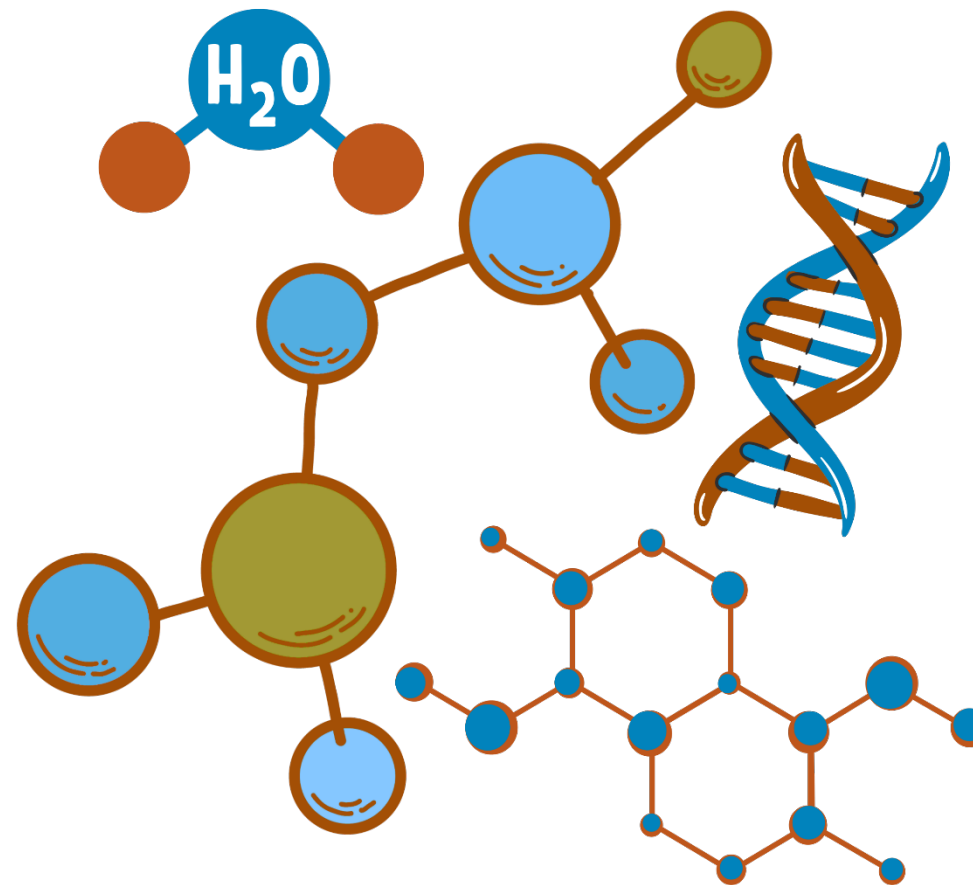


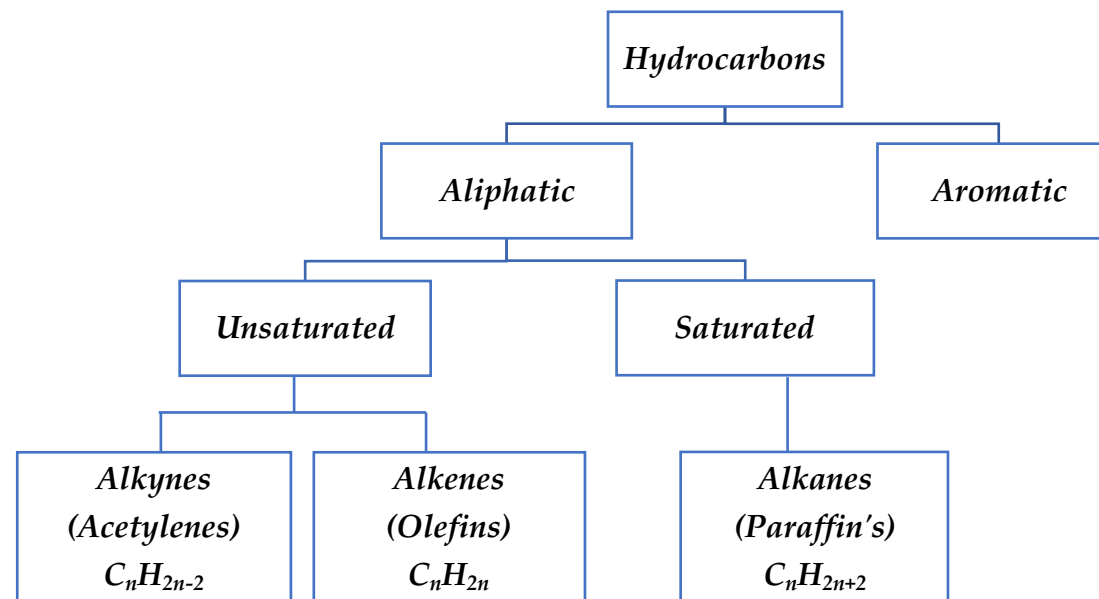
Chapter 2: Structure and Classification of Organic Compounds



