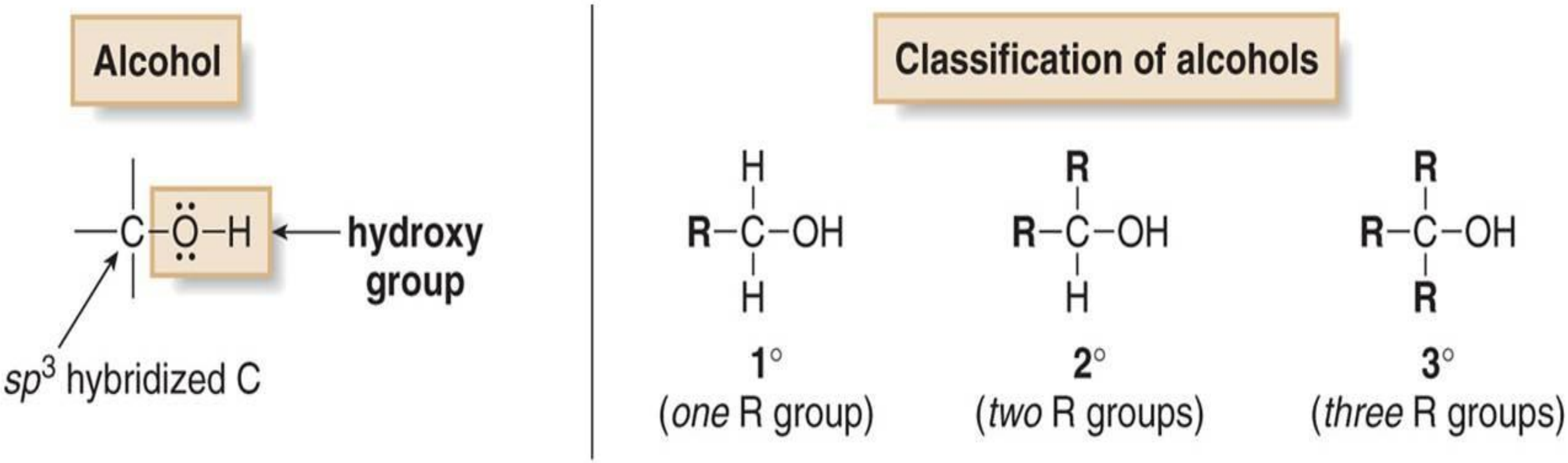
Organic Chemistry

Alcohols, Ethers, and Epoxides

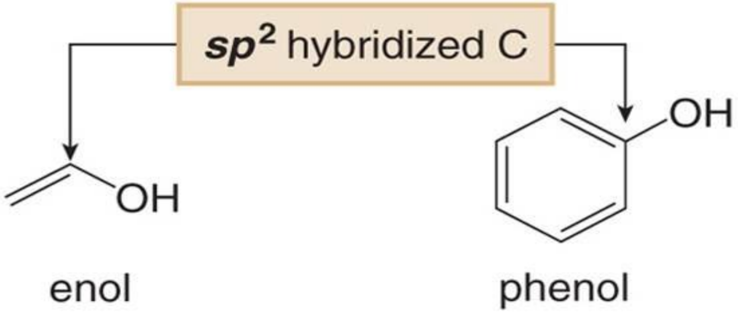
Alcohols—Structure and Bonding

- **Alcohols** contain a hydroxy group (OH) bonded to an *sp*^{3} hybridized carbon.
- They are classified according to the number of alkyl groups attached to carbon bearing the OH.

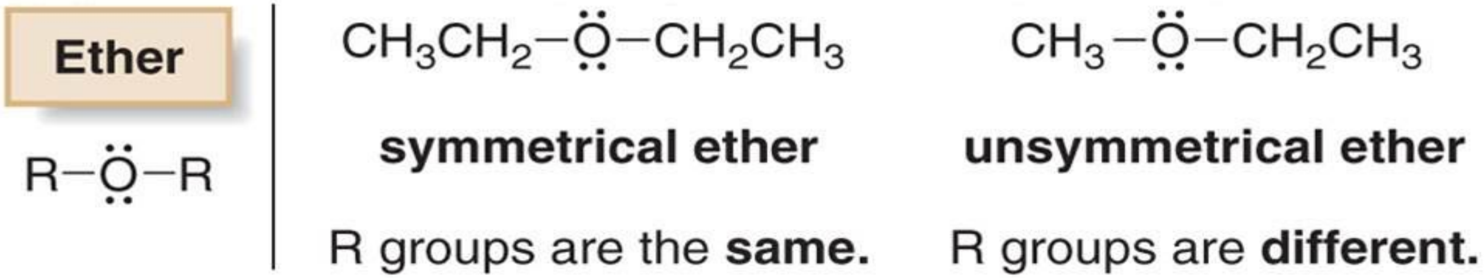


Enols, Phenols, and Ethers

- **Compounds having a hydroxy group on a *sp*^{2} hybridized carbon—enols and phenols—undergo different reactions than alcohols.**



- **Ethers have two alkyl groups bonded to an oxygen atom.**



Ether

$R-\ddot{\underset{..}{O}}-R$

$CH_3CH_2-\ddot{\underset{..}{O}}-CH_2CH_3$

symmetrical ether

R groups are the **same.**

$CH_3-\ddot{\underset{..}{O}}-CH_2CH_3$

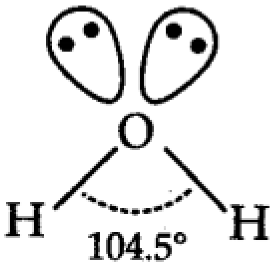
unsymmetrical ether

R groups are **different.**

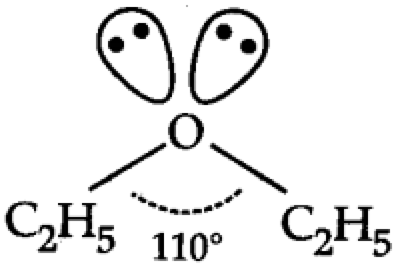
Epoxides

- **Epoxides** are ethers having the oxygen atom in a three-membered ring.

- **Epoxides** are also called **oxiranes**.



Water



Diethyl ether

epoxide or oxirane

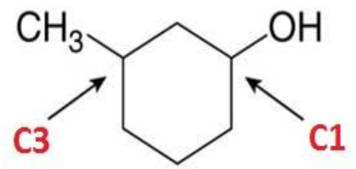
- The C-O-C bond angle for an epoxide must be 60°, a considerable deviation from the tetrahedral bond angle of 109.5°.

- Thus, **epoxides** have angle strain, making them more reactive than other ethers.

- Nucleophiles attack the electrophilic C of the C-O bond causing it to break, resulting in ring opening. **Epoxides** can react with a large range of nucleophiles.

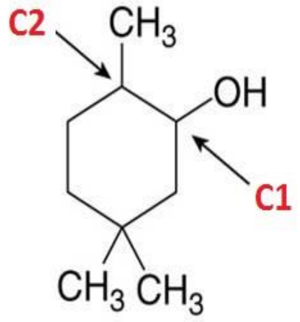
Naming Alcohols Attached to Rings

- **When an OH group is bonded to a ring, the ring is numbered beginning with the OH group.**
- **Because the functional group is at C1, the 1 is usually omitted from the name.**
- **The ring is then numbered in a clockwise or counterclockwise fashion to give the next substituent the lowest number.**



3-methylcyclohexanol

[The OH group is at C1; the second substituent (CH_3) gets the lower number.]

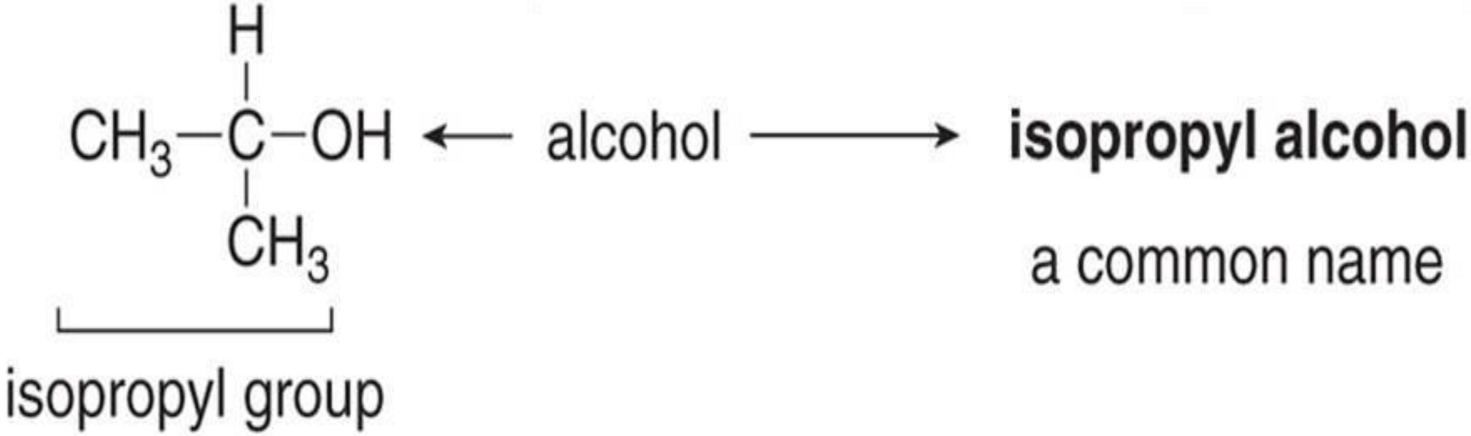


2,5,5-trimethylcyclohexanol

[The OH group is at C1; the second substituent (CH_3) gets the lower number.]

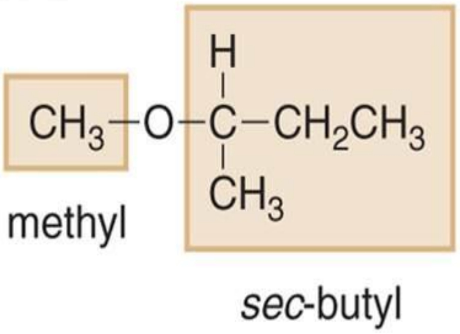
Common Names of Alcohols

- **Common names are often used for simple alcohols. To assign a common name:**
  - **Name all the carbon atoms of the molecule as a single alkyl group.**
  - **Add the word alcohol, separating the words with a space.**



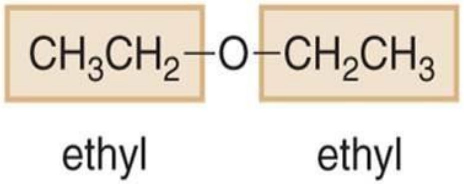
Naming Ethers

- **Simple ethers are usually assigned common names. To do so:**
  - **Name both alkyl groups bonded to the oxygen, arrange these names alphabetically, and add the word ether.**
  - **For symmetrical ethers, name the alkyl group and add the prefix “di-”.**

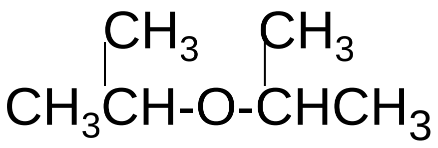


***sec*-butyl methyl ether**

[Alphabetize the **b** of **butyl** before the **m** of **methyl**.]



diethyl ether

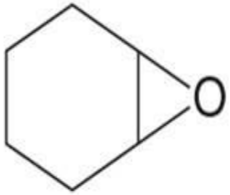


$$\begin{array}{c} CH_3CH_3 \\ || \\ CH_3CH\text{-}O\text{-}CHCH_3 \end{array}$$

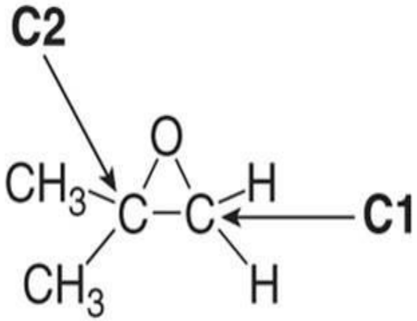
diisopropyl ether

Naming Epoxides

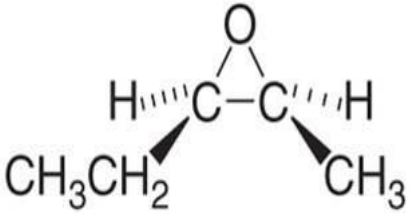
- Epoxides can be named in three different ways—epoxyalkanes, oxiranes, or alkene oxides.
- To name an epoxide as an epoxyalkane, first name the alkane chain or ring to which the O atom is attached, and use the prefix "epoxy" to name the epoxide as a substituent.
- Use two numbers to designate the location of the atoms to which the O is bonded.



1,2-epoxycyclohexane



1,2-epoxy-2-methylpropane



cis-2,3-epoxypentane

Physical Properties

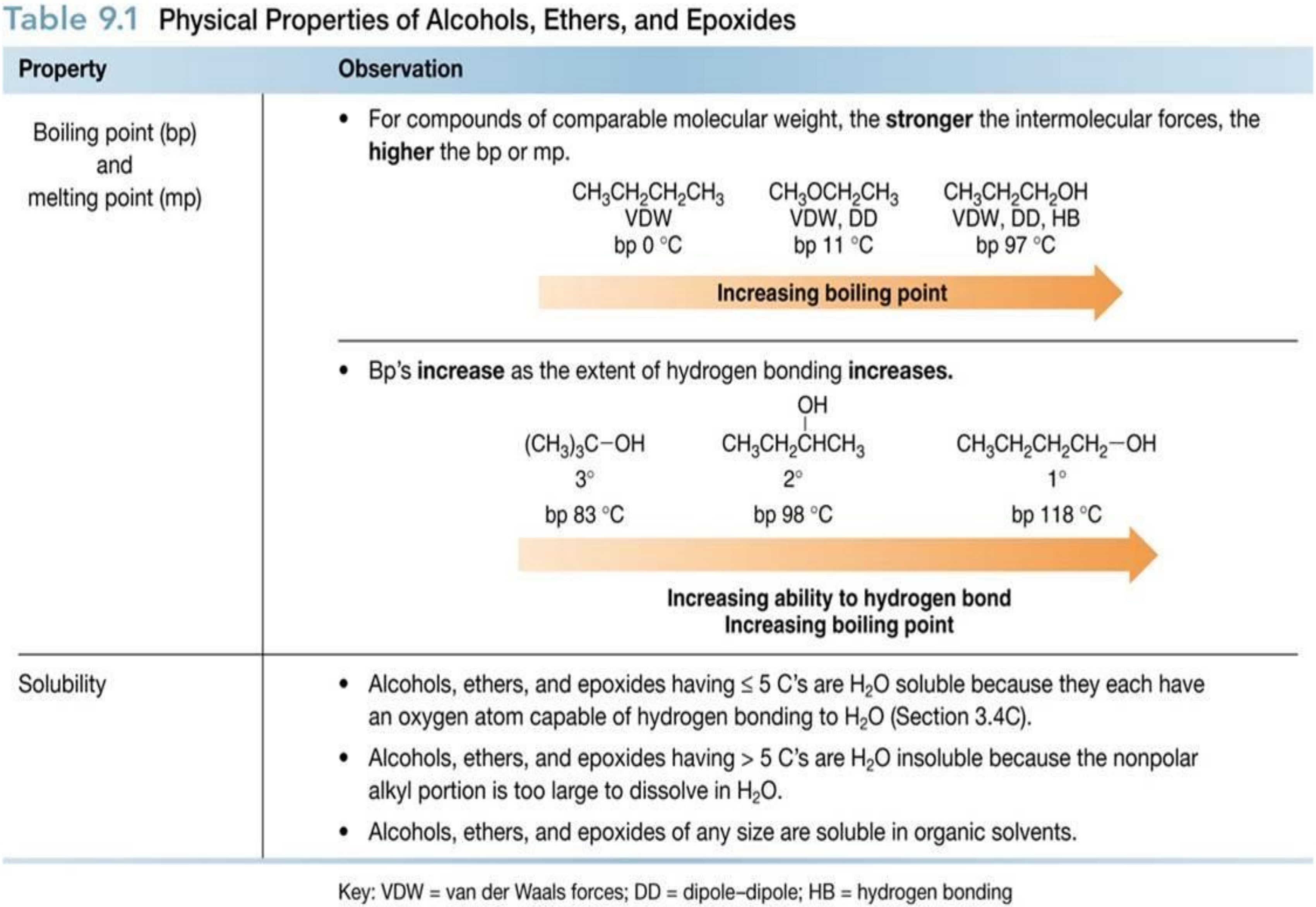


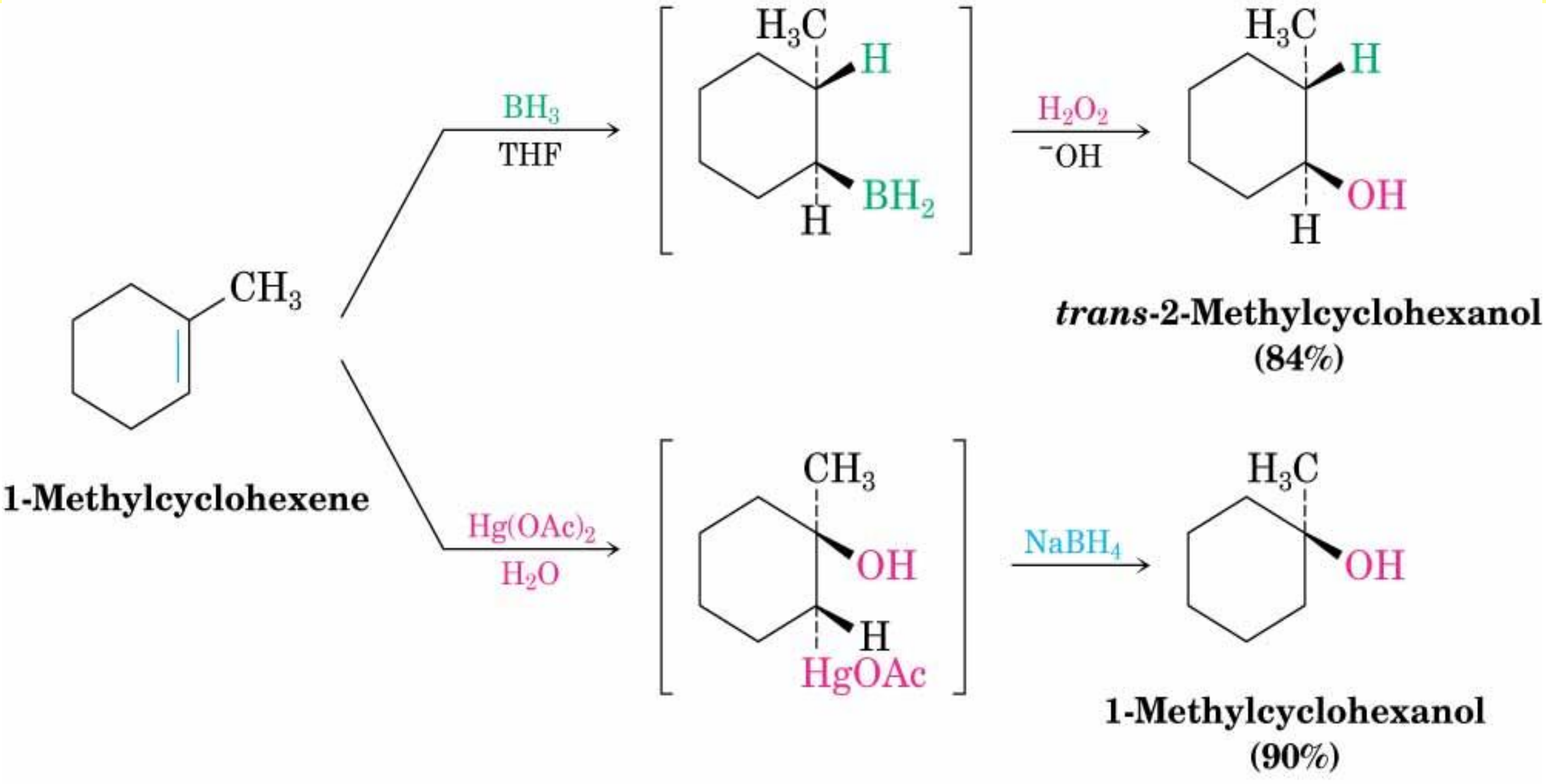
Table 9.1 Physical Properties of Alcohols, Ethers, and Epoxides

Property	**Observation**
Boiling point (bp) and melting point (mp)	• For compounds of comparable molecular weight, the **stronger** the intermolecular forces, the **higher** the bp or mp. $CH_3CH_2CH_2CH_3$ VDW bp 0 °C $CH_3OCH_2CH_3$ VDW, DD bp 11 °C $CH_3CH_2CH_2OH$ VDW, DD, HB bp 97 °C **Increasing boiling point**
	• Bp's **increase** as the extent of hydrogen bonding **increases.** $(CH_3)_3C{-}OH$ 3° bp 83 °C $CH_3CH_2\overset{OH}{\overset{\vert}{C}}HCH_3$ 2° bp 98 °C $CH_3CH_2CH_2CH_2{-}OH$ 1° bp 118 °C **Increasing ability to hydrogen bond** **Increasing boiling point**
Solubility	• Alcohols, ethers, and epoxides having ≤ 5 C's are H_2O soluble because they each have an oxygen atom capable of hydrogen bonding to H_2O (Section 3.4C). • Alcohols, ethers, and epoxides having > 5 C's are H_2O insoluble because the nonpolar alkyl portion is too large to dissolve in H_2O. • Alcohols, ethers, and epoxides of any size are soluble in organic solvents.

Key: VDW = van der Waals forces; DD = dipole–dipole; HB = hydrogen bonding

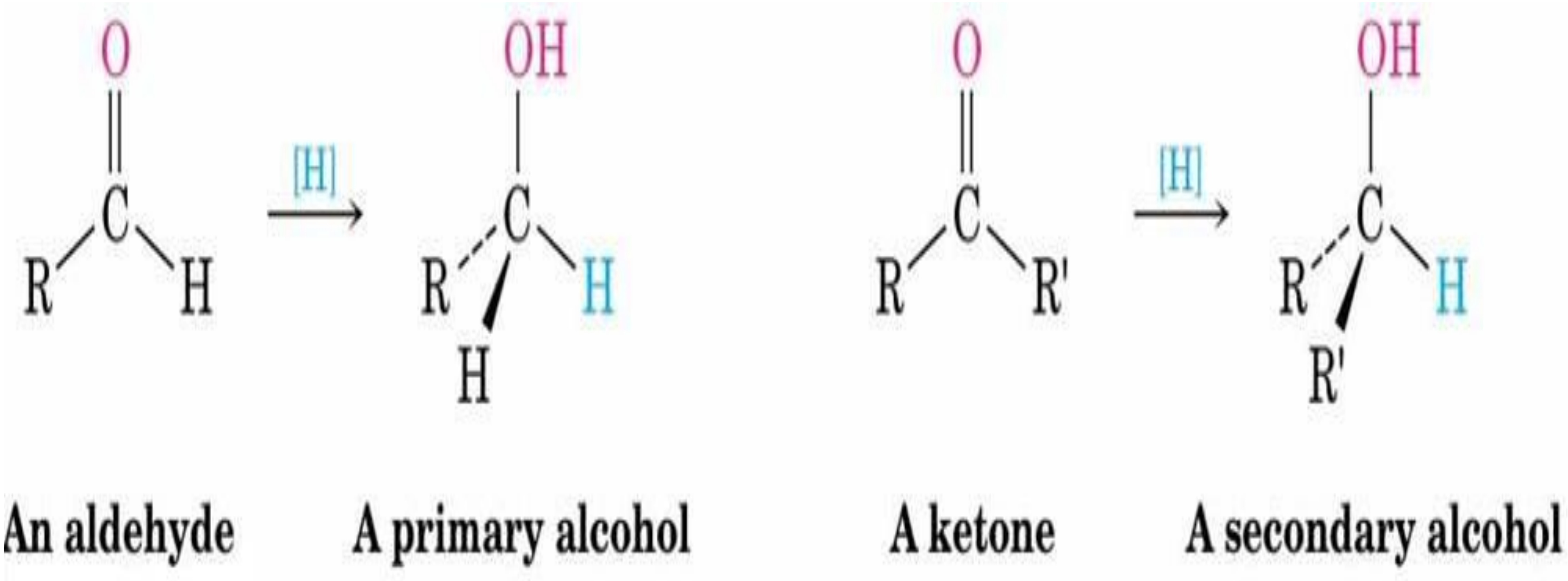
Preparation of Alcohols by Regiospecific Hydration of Alkenes

- **Hydroboration/oxidation: *syn*, non-Markovnikov hydration**
- **Oxymercuration/reduction: Markovnikov hydration**



