

# ORGANIC CHEMISTRY II

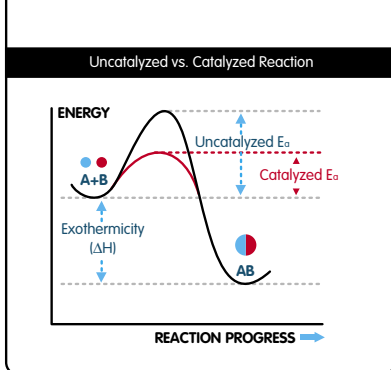
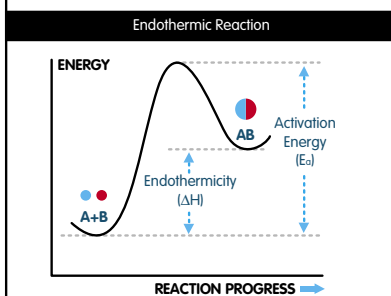
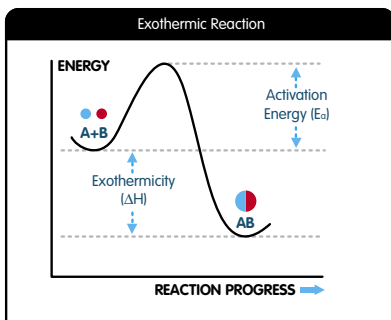
## (ORGANIC CHEMISTRY REACTIONS)

### REACTIONS

#### REACTION COORDINATE DIAGRAM

Plot of energy versus reaction progress

- A. Activation energy ( $E_a$ ):** Energy barrier that reactants must overcome in order to react; energy difference between the reactants and the transition state.
- B. Transition state:** Arrangement of atoms that represents the highest energy point along the path from reactants to products; exists for an infinitesimally short time.
- 1. Hammond postulate:** The transition state in a reaction will more closely resemble whichever species (reactants or products) it is closest to in energy.
- C. Reactive intermediate:** Chemical species that exists in a potential energy well along the path from reactants to products; has a finite lifetime and is more stable than a transition state.



#### INCREASING REACTION RATES

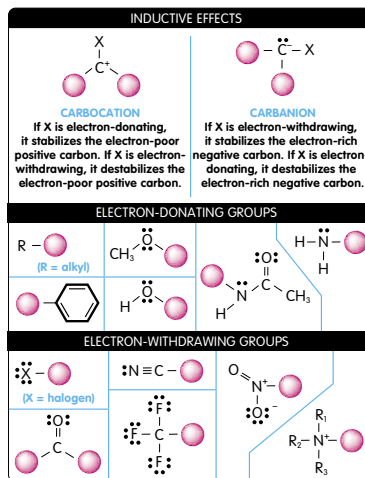
- A. Catalysts:** Substances that increase the rate of a reaction by lowering activation energy, but are not consumed in the reaction; catalysts lower activation energy either by stabilizing the transition state or destabilizing reactants.
- B. Solvent:** The solvent in which a reaction takes place can increase the rate of a reaction either by stabilizing the transition state or destabilizing reactants.
- 1. Protic solvents:** Solvents containing hydrogen atoms not bonded to carbon; can participate in reactions by donating protons.
- 2. Aprotic solvents:** Solvents that do not contain hydrogen atoms or that contain hydrogen atoms bonded to carbon.
- Polar solvents stabilize charged and polar molecules.
  - Nonpolar solvents stabilize nonpolar molecules.

POLAR AND NONPOLAR SOLVENTS	
APROTIC SOLVENTS	PROTIC SOLVENTS
 Dimethyl sulfoxide (DMSO)	 water
 Dimethyl formamide (DMF)	 Formic acid
 Chloroform	 Methanol
 Diethyl ether	 Ethanol
 Benzene	 Acetic acid
 Hexane	

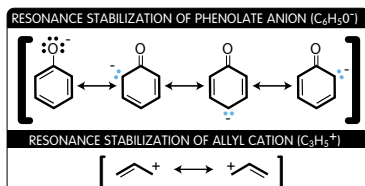
- C. Temperature:** Reaction rates increase with elevating temperature, as additional heat energy can be used to carry reactants over the activation energy barrier.
- D. Light:** Light is often used to initiate radical reactions, as it can induce homolytic cleavage of covalent bonds.

#### TYPES OF REACTIONS

- A. Concerted reaction:** Reactants are converted to products through a single transition state.
- B. Stepwise reaction:** Reactants are converted to products through one or more steps, which involve one or more reactive intermediates.
- 1. Stabilization of reactive intermediates:**
- a. Inductive effects:** Atoms and functional groups within a molecule can "donate" or "withdraw" electron density through  $\sigma$  bonds to compensate for changes caused by formation of the reactive intermediate.