Chapter 2: Structure and Classification of Organic Compounds

1. Aliphatic Hydrocarbons: Alkanes, Alkenes, Alkynes

- Hydrocarbons are compounds that contain only carbon and hydrogen atoms.



- Aliphatic hydrocarbons** are subdivided into:

- Saturated hydrocarbons**

- **Alkanes;** C_nH_{2n+2} (contain carbon-carbon single bond)
- **Cycloalkanes;** C_nH_{2n} (contain carbon-carbon single bond in a single ring)

Alkanes and cycloalkanes are so similar that many of their properties can be considered side by side.

- Unsaturated hydrocarbons**

- **Alkenes;** C_nH_{2n} (contain carbon-carbon double bond)
- **Alkynes;** C_nH_{2n-2} (contain carbon-carbon triple bond)



Chapter 2: Structure and Classification of Organic Compounds

1. Aliphatic Hydrocarbons

1.1. Alkanes

- **Alkanes**, whose molecules contain only single bonds, are referred to as saturated compounds because these compounds contain the maximum number of hydrogen atoms that the carbon compound can possess.
- Alkanes have the general formula C_nH_{2n+2}
- **Cycloalkanes**: are alkanes in which all or some of the carbon atoms are arranged in a ring. cycloalkanes containing a single ring have two fewer hydrogen atoms.
- Cycloalkanes have the general formula C_nH_{2n}
- **Sources of Alkanes**: Natural gas and petroleum are the primary sources of alkanes.
- Methane, the simplest alkane, is a key component of natural gas.