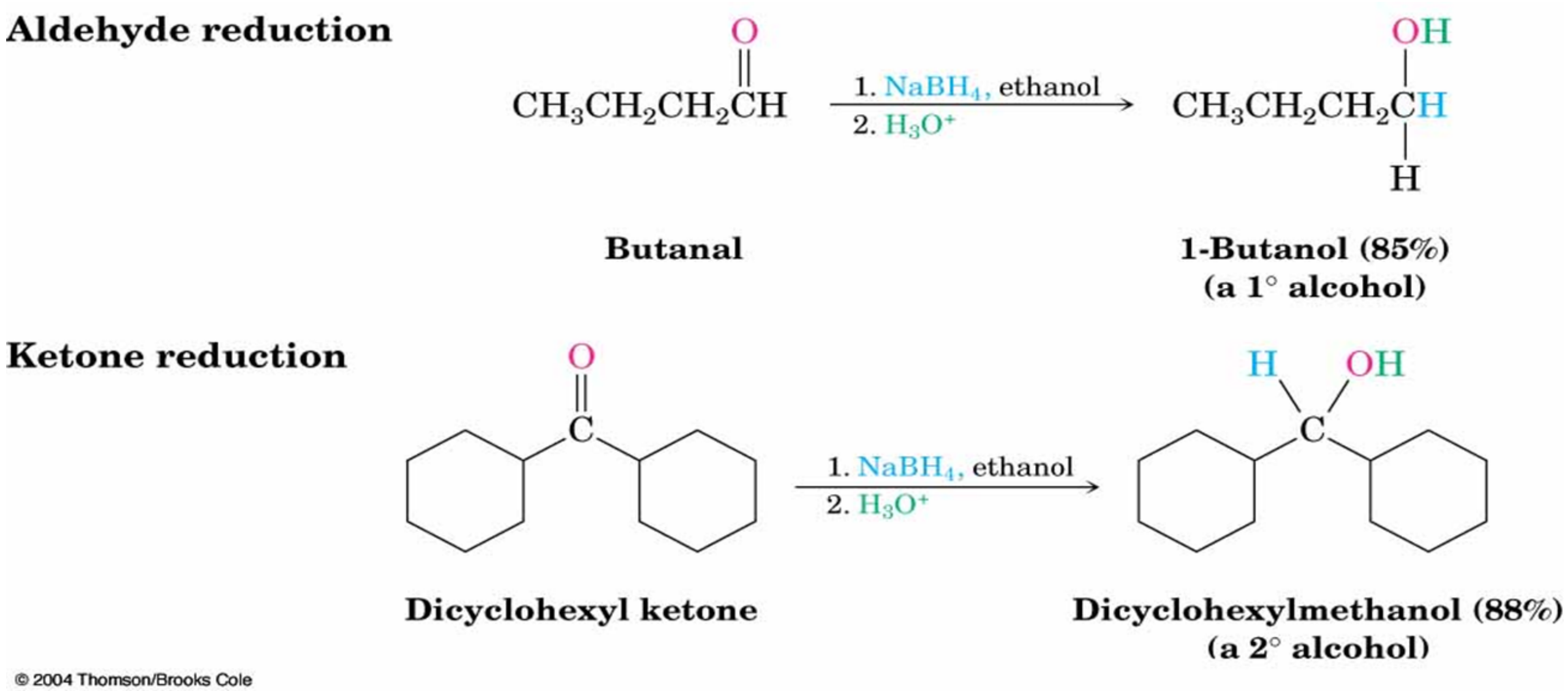
Reduction of Aldehydes and Ketones

- **Aldehydes give primary alcohols**
- **Ketones give secondary alcohols**



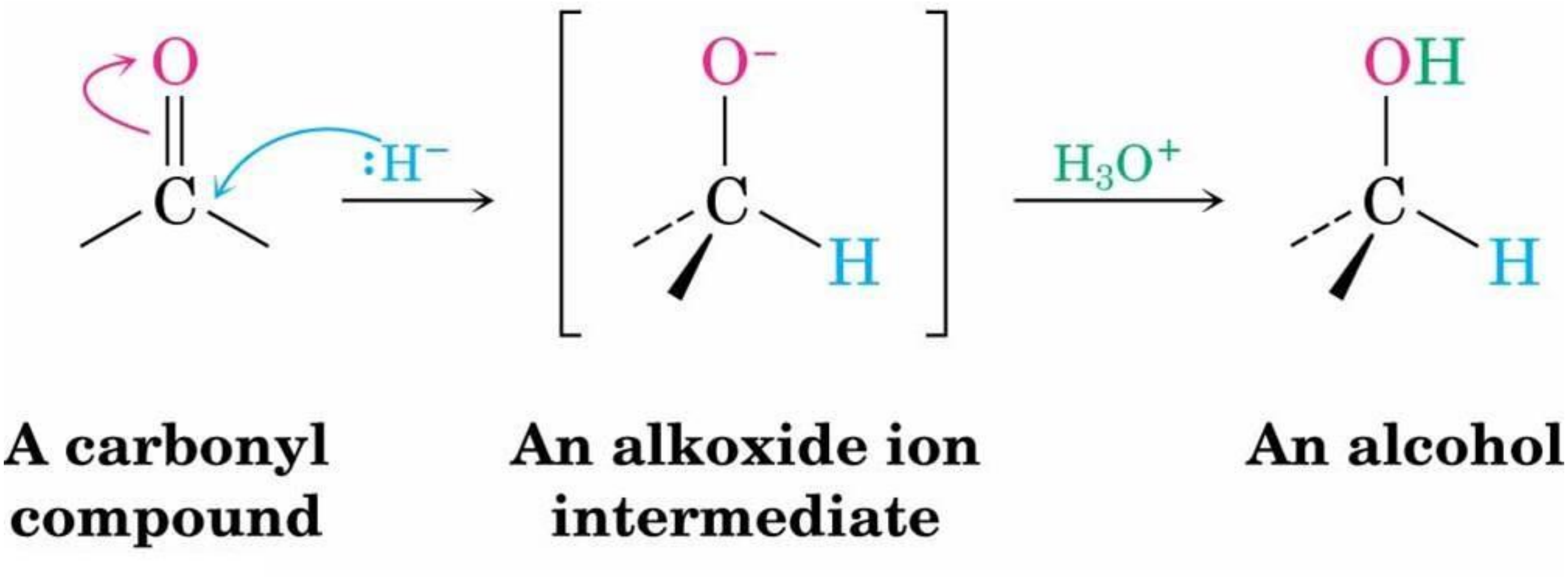
Reduction Reagent: Sodium Borohydride

- **Sodium Borohydride ($NaBH_4$) is not sensitive to moisture and it does not reduce other common functional groups.**
- **Lithium aluminum hydride ($LiAlH_4$) is more powerful, less specific, and very reactive with water.**
- **Both add the equivalent of “H^-”.**



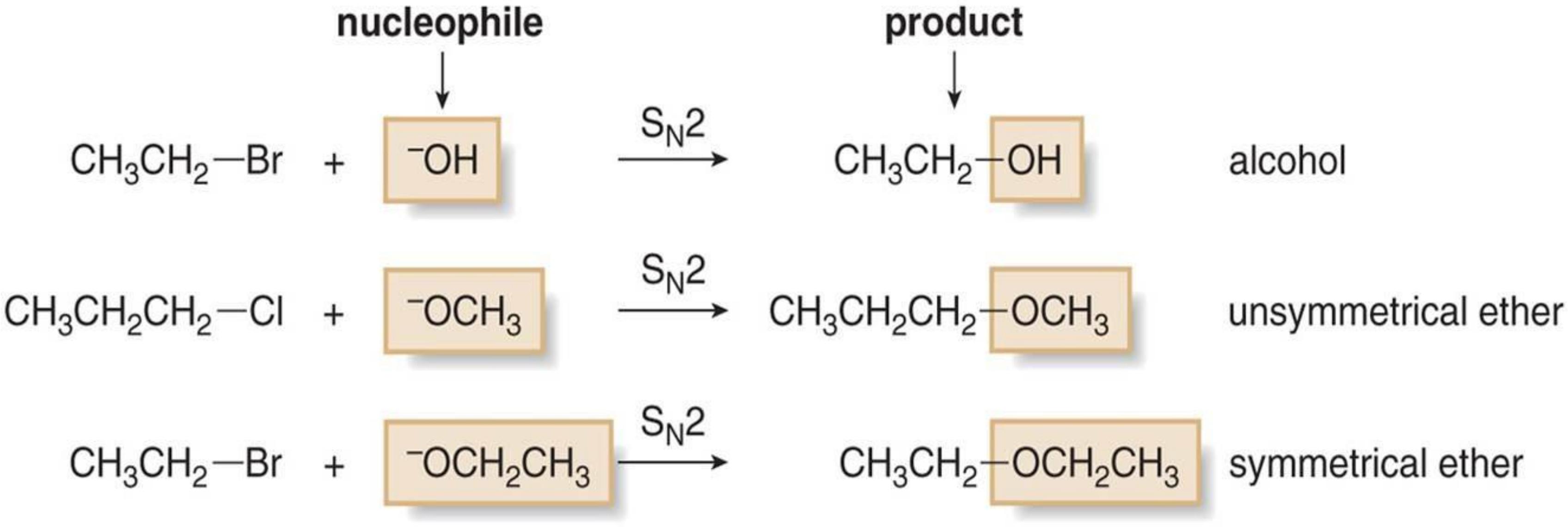
Mechanism of Reduction

- **The reagent adds the equivalent of hydride to the carbon of C=O and polarizes the group as well**



Preparation of Alcohols and Ethers

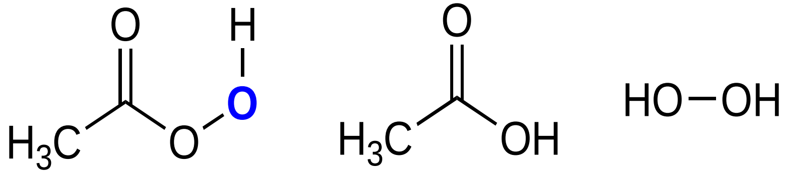
- **Alcohols and ethers are both common products of nucleophilic substitution.**



- **The preparation of ethers by the method shown in the last two equations is called the Williamson ether synthesis.**

Forming Epoxides from Alkenes

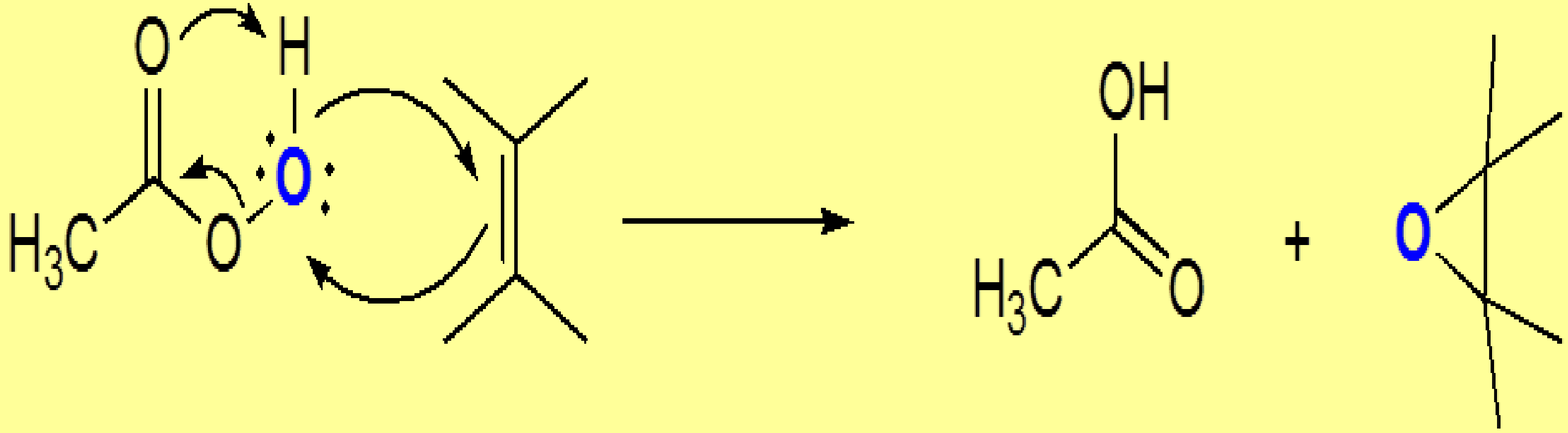
Epoxidation of Alkenes: Reaction of an alkene with a peroxyacid: peroxyacetic acid



peroxyacetic acid

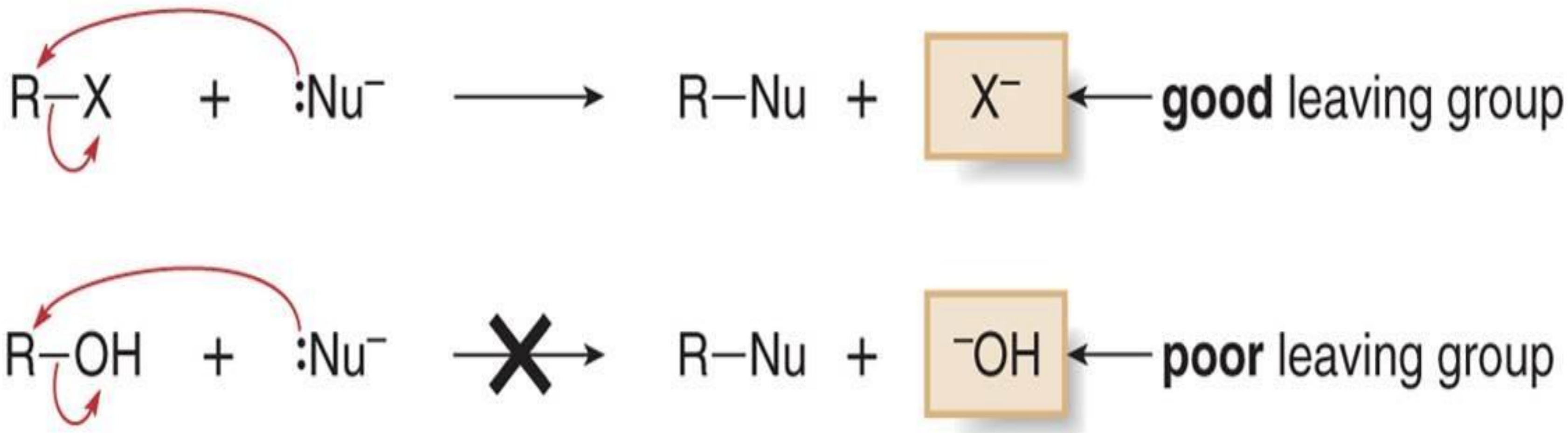
acetic acid

peroxide



OH as a Leaving Group

- **Unlike alkyl halides in which the halogen atom (X) serves as a good leaving group, the OH group in alcohols is a very poor leaving group.**



- **For an alcohol to undergo nucleophilic substitution, OH must be converted into a better leaving group.**

Dehydration and Alcohol Substitution

- More substituted alcohols dehydrate more easily, giving rise to the following order of reactivity.

$RCH_2{-}OH$ 1°

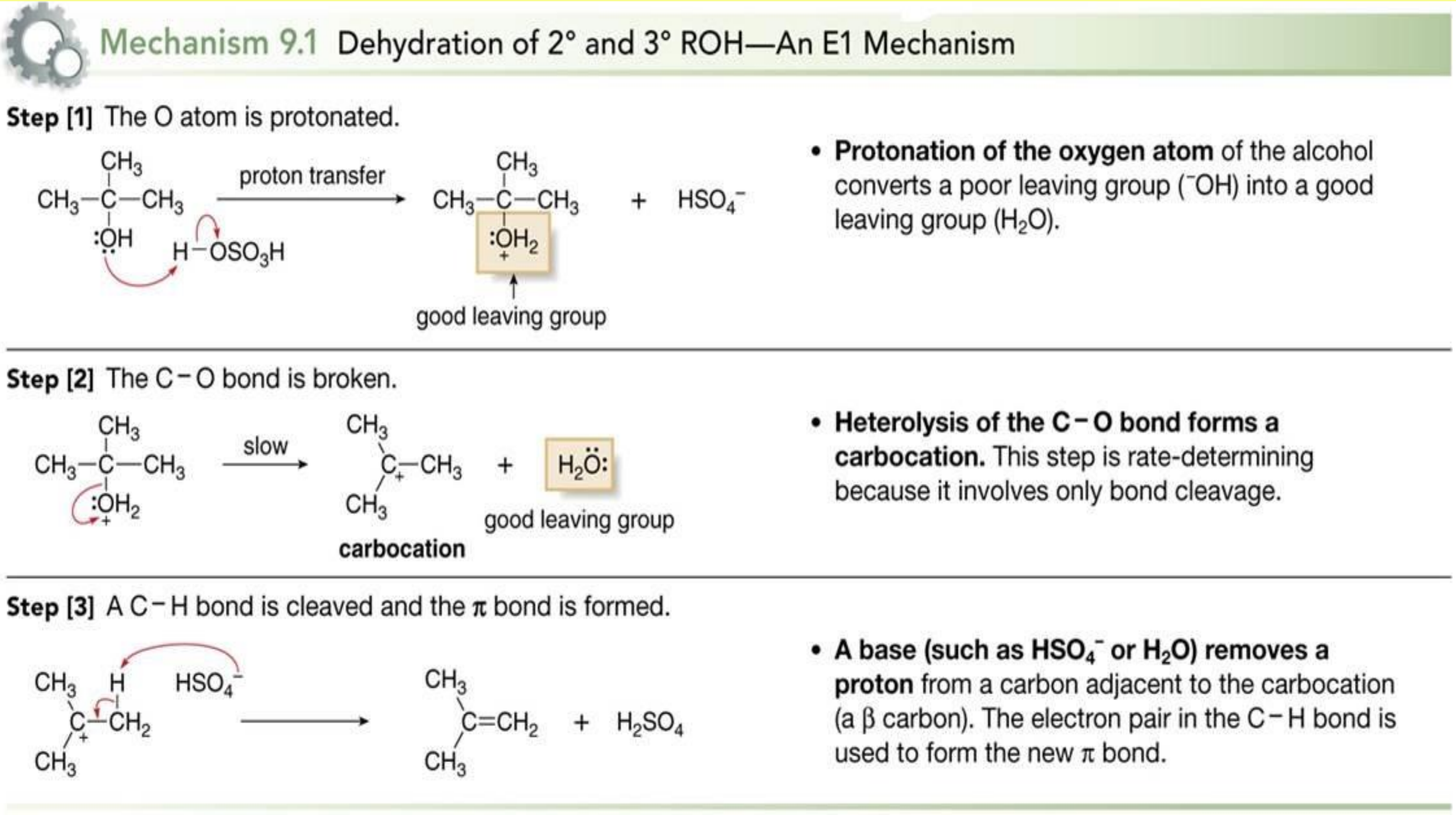
$R_2CH{-}OH$ 2°

$R_3C{-}OH$ 3°

Increasing rate of dehydration

Dehydration by E1 Mechanism

- 2° and 3° alcohols react by an E1 mechanism, whereas 1° alcohols react by an E2 mechanism.



Mechanism 9.1 Dehydration of 2° and 3° ROH—An E1 Mechanism

Step [1] The O atom is protonated.

- **Protonation of the oxygen atom** of the alcohol converts a poor leaving group (^-OH) into a good leaving group (H_2O).

Step [2] The C–O bond is broken.

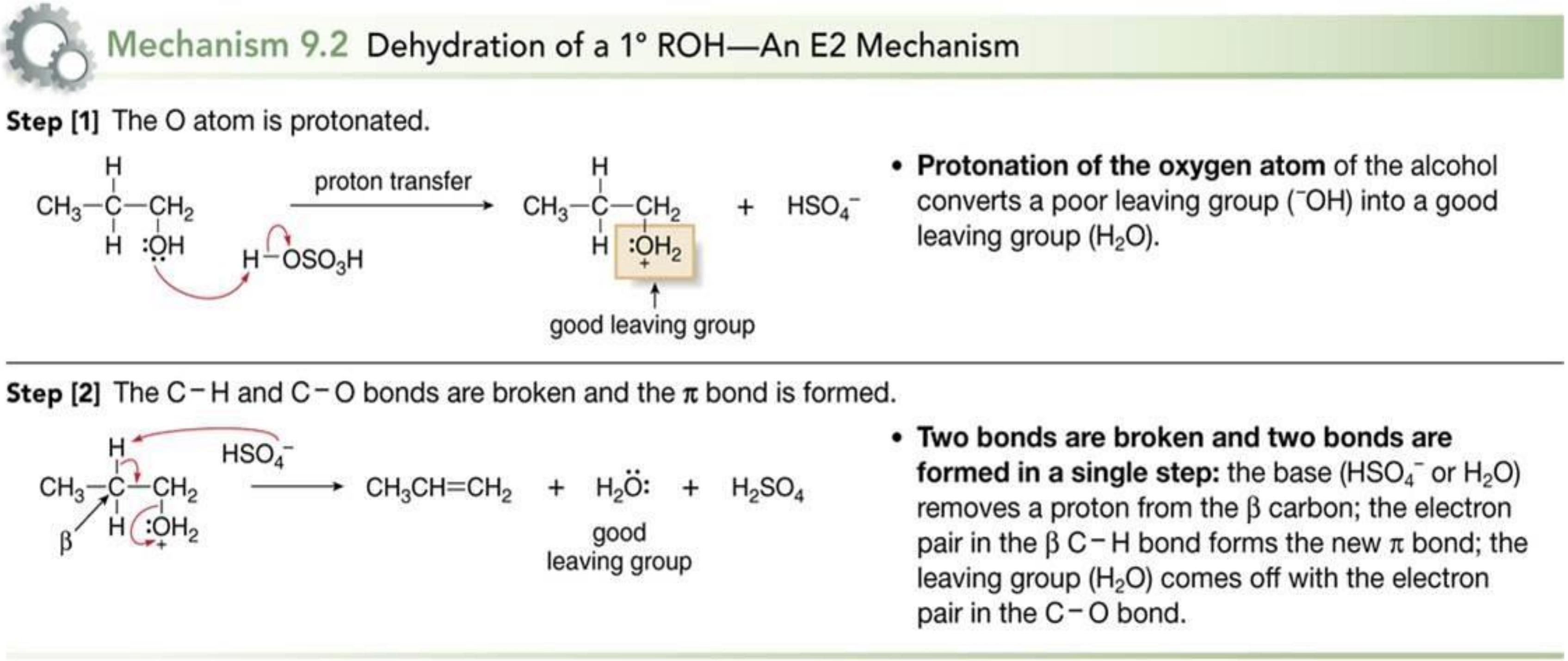
- **Heterolysis of the C–O bond forms a carbocation.** This step is rate-determining because it involves only bond cleavage.

Step [3] A C–H bond is cleaved and the π bond is formed.

- **A base (such as HSO_4^- or H_2O) removes a proton** from a carbon adjacent to the carbocation (a β carbon). The electron pair in the C–H bond is used to form the new π bond.

E2 Dehydration of 1º Alcohols

- **Since 1° carbocations are highly unstable, their dehydration cannot occur by an E1 mechanism involving a carbocation intermediate.**
- **However, 1° alcohols undergo dehydration by way of an E2 mechanism.**



Mechanism 9.2 Dehydration of a 1° ROH—An E2 Mechanism

Step [1] The O atom is protonated.

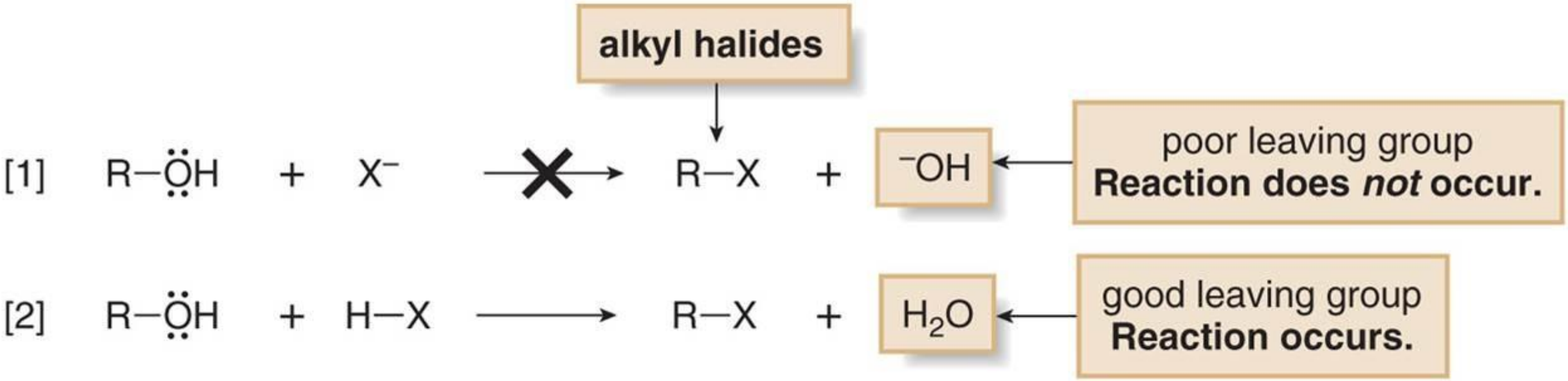
- **Protonation of the oxygen atom** of the alcohol converts a poor leaving group (^-OH) into a good leaving group (H_2O).

Step [2] The C–H and C–O bonds are broken and the π bond is formed.

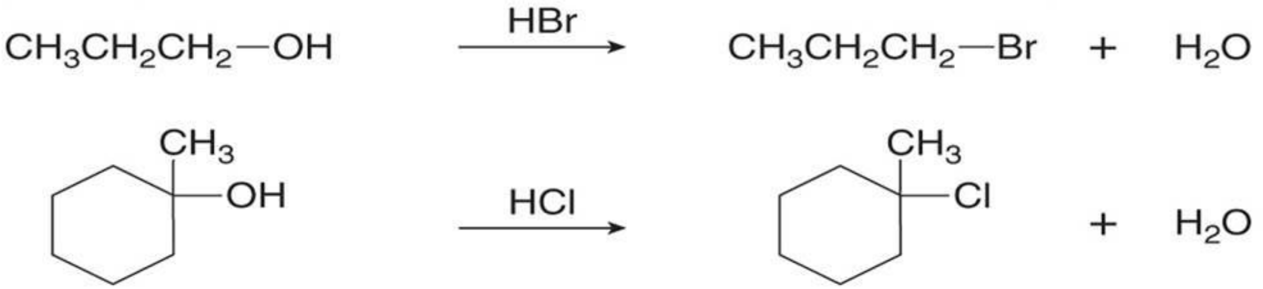
- **Two bonds are broken and two bonds are formed in a single step:** the base (HSO_4^- or H_2O) removes a proton from the β carbon; the electron pair in the β C–H bond forms the new π bond; the leaving group (H_2O) comes off with the electron pair in the C–O bond.