- b. Sterics:** Bulky, functional groups in a molecule can physically hinder intermolecular and intramolecular interactions that would stabilize a reactive intermediate.
- c. Resonance:** Intermediates that have resonance forms are stabilized by the delocalization of charge or radical character.



- 2. Types of reactive intermediates in organic chemistry:**

- a. Carbocation:** Electron-deficient species containing a positively charged carbon atom with three substituents (for a total of six valence electrons); carbocations have trigonal planar geometry and are electrophilic.
- b. Radical:** Electron-deficient species in which an atom has an unpaired electron.

**Factors affecting carbocation and carbon radical stability:**

**Substitution:** Alkyl substituents donate electron density and delocalize positive charge or electron deficiency to stabilize carbocations and carbon radicals; in terms of carbocation stability, tertiary > secondary > primary > methyl.

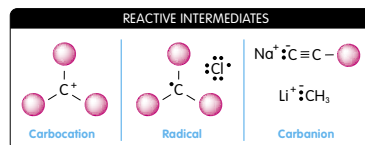
**Resonance:** Stabilizes carbocations and carbon radicals by delocalizing positive charge or electron-deficiency over a larger area.

- c. Carbanion:** Chemical species containing a negatively-charged carbon atom with three substituents plus an unshared electron pair (for a total of eight valence electrons); carbanions are nucleophilic.

**Factors affecting carbanion stability:**

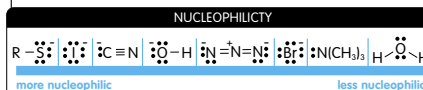
**Hybridization:** Because electrons are closer to the nucleus in s orbitals than in p orbitals, stabilization of carbanions increases as the s character of the orbital holding the unshared electron pair increases; in terms of carbanion stability,  $sp > sp^2 > sp^3$ .

**Resonance:** Stabilizes carbanions by delocalizing negative charge over a larger area.



#### REACTION MECHANISMS

- A. Mechanism:** Way in which bonds are broken and formed during the course of a reaction; reaction mechanisms show movement of electrons and formation of intermediates by which reactants are converted to products.
- B. Curved arrow notation:** Use of curved arrows to indicate the flow of electrons in a reaction mechanism; full-headed arrows denote movement of an electron pair; half-headed arrows denote movement of a single electron.
- Movement of electrons is accompanied by the movement of any atoms or groups associated with those electrons.
- C. Heterolytic cleavage:** Breaking of a covalent bond in which both bonding electrons become associated with one of the atoms involved in the bond.
- D. Heterogenic bond formation:** Formation of a covalent bond in which both bonding electrons are donated by one of the atoms in the bond.
- Nucleophile:** Chemical species that is electron-rich and can donate an electron lone pair to a covalent bond in heterogenic bond formation.
- 1.** Any species carrying an electron lone pair can act as a nucleophile.
- 2.** The nucleophilicity of a species depends on a number of factors, but it follows some general trends.
- a.** There is some correlation between the basicity of a species and its nucleophilicity.
- b.** Nucleophilicity increases moving down a group in the Periodic Table (e.g., Br<sup>-</sup> is more nucleophilic than Cl<sup>-</sup>, and HS<sup>-</sup> is more nucleophilic than HO<sup>-</sup>).

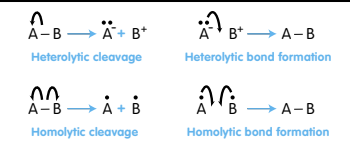


**Electrophile:** Chemical species that is electron-poor and can accept an electron lone pair from a nucleophile in heterogenic bond formation.

- E. Polar reactions:** Reactions whose mechanisms involve heterolytic cleavage and heterogenic bond formation.
- F. Homolytic cleavage:** Breaking of a covalent bond in which both atoms involved in the bond receive one bonding electron.
- G. Homogenic bond formation:** Formation of a covalent bond in which each bonding atom donates one electron to the bond.
- H. Nonpolar reactions:** Reactions whose mechanisms involve homolytic cleavage and/or homogenic bond formation.