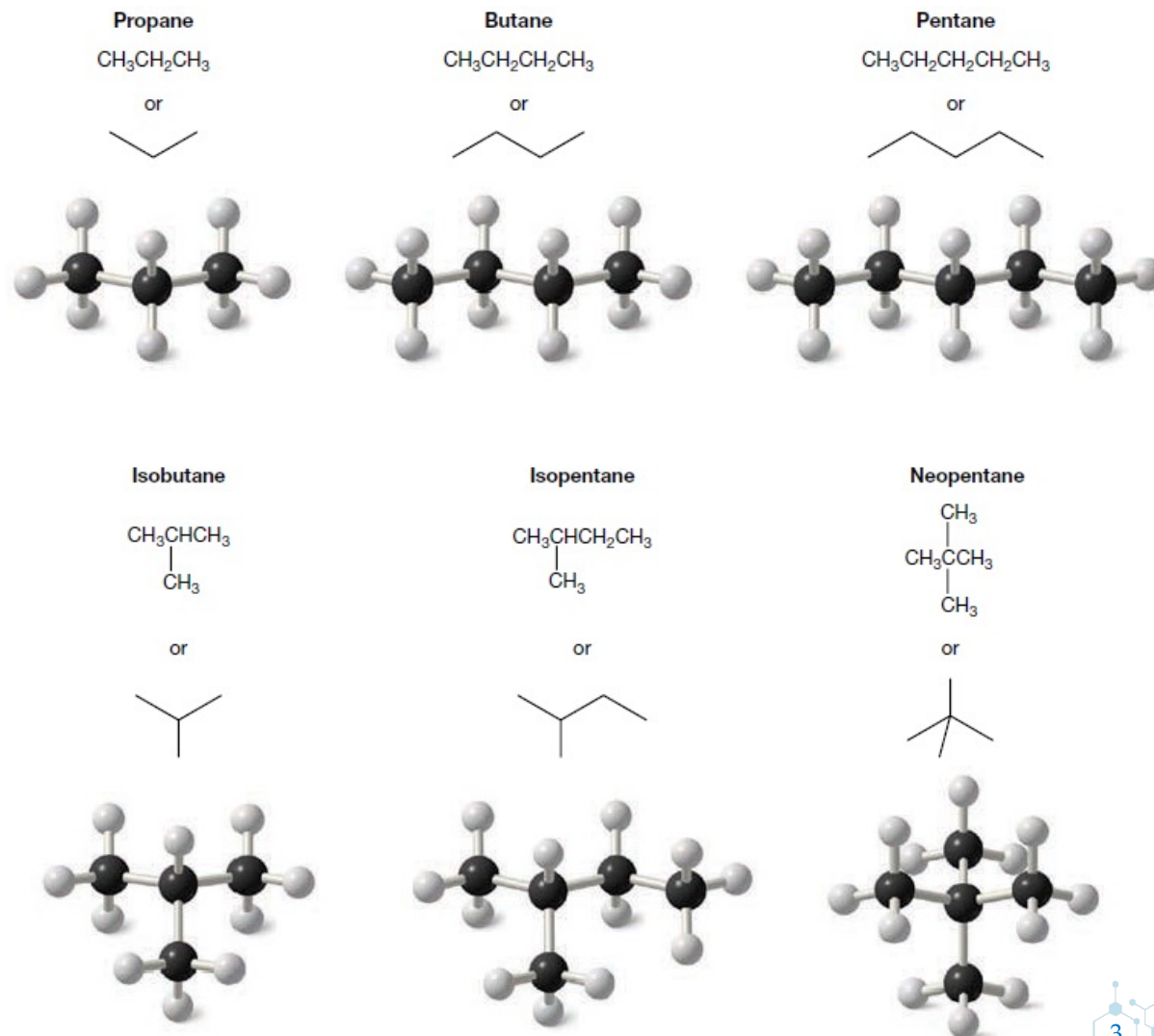
Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH ₄	CH ₄	1
ethane	2	C ₂ H ₆	CH ₃ CH ₃	1
propane	3	C ₃ H ₈	CH ₃ CH ₂ CH ₃	1
butane	4	C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₃	2
pentane	5	C ₅ H ₁₂	CH ₃ (CH ₂) ₃ CH ₃	3
hexane	6	C ₆ H ₁₄	CH ₃ (CH ₂) ₄ CH ₃	5
heptane	7	C ₇ H ₁₆	CH ₃ (CH ₂) ₅ CH ₃	9
octane	8	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	18
nonane	9	C ₉ H ₂₀	CH ₃ (CH ₂) ₇ CH ₃	35
decane	10	C ₁₀ H ₂₂	CH ₃ (CH ₂) ₈ CH ₃	75

1. Aliphatic Hydrocarbons

1.1. Alkanes

1.1.1. Shapes Alkanes

- A general **tetrahedral orientation** of groups and thus sp^3 hybridization is the rule for the carbon atoms of all alkanes and cycloalkanes.
- **Straight-chain:**
Alkanes like butane, as an example, have a zigzag structure due to their tetrahedral carbon atoms. A more accurate term is "unbranched," meaning no carbon is bonded to more than two others.
- **Branched-chain alkanes:**
Isobutane, isopentane, and neopentane are examples of branched-chain alkanes. In neopentane the central carbon atom is bonded to four carbon atoms.