Conversion of Alcohols to Alkyl Halides with HX

- **Substitution reactions do not occur with alcohols unless ⁻OH is converted into a good leaving group.**



- **The reaction of alcohols with HX (X = Cl, Br, I) is a general method to prepare 1°, 2°, and 3° alkyl halides.**

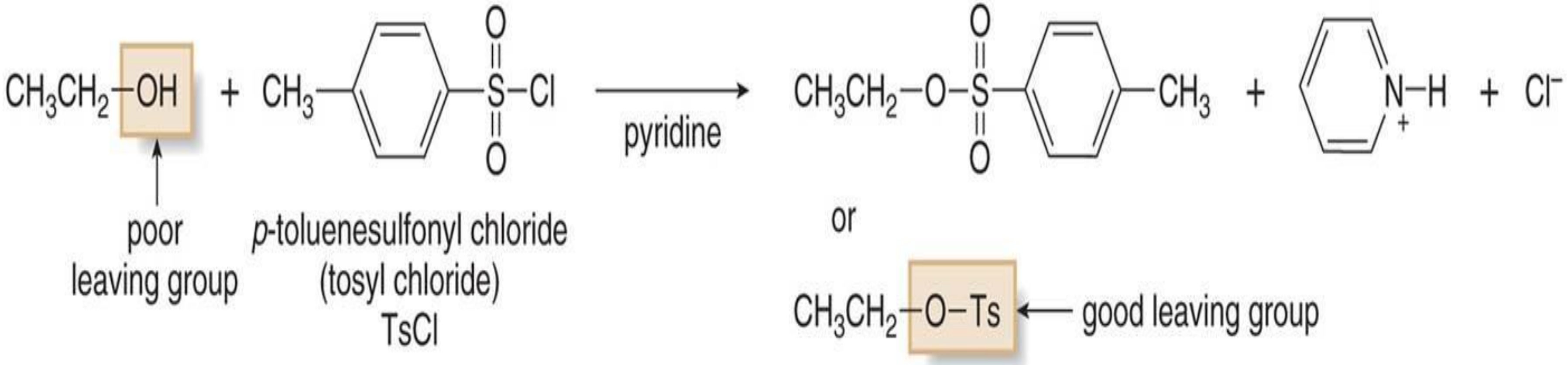


Conversion of Alcohols to Alkyl Halides with $SOCl_2$ and PBr_3

- **Primary and 2° alcohols can be converted to alkyl halides using $SOCl_2$ and PBr_3.**
- **$SOCl_2$ (thionyl chloride) converts alcohols into alkyl chlorides.**
- **PBr_3 (phosphorus tribromide) converts alcohols into alkyl bromides.**
- **Both reagents convert ^{-}OH into a good leaving group in situ—that is, directly in the reaction mixture—as well as provide the nucleophile, either Cl^{-} or Br^{-}, to displace the leaving group.**

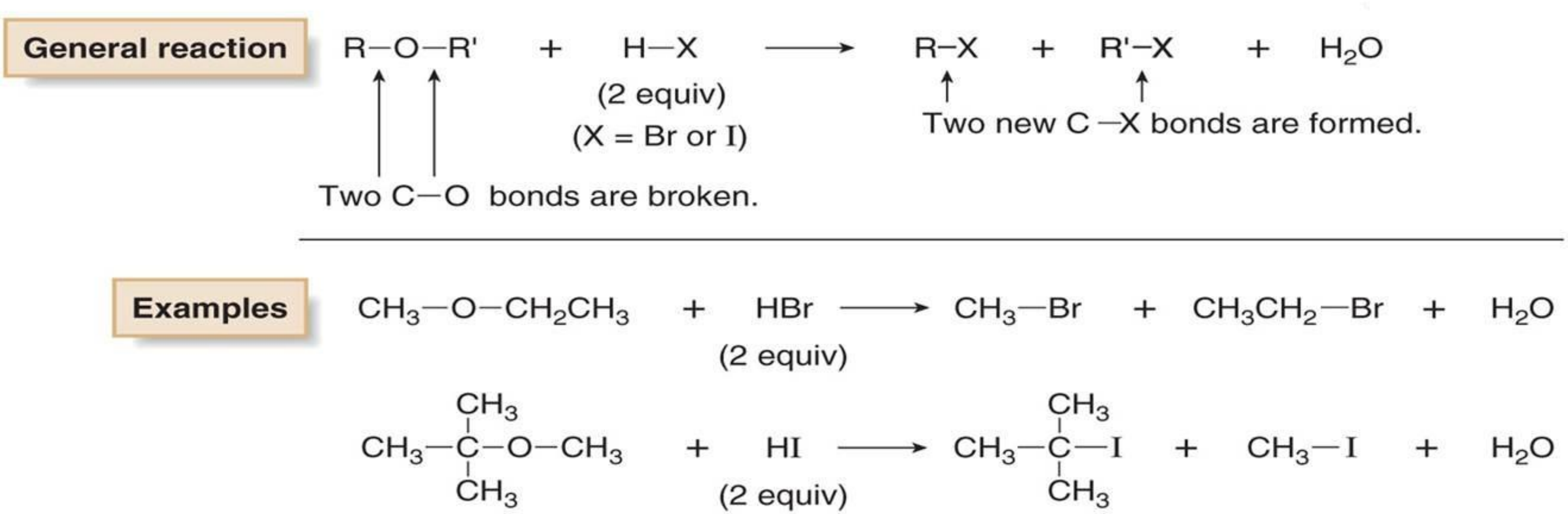
Formation and Use of Tosylates

- **Alcohols are converted to tosylates by treatment with *p*-toluenesulfonyl chloride (TsCl) in the presence of pyridine.**
- **This process converts a poor leaving group (¯OH) into a good one (¯OTs).**
- **Tosylate is a good leaving group because its conjugate acid, *p*-toluenesulfonic acid ($CH_3C_6H_4SO_3H$, TsOH) is a strong acid (pK_a = –7).**



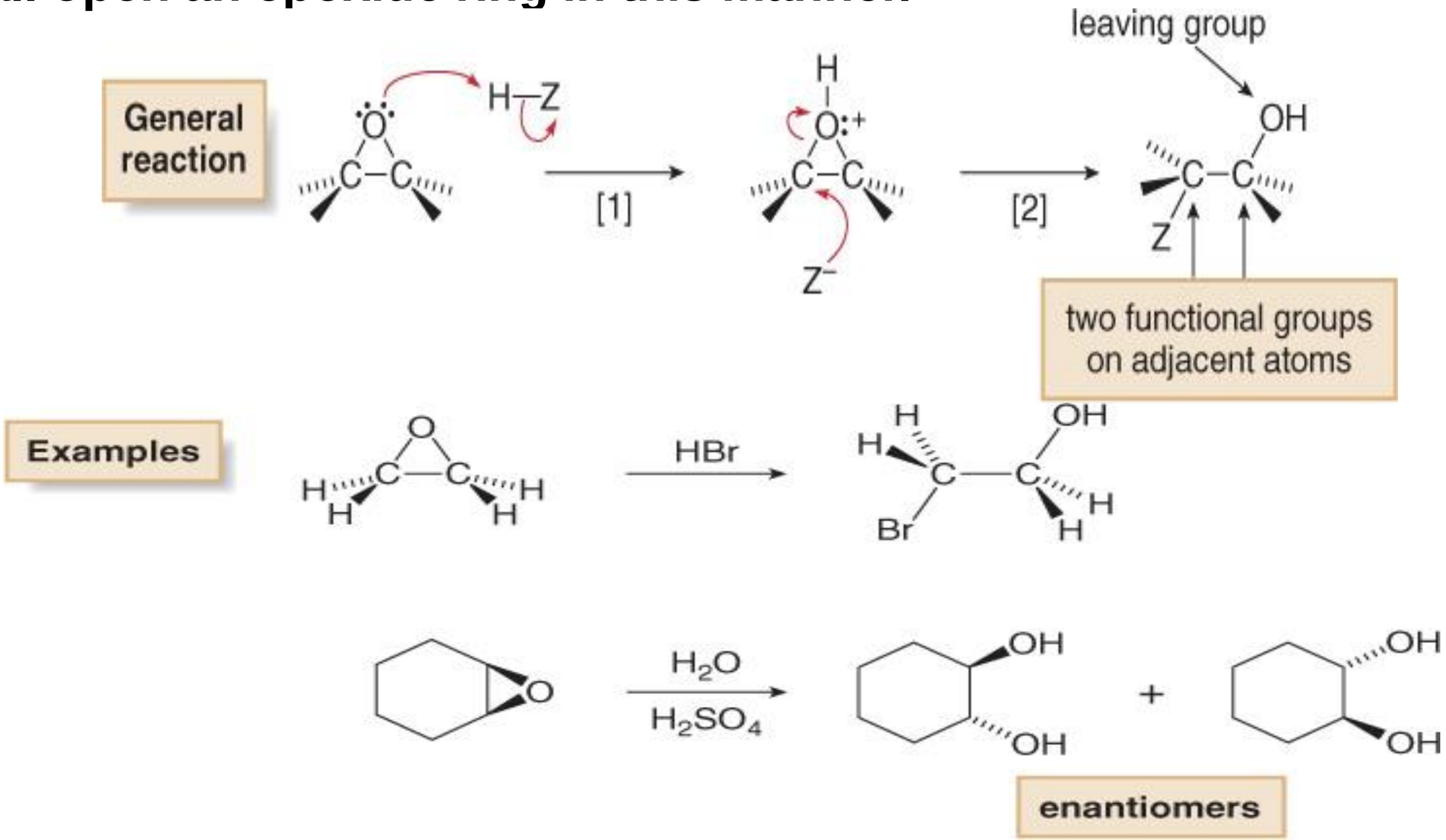
Reaction of Ethers with Strong Acid

- In order for ethers to undergo substitution or elimination reactions, their poor leaving group must first be converted into a good leaving group by reaction with strong acids such as HBr and HI.
- HBr and HI are strong acids that are also sources of good nucleophiles (Br^- and I^-, respectively).
- When ethers react with HBr or HI, both C-O bonds are cleaved and two alkyl halides are formed as products.



Acidic Epoxide Ring Opening

- Acids HZ that contain a nucleophile Z also open epoxide rings by a two-step sequence.
- HCl, HBr, and HI, as well as H_2O and ROH in the presence of acid, all open an epoxide ring in this manner.

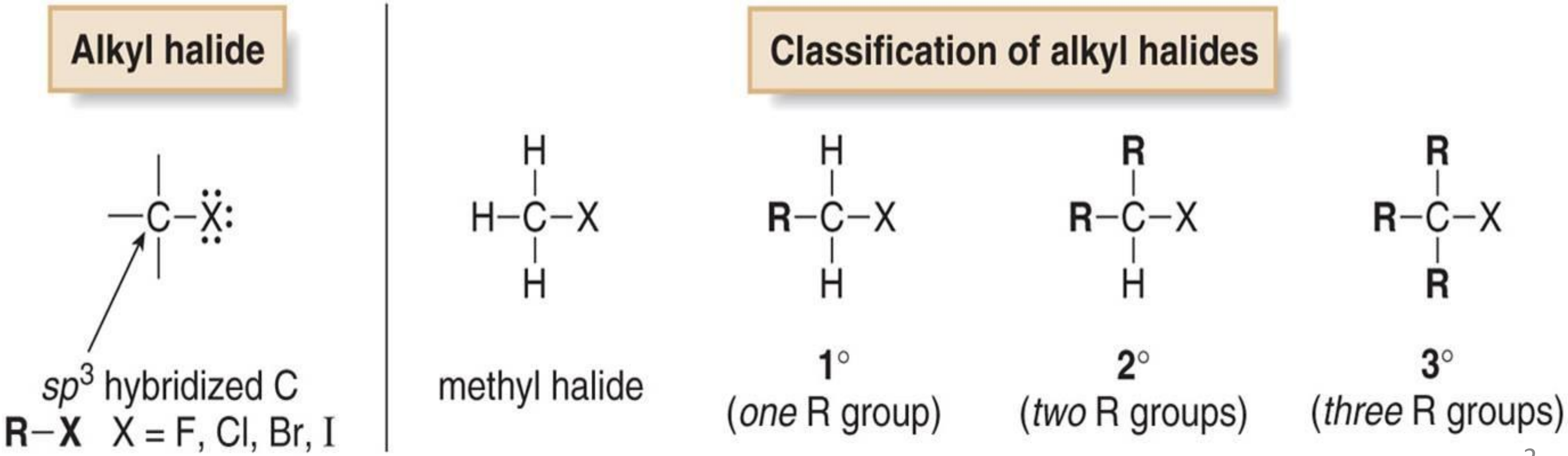


Alkyl Halides

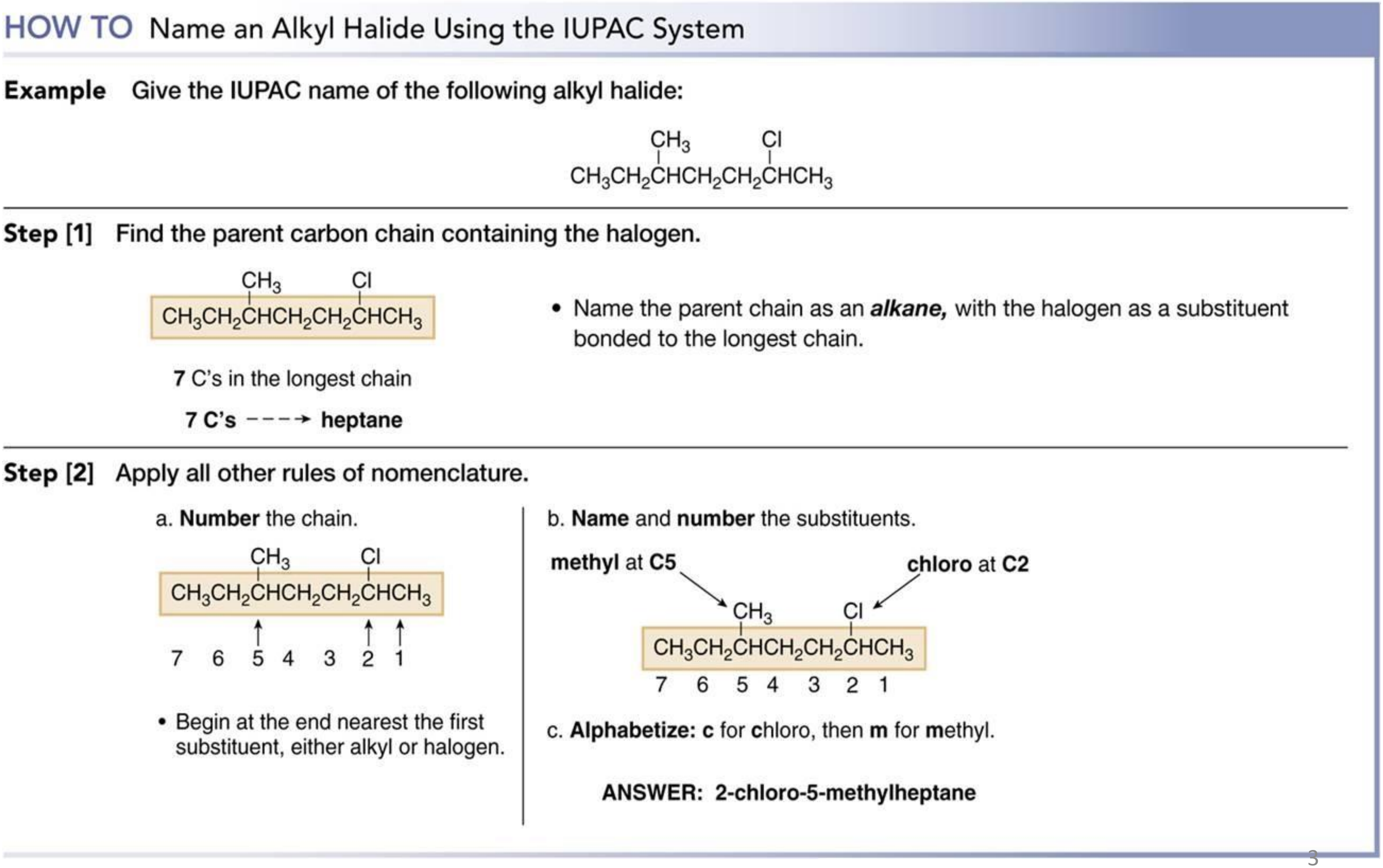
Organic chemistry

1st class students

- **INTRODUCTION**:
- Alkyl halides are organic molecules containing a halogen atom bonded to an *sp*^{3} hybridized carbon atom.
- The halogen atom in halides is often denoted by the symbol; X.
- Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°), depending on the number of carbons bonded to the carbon with the halogen atom.



Nomenclature



HOW TO Name an Alkyl Halide Using the IUPAC System

Example Give the IUPAC name of the following alkyl halide:

$$CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3$$

Step [1] Find the parent carbon chain containing the halogen.

$$\boxed{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3}$$

7 C's in the longest chain

7 C's - - - → **heptane**

- Name the parent chain as an ***alkane,*** with the halogen as a substituent bonded to the longest chain.

Step [2] Apply all other rules of nomenclature.

a. **Number** the chain.

$$\boxed{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3}$$

7 6 5 4 3 2 1

- Begin at the end nearest the first substituent, either alkyl or halogen.

b. **Name** and **number** the substituents.

methyl at **C5** **chloro** at **C2**

$$\boxed{CH_3CH_2\overset{\overset{CH_3}{|}}{C}HCH_2CH_2\overset{\overset{Cl}{|}}{C}HCH_3}$$

7 6 5 4 3 2 1

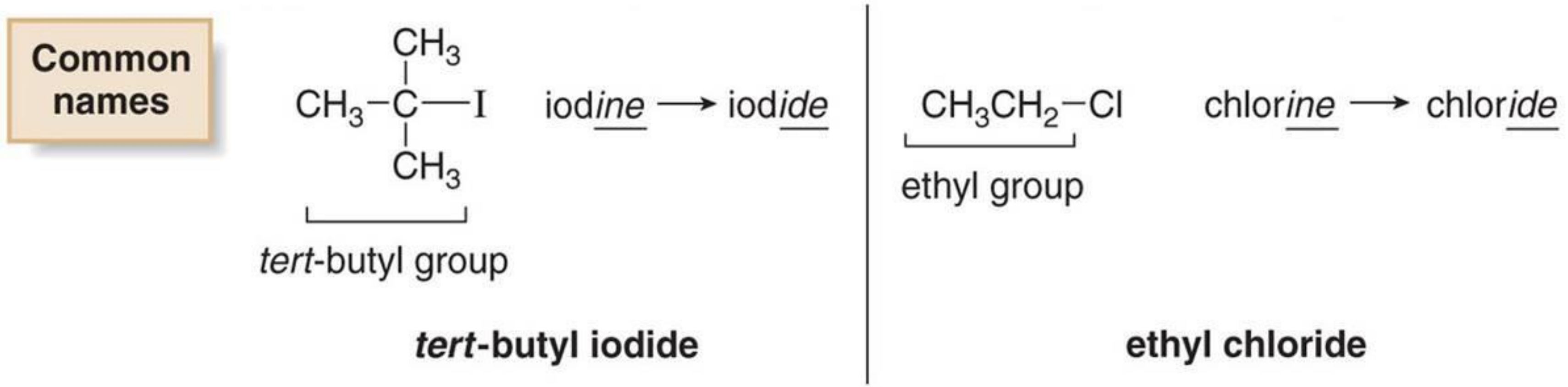
c. **Alphabetize: c** for **c**hloro, then **m** for **m**ethyl.

ANSWER: 2-chloro-5-methylheptane

Common Names of Alkyl Halides

- Common names are often used for simple alkyl halides.
- To assign a common name:

    1. Name all the carbon atoms of the molecule as a single alkyl group.
    2. Name the halogen bonded to the alkyl group.
    3. Combine the names of the alkyl group and halide, separating the words with a space.



Physical Properties of Alkyl Halides

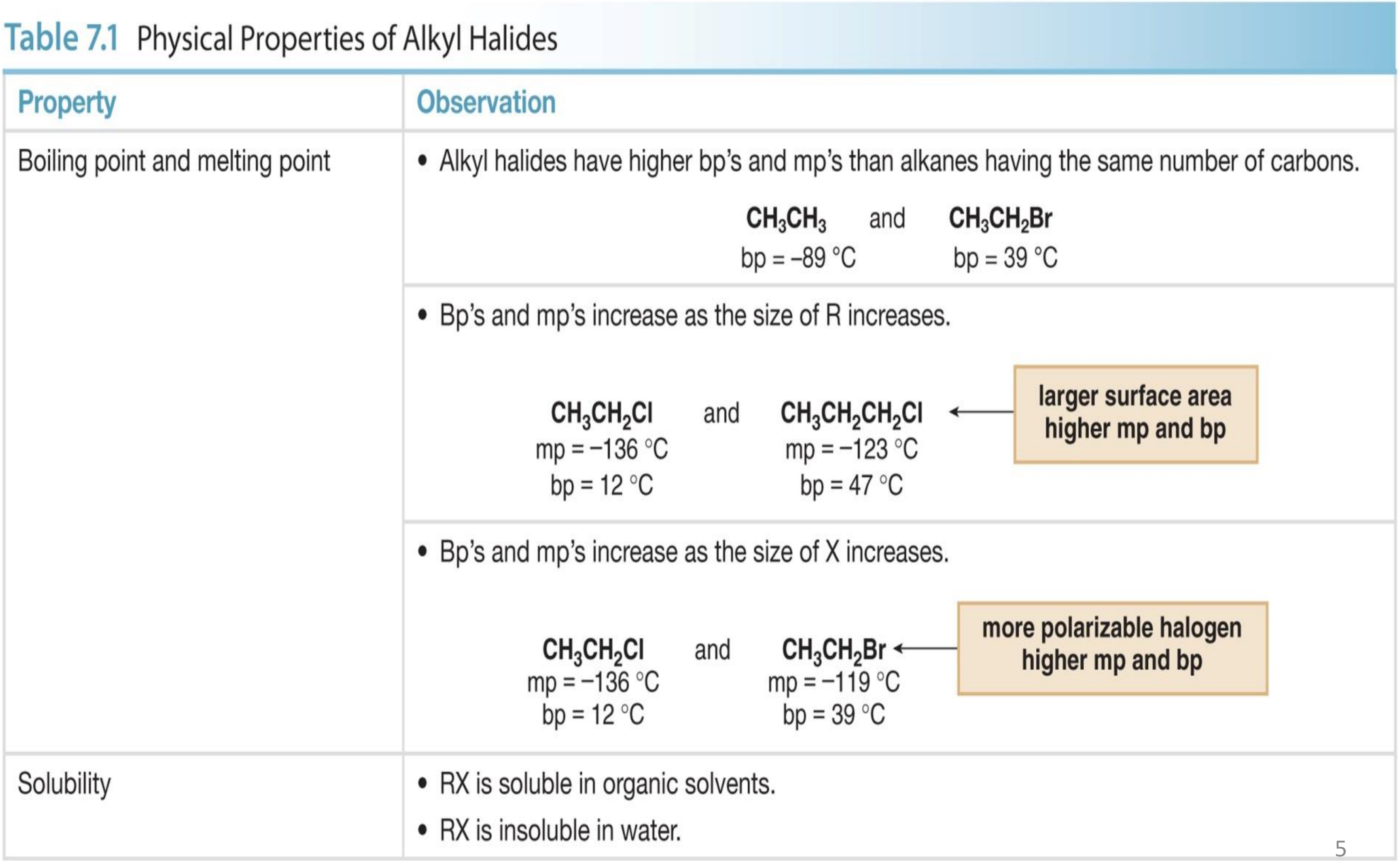


Table 7.1 Physical Properties of Alkyl Halides

Property	Observation
Boiling point and melting point	• Alkyl halides have higher bp's and mp's than alkanes having the same number of carbons. CH_3CH_3 bp = –89 °C and CH_3CH_2Br bp = 39 °C
	• Bp's and mp's increase as the size of R increases. CH_3CH_2Cl mp = –136 °C, bp = 12 °C and $CH_3CH_2CH_2Cl$ mp = –123 °C, bp = 47 °C ← larger surface area higher mp and bp
	• Bp's and mp's increase as the size of X increases. CH_3CH_2Cl mp = –136 °C, bp = 12 °C and CH_3CH_2Br mp = –119 °C, bp = 39 °C ← more polarizable halogen higher mp and bp
Solubility	• RX is soluble in organic solvents. • RX is insoluble in water.

