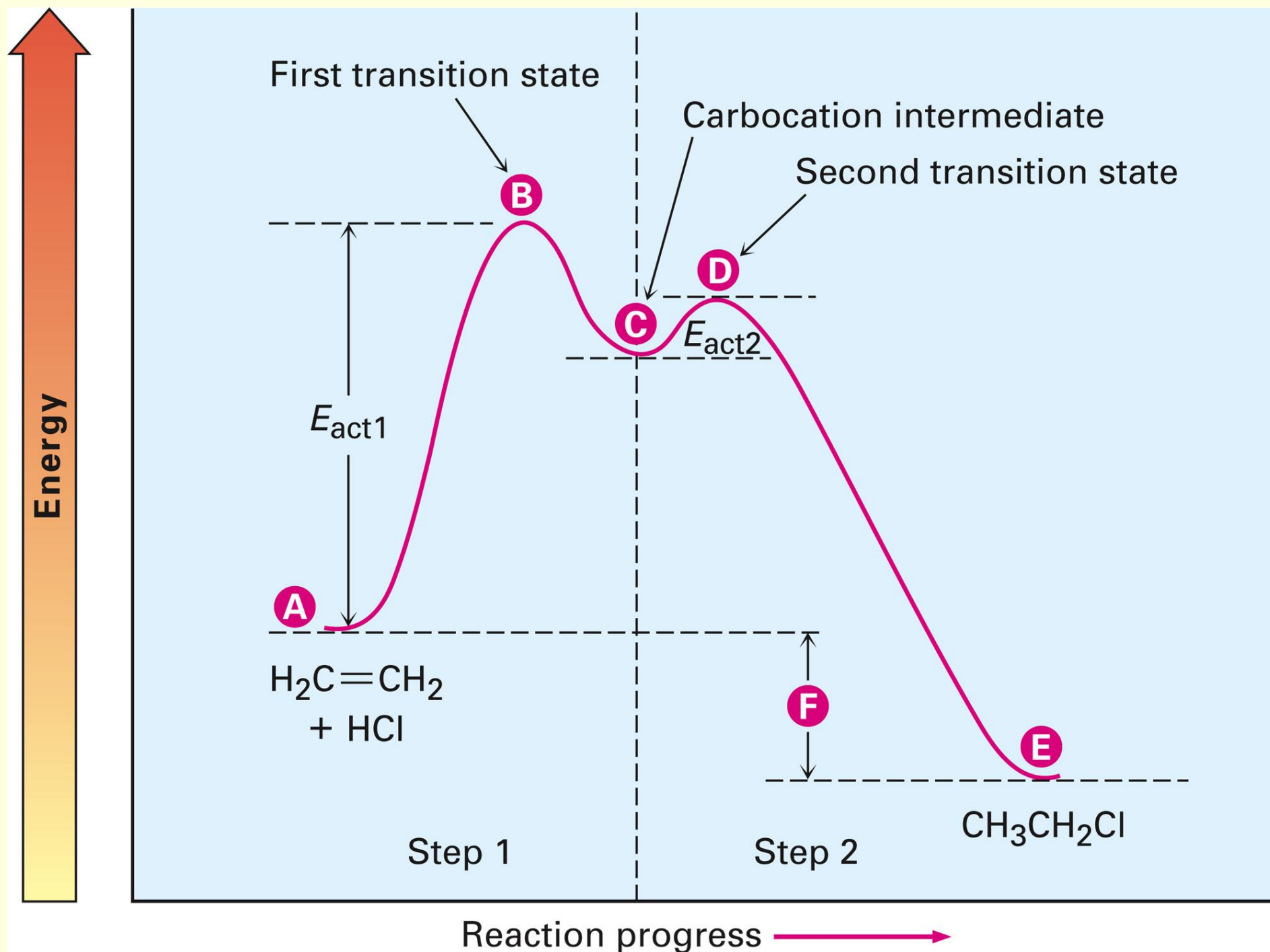


## 3.8 Describing a Reaction: Transition States and Intermediates

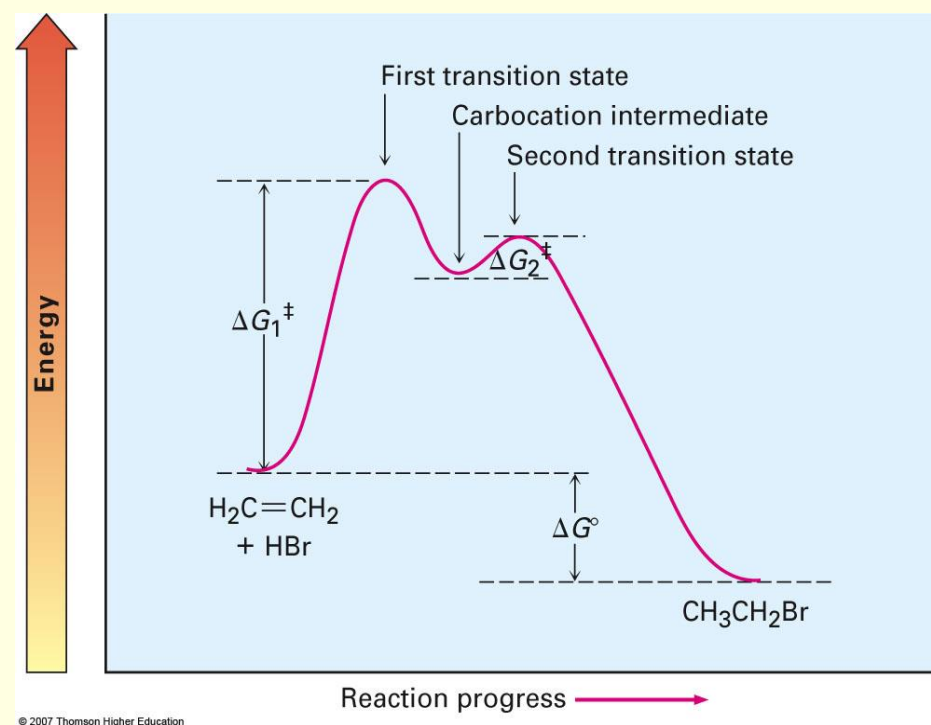
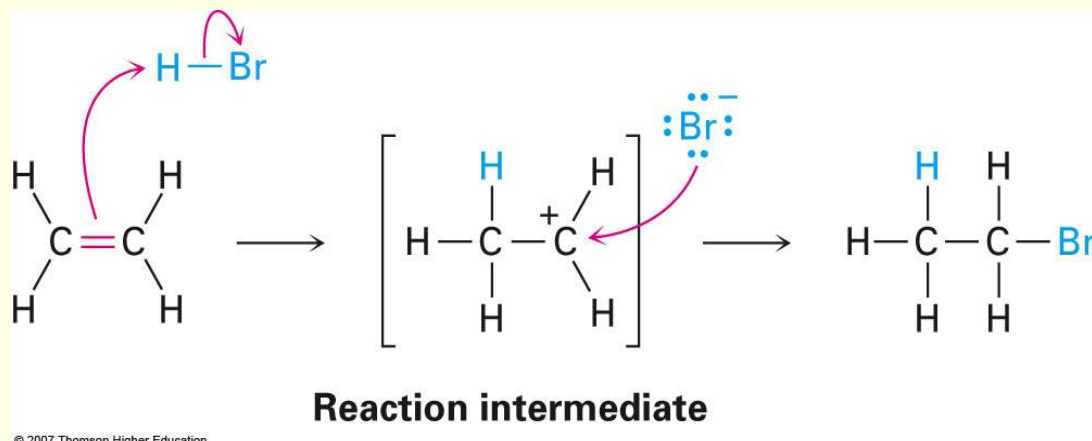


- The highest energy point in a reaction step is called the **transition state**
- The energy needed to go from reactant to transition state is the **activation energy** ( $\Delta G^\ddagger$ )





- If a reaction occurs in more than one step, it must involve species that are neither the reactant nor the final product
- These are called **reaction intermediates** or simply “intermediates”
- Each step has its own free energy of activation
- The complete diagram for the reaction shows the free energy changes associated with an intermediate



## 3.9 Describing a Reaction: Catalysis

Catalyst: a substance that increases the **rate of a chemical transformation**