1. Aliphatic Hydrocarbons

1.1. Alkanes

1.1.2. How to classify carbon and hydrogen atoms

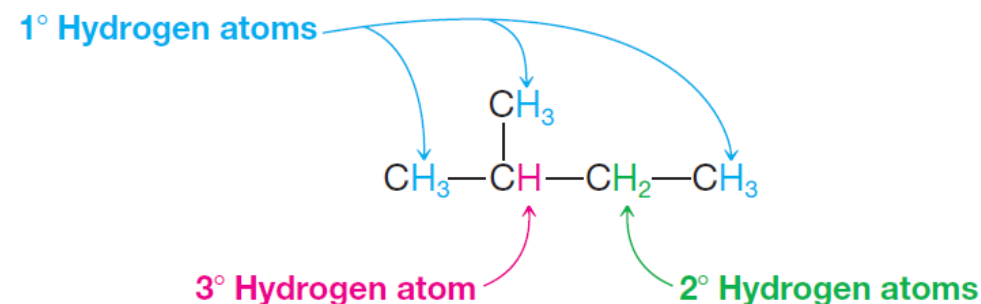
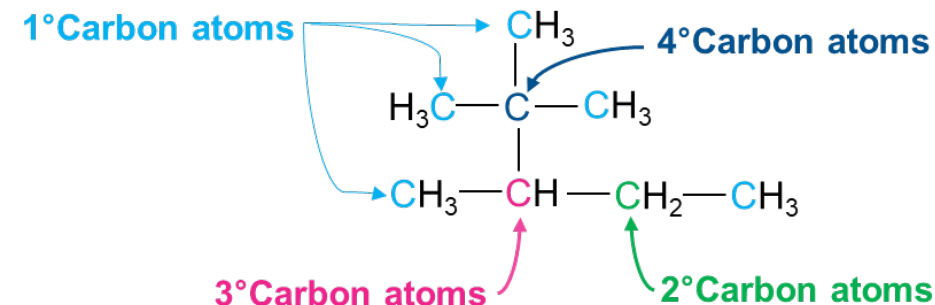
- A **primary (1°) carbon** is one that is bonded to only one other carbon.
- A **secondary (2°) carbon** is one that is bonded to two other carbons.
- A **tertiary (3°) carbon** is one that is bonded to three other carbons.

- The **hydrogen atoms** of an alkane are classified based on the carbon atom to which they are attached.

A hydrogen atom attached to a primary carbon atom is a **primary (1°)** hydrogen atom, and so forth.

- **Example:**

2-methylbutane, has **primary (1°)** , **secondary (2°)**, and **tertiary (3°)** carbon and hydrogen atoms.

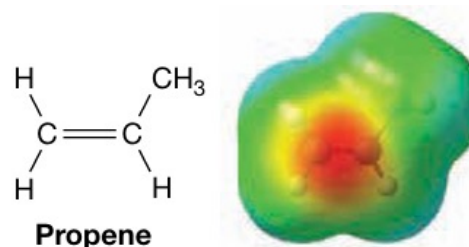
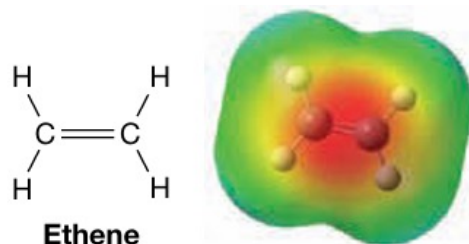


Chapter 2: Structure and Classification of Organic Compounds

1. Aliphatic Hydrocarbons

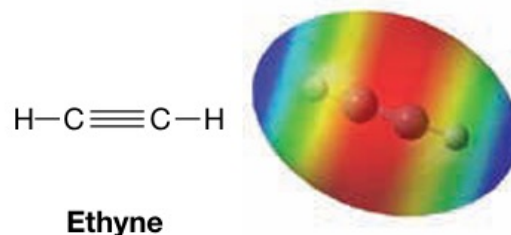
1.2. Alkenes

- Alkenes are hydrocarbons containing a carbon-carbon double bond, historically called olefins.
- General formula is C_nH_{2n} .
- The simplest alkene, ethene (ethylene) (C_2H_4),



1.3. Alkynes

- Hydrocarbons whose molecules contain the carbon-carbon triple bond and called acetylenes.
- The simplest member, acetylene $HC\equiv CH$.

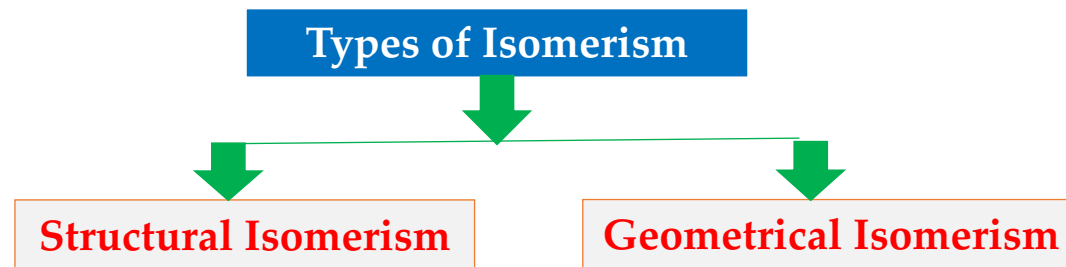


Chapter 2: Structure and Classification of Organic Compounds

1. Aliphatic Hydrocarbons

1.4. Isomerism

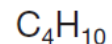
- **Isomers** are different compounds with identical molecular formulas.