Preparation of Alkyl Halides from Alcohols and Hydrogen Halides

$$ROH + HX \rightarrow RX + HOH$$

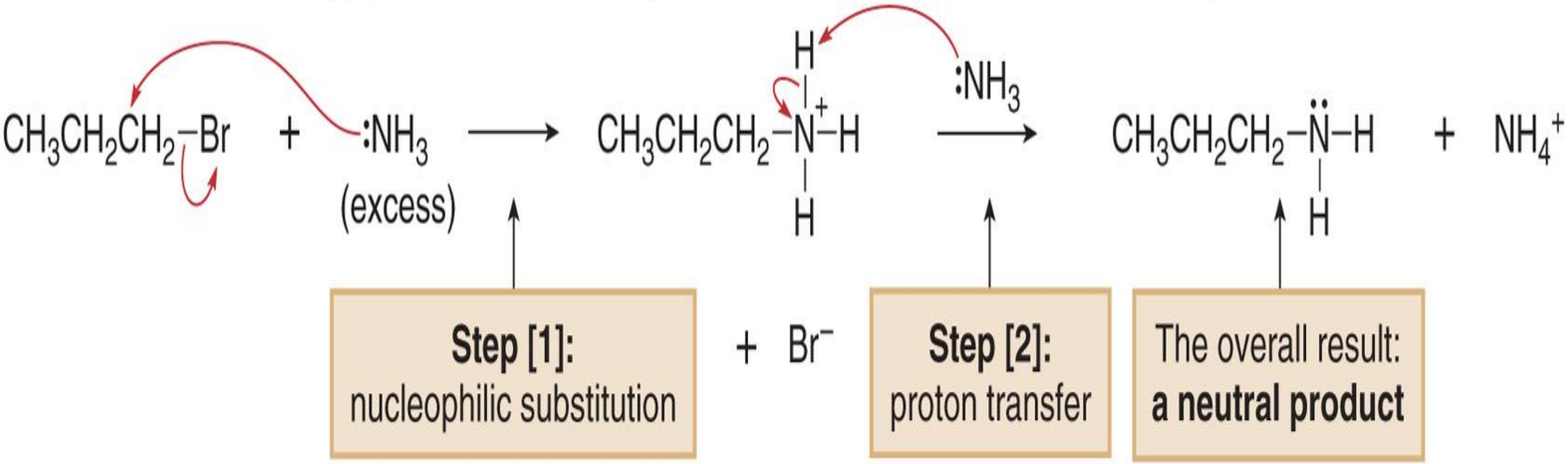
Hydrogen halide reactivity

HI	HBr	HCl	HF
most reactive			least reactive

Alcohol reactivity

R_3COH	R_2CHOH	RCH_2OH	CH_3OH
Tertiary	Secondary	Primary	Methanol
most reactive			least reactive

Drawing Products of Nucleophilic Substitution Reactions

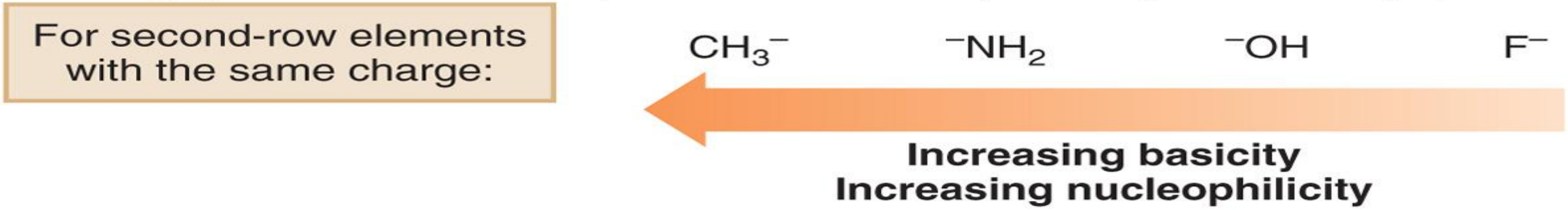


The overall effect of any nucleophilic substitution is the replacement of the leaving group by the nucleophile.

Nucleophilicity Parallels Basicity

Nucleophilicity parallels basicity in three instances:

1. For two nucleophiles with the same nucleophilic atom, the stronger base is the stronger nucleophile.
    - The relative nucleophilicity of HO$^-$ and CH_3COO^-, is determined by comparing the pK_a values of their conjugate acids (H_2O = 15.7, and CH_3COOH = 4.8).
    - HO$^-$ is a stronger base and stronger nucleophile than CH_3COO^-.
2. A negatively charged nucleophile is always a stronger nucleophile than its conjugate acid.
    - HO$^-$ is a stronger base and stronger nucleophile than H_2O.
3. Right-to-left across a row of the periodic table, nucleophilicity increases as basicity increases:



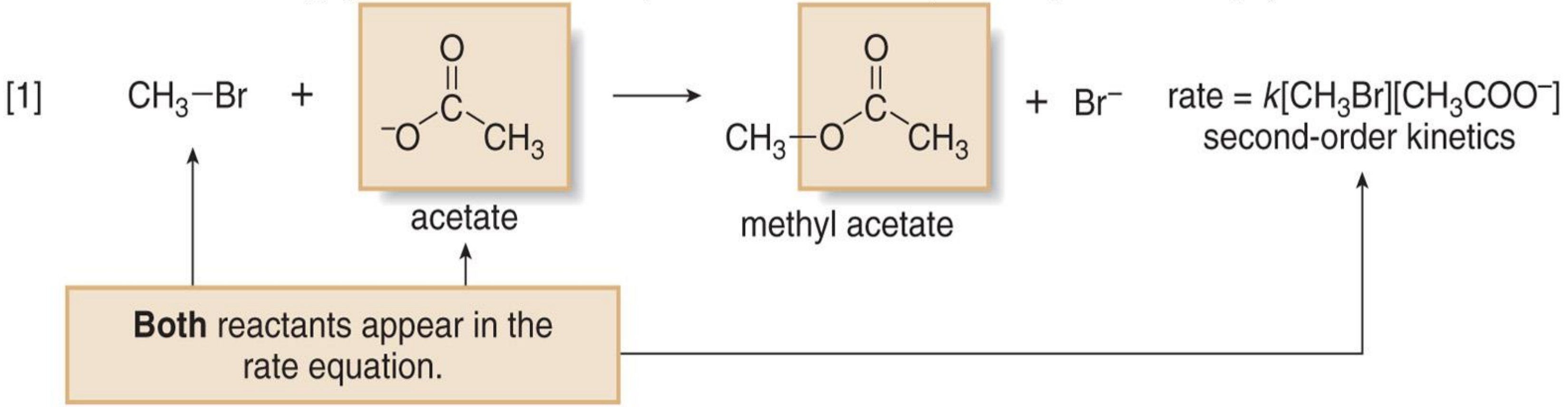
For second-row elements with the same charge:

CH_3^- $\quad$ $^-NH_2$ $\quad$ ^-OH $\quad$ F^-

Increasing basicity
Increasing nucleophilicity

Kinetics and Mechanisms

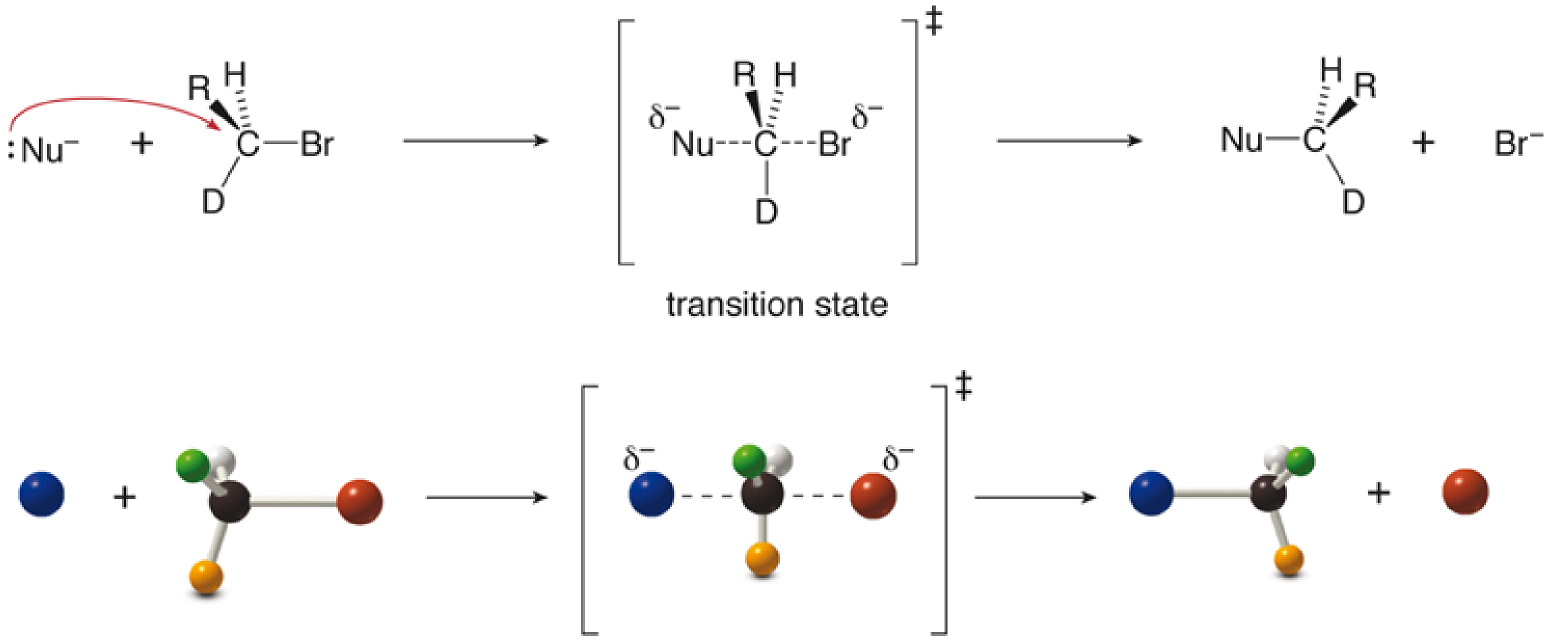
- Consider reaction 1 below:



- Kinetic data show that the rate of **reaction1** depends on the concentration of both reactants, which suggests a bimolecular reaction with a one-step mechanism.
- This is an example of an **S_N2** (substitution nucleophilic bimolecular) mechanism.

Stereochemistry

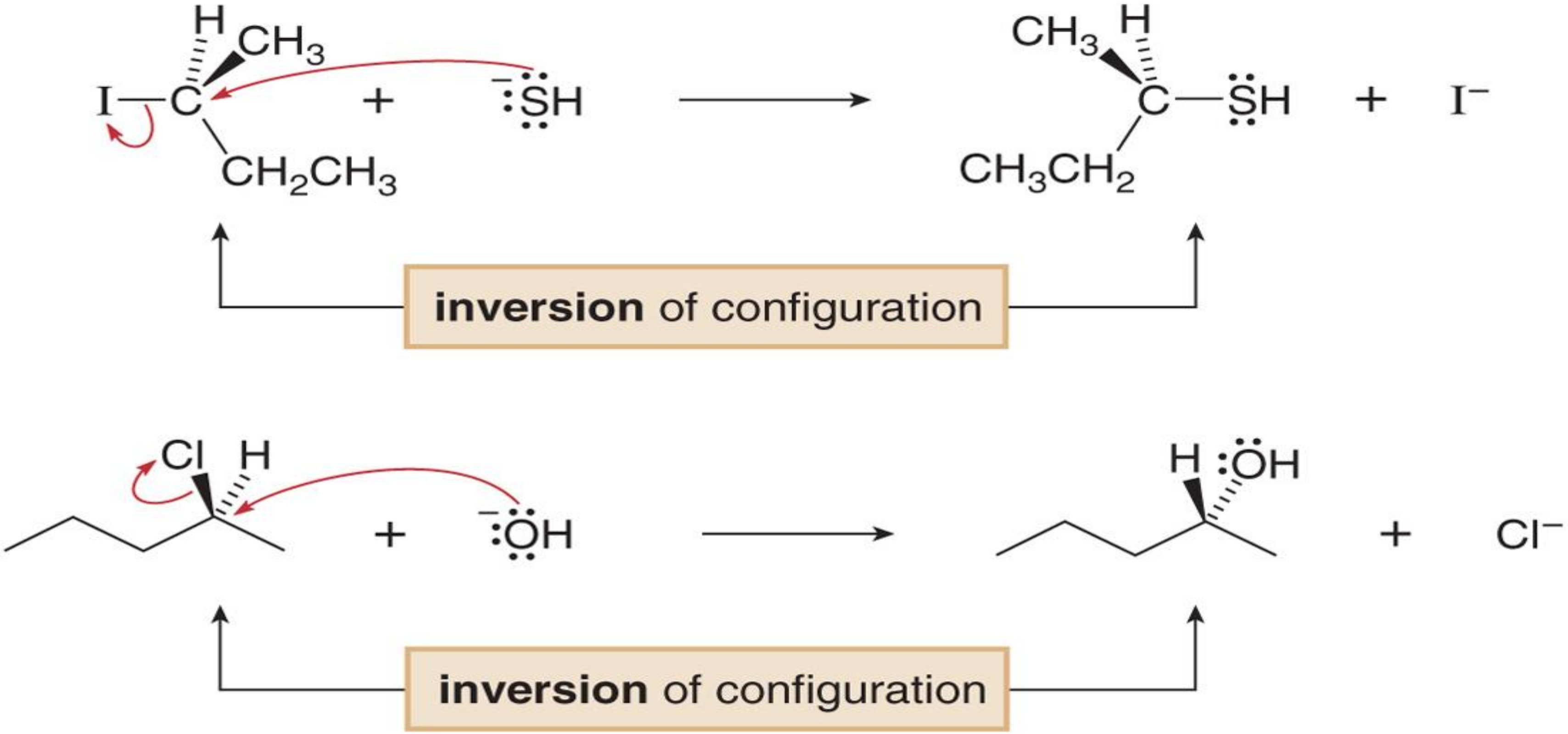
- **All S_N2 reactions proceed with backside attack of the nucleophile, resulting in inversion of configuration at a stereogenic center.**



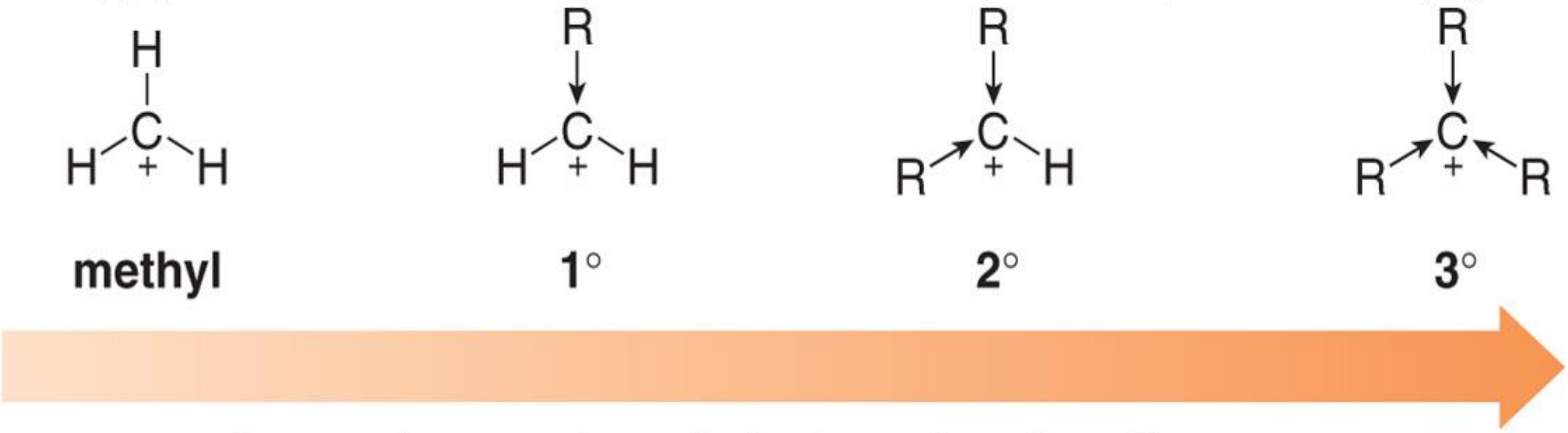
:Nu⁻ and Br⁻ are 180Υaway from each other, on either side of a plane containing R, H, and D.

Inversion in S_N2 Reactions

- **Two examples showing inversion of configuration at a stereogenic center.**



Carbocation Stability



Increasing number of electron-donating R groups
Increasing carbocation stability

Alkyl groups are electron donor groups that stabilize a positive charge because they contain several σ bonds, each containing electron density.
As a result, alkyl groups are more polarizable than a hydrogen atom, and better able to donate electron density.
In general, the more alkyl groups attached to a carbon with a positive charge, the more stable the cation will be.

Predicting the Mechanism of Nucleophilic Substitutions Reactions

- **Four factors are relevant in predicting whether a given reaction is likely to proceed by an S_N1 or an S_N2 mechanism:**

  1. **The alkyl halide—CH_3X, RCH_2X, R_2CHX or R_3CX**
  2. **The nucleophile—strong or weak**
  3. **The leaving group—good or poor**
  4. **The solvent—protic or aprotic**

Predicting S_N1 or an S_N2–Summary

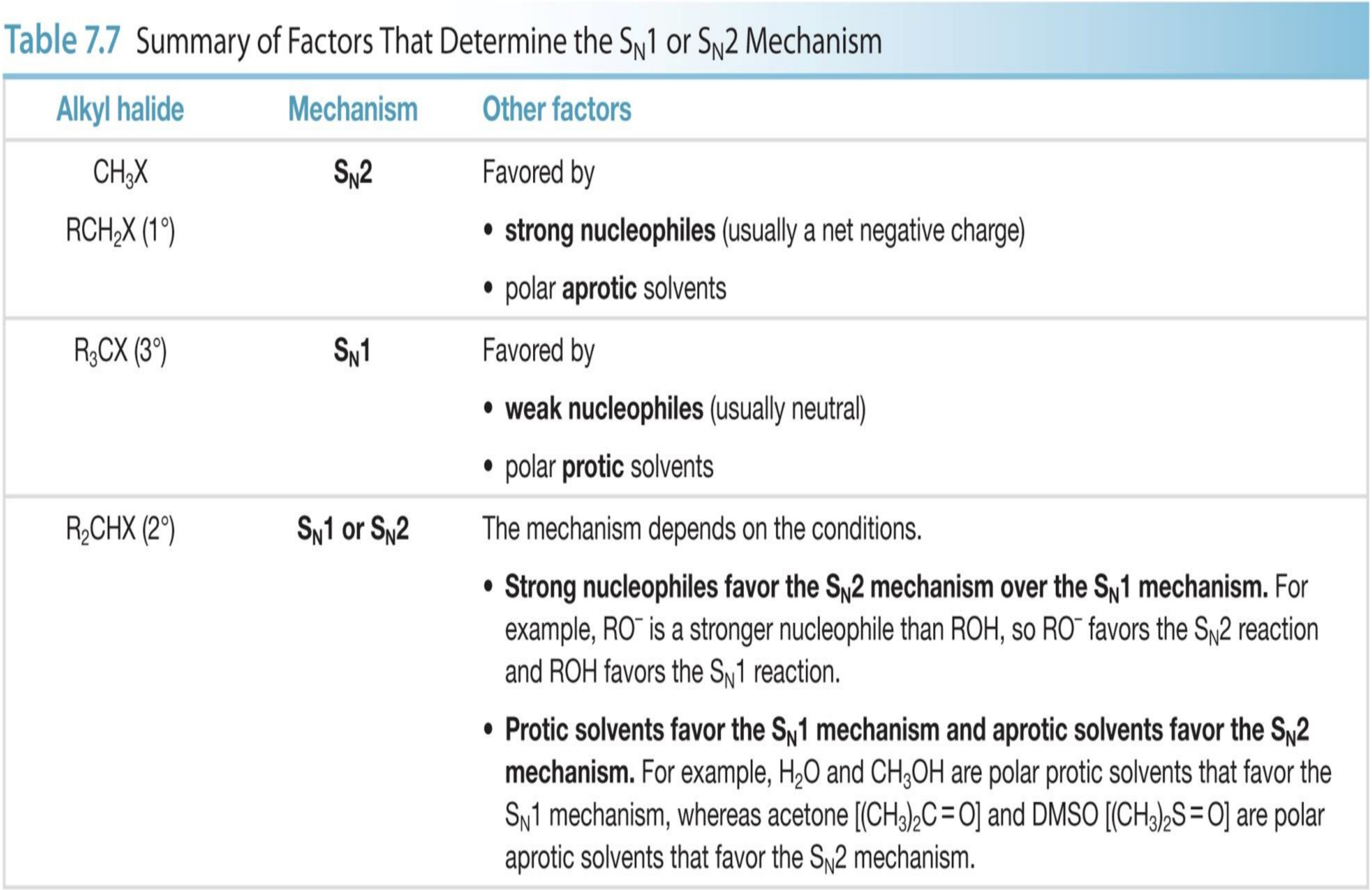


Table 7.7 Summary of Factors That Determine the S_N1 or S_N2 Mechanism

Alkyl halide	Mechanism	Other factors
CH_3X RCH_2X (1°)	**S_N2**	Favored by • **strong nucleophiles** (usually a net negative charge) • polar **aprotic** solvents
R_3CX (3°)	**S_N1**	Favored by • **weak nucleophiles** (usually neutral) • polar **protic** solvents
R_2CHX (2°)	**S_N1 or S_N2**	The mechanism depends on the conditions. • **Strong nucleophiles favor the S_N2 mechanism over the S_N1 mechanism.** For example, RO^- is a stronger nucleophile than ROH, so RO^- favors the S_N2 reaction and ROH favors the S_N1 reaction. • **Protic solvents favor the S_N1 mechanism and aprotic solvents favor the S_N2 mechanism.** For example, H_2O and CH_3OH are polar protic solvents that favor the S_N1 mechanism, whereas acetone $[(CH_3)_2C=O]$ and DMSO $[(CH_3)_2S=O]$ are polar aprotic solvents that favor the S_N2 mechanism.

Organic Synthesis Using Alkyl Halides

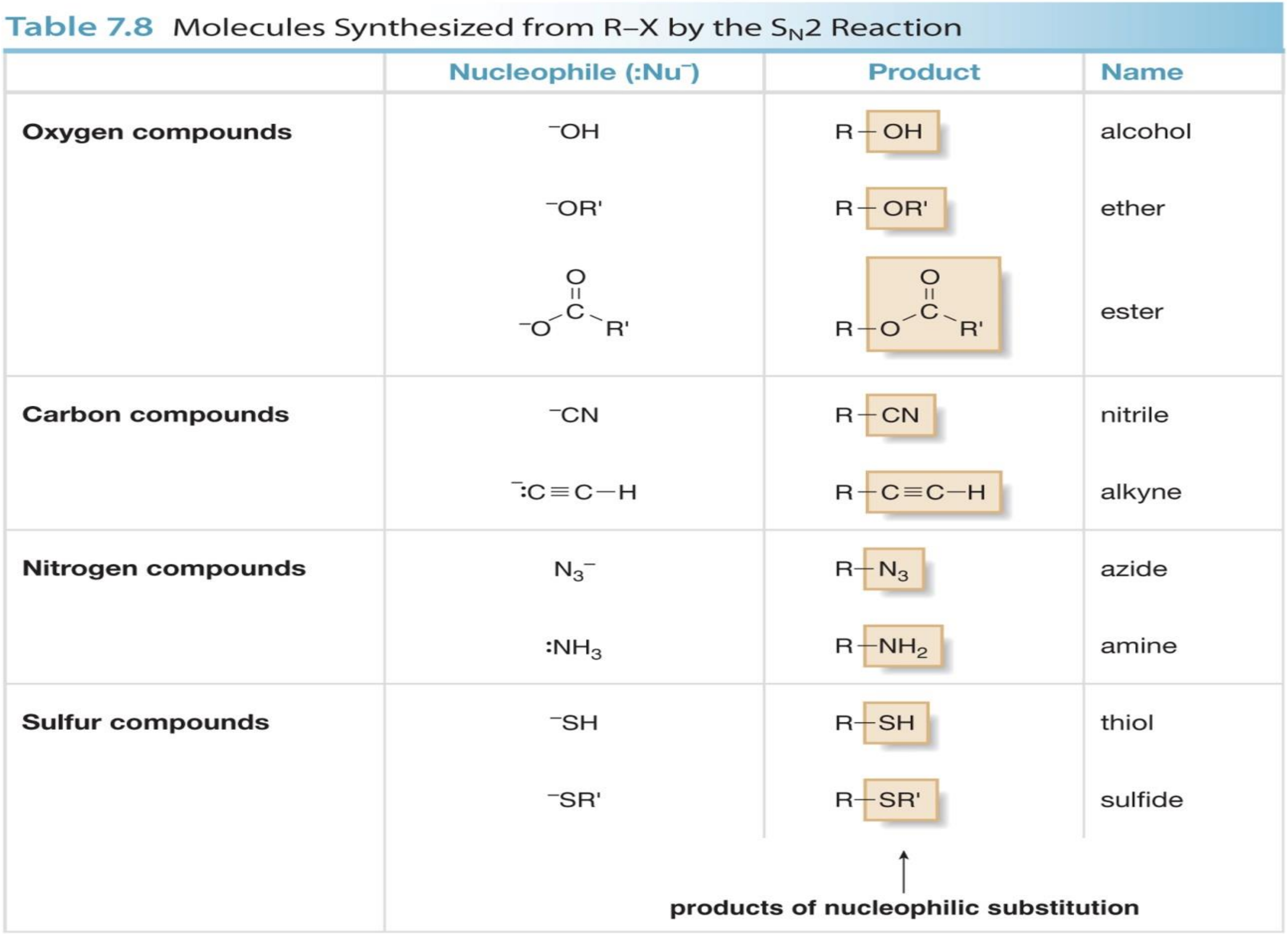
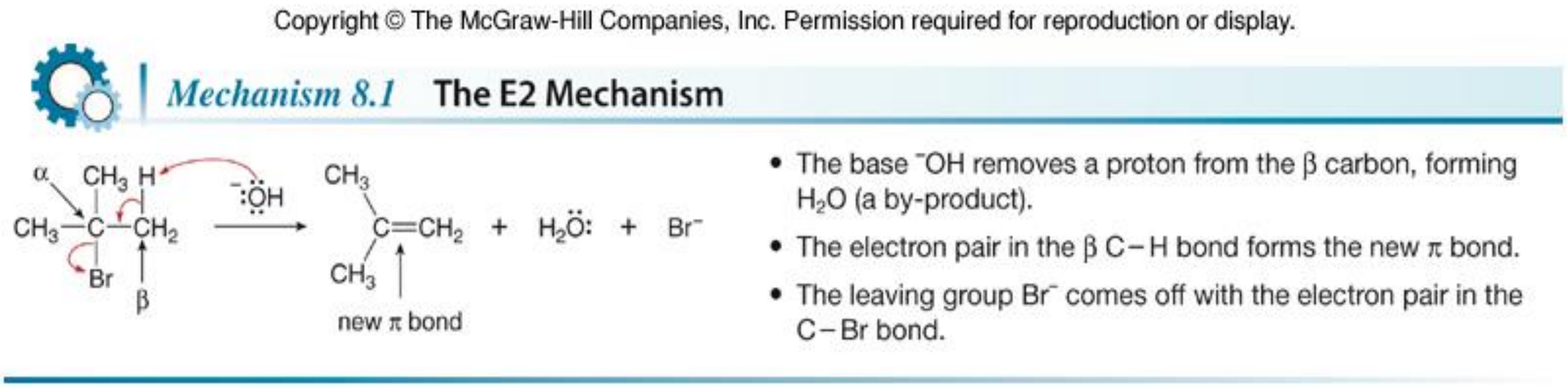


Table 7.8 Molecules Synthesized from R–X by the S_N2 Reaction

	Nucleophile (:Nu^-)	Product	Name
Oxygen compounds	^{-}OH	$R-OH$	alcohol
	$^{-}OR'$	$R-OR'$	ether
	$^{-}O-\overset{O}{\overset{\|}{C}}-R'$	$R-O-\overset{O}{\overset{\|}{C}}-R'$	ester
Carbon compounds	^{-}CN	$R-CN$	nitrile
	$^{-}{:}C{\equiv}C-H$	$R-C{\equiv}C-H$	alkyne
Nitrogen compounds	N_3^-	$R-N_3$	azide
	$:NH_3$	$R-NH_2$	amine
Sulfur compounds	^{-}SH	$R-SH$	thiol
	$^{-}SR'$	$R-SR'$	sulfide

E2 reaction

- The most common mechanism for dehydrohalogenation is the E2 mechanism.
- It exhibits second-order kinetics, and both the alkyl halide and the base appear in the rate equation, i.e.,
- rate = $k[(CH_3)_3CBr][^{-}OH]$
- The reaction is concerted—all bonds are broken and formed in a single step.