## REACTIONS (CONTINTUED)

### HETEROLYTIC AND HOMOLYTIC CLEAVAGE AND BOND FORMATION



## ACIDS AND BASES IN ORGANIC REACTIONS

### A. Definitions of Acids and Bases

#### Arrhenius

Acids: Compounds that produce  $H_3O^+$  in water

Bases: Compounds that produce  $OH^-$  in water

#### Lewis

Acids: Electron-pair acceptors

Bases: Electron-pair donors

#### Bronsted-Lowry

Acids: Proton ( $H^+$ ) donors

Bases: Proton ( $H^+$ ) acceptors

**B. Conjugate acid:** For a base 'B-', its protonated form 'HB' is said to be the "conjugate acid" of 'B-'.

**C. Conjugate base:** For an acid 'HA', its deprotonated form 'A-' is said to be the "conjugate base" of 'HA'.

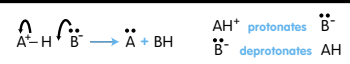
**D. Protonation:** Formation of a covalent bond between a proton ( $H^+$ ) donated by a Bronsted-Lowry acid and an atom that either has an unshared electron pair or is participating in a  $\pi$  bond.

- Protonation is favored if the compound donating the proton is a stronger acid than the compound that would be formed by protonation.

**E. Deprotonation:** Removal of a proton ( $H^+$ ) from a molecule by a Bronsted-Lowry base.

- Deprotonation is favored if the compound removing the proton is a stronger base than the compound that would be formed by deprotonation.

### PROTONATION AND DEPROTONATION



## SUBSTITUTION REACTIONS AND MECHANISMS

**A. Substitution reaction:** Reaction in which a reactant molecule has one of its functional groups replaced by a functional group from another reactant molecule.

- Leaving group:** Functional group that is replaced in a substitution reaction; in organic substitution reactions, good leaving groups make weak bonds with carbon and can readily accept the electrons they receive from heterolytic cleavage of their bond with carbon.

### LEAVING GROUPS



**B.  $S_N1$  reaction:** Stepwise substitution reaction that proceeds through a carbocation intermediate.

**Step 1:** One reactant is converted to a carbocation by the loss of a leaving group; Step 1 is the slow step in an  $S_N1$  reaction, and its speed determines the overall reaction rate.

**Step 2:** A nucleophile bonds to the positively charged carbon atom on the carbocation.

#### Stereochemistry of $S_N1$ reactions

When a chiral center results from an  $S_N1$  reaction, the S and R forms of the chiral center are formed in a 50:50 mixture called a racemic mixture. A racemic mixture is formed because the nucleophile can add to either side of the carbocation intermediate.

#### Factors influencing $S_N1$ reaction rates

**Carbocation stability:** The more substituted the carbocation intermediate of an  $S_N1$  reaction is, the more stable it is, and the faster the reaction proceeds; likewise, the more resonance-stabilized the carbocation intermediate of an  $S_N1$  reaction is, the faster the reaction proceeds.

- Because of carbocation stability considerations,  $S_N1$  reactions generally occur only when the carbocation intermediate is tertiary (or in some cases secondary) or resonance-stabilized.

**Leaving group:** The better the leaving group on an  $S_N1$  reactant, the lower the activation energy for Step 1, and the faster the reaction.

**Solvent polarity:** Polar solvents stabilize charge; the more polar the solvent in which the reaction takes place, the more stable the carbocation intermediate, and the faster the reaction.

**C.  $S_N2$  reaction:** A concerted substitution reaction in which a nucleophile bonds to a carbon atom and displaces another substituent on that carbon atom.

- In an  $S_N2$  reaction, the nucleophile approaches the target carbon atom from the side of the molecule that is opposite the substituent it displaces; this type of approach is known as back-side attack.

#### Stereochemistry of $S_N2$ reactions

Back-side attack leads to inversion of the stereochemical configuration at the attacked carbon atom.

#### Factors influencing $S_N2$ reaction rates

**Sterics:** The larger the substituents bonded to the target carbon in an  $S_N2$  reaction, the more difficult it is for the nucleophile to approach the target carbon and start bonding to it to displace the leaving group; as a result, the more substituted the target carbon, the slower the reaction.

- Because of steric considerations,  $S_N2$  reactions generally only occur at methyl or primary (or sometimes secondary) carbon atoms.

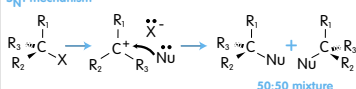
**Nucleophilicity:** The stronger the nucleophile in an  $S_N2$  reaction, the lower the activation energy for the reaction, and the faster the reaction.

**Leaving group:** The better the leaving group on an  $S_N2$  reactant, the lower the activation energy for the reaction, and the faster the reaction.

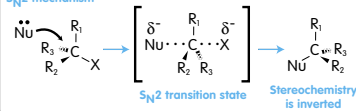
**Solvent polarity:** Polar solvents stabilize charge; if the reactant nucleophile is uncharged, then only the charged transition state is stabilized by polar solvent, so activation energy decreases and reaction rate increases with increasing solvent polarity; if the reactant nucleophile is charged, then it is stabilized by polar solvent more so than the charged transition state, so activation energy increases and reaction rate decreases with increasing solvent polarity.