Mechanism 8.1 The E2 Mechanism

- The base ^{-}OH removes a proton from the β carbon, forming H_2O (a by-product).
- The electron pair in the β C–H bond forms the new π bond.
- The leaving group Br^{-} comes off with the electron pair in the C–Br bond.

Characteristic of the E2 Mechanism

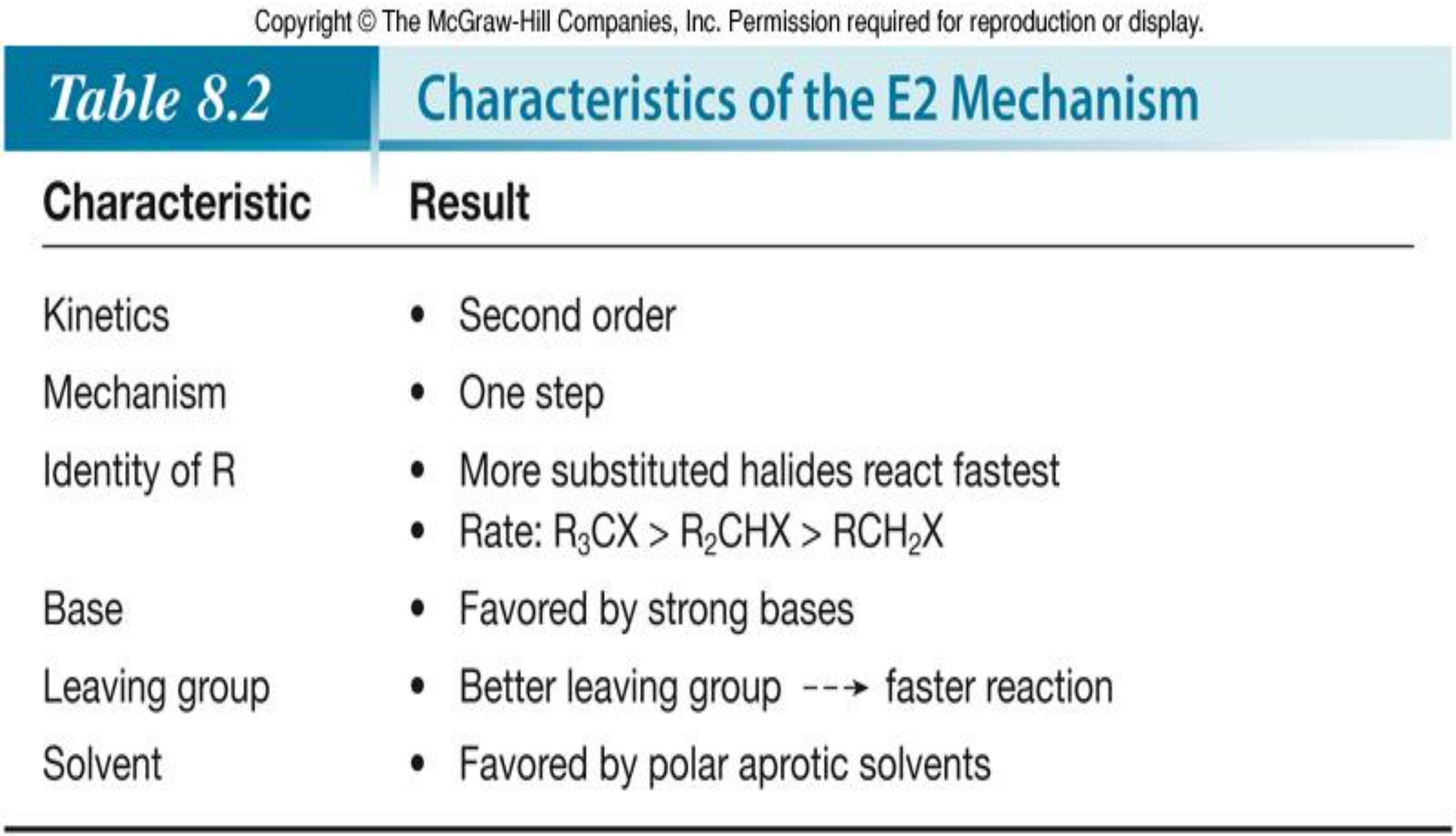
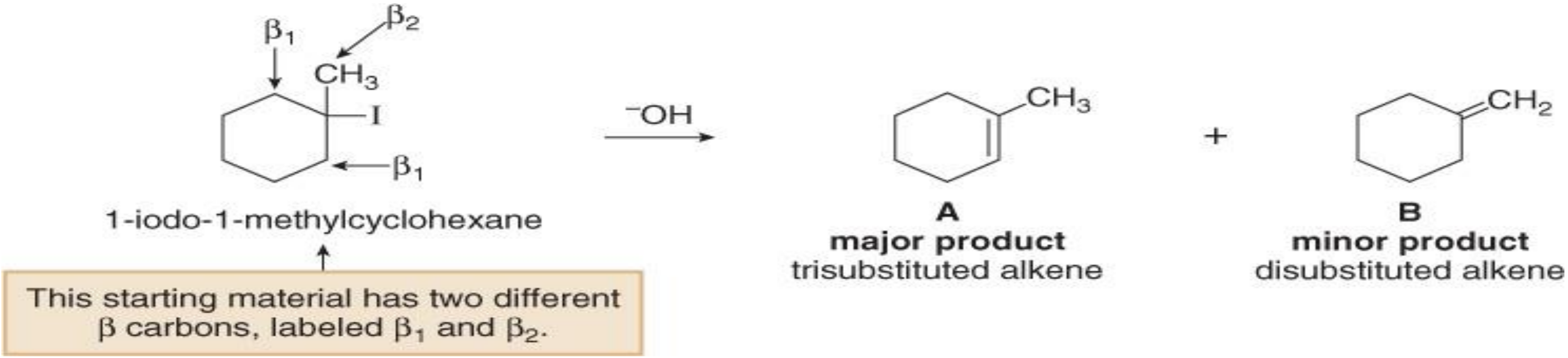


Table 8.2 Characteristics of the E2 Mechanism

Characteristic	Result
Kinetics	• Second order
Mechanism	• One step
Identity of R	• More substituted halides react fastest • Rate: $R_3CX > R_2CHX > RCH_2X$
Base	• Favored by strong bases
Leaving group	• Better leaving group --→ faster reaction
Solvent	• Favored by polar aprotic solvents

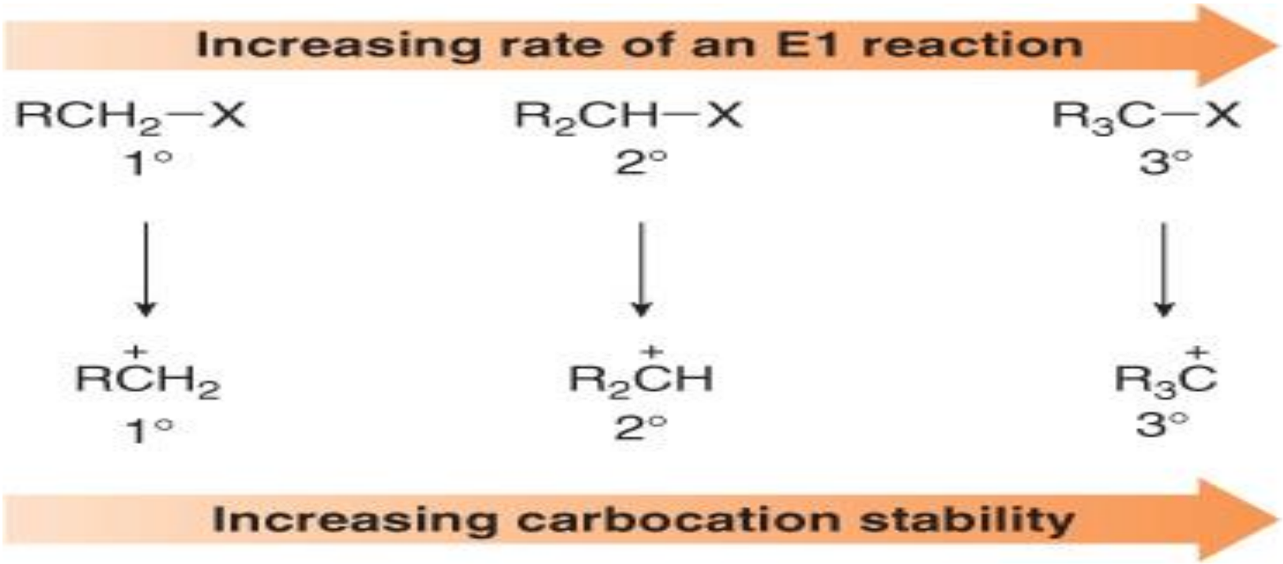
The Zaitsev Rule

- **The Zaitsev (Saytzeff) Rule**
- Recall that when alkyl halides have two or more different β carbons, more than one alkene product is formed.
- When this happens, one of the products usually predominates.
- The major product is the more stable product—the one with the more substituted double bond.
- This phenomenon is called the Zaitsev rule.



Factors in E1 reactions

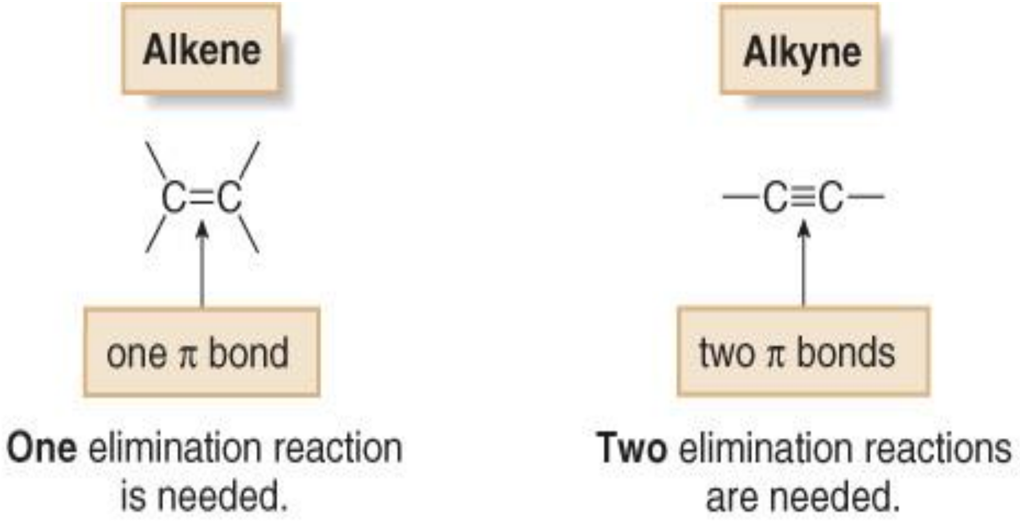
- The rate of an E1 reaction increases as the number of R groups on the carbon with the leaving group increases.



- The strength of the base usually determines whether a reaction follows the E1 or E2 mechanism. Strong bases like ^-OH and ^-OR favor E2 reactions, whereas weaker bases like H_2O and ROH favor E1 reactions.

E2 Reactions and aklene, Alkyne Synthesis

- A single elimination reaction produces a π bond of an alkene. Two consecutive elimination reactions produce two π bonds of an alkyne.



Alkene

one π bond

One elimination reaction is needed.

Alkyne

two π bonds

Two elimination reactions are needed.

◆ Alkynes are prepared by two successive dehydrohalogenation reactions.

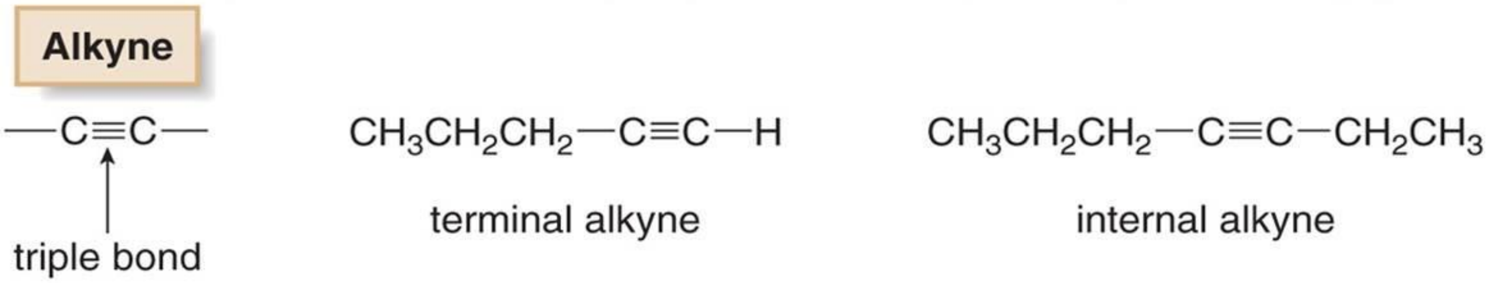
Organic chemistry

Alkynes

$$-C\equiv C-$$

Alkyne Structure

- **Alkynes contain a carbon-carbon triple bond.**
- **An alkyne has the general molecular formula C_nH_{2n-2}, giving it <u>four</u> fewer hydrogens than the maximum possible for the number of carbons present.**
- **The triple bond introduces two degrees of unsaturation.**
- **Terminal alkynes have the triple bond at the end of the carbon chain so that a hydrogen atom is directly bonded to a carbon atom of the triple bond.**
- **Internal alkynes have a carbon atom bonded to each carbon atom of the triple bond.**



$CH_3CH_2CH_2—C≡C—H$

terminal alkyne

$CH_3CH_2CH_2—C≡C—CH_2CH_3$

internal alkyne

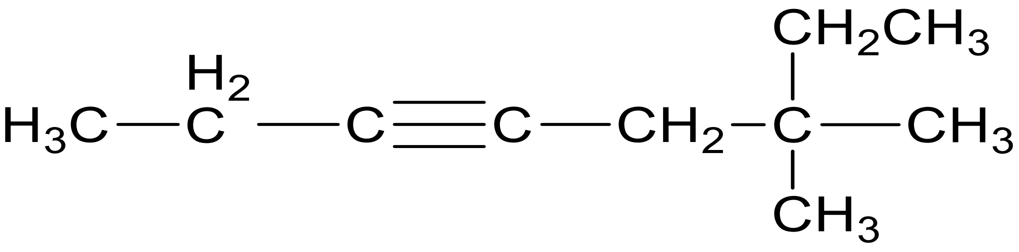
Nomenclature

- **Alkynes are named in the same general way that alkenes are named.**

- **In the IUPAC system, change the –*ane* ending of the parent alkane name to the suffix –*yne*.**

- **Choose the longest continuous chain that contains both atoms of the triple bond and number the chain to give the triple bond the lower number.**

Example: Give the IUPAC name of the following alkyne:



$$H_3C-\overset{H_2}{C}-C\equiv C-CH_2-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_2CH_3}{C}}-CH_3$$

Physical Properties of Alkynes

The physical properties of alkynes resemble those of hydrocarbons of similar shape and molecular weight.

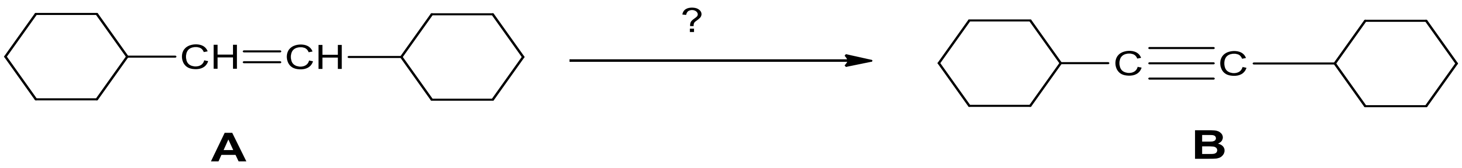
1. Alkynes have low melting points and boiling points.

2. Melting point and boiling point increase as the number of carbons increases.

3. Alkynes are soluble in organic solvents and insoluble in water.

Example: Preparation of Alkynes from Alkenes

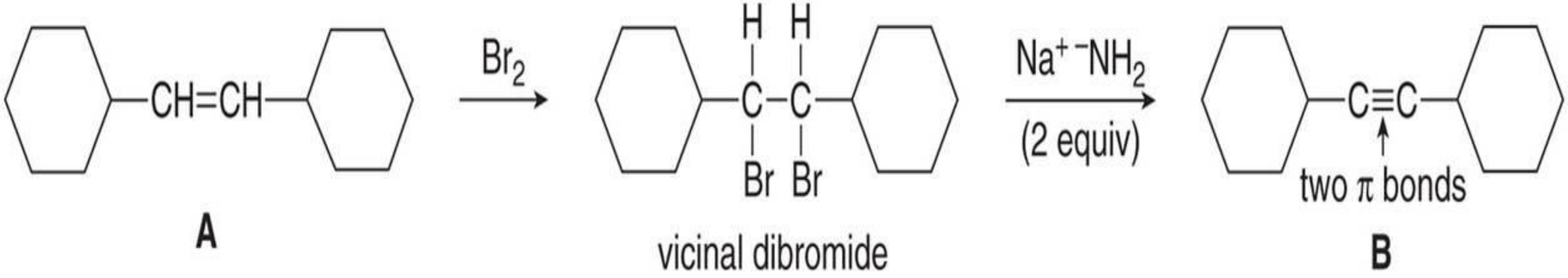
Convert alkene A into alkyne B by stepwise method.



- Since vicinal dihalides are readily made from alkenes, one can convert an alkene to the corresponding alkyne in a two-step process involving:

. **Addition of X_2 (halogenation) forms vicinal dihalide.**

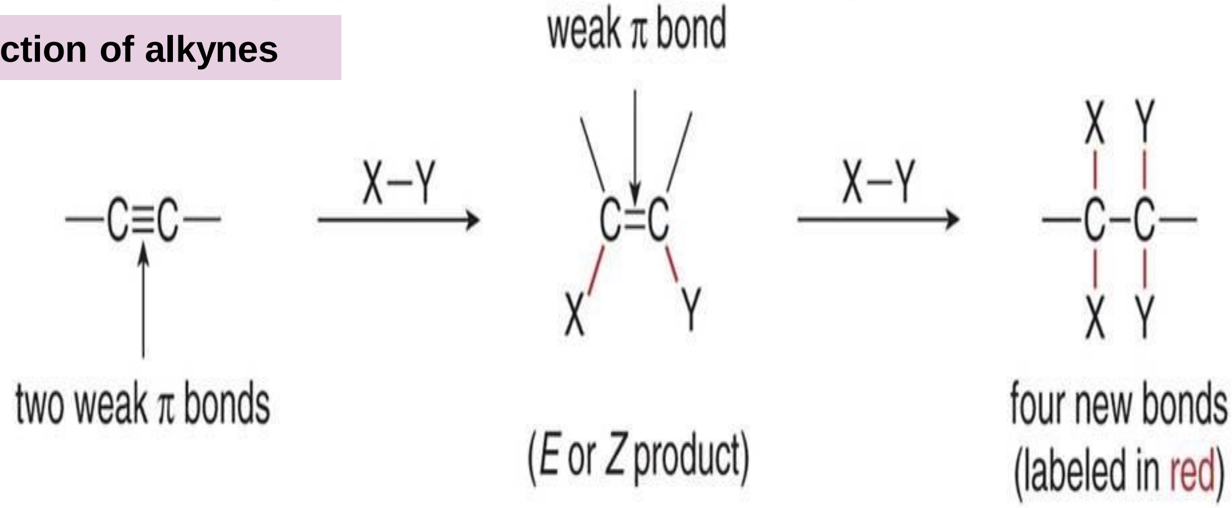
- **Elimination of two equivalents of HX forms two π bonds.**



1. Addition Reactions of Alkynes

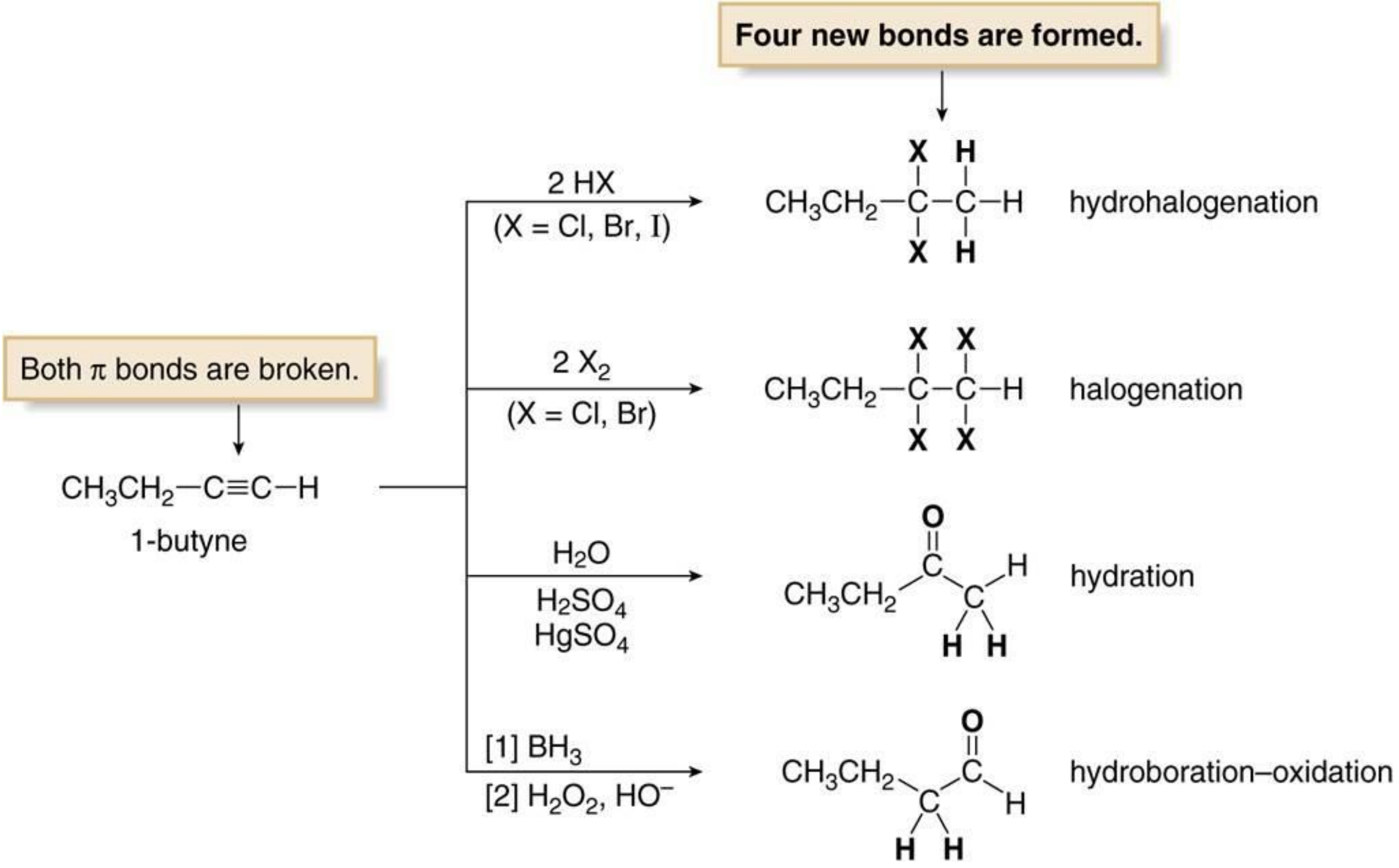
- **Like alkenes, alkynes undergo addition reactions because they contain relatively weak π bonds.**
- **Two sequential reactions can take place: addition of one equivalent of reagent forms an alkene, which can then add a second equivalent of reagent to yield a product having four new bonds.**

General addition reaction of alkynes



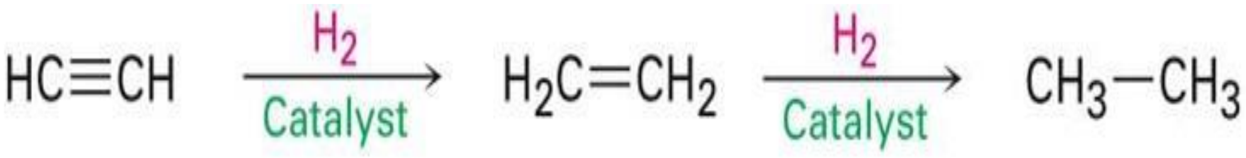
Four Addition Reactions of Alkynes

Alkynes react with electrophiles. Four addition reactions are illustrated in this figure using 1- butyne as starting material.



Reduction of alkynes

- Alkynes are reduced to alkanes by addition of H_2 over a metal catalyst.
- The reaction occurs in two steps through an alkene intermediate.
- Complete reduction to the alkane occurs when palladium on carbon (Pd/C) is used as catalyst

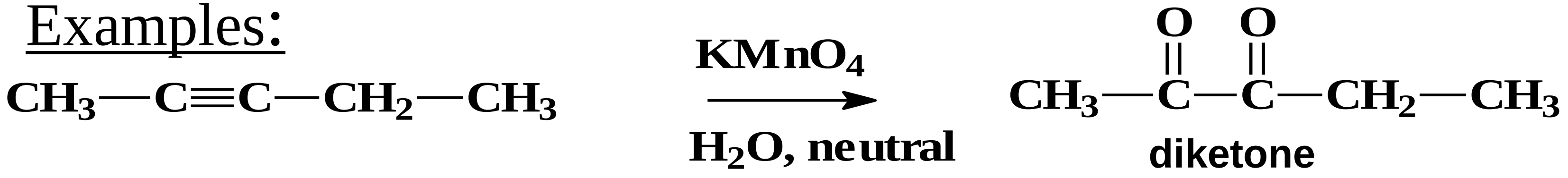


$$HC{\equiv}CH \xrightarrow[\text{Catalyst}]{H_2} H_2C{=}CH_2 \xrightarrow[\text{Catalyst}]{H_2} CH_3{-}CH_3$$

Oxidation Reaction of Alkynes with $KMnO_4$

- Alkynes are oxidized by the same reagents that oxidize alkenes. Disubstituted alkynes react with potassium permanganate to yield vicinal diketones (1,2-diketones) in mild conditions. While, warm and basic $KMnO_4$ cleaves the triple bond.
- Examples:

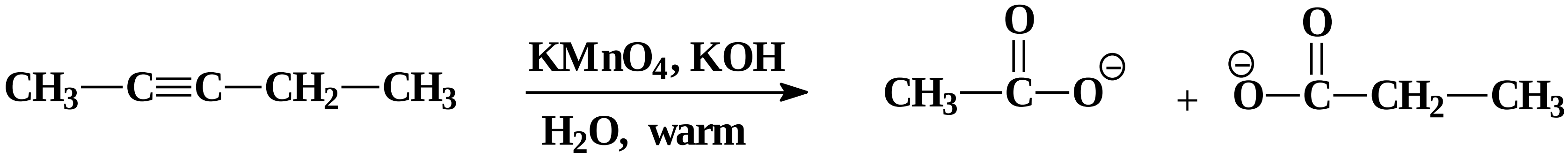
A.



$$CH_3-C\equiv C-CH_2-CH_3 \xrightarrow[H_2O,\ neutral]{KMnO_4} CH_3-\overset{\overset{O}{\|}}{C}-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

Note: **Mild conditions; dilute and neutral.**

B.

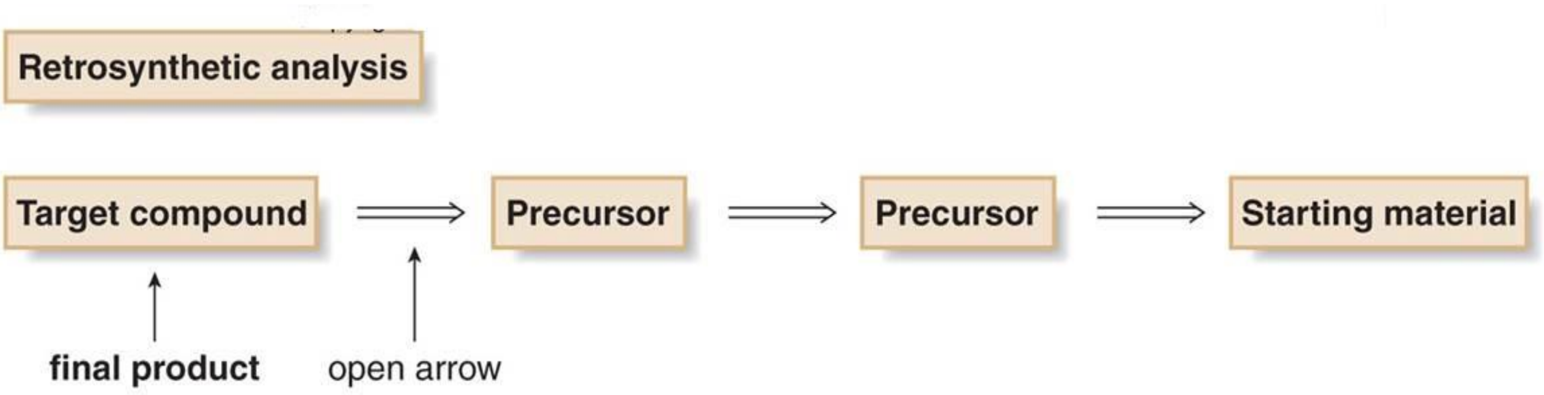


$$CH_3-C\equiv C-CH_2-CH_3 \xrightarrow[H_2O,\ warm]{KMnO_4,\ KOH} CH_3-\overset{\overset{O}{\|}}{C}-O^{\ominus} + {}^{\ominus}O-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

Note: **Harsher conditions; warm and basic.**

Retrosynthetic Analysis

- **Retrosynthetic analysis is the method of working backwards from a target compound to starting materials.**
- **To write a synthesis working backwards, an open arrow (⇒) is used to indicate that the product is drawn on the left and the starting material on the right.**

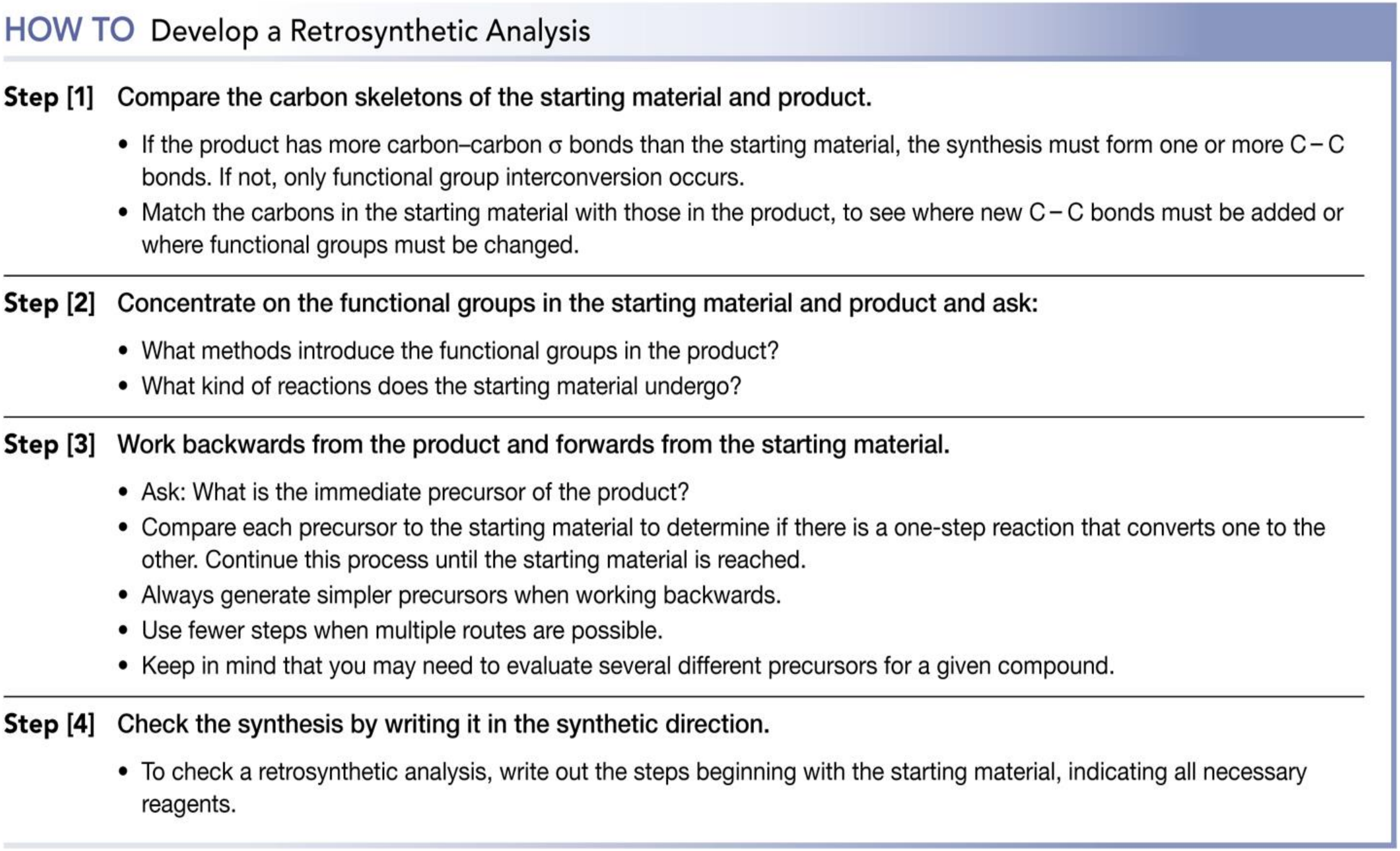


- **In designing a synthesis, reactions are often divided into two categories:**

1. Those that form new carbon-carbon bonds.

2. Those that convert one functional group into another—that is, functional group interconversions.

Steps to Develop a Retrosynthetic Analysis



HOW TO Develop a Retrosynthetic Analysis

Step [1] **Compare the carbon skeletons of the starting material and product.**

- If the product has more carbon–carbon σ bonds than the starting material, the synthesis must form one or more C–C bonds. If not, only functional group interconversion occurs.
- Match the carbons in the starting material with those in the product, to see where new C–C bonds must be added or where functional groups must be changed.

Step [2] **Concentrate on the functional groups in the starting material and product and ask:**

- What methods introduce the functional groups in the product?
- What kind of reactions does the starting material undergo?

Step [3] **Work backwards from the product and forwards from the starting material.**

- Ask: What is the immediate precursor of the product?
- Compare each precursor to the starting material to determine if there is a one-step reaction that converts one to the other. Continue this process until the starting material is reached.
- Always generate simpler precursors when working backwards.
- Use fewer steps when multiple routes are possible.
- Keep in mind that you may need to evaluate several different precursors for a given compound.

Step [4] **Check the synthesis by writing it in the synthetic direction.**

- To check a retrosynthetic analysis, write out the steps beginning with the starting material, indicating all necessary reagents.

Analytical chemistry

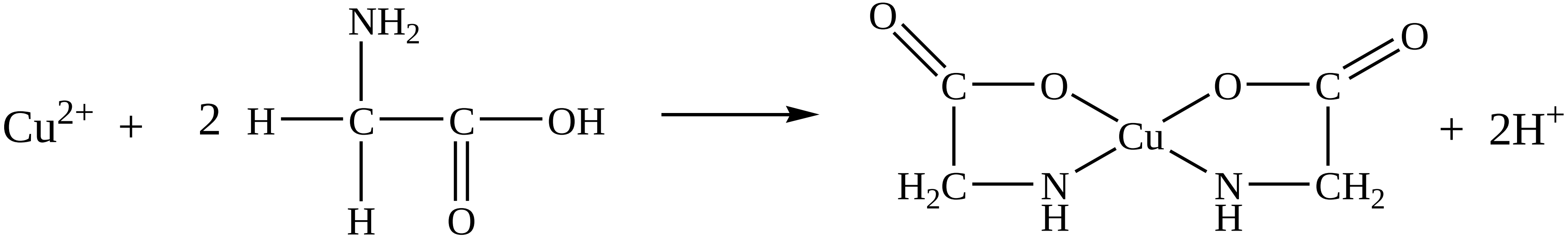
First class students

Complexation and Precipitation Reactions and Titrations

- Complex-formation reactions are widely used in analytical chemistry.
- One of the first uses of these reactions was for titrating cations.
- In addition, many complexes are colored or absorb ultraviolet radiation; the formation of these complexes is often the basis for spectrophotometric determinations.

- Some complexes are sparingly soluble and can be used in gravimetric analysis.
- Complexes are also widely used for extracting cations from one solvent to another and for dissolving insoluble precipitates.
- The most useful complex forming reagents are organic compounds that contain several electron donor groups that form multiple covalent bonds with metal ions.

- **Complexometric method**: titrimetric methods based on complex formation.
- **Chelate**: when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-member heterocyclic ring.
- The copper complex of glycine; the copper bonds to both the oxygen of the carboxyl group and the nitrogen of amine group:



Glycine

Cu^{2+} complex with glycine

Types of ligands

- Unidentate: a ligand that has a single donor group Ex: NH_3
- Bidentate: a ligand that has two groups available for covalent bonding Ex: glycine
- Tridentate, tetradentate, pentadentate, and hexadentate chelating agents are also known.

Macrocycles Ligands

- Another important type of complex is formed between metal ions and cyclic organic compounds(**macrocycles**).
- These molecules contain nine or more atoms in the cycle and include at least three heteroatoms, usually oxygen, nitrogen or sulfur.
- Crown ethers, such as 18-crown-6 and dibenzo-18-crown-6 are examples of organic macrocycles.
- The selectivity of a ligand for one metal ion over another relates to the stability of the complexes formed.

Complexation Equilibria

Complexation reactions involve a metal ion M reacting with a ligand L to form a complex ML.

$$M + L \rightleftharpoons ML$$

Complexation reactions occur in a stepwise fashion, and the reaction above is often followed by additional reactions:

$$\begin{array}{cccc} ML & + \; L & \rightleftharpoons & ML_2 \\ ML_2 & + \; L & \rightleftharpoons & ML_3 \\ \vdots & \vdots & & \vdots \\ ML_{n-1} & + \; L & \rightleftharpoons & ML_n \end{array}$$

Organic Complexing Agents

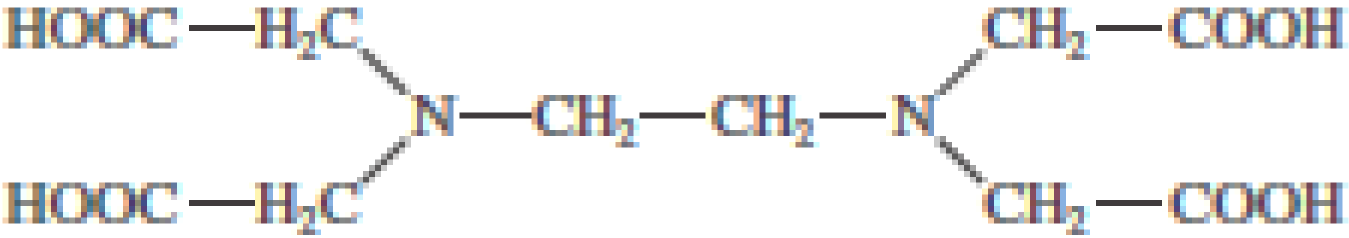
- Several different organic complexing agents have become important in analytical chemistry because of their inherent sensitivity and potential selectivity in reacting with metal ions.
- Organic reagents are particularly useful in precipitating metal and in extracting metal from one solvent to another.
- The most useful organic reagents form chelate complexes with metal ions.

AMINOCARBOXYLIC ACID TITRATIONS

- Tertiary amines that also contain carboxylic acid groups form remarkably stable chelates with many metal ions.
- Gerold Schwarzenbach, a Swiss chemist, first recognized their potential as analytical reagents in 1945.

Ethylenediaminetetraacetic Acid (EDTA)

- Ethylenediaminetetraacetic acid, which is also called (ethylenedinitrilo)tetraacetic acid.
- It is commonly shortened to EDTA, is the most widely used complexometric titrant. Fully protonated EDTA has the structural formula



Structural formula of EDTA.

EDTA Species

- The various EDTA species are often abbreviated H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-}.
- H_4Y is the major component in very acidic solutions.
- The fully unprotonated form Y^{4-} is a significant component only in very basic solutions (pH> 10).
- Throughout the pH range of 3 to 10, the species H_2Y^{2-} and HY^{3-} are predominant.
- See figure **17F-1**

Reagents for EDTA Titrations

- The free acid H_4Y and the dihydrate of the sodium salt, $Na_2H_2Y.\ 2H_2O$, are commercially available in reagent quality.
- However, the free acid is not very soluble in water, the dihydrate, $Na_2H_2Y.\ 2H_2O$, is most commonly used to prepare standard solutions.

Complexes of EDTA and Metal Ions

- Solutions of EDTA are particularly valuable as titrants because the EDTA *combines with metal ions stoichiometry in a 1:1 ratio regardless of the charge on the cation*. For example, the silver and aluminum complexes are formed by the reactions

$$Ag^{+} + Y^{4-} \rightleftharpoons AgY^{3-}$$

$$Al^{3+} + Y^{4-} \rightleftharpoons AlY^{-}$$

- In general, we can write the reaction of the EDTA anion with a metal ion M^{n+}
- $M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\,[Y^{4-}]}$$

K_{MY} the formation constants for common EDTA complexes.

Equilibrium Calculations Involving EDTA

- A titration curve for the reaction of a cation M^{n+} with EDTA consists of a plot of pM (pM = $-\log[M^{n+}]$) versus reagent volume. In the early stage of a titration, values for pM are readily computed by assuming that the equilibrium concentration of M^{n+} is equal to its analytical concentration, which is found from stoichiometric data.

The Derivation of Conditional Formation Constant

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{(n-4)+}$$

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}][Y^{4-}]} \qquad \text{.............................. 1}$$

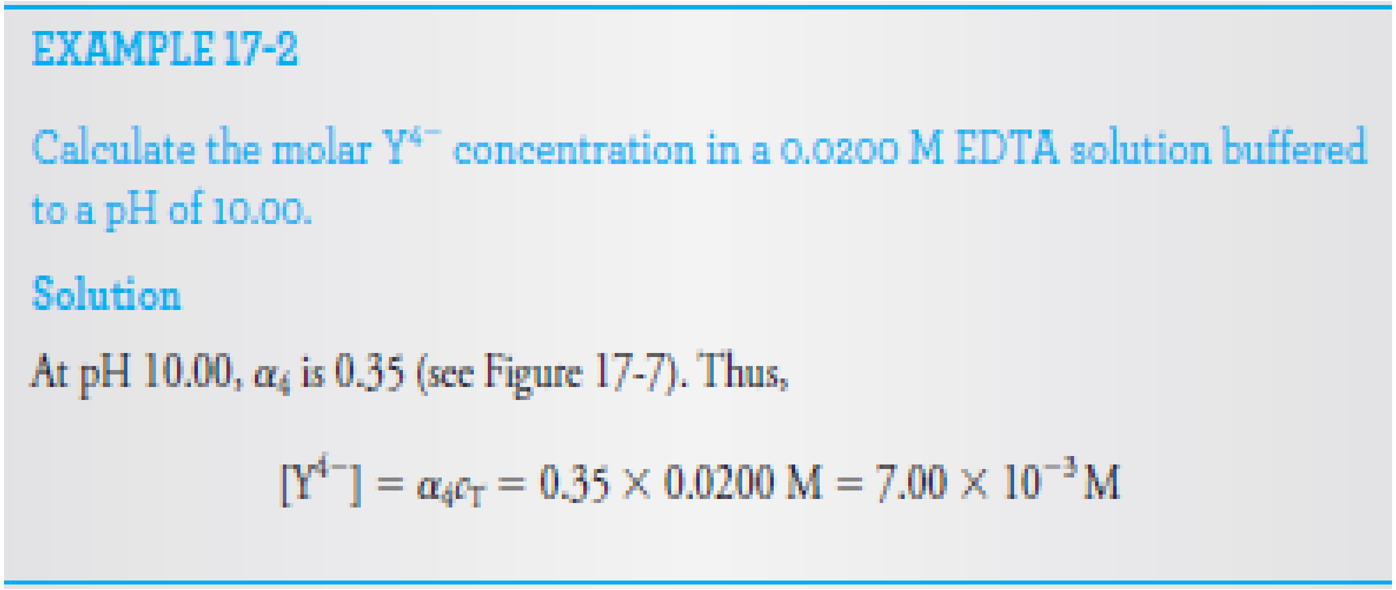
$$\alpha_4 = \frac{[Y^{4-}]}{C_T} \qquad \text{.............................. 2}$$

$$K_{MY} = \frac{[MY^{(n-4)+}]}{[M^{n+}]\,\alpha_4 C_T}$$

$$K'_{MY} = K_{MY}\,\alpha_4 = \frac{[MY^{(n-4)+}]}{[M^{n+}]\,C_T} \qquad \text{.............................. 3}$$

By using Eq no. 2

$$\alpha_4 = \frac{[Y^{4-}]}{c_T}$$



EXAMPLE 17-2

Calculate the molar Y^{4-} concentration in a 0.0200 M EDTA solution buffered to a pH of 10.00.

Solution

At pH 10.00, α_4 is 0.35 (see Figure 17-7). Thus,

$$[Y^{4-}] = \alpha_4 c_T = 0.35 \times 0.0200\ M = 7.00 \times 10^{-3}\ M$$

EDTA Titration Curves

Example 17-5

Use a spreadsheet to construct the titration curve of pCa versus volume of EDTA for 50.00mL of 0.00500M Ca^{2+} being titrated with 0.0100M EDTA in a solution buffered to a constant pH of 10.0.

Solution:

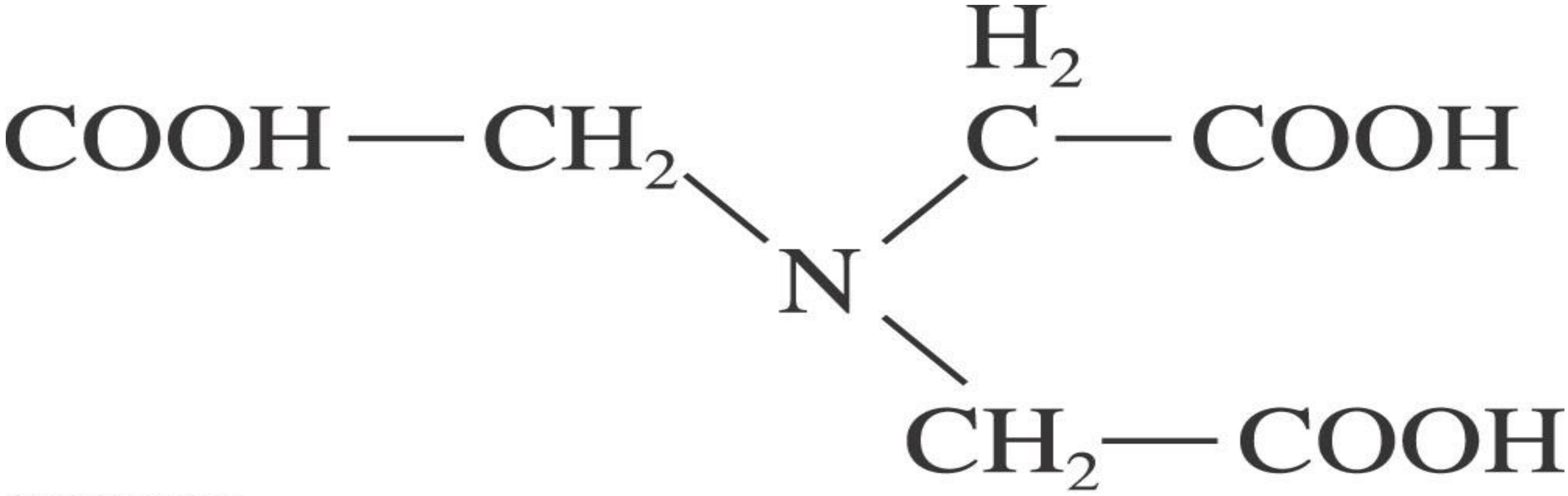
- We need the conditional formation constant for the CaY complex. This constant is obtained from the formation constant of the complex (Table 17-4) and the α_4 value for EDTA at pH 10 (see Figure 17-7). If we substitute into Equation no. 3, we get:

$$K'_{\mathrm{CaY}} = \frac{[\mathrm{CaY}^{2-}]}{[\mathrm{Ca}^{2+}]c_T} = \alpha_4 K_{\mathrm{CaY}}$$

$$= 0.35 \times 5.0 \times 10^{10} = 1.75 \times 10^{10}$$

Nitrilotriacetic acid

- Nitrilotriacetic acid (NTA) is the second most common aminopolycarboxylic acid used for titrations. It is a tetradentate chelating agent and has the structure



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Analytical Chemistry

Precipitation Titrations

1st class students

د. مي محمد جواد

Precipitation Titrations

- Precipitation titrations are based on reactions that yield ionic compounds of limited solubility. Precipitation titrimetry is one of the oldest analytical techniques. The slow rate of formation of most precipitates, however, limits the number of precipitating agents that can be used in titrations to a handful.