### NUCLEOPHILIC SUBSTITUTION REACTION MECHANISMS

#### $S_N1$ mechanism



#### $S_N2$ mechanism

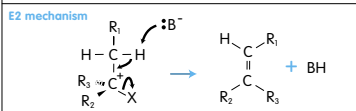
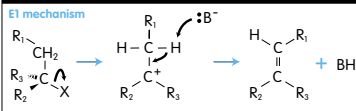


$S_N1$  reactions occur with a loss of stereochemistry (because the reactant goes through a planar intermediate), while  $S_N2$  reactions occur with inversion of stereochemistry.

## ELIMINATION REACTIONS AND MECHANISMS

**A. Elimination reaction:** Reaction in which one reactant molecule decomposes into two smaller products that contain all the atoms of the original reactant.

### ELIMINATION REACTION MECHANISMS



**B. E1 reaction:** Stepwise elimination reaction that proceeds through a carbocation intermediate.

- Step 1:** A reactant is converted to a carbocation by loss of a leaving group; Step 1 is the slow step in an E1 reaction, and its speed determines the overall reaction rate.

- Step 2:** A carbon atom adjacent to the carbocation's positively charged carbon atom is deprotonated by base,

and the electrons from this broken C-H bond are used to form a  $\pi$ -bond to the positively charged carbon atom.

**C. E2 reaction:** Concerted elimination reaction in which one carbon atom loses a hydrogen atom to base, the electrons from this broken C-H bond are used to form a  $\pi$ -bond from the deprotonated carbon to an adjacent carbon atom, and this adjacent carbon atom loses a leaving group simultaneously.

## ADDITION REACTIONS AND MECHANISMS

**A. Addition reaction:** Reaction in which two reactant molecules join to give a product that contains all the atoms of the original reactants.

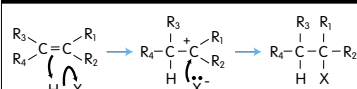
#### Orientation of addition reactions

- Syn addition:** Two groups add to the same side of a multiple bond in an addition reaction.
- Anti addition:** Two groups add to opposite sides of a multiple bond in an addition reaction.
- Markovnikov addition:** A compound HX adds to a multiple bond such that X bonds to the more substituted carbon.
- Anti-Markovnikov addition:** A compound HX adds to a multiple bond such that X bonds to the less substituted carbon.

**B. Electrophilic addition reaction:** Stepwise reaction in which an electrophile and a nucleophile add to the carbon atoms participating in a double bond to give a saturated product.

- Step 1:** An electrophile adds to one carbon atom participating in a double bond to give a carbocation intermediate.
- Step 2:** A nucleophile bonds to the positively charged carbon atom on the carbocation.

### ELECTROPHILIC ADDITION MECHANISM



H adds to the double bond to generate the most stable carbocation

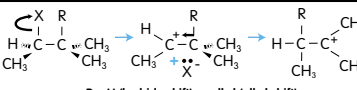
## REARRANGEMENT REACTIONS AND MECHANISMS

**A. Rearrangement:** Reaction in which connectivity of atoms or groups in a molecule is altered by the movement of atoms or groups within the molecule.

**B. Hydrogen shift:** Rearrangement in which a hydrogen atom moves from one carbon atom to an adjacent carbon atom; occurs in carbocations when a more stable carbocation results from the shift.

**C. Alkyl shift:** Rearrangement in which an alkyl group moves from one carbon atom to an adjacent carbon atom; occurs in carbocations when a more stable carbocation results from the shift.

### SHIFT REACTION MECHANISM



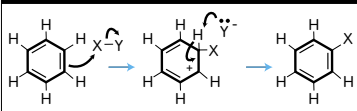
R = H (hydride shift) or alkyl (alkyl shift)  
Mechanisms for hydride and methyl shift rearrangement reactions. Hydride and methyl shifts lead to the conversion of a carbocation to a more stable carbocation.

## AROMATIC SUBSTITUTION REACTIONS

**A. Electrophilic Aromatic Substitution:** Stepwise reaction in which an electrophile replaces a hydrogen atom on an aromatic ring.

- Step 1:** An electrophile adds to one of the carbon atoms in an aromatic ring to yield a resonance-stabilized carbocation intermediate.
- Step 2:** The carbon atom to which the electrophile has been added (i.e., the one adjacent to the positively charged carbon atom) loses a hydrogen atom to base, and the electrons from this broken C-H bond are used to form a  $\pi$ -bond to the positively charged carbon atom.

### ELECTROPHILIC AROMATIC SUBSTITUTION MECHANISM

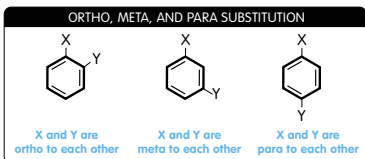


Mechanism for electrophilic aromatic substitution to replace a hydrogen atom on a benzene ring with another substituent.

# REACTIONS (CONTINUED)

## Orientation of electrophilic aromatic substitution reactions

- In electrophilic aromatic substitution reactions involving a substituted benzene ring, the electrophile can add to a benzene ring in one of three distinct ways (**ortho**, **meta**, or **para**) relative to a substituent already on the ring.

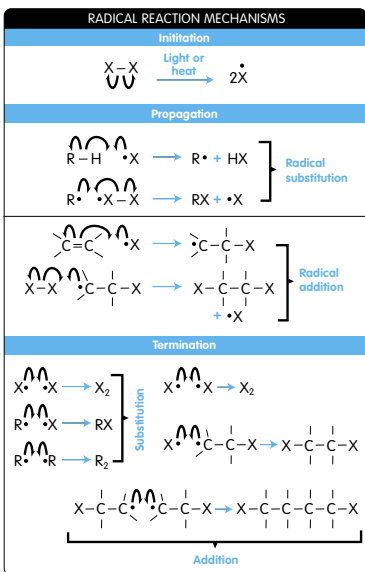


## RADICAL REACTIONS

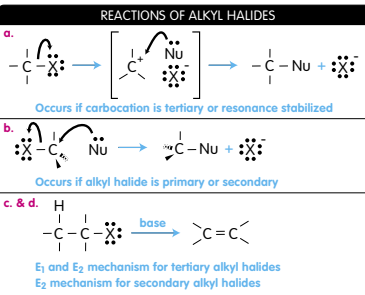
**A. Chain reaction:** Type of reaction in which one reaction cycle generates a product that is consumed in the next reaction cycle; radical reactions generally occur via a chain reaction mechanism.

### Radical reactions occur in three steps

- Initiation:** Light or heat is used to induce homolytic bond cleavage to produce two radical species.
  - Propagation:** A radical from the initiation step reacts with a neutral reactant molecule to generate another radical; this radical reacts with another neutral reactant molecule to generate the final reaction product plus another radical that can be used to start the next propagation step.
  - Termination:** Two radicals from the propagation step bond to each other to yield a neutral atom. No radical species is formed to start the next propagation step.
- B. Radical addition:** Reaction in which a radical species forms a bond to an unsaturated carbon atom.
- C. Radical substitution:** Reaction in which a radical species replaces a substituent on a carbon atom.



## CLASSES OF ORGANIC MOLECULES AND THEIR REACTIONS



### A. Alkyl halides

#### Reactive characteristics of alkyl halides

- Because halogens are more electronegative than carbon, the carbon atom in a carbon-halogen bond is electron-poor.

### Reactions involving alkyl halides

- S<sub>N</sub>1 reaction with a nucleophile displacing the halogen atom
- S<sub>N</sub>2 reaction with a nucleophile displacing the halogen atom
- E1 reaction with a base to form the most substituted alkene possible
- E2 reaction with a base to form the most substituted alkene possible

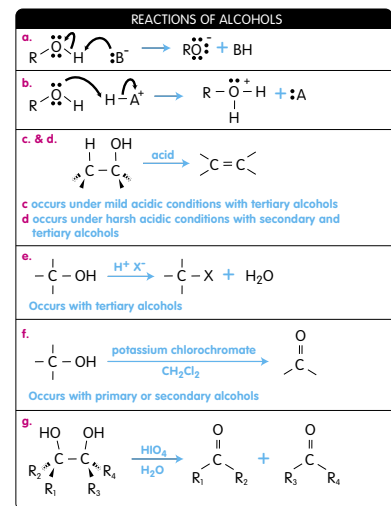
### B. Alcohols

#### Reactive characteristics of alcohols

- Because oxygen is somewhat more electronegative than carbon, the carbon atom in a carbon-oxygen bond is somewhat electron-poor.
- Alcohols are weakly acidic and weakly basic. They can be protonated by strong acids to yield oxonium ion (ROH<sub>2</sub><sup>+</sup>) or deprotonated by strong bases to yield alkoxide ion (RO<sup>-</sup>).