- The most widely used and important precipitating reagent, **silver nitrate**, which is used for the determination of the halogens, the halogen-like anions, mercaptans (Thiols), fatty acids. Titrations with silver nitrate are sometimes called **argentometric titrations**.

The Shapes of Titration Curves

- Titration curves for precipitation reactions are calculated in a completely analogous way to the methods for titrations involving strong acids and strong bases.
- The titration curves for precipitation reactions usually consist of a plot of pAg versus volume of the silver reagent (usually $AgNO_3$). **Example 17-1** illustrates how p-functions are obtained for the preequivalence-point region, the postequivalence -point region, and the equivalence point for a typical precipitation titration.

- **Example 17-1**
- Calculate the silver ion concentration in terms of pAg during the titration of 50.00 mL of 0.05000 M NaCl with 0.1000 M $AgNO_3$ after the addition of the following volumes of reagent: (a) in the preequivalence point region at 10.00 mL, (b) at the equivalence point (25.00 mL), (c) after the equivalence point at 26.00 mL. For AgCl, $K_{sp} = 1.82 \times 10^{-10}$.

$$\mathrm{Ag}^+(aq) + \mathrm{Cl}^-(aq) \rightleftharpoons \mathrm{AgCl}(s)$$

$$K_{sp} = [Ag^+][Cl^-]$$

NOTE: The solubility product constant, Ksp, is the equilibrium constant for a solid substance dissolving in an aqueous solution. It represents the level at which a solute dissolves in solution. The more soluble a substance is, the higher the Ksp value it has.

(b) Equivalence Point pAg

At the equivalence point, $[Ag^+] = [Cl^-]$, and $[Ag^+][Cl^-] = K_{sp} = 1.82 \times 10^{-10} = [Ag^+]^2$

$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{1.82 \times 10^{-10}} = 1.35 \times 10^{-5}$$

$$pAg = -\log(1.35 \times 10^{-5}) = 4.87$$

(c) Postequivalence-Point Region

At 26.00 mL of $AgNO_3$, Ag^+ is in excess so

$$[Ag^+] = c_{AgNO_3} = \frac{(26.00 \times 0.1000 - 50.00 \times 0.05000)}{76.00} = 1.32 \times 10^{-3}\ M$$

$$pAg = -\log(1.32 \times 10^{-3}) = 2.88$$

Additional results in the postequivalence-point region are obtained in the same way and are shown in Table 17-2. The titration curve can also be derived from the charge-balance equation as shown for an acid/base titration in Feature 14-1.

The Effect of Concentration on Titration Curves

- The effect of reagent and analyte concentration on titration curves can be seen in the data in Table 17-2 and the two curves shown in **Figure 17-2**. With 0.1000 M AgNO3 (Curve *A*), the change in pAg in the equivalence-point region is large, about 2 pAg units. With the 0.01000 M reagent, the change is about 1 pAg unit, but still pronounced.

The Effect of Reaction Completeness on Titration Curves

- **Figure 17-3** illustrates the effect of solubility product on the sharpness of the end point for titrations with 0.1 M silver nitrate. Note that the change in pAg at the equivalence point becomes greater as the solubility products become smaller, that is, as the reaction between the analyte and silver nitrate becomes more complete.
- By choosing an indicator that changes color in the pAg region of 4 to 6, titration of chloride ions should be possible with a minimal titration error.

End Points for Argentometric Titrations

- Three types of end points are: (1) chemical, (2) potentiometric, (3) amperometric.
- In this section, we describe the chemical indicator methods.
- The chemical end point consists of a color change or the appearance or disappearance of turbidity. **The requirements** are (1) the color change should occur over a limited range in the p-function, and (2) the color change should take place within the steep portion of the titration curve.

The Volhard Method (Colored Complex)

- The **Volhard method** is one of the most common argentometric methods. In this method, silver ions are titrated with a standard solution of thiocyanate ion:

$$Ag^{+} + SCN^{-} \rightleftharpoons AgSCN_{(s)}$$

- The most important application of the Volhard method is the indirect determination of halide ions example chloride ion. A measured excess of standard silver nitrate solution is added to the sample, and the excess silver is determined by back-titration with a standard thiocyanate solution.

Formation of a Colored Precipitate
The Mohr Method

- Sodium chromate can serve as an indicator for the argentometric determination of chloride, bromide, and cyanide ions by reacting with silver ion to form a brick-red silver chromate (Ag_2CrO_4) precipitate in the equivalence-point region. The reactions involved in the determination of chloride and bromide (X^-) are:

titration reaction: $Ag^+ + X^- \rightleftharpoons AgX_{(s)}$ [white]

indicator reaction: $2Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_{4(s)}$ [red]

Adsorption Indicators: The Fajans Method

- The **Fajans** method uses an adsorption indicator, an organic compound that adsorbs onto or desorbs from the surface of the solid in a precipitation titration.

INTRODUCTION

Analytical Chemistry deals with methods for determining the chemical composition of samples.

Qualitative Analysis (identification) provides information about the identity of species or functional groups in the sample (an analyte can be identified).

Quantitative Analysis provides numerical information of analyte (quantitate the exact amount or concentration), which is done either

1. Classical Methods of analysis: Wet chemical methods such as precipitation, extraction, distillation, boiling or melting points, gravimetric and titrimetric or volumetric measurements.

2. Instrumental Methods of analysis: Analytical measurements (conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, fluorescence etc.) are made using instrumentation.

Types of Instrumental Methods

1. Spectroscopic methods:
   a. Atomic spectroscopy
   b. Molecular spectroscopy
2. Chromatographic methods (separations).
3. Electrochemistry.

Gravimetric methods of analysis

are quantitative methods that are based on determining the mass of a pure compound to which the analyte is chemically related. Or

- By adding excess Cl^- to the sample, essentially all of the Pb^{+2} will precipitate as $PbCl_2$.
- Mass of $PbCl_2$ is then determined.

- used to calculate the amount of Pb^{+2} in original solution

Classifications of Gravimetric methods

1-Precipitation gravimetry, the analyte is separated from a solution of the sample as a precipitate and is converted to a compound of known composition that can be weighed.

2-Volatilization gravimetry, the analyte is separated from other constituents of a sample by conversion to a gas of known chemical composition. The weight of this gas then serves as a measure of the analyte concentration.

3-Electrogravimetry, the analyte is separated by deposition on an electrode by an electrical current. The mass of this product then provides a measure of the analyte concentration.

Properties of Gravimetric Analysis

- Traditional Method.
- Cheap, easily available apparatus, simple to carry out.
- Slow, especially when accurate results are required.
- A wide range of sample concentrations (ng - kg).
- No calibration required (except for the balance).
- Accurate.

Precipitation Gravimetry

In precipitation gravimetry, the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, converted to a product of known composition by suitable heat treatment, and weighed. For example, a precipitation method for determining calcium in natural water is one of the official methods of the Association of Official Analytical Chemists. In this technique, an excess of oxalic acid ($H_2C_2O_4$) is added to an aqueous solution of the sample. Ammonia (NH_3) is then added, which neutralizes the acid and causes essentially all of the calcium in the sample to precipitate as calcium oxalate (CaC_2O_4).

The reactions are:

$$2NH_3 + H_2C_2O_4 \longrightarrow 2NH_4^{+} + C_2O_4^{-2}$$

$$Ca^{+2}\,(aq) + C_2O_4^{-2}\,(aq) \longrightarrow CaC_2O_4\,(s)$$

The precipitate, CaC_2O_4 is filtered using a weighted filtering crucible, then dried and ignited. The process converts the precipitate entirely to calcium oxide. The reaction is:

$$CaC_2O_4\,(s) \xrightarrow{\Delta} CaO\,(s) + CO\,(g) + CO_2\,(g)$$

After cooling, the crucible and precipitate are weighed, and the mass of calcium oxide is determined by subtracting the known mass of the crucible. The calcium content of the sample is then computed.

Procedure for gravimetric analysis (Precipitation gravimetry)

The steps required in gravimetric analysis, can be summarized as follows:

1. Preparation of the solution, by dissolving the sample
2. Precipitation
3. Digestion
4. Filtration
5. Washing
6. Drying or igniting
7. Weighing
8. Calculation

Properties of precipitates and precipitating reagents

Properties precipitating reagents

Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte. Specific reagents, which are rare, react only with a single chemical species. Selective reagents, which are more common, react with a limited number of species.

An example of a selective reagent is $AgNO_3$. The only common ions that it precipitates from acidic solution are Cl^-, Br^-, I^-, and SCN^-.
Dimethylglyoxime (DMG) is a specific reagent that precipitates only Ni^{+2} from alkaline solutions.

Properties of good precipitates

1. Easily filtered and washed free of contaminants.
2. Of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing.
3. Unreactive with constituents of the atmosphere.
4. of known chemical composition after it is dried or, if necessary, ignited.

Particle Size and Filterability of Precipitates

Why we prefer precipitates of large particles?

Precipitates consisting of ***large particles*** are generally desirable for gravimetric work because these particles are

1. easy to filter
2. easy to wash
3. Free of impurities.
4. In addition, precipitates of this type are usually purer than are precipitates made up of fine particles.

Factors that determine the particle size of precipitates

Physical nature of precipitate will be determined by relative rates of nucleation and particle growth and the particle size of solids formed by precipitation varies enormously, which are the following types:

1-*Colloidal suspensions* (the nucleation **faster** than particle growth)

- Whose tiny particles are invisible to the naked eye (10^{-7} - 10^{-4} cm in diameter).
- Colloidal particles show no tendency to settle from solution
- Not easily filtered.

2-*Crystalline suspension* (the particle growth **faster** than nucleation)

- Particles with dimensions on the order of tenths of a millimeter or greater.
- The temporary dispersion of such particles of a tend to settle spontaneously,
- Easily filtered.

Scientists have studied precipitate formation for many years, but the mechanism of the process is still not fully understood. It is certain, however, that the particle size of a precipitate is influenced by such experimental variables as ***precipitate solubility***, ***temperature***, ***reactant concentrations,*** and ***rate at which reactants are mixed***. The net effect of these variables can be accounted for, at least qualitatively, by assuming that the particle size is related to a single property of the system called the **relative supersaturations**, where:

$$\textbf{Relative supersaturations} = \frac{Q - S}{S} \text{ ……..Von Weimarn equation}$$

In this equation, ***Q*** is the concentration of the solute at any instant and ***S*** is its equilibrium solubility.

Generally, precipitation reactions are slow, so that even when a precipitating reagent is added drop by drop to a solution of an analyte, some supersaturation is likely. Experimental evidence indicated that the particle size of a precipitate varies inversely (inversely proportional) with the relative supersaturation during the time when the reagent is being introduced.

Supersaturated solution *is an unstable solution that contains a higher solute concentration than a saturated solution.*

Relationship between Supersaturation & Nucleation:

Thus, when ($Q - S$)/S is large, **many small crystals**, the precipitate tends to be colloidal, high surface area, more adsorption of impurities.

When ($Q - S$)/S is small, **fewer, larger crystals** a crystalline solid particles is more likely, low surface area, less adsorption of impurities.

Obviously, then, we want to keep Q low and S high during precipitation.

Several steps are commonly taken to maintain ***favorable conditions for precipitation or the experimental control of particle size.***

Keep Q low by:

1. Precipitate from ***dilute solution***.
2. Add ***dilute*** precipitating reagents ***slowly***, with effective ***stirring***. Stirring prevents local excesses of the reagent.

Keep S high by:

1. Precipitate from ***hot solution***. The solubility should not be too great or the precipitation will not be quantitative. The bulk of the precipitation may be performed in the hot solution, and then the solution may be cooled to make the precipitation quantitative.
2. Precipitate at as ***low*** a pH as is possible to maintain quantitative precipitation. Many precipitates are more soluble in the acid medium, and

this slows the rate of precipitation. They are more soluble because the anion of the precipitate combines with protons in the solution.

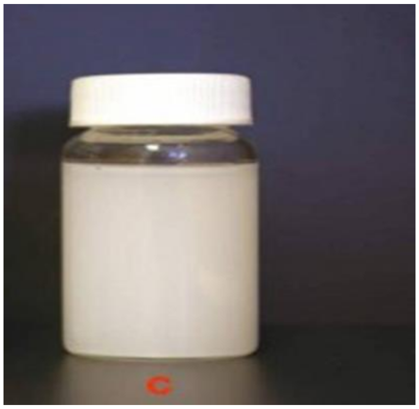
Mechanism of Precipitate Formation

The precipitates form in two ways: by **nucleation** and by **particle growth.**
In **nucleation**, a few ions, atoms, or molecules (perhaps as few as four or five) come together to form a stable solid (form small aggregates).

Particle growth : addition of molecules to a nucleus to form a crystal.

- If nucleation is faster than particle growth:

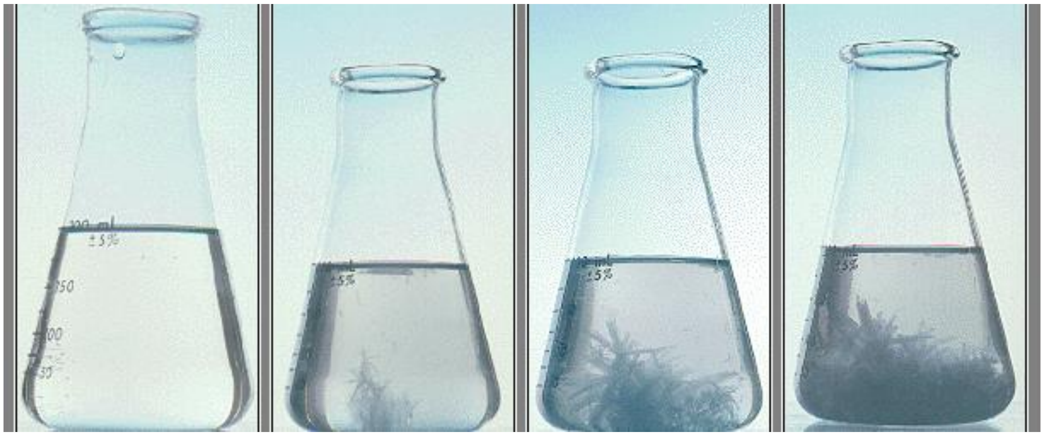
- a large number of small aggregates occur giving colloidal suspensions



Colloidal suspension

- If particle growth is faster than nucleation:

- only a few, large particles form giving pure crystals



Crystal formation

Colloidal Precipitates

Individual colloidal particles are 1. so small that they are not retained by ordinary filters. Moreover, 2. Brownian motion prevents their settling out of solution under the influence of gravity. Fortunately, however, we can coagulate, or agglomerate, the individual particles of most colloids to give a filterable, amorphous mass that will settle out of solution.

Why colloidal suspensions are stable and do not coagulate spontaneously?

Colloidal suspensions are stable because all of the particles of the colloid are either 1. positively or negatively charged and thus repel one another. 2.Colloidal particles are very small and have a very large surface-to-mass ratio, which promotes surface adsorption.

(***adsorption*** *is the process by which ions are retained on the* ***surface of a solid****).*

For example, when silver nitrate is first added to a solution containing chloride ion (ex: HCl), the colloidal particles of the precipitate are negatively charged as a result of adsorption of some of the excess chloride ions. This charge, though, becomes positive when enough silver nitrate has been added to provide an excess of silver ions. **Figure 1** shows a colloidal silver chloride particle in a solution that contains an excess of silver nitrate. Attached directly to the solid surface is the **primary adsorption layer**, which consists mainly of adsorbed silver ions. Surrounding the charged particle is a layer of solution, called the **counter-ion layer (secondary adsorption layer)**, which contains sufficient excess of negative ions (principally nitrate) to just balance the charge on the surface of the particle. The primarily adsorbed silver ions and the negative counter-ion layer constitute an **electric double layer** that imparts stability to the colloidal suspension. As colloidal particles approach one another, this double layer exerts an electrostatic repulsive force that prevents particles from colliding and adhering (figure 4).

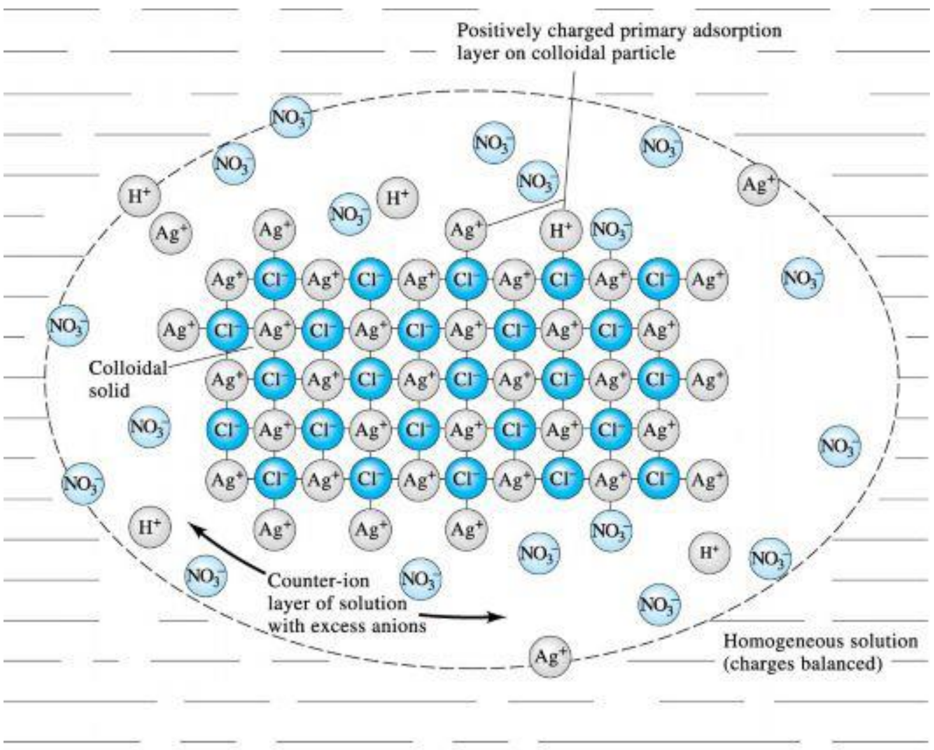


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Fig 1: A colloidal silver chloride particle suspended in a solution of silver nitrate

Coagulation of Colloids

Coagulation can be hastened by **1.** ***Heating***, decreases the number of adsorbed ions and thus the thickness of the double layer and the particles may also gain enough kinetic energy at the higher temperature to overcome the barrier to close approach imposed by the double layer.

By **2.** ***Stirring*** should be combined with heating and by **3.** ***Adding an electrolyte*** to the medium, this will lead to the concentration of counter-ions increases in the vicinity of each particle. As a result, the volume of solution that contains sufficient counter-ions to balance the charge of the primary adsorption layer decreases. The net effect of adding an electrolyte is thus shrinkage of the counter-ion layer. The particles can then approach one another more closely and agglomerate.

Peptization of Colloids

Peptization is the process by which a coagulated colloid reverts to its original dispersed state. When a coagulated colloid is washed, some of the electrolyte responsible for its coagulation is leached from the internal liquid in contact with the solid particles. Peptization is the reverse of coagulation (the precipitate reverts to a colloidal state and is lost). It is avoided by washing with a solution containing an electrolyte that volatilizes (ex: HNO_3, HCl, NH_3) when the precipitate is dried or ignited.

For example, silver chloride is usually washed with a dilute solution of nitric acid. While the precipitate no doubt becomes contaminated with acid, no harm is done, since the nitric acid is lost during the drying step.

Practical Treatment of Colloidal Precipitates

Colloids are best precipitated from **hot**, **stirred** solutions containing **sufficient electrolyte** to ensure coagulation. The filterability of a coagulated colloid frequently improves if it is allowed to stand for an **hour or more** in contact with the hot solution from which it was formed. This process is known as ***digestion.***

Digestion *is a process in which a precipitate is heated for an hour or more in the solution from which it was formed (the mother liquor).*

Mother liquor *is the solution from which a precipitate was formed.*

Crystalline Precipitates

Crystalline precipitates are generally more easily filtered and purified than are coagulated colloids. In addition, the size of individual crystalline particles, and thus their filterability, can be controlled to a degree.

Methods of Improving Particle Size and Filterability

The particle size of crystalline solids can often be improved significantly by minimizing Q or maximizing S or both as mentioned previously.

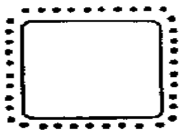
Digestion of crystalline precipitates (without stirring) for some time after formation often yields a purer, more filterable product.

Coprecipitation

Coprecipitation is a process in which *otherwise soluble* compounds are removed from solution during precipitate formation.

Or it is a process in which *normally soluble* compounds are carried out of solution by a precipitate.
There are four types of coprecipitation:

1. Surface adsorption.
2. Mixed-crystal formation (inclusion).
3. Occlusion.
4. Mechanical entrapment.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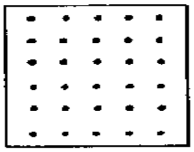
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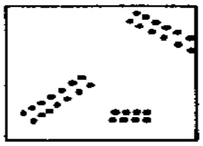
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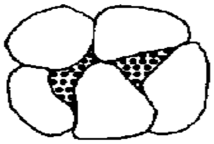
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1. Surface Adsorption

Adsorption is often the major source of contamination in coagulated colloids but of no significance in crystalline precipitates.

Because of the colloidal precipitates are with high surface area.
Example: in determination of Cl^-, AgCl ppt. is contaminated with Ag^+ (primary layer) and $NO3^-$ (counter-ion layer).
The effect: AgNO3 is coprecipitation with AgCl.

***Minimizing Adsorbed Impurities on Colloids*:**

The purity of many coagulated colloids is improved by
***A*. *Digestion*.** During this process, water is expelled from the solid to give a denser mass (particle size increased) that has a smaller specific surface area for adsorption.
B. Washing a coagulated colloid with a solution containing a volatile electrolyte may also be helpful because any nonvolatile electrolyte added earlier to cause coagulation is displaced by the volatile species.

C. Reprecipitation **(*double precipitation*):** A drastic but effective way to minimize the effects of adsorption. In this process, the filtered solid is redissolved in fresh solvent and reprecipitated.

2. ***Mixed-crystal formation(inclusion)***

In mixed-crystal formation, one of the ions in the crystal lattice of a solid is replaced by an ion of another element. For this exchange to occur, it is necessary that the two ions have the same charge and that their sizes differ by no more than about 5% and the salt of the same crystal class. This problem occurs with both colloidal suspensions and crystalline precipitates. Example (lead ion replace some of the barium ion). In order to *minimizing* this type of coprecipitation:

· the interfering ion may have to be separated before the final precipitation step.

· a different precipitating reagent that does not give mixed crystals with the ions interested may be used.

3. ***Occlusion***

When a crystal is growing rapidly during precipitate formation, foreign ions in the counter-ion layer may become trapped, or *occluded*, within the growing crystal.

4. ***Mechanical entrapment*** occurs when crystals lie close together during growth. Several crystals grow together and in so doing trap a portion of the solution in a tiny pocket.

Both *occlusion* and *mechanical entrapment* are at a minimum when the rate of precipitate formation is low, that is, under conditions of low supersaturation. In addition, digestion often reduces the effects of these types of coprecipitation.

Coprecipitation Errors

Coprecipitated impurities may cause either negative or positive errors in an analysis. If the contaminant is not a compound of the ion being determined, a positive error will always result. Therefore, a positive error is observed whenever colloidal silver chloride adsorbs silver nitrate during a chloride analysis.

Precipitation from Homogeneous Solution

Precipitation from homogeneous solution is a technique in which a precipitating agent is generated in a solution of the analyte by a slow chemical reaction. Local reagent excesses do not occur because the precipitating agent appears gradually and homogeneously throughout the solution and reacts immediately with the analyte. As a result, the relative supersaturation is kept low during the entire precipitation. In general, homogeneously formed precipitates, both colloidal and crystalline, are better suited for analysis than a solid formed by direct addition of a precipitating reagent.

Urea is often used for the homogeneous generation of hydroxide ion. The reaction can be expressed by the equation

$$(H_2N)_2CO + 3H_2O \longrightarrow CO_2 + 2NH_4^+ + 2OH^-$$

Representative methods based on precipitation by homogeneously generated reagents are given in Table 12-1.