#### Reactions involving alcohols

- Deprotonation by strong bases to form alkoxide ion
- Protonation by strong acids to form oxonium ion
- Acid-catalyzed dehydration of tertiary alcohols (E1 mechanism)
- Acid-catalyzed dehydration of tertiary alcohols (E2 mechanism)
- Acid-catalyzed conversion of tertiary alcohols to alkyl halides (S<sub>N</sub>1 mechanism)
- Oxidation of primary and secondary alcohols to yield carbonyls
- Cleavage of the carbon-carbon bond in a 1,2-diol to yield two carbonyl compounds



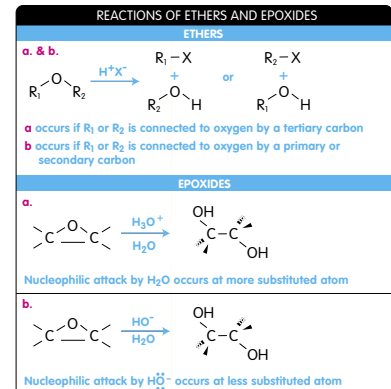
### C. Ethers and epoxides

#### Reactive characteristics of ethers and epoxides

- Because oxygen is somewhat more electronegative than carbon, the carbon atom in a carbon-oxygen bond is somewhat electron-poor.
- Ethers are weakly basic. The oxygen atom in an ether can be protonated by strong acids.
- Because of their large amount of ring strain, epoxides are highly reactive and can undergo nucleophilic attack at an electrophilic carbon to open the epoxide ring.

#### Reactions involving ethers

- Acid-catalyzed cleavage of tertiary ethers (S<sub>N</sub>1 mechanism)
- Acid-catalyzed cleavage of primary and secondary ethers (S<sub>N</sub>2 mechanism)



### Reactions involving epoxides

- Acid-catalyzed ring opening (S<sub>N</sub>1 mechanism)
- Base-catalyzed ring opening (S<sub>N</sub>2 mechanism)

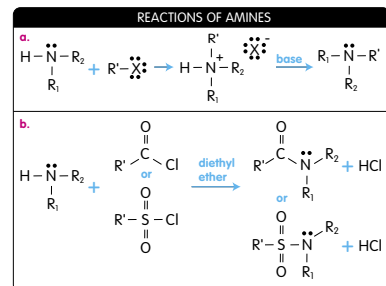
### D. Amines

#### Reactive characteristics of amines

- Amines are basic and nucleophilic because of the lone pair of electrons on nitrogen.

#### Reactions involving amines

- Alkylation of amines by alkyl halides (S<sub>N</sub>2 mechanism)
- Nucleophilic attack on an acid chloride/sulfonyl chloride (S<sub>N</sub>2 mechanism)



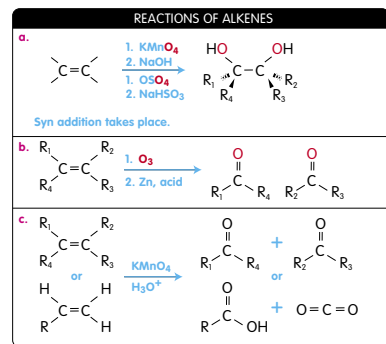
### E. Alkenes

#### Reactive characteristics of alkenes

- Because carbon-carbon double bonds are electron-rich, alkenes can act as nucleophiles and donate electrons to electrophiles.

#### Reactions involving alkenes

- Addition of a hydroxyl group to each carbon in a double bond by treatment with KMnO<sub>4</sub> or OsO<sub>4</sub> and NaHSO<sub>3</sub>
- Cleavage of alkenes by treatment with ozone (O<sub>3</sub>) followed by zinc in acetic acid
- Cleavage of alkenes by KMnO<sub>4</sub> in neutral or acidic solution



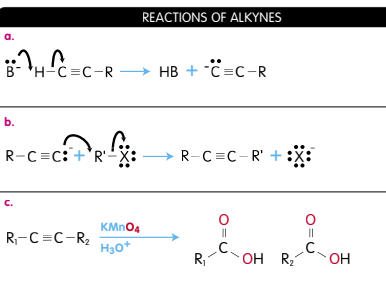
### F. Alkynes

#### Reactive characteristics of alkynes

- Because carbon-carbon double bonds are electron-rich, alkenes can act as nucleophiles and donate electrons to electrophiles.
- Terminal alkynes (i.e., alkynes in which a triple-bonded carbon is also bonded to a hydrogen atom) are weakly acidic and can be deprotonated by strong bases to yield acetylide anion (RCC<sup>-</sup>).

#### Reactions involving alkynes

- Deprotonation of a terminal alkyne by strong base (:B<sup>-</sup>)
- Alkylation of acetylide by alkyl halides (S<sub>N</sub>2 mechanism)
- Cleavage of alkynes by O<sub>3</sub> or KMnO<sub>4</sub> in neutral or acidic solution



#### Reactions common to alkenes and alkynes

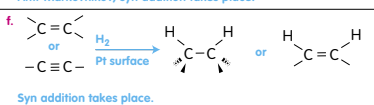
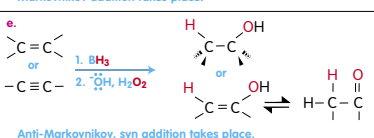
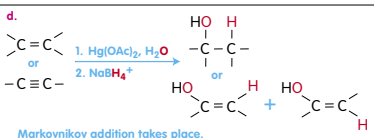
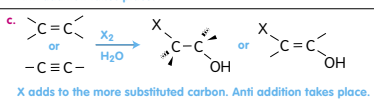
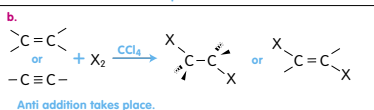
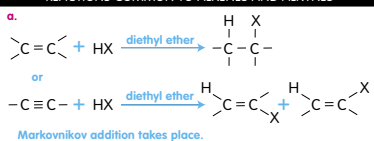
- Electrophilic addition of HX (X = halogen) across a double or triple bond
- Addition of Cl<sub>2</sub> or Br<sub>2</sub> across a double or triple bond via

# REACTIONS (CONTINUED)

nucleophilic attack on a cationic three-membered ring intermediate ( $S_N2$  mechanism)

- Addition of Cl or Br and a hydroxide group across a double or triple bond via nucleophilic attack on a cationic three-membered ring intermediate ( $S_N2$  mechanism)
- Addition of water across a double or triple bond via nucleophilic attack on an organomercury intermediate ( $S_N2$  mechanism)
- Hydroboration-oxidation of a double or triple bond
- Platinum-catalyzed hydrogenation of a double or triple bond

## REACTIONS COMMON TO ALKENES AND ALKYNES

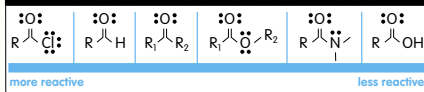


## G. Carbonyls

### Reactive characteristics of carbonyls

- The  $\pi$  bond between carbon and oxygen in a carbonyl is weaker than a  $\sigma$  bond, and more of the electron density from the  $\pi$  bond is associated with the more electronegative oxygen atom. As a result, the carbon atom is electron-poor and can undergo nucleophilic attack.
- Because the carbonyl carbon is electron-poor, groups bonded to the carbonyl carbon atom make the carbonyl more reactive if they are electron withdrawing, and less reactive if they are electron-donating.

### RELATIVE CARBONYL REACTIVITY TO ATTACK BY A NUCLEOPHILE



### Reactions involving aldehydes and ketones

- Nucleophilic attack by hydride ion or a carbanion
- Nucleophilic attack by HCN
- Acid-catalyzed nucleophilic attack by a primary amine
- Acid-catalyzed nucleophilic attack by a secondary amine
- Acid-catalyzed nucleophilic attack by alcohols or thiols
- Addition of a phosphorus ylide
- Nucleophilic attack by HCN/amine/carbanion to the  $\beta$  carbon of an  $\alpha,\beta$ -unsaturated aldehyde or ketone

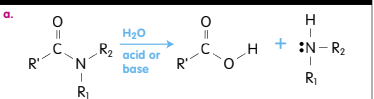
### Reactions involving carboxylic acids

- Deprotonation by base ( $B^-$ )
- Nucleophilic attack by hydride ion
- Acid-catalyzed nucleophilic attack by an alcohol
- Treatment with thionyl chloride ( $SOCl_2$ ) to yield an acid chloride

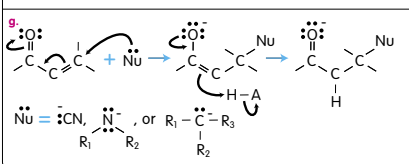
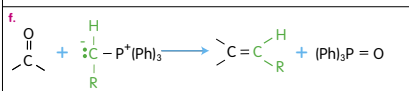
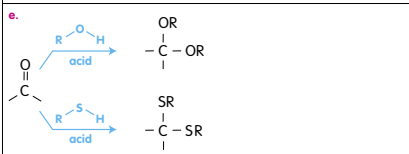
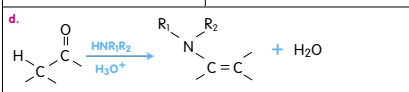
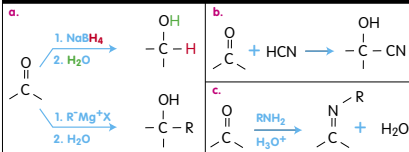
### Reactions involving amides