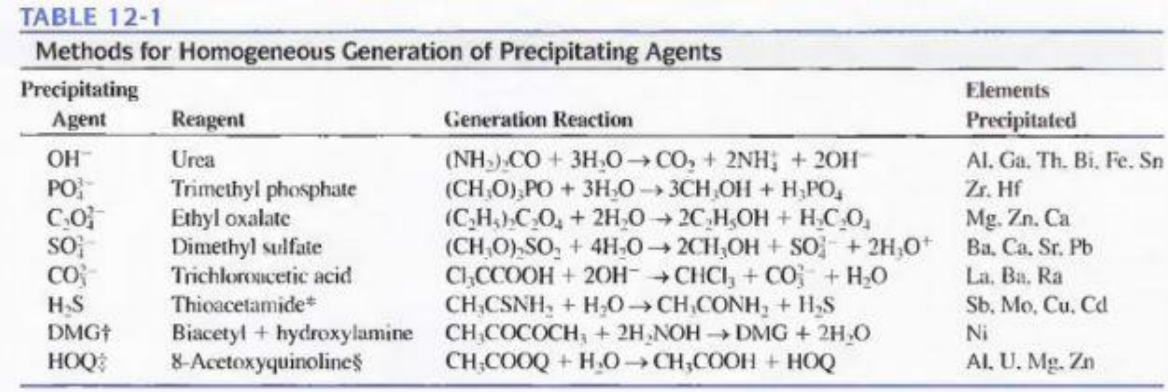


TABLE 12-1

Methods for Homogeneous Generation of Precipitating Agents

Precipitating Agent	Reagent	Generation Reaction	Elements Precipitated
OH^-	Urea	$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3PO + 3H_2O \rightarrow 3CH_3OH + H_3PO_4$	Zr, Hf
$C_2O_4^{2-}$	Ethyl oxalate	$(C_2H_5)_2C_2O_4 + 2H_2O \rightarrow 2C_2H_5OH + H_2C_2O_4$	Mg, Zn, Ca
SO_4^{2-}	Dimethyl sulfate	$(CH_3O)_2SO_2 + 4H_2O \rightarrow 2CH_3OH + SO_4^{2-} + 2H_3O^+$	Ba, Ca, Sr, Pb
CO_3^{2-}	Trichloroacetic acid	$Cl_3CCOOH + 2OH^- \rightarrow CHCl_3 + CO_3^{2-} + H_2O$	La, Ba, Ra
H_2S	Thioacetamide*	$CH_3CSNH_2 + H_2O \rightarrow CH_3CONH_2 + H_2S$	Sb, Mo, Cu, Cd
DMG†	Biacetyl + hydroxylamine	$CH_3COCOCH_3 + 2H_2NOH \rightarrow DMG + 2H_2O$	Ni
HOQ‡	8-Acetoxyquinoline§	$CH_3COOQ + H_2O \rightarrow CH_3COOH + HOQ$	Al, U, Mg, Zn

Drying and Ignition of Precipitates

After filtration, a gravimetric precipitate is heated until its mass becomes constant. Heating removes the solvent and any volatile species carried down with the precipitate. Some precipitates are also ignited to decompose the solid and form a compound of known composition more suitable form for weighing. This new Compound is often called the ***weighing form***.

The temperature required to dehydrate a precipitate completely may be as low as 100°C or as high as 1000°C.
Example : AgCl – drying in over 100 – 130 ̊C to remove physically-bound water.
_ Higher temp. is necessary if water is trapped in crystals / chemically-bound water / or ensure appropriate chemical changes
- $MgNH_4PO_4 \cdot 6H_2O \longrightarrow Mg_2P_2O_7$ 900 ̊C
- $CaC_2O_4 \longrightarrow CaO$ 1100 ̊C

Calculation of Results from Gravimetric Data

The results of a gravimetric analysis are generally computed from two experimental measurements: the mass of sample and the mass of a product of known composition. The examples that follow illustrate how such computations are carried out.

Calculations:

$$\%\ \text{analyte} = \frac{\text{Mass analyte}}{\text{Mass sample}} \times 100$$

Mass analyte = Mass ppt. × Gravimetric Factor (GF)

note: ppt. means precipitate

$$\%\ \text{analyte} = \frac{\text{Mass ppt.}}{\text{Mass sample}} \times \text{GF} \times 100$$

$$\text{Gravimetric factor} = \frac{\text{f w analyte (g/mol)}}{\text{f w ppt. weighed (g/mol)}} \times \frac{a}{b}$$

(*analyte or sought*)

a = number of moles of analyte

b = number of moles of ppt.

Example 1: How many grams of Cl (fw= 35.45 g/mol) are contained in a ppt. of AgCl (fw= 143.3 g/mol) that weighs 0.204g?

Solution: $Ag^+ + Cl^- \longrightarrow AgCl$ (ppt.)

Wt Cl^-= wt AgCl (ppt.) × G.F

$$= 0.204g \times \frac{\text{fw } \mathbf{Cl} \text{ (analyte) (g/mol)}}{\text{fw } \mathbf{AgCl} \text{ (ppt.)(g/mol)}} \times \frac{a}{b}$$

$$= 0.204g \times \frac{35.45}{143.3} \times \frac{1}{1}$$

$$=0.0505 \text{ g}$$

Example 2: To what weight of $AlCl_3$ (fw=133.3 g/mol) would 0.254 g of AgCl correspond?

Solution:

$AlCl_3 \longrightarrow 3$ AgCl ppt.

$$\text{Wt } AlCl_3 = 0.254g \times \frac{\text{F w } \mathbf{AlCl_3} \text{ (analyte)}}{\text{F w } \mathbf{AgCl} \text{ (ppt.)(g/mol)}} \times \frac{a}{b}$$

$$= 0.254 \times \frac{133.3}{143.3} \times \frac{1}{3} = 0.0787 \text{ g weight } AlCl_3$$

Applications of Gravimetric Methods

Gravimetric methods have been developed for most inorganic anions and cations, as well as for such neutral species as water, sulfur dioxide, carbon dioxide, and iodine. A variety of organic substances can also be determined gravimetrically. Examples include lactose in milk products, salicylates in drug preparations, phenolphthalein in laxatives, nicotine in pesticides, cholesterol in cereals, and benzaldehyde in almond extracts. Indeed, gravimetric methods are among the most widely applicable of all analytical procedures.

Inorganic Precipitating Agents

These reagents typically form slightly soluble salts or hydrous oxides with the analyte. As you can see from the many entries for each reagent, few inorganic reagents are selective. See table 12-2

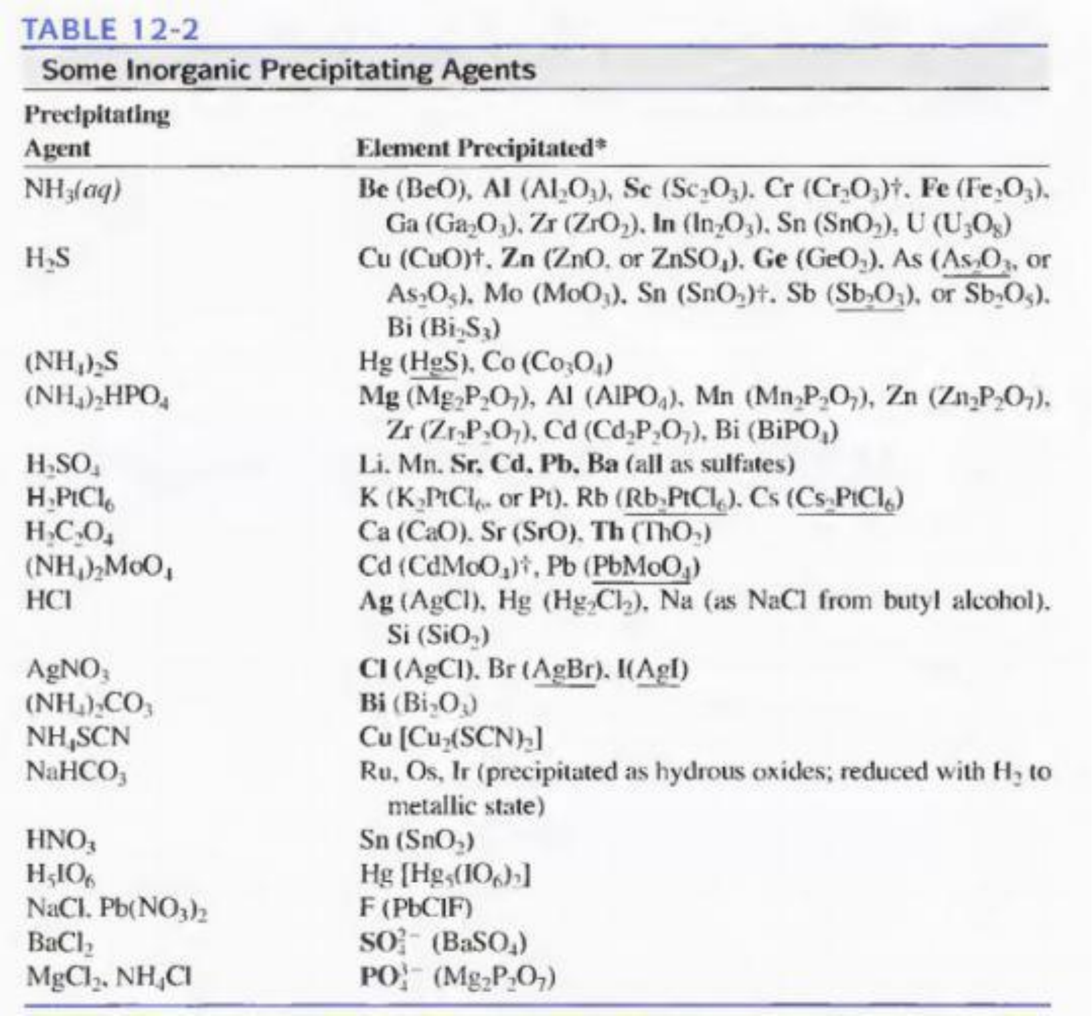


TABLE 12-2

Some Inorganic Precipitating Agents

Precipitating Agent	Element Precipitated*
$NH_3(aq)$	**Be** (BeO), **Al** (Al_2O_3), **Sc** (Sc_2O_3), **Cr** (Cr_2O_3)†, **Fe** (Fe_2O_3), Ga (Ga_2O_3), Zr (ZrO_2), **In** (In_2O_3), Sn (SnO_2), U (U_3O_8)
H_2S	Cu (CuO)†, **Zn** (ZnO, or $ZnSO_4$), **Ge** (GeO_2), As ($\underline{As_2O_3}$, or As_2O_5), Mo (MoO_3), Sn (SnO_2)†, Sb ($\underline{Sb_2O_3}$), or Sb_2O_5), Bi (Bi_2S_3)
$(NH_4)_2S$	Hg ($\underline{HgS}$), Co (Co_3O_4)
$(NH_4)_2HPO_4$	**Mg** ($Mg_2P_2O_7$), Al ($AlPO_4$), Mn ($Mn_2P_2O_7$), Zn ($Zn_2P_2O_7$), Zr ($Zr_2P_2O_7$), Cd ($Cd_2P_2O_7$), Bi ($BiPO_4$)
H_2SO_4	Li, Mn, **Sr, Cd, Pb, Ba** (all as sulfates)
H_2PtCl_6	K (K_2PtCl_6, or Pt), Rb ($\underline{Rb_2PtCl_6}$), Cs ($\underline{Cs_2PtCl_6}$)
$H_2C_2O_4$	Ca (CaO), Sr (SrO), **Th** (ThO_2)
$(NH_4)_2MoO_4$	Cd ($CdMoO_4$)†, Pb ($\underline{PbMoO_4}$)
HCl	**Ag** (AgCl), Hg (Hg_2Cl_2), Na (as NaCl from butyl alcohol), Si (SiO_2)
$AgNO_3$	**Cl** (AgCl), Br ($\underline{AgBr}$), I($\underline{AgI}$)
$(NH_4)_2CO_3$	**Bi** (Bi_2O_3)
NH_4SCN	Cu [$Cu_2(SCN)_2$]
$NaHCO_3$	Ru, Os, Ir (precipitated as hydrous oxides; reduced with H_2 to metallic state)
HNO_3	Sn (SnO_2)
H_5IO_6	Hg [$Hg_5(IO_6)_2$]
NaCl, $Pb(NO_3)_2$	F (PbClF)
$BaCl_2$	**SO_4^{2-}** ($BaSO_4$)
$MgCl_2$, NH_4Cl	**PO_4^{3-}** ($Mg_2P_2O_7$)

*Boldface type indicates that gravimetric analysis is the preferred method for the element or ion. An underscore indicates the most reliable gravimetric method.

Reducing Agents

These types of reagents convert an analyte to its elemental form for weighing. Table 12-3

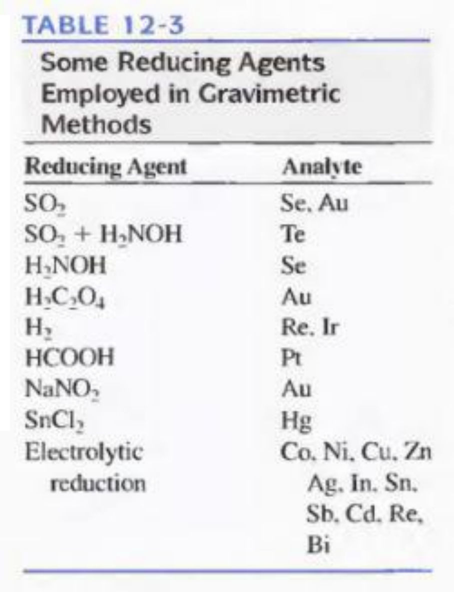


TABLE 12-3

Some Reducing Agents Employed in Gravimetric Methods

Reducing Agent	Analyte
SO_2	Se, Au
$SO_2 + H_2NOH$	Te
H_2NOH	Se
$H_2C_2O_4$	Au
H_2	Re, Ir
HCOOH	Pt
$NaNO_2$	Au
$SnCl_2$	Hg
Electrolytic reduction	Co, Ni, Cu, Zn Ag, In, Sn, Sb, Cd, Re, Bi

Organic Precipitating Agents

Numerous organic reagents have been developed for the gravimetric determination of inorganic species. Some of these reagents are significantly *more selective* in their reactions than are most of the inorganic reagents.

There are two types of organic reagents: one forms slightly soluble nonionic products called **coordination compounds**, and the other forms products in which the bonding between the inorganic species and the reagent is largely ionic.

Advantages of organic reagents

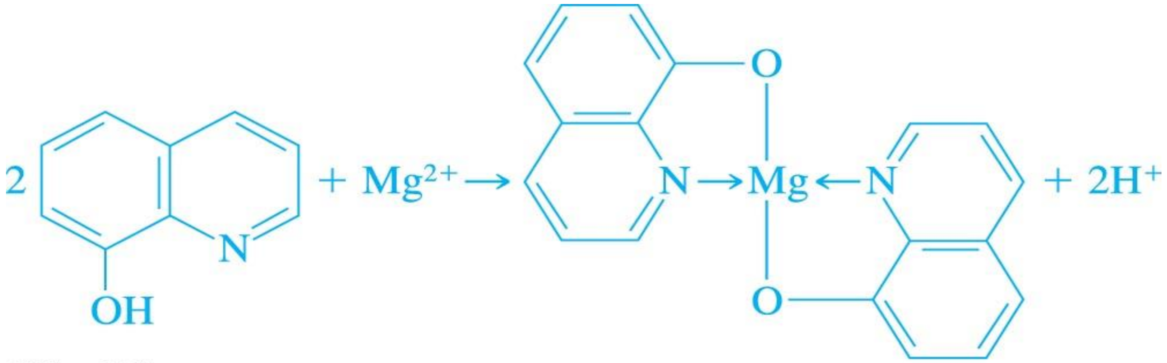
1. PPT products sparingly soluble in water
2. Colored
3. High molecular masses, so more ppt

Organic reagents that yield sparingly soluble coordination compounds typically contain at least two functional groups. Each of these groups is capable of bonding with a cation by donating a pair of electrons. The functional groups are located in the molecule such that a five- or six-membered ring results from the reaction. Reagents that form compounds of this type are called **chelating agents** and their products are called **chelates.**

Metal chelates are relatively nonpolar and, as a consequence, have solubilities that are low in water but high in organic liquids. Usually, these compounds possess low densities and are often intensely colored. Because they are not wetted by water, coordination compounds are easily freed of moisture at low temperatures. Two widely used chelating reagents are described in the paragraphs that follow.

8-Hydroxyquinoline (oxine)

Approximately two dozen cations (24 cations) form sparingly soluble chelates with 8- hydroxyquinoline. The structure of magnesium 8-hydroxyquinolate is typical of these chelates



8- hydroxyquinoline
(chelating agent)

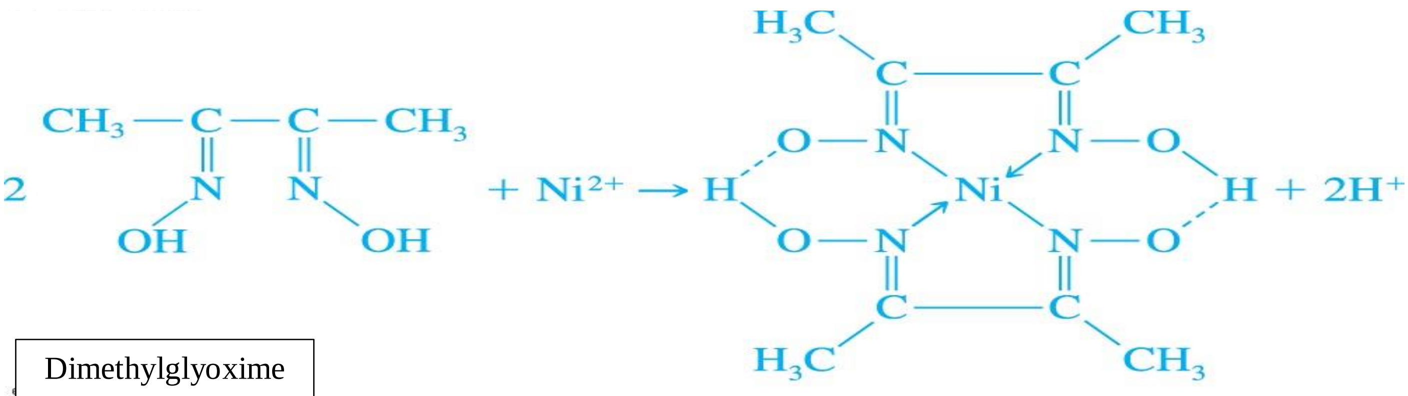
Magnesium 8-hydroxyquinolate
(chelate)

The solubilities of metal 8-hydroxyquinolates vary widely from cation to cation and are pH dependent because 8-hydroxyquinoline is always deprotonated during a chelation reaction. Therefore, we can achieve a considerable degree of selectivity in the use of 8-hydroxyquinoline by controlling pH.

Dimethylglyoxime

Dimethylglyoxime is an organic precipitating agent of unparalleled specificity. Only nickel (II) is precipitated from a weakly alkaline solution.

General chemical equation: $Ni^{2+} + 2H_2DMG \longrightarrow Ni(HDMG)_2 + 2H^+$



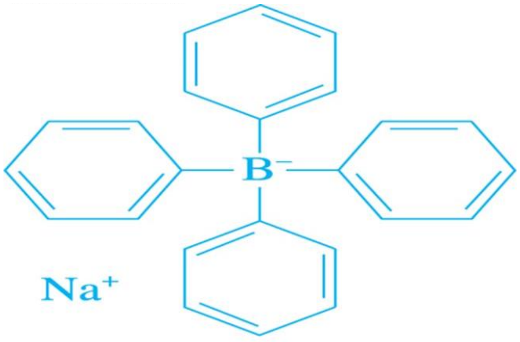
Dimethylglyoxime
(H_2DMG)

Ni($HDMG)_2$ Characteristic bright red ppt

This precipitate is so bulky that only small amounts of nickel can be handled conveniently. It also has an exasperating tendency to creep up the sides of the container as it is filtered and washed. The solid is conveniently dried at 110°C and has the composition $C_8H_{14}N_4NiO_4$.

Sodium Tetraphenylborate

Sodium tetraphenylborate, $(C_6H_5)_4B^-Na^+$, is an important example of an organic precipitating reagent that forms salt-like precipitates. In cold mineral acid solutions, it is a near-specific precipitating agent for potassium and ammonium ions. The precipitates have stoichiometric composition and contain one mole of potassium or ammonium ion for each mole of tetraphenylborate ion. These ionic compounds are easily filtered and can be brought to constant mass at 105°C to 120°C.



Sodium tetraphenyl borate

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Volatilization Gravimetry

Definition: In this analysis the ***analyte*** or its ***decomposition products*** are volatilized at a suitable temperature. The volatile product is then collected and weighed, or, alternatively, the mass of the product is determined indirectly from the loss in mass of the sample.

The two most common gravimetric methods based on volatilization are those for determining water and carbon dioxide. Water is quantitatively distilled from many materials by heating. In direct determination, water vapor is collected on any of several solid desiccants, and its mass is determined from the mass gain of the desiccant. The indirect method in which the amount of water is determined by the loss of mass of the sample during heating is less satisfactory because it must be assumed that water is the only component that is volatilized. This assumption can present problems, however, if any component of the precipitate is volatile. Nevertheless, the indirect method is widely used to determine water in items of commerce.

An example of a gravimetric procedure involving volatilization of carbon dioxide is the determination of the sodium hydrogen carbonate content of antacid tablets. A weighed sample of the finely ground tablets is treated with dilute sulfuric acid to convert the sodium hydrogen carbonate (sodium bicarbonate) to carbon dioxide:

$$NaHCO_3\,(aq) + H_2SO_4\,(aq) \longrightarrow CO_2(g) + H_2O(l) + NaHSO_4(aq)$$

As shown in *Figure 12-8*, this reaction is carried out in a flask connected first to a tube containing $CaSO_4$ that removes water vapor from the initial reaction stream to produce a stream of pure CO_2 in nitrogen. These gases then pass through a weighed absorption tube containing the absorbent Ascarite II, which consists of sodium hydroxide absorbed on a nonfibrous silicate. This material retains carbon dioxide by the reaction:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

The absorption tube must also contain a desiccant such as $CaSO_4$ to prevent loss of the water produced by this last reaction.

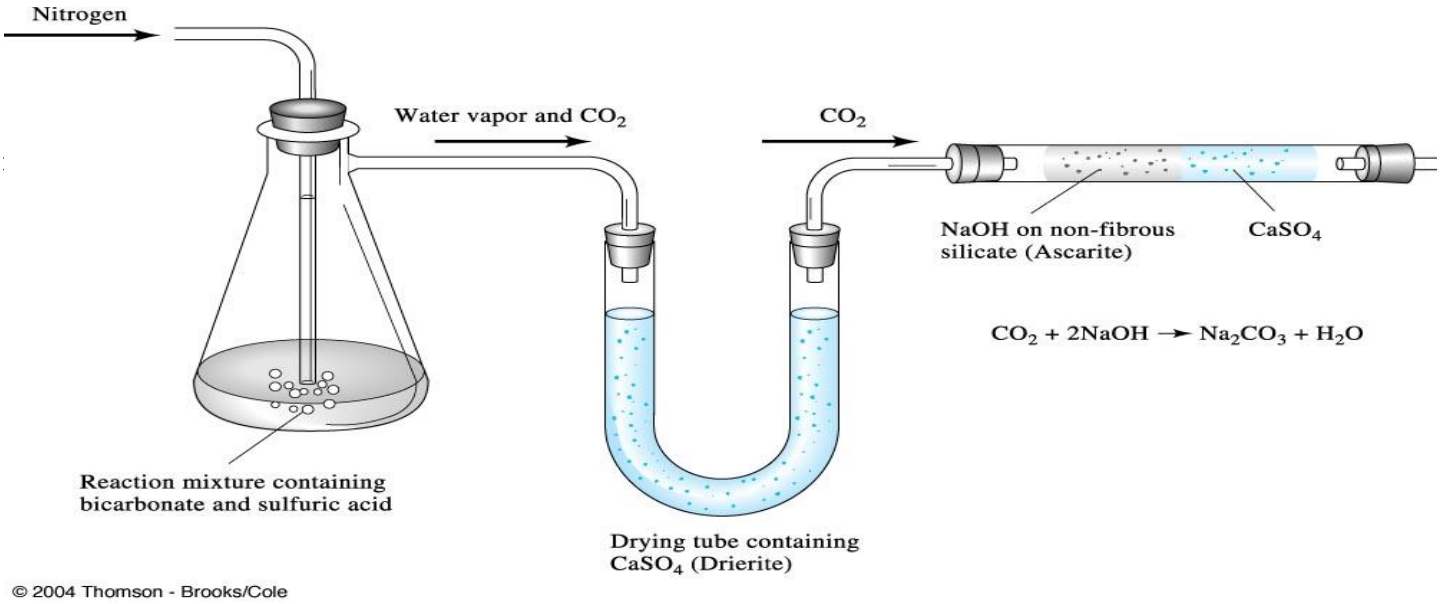

Figure 12-8 Apparatus for determining the sodium hydrogen carbonate content of antacid tablets by a gravimetric volatilization procedure.

Sulfides and **sulfites** can also be determined by **volatilization**. Hydrogen sulfide (H_2S) or sulfur dioxide (SO_2) evolved from the sample after treatment with acid is collected in a suitable absorbent.

Finally, the **classical method for the determination of carbon and hydrogen in organic compounds is a gravimetric volatilization procedure** in which the combustion products (H_2O and CO_2) are collected selectively on weighed absorbents. The increase in mass serves as the analytical variable.