- Acid or base-catalyzed nucleophilic attack by water

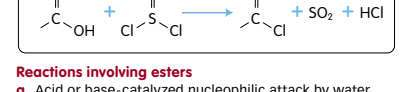
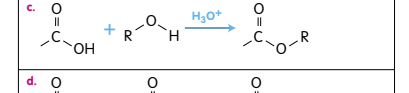
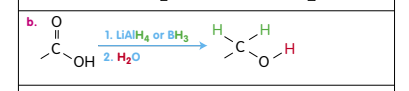
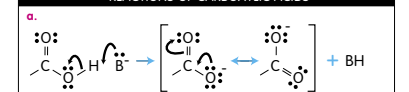
### REACTIONS OF AMIDES



## REACTIONS OF ALDEHYDES AND KETONES



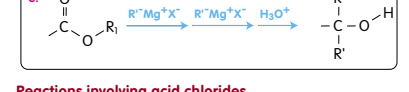
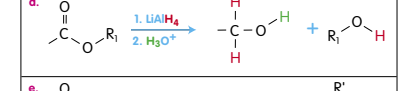
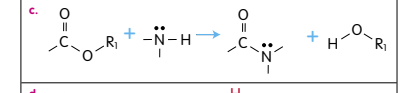
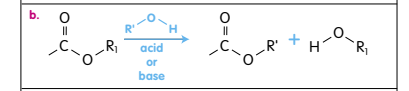
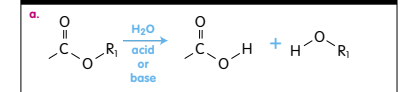
## REACTIONS OF CARBOXYLIC ACIDS



### Reactions involving esters

- Acid or base-catalyzed nucleophilic attack by water
- Acid or base-catalyzed nucleophilic attack by an alcohol
- Nucleophilic attack by an amine
- Nucleophilic attack by hydride ion
- Nucleophilic attack by a carbanion

## REACTIONS OF ESTERS



### Reactions involving acid chlorides

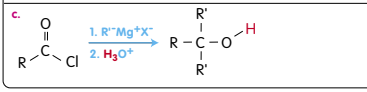
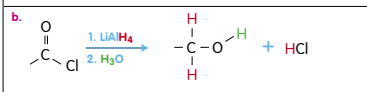
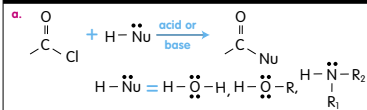
- Nucleophilic attack by an alcohol or amine
- Nucleophilic attack by hydride ion
- Nucleophilic attack by a carbanion

## H. Aromatic molecules

### Reactions involving aromatic molecules

- Halogenation

## REACTIONS OF ACID CHLORIDES



## b. Nitration

### Reactions involving nitrated aromatic systems

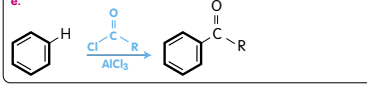
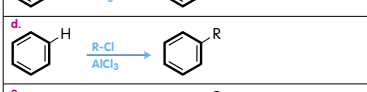
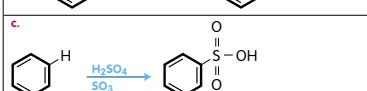
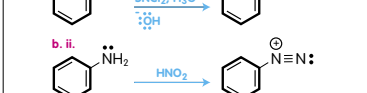
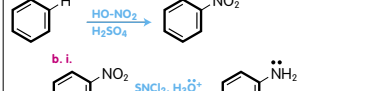
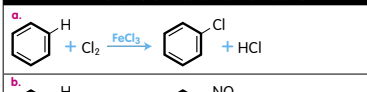
- Reduction to primary amines
- Diazotization followed by addition to another aromatic system or conversion to other functional groups

## c. Sulfonation

## d. Alkylation

## e. Acylation

## REACTIONS OF AROMATIC MOLECULES



### Effect of substituents on reactivity and regiochemistry in aromatic substitution reactions

- A substituent on an aromatic ring can either activate or deactivate the ring toward aromatic substitution; electron-donating substituents activate an aromatic ring by stabilizing the reaction's carbocation intermediate, while electron-withdrawing substituents deactivate an aromatic ring by destabilizing the reaction's carbocation intermediate.
- A substituent on an aromatic ring can direct a substitution reaction to occur either meta to itself, or both ortho and para to itself; whether a substituent is meta or ortho/para directing depends on how it affects the relative stabilities of the carbocation intermediates leading to meta and ortho/para substitution.

### ACTIVATING/DEACTIVATING ORTHO/META/PARA DIRECTORS