1.4.1. Structural or constitutional isomers

- **Structural isomers** have the same molecular formula but different in the sequence of atoms bonded to each other.
- Examples:

Molecular formula

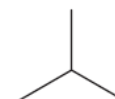


Constitutional isomers

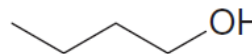
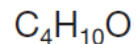


Butane

and

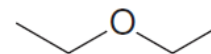


2-Methylpropane



1-Butanol

and



Diethyl ether

Chapter 2: Structure and Classification of Organic Compounds

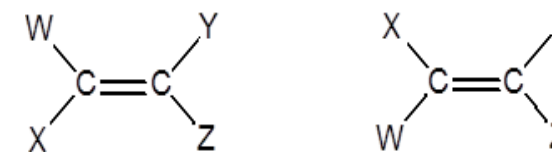
1. Aliphatic Hydrocarbons

1.4. Isomerism

1.4.2. Geometric Isomerism in Alkenes

A) The (cis)–(trans) System for Alkene when W differs from X and Y from Z,

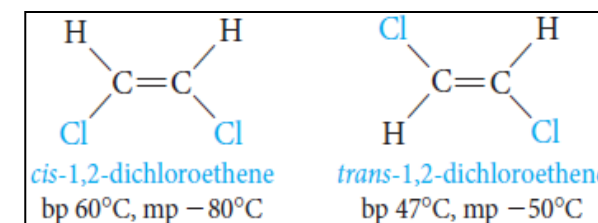
Alkenes exist as geometric isomers



Geometric isomers

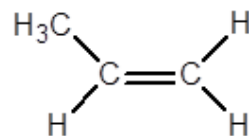
- In **alkenes**, **geometric isomerism** is due to **restricted rotation about the carbon - carbon double bond**.

- cis isomer**; when two similar groups are on the **same side or same side** of the double bond.
- trans isomer**; when two similar groups are on the **opposite direction or opposite sides** of the double bond.

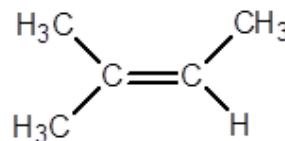


- They have **different physical properties** and can be separated by **fractional crystallization or distillation**.

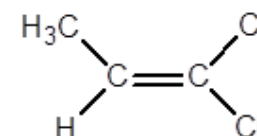
B) If (W = X or Y = Z), geometric isomerism is not possible.



Propene



2-Methyl-2-butene



1,1-Dichloropropene

1. Aliphatic Hydrocarbons

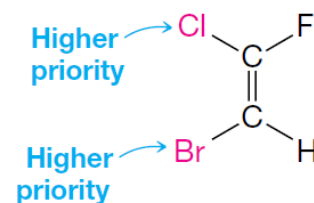
1.4. Isomerism

1.4.2. Geometric Isomerism in Alkenes

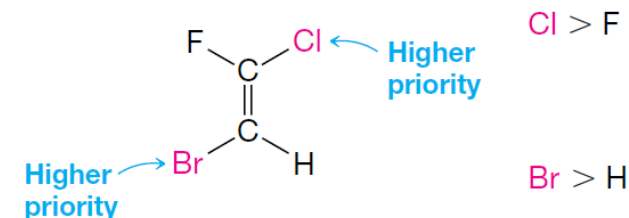
C) The (E)–(Z) System for Alkene

■ How To Use the (E)–(Z) System

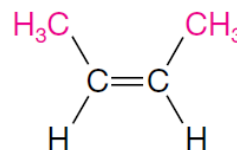
1. Examine the two groups attached to one carbon atom of the double bond.
2. Repeat that operation at the other carbon atom.
3. Compare the group of higher priority on one carbon atom with the group of higher priority on the other carbon atom.
4. **(Z)** from the German word **zusammen**, meaning **together**; if the two groups of higher priority are on the same side of the double bond.
5. **(E)** from the German word **entgegen**, meaning **opposite**; If the two groups of higher priority are on opposite sides of the double bond.



(Z)-2-Bromo-1-chloro-1-fluoroethene



(E)-2-Bromo-1-chloro-1-fluoroethene



(Z)-2-Butene or (Z)-but-2-ene
(cis-2-butene)



(E)-2-Butene or (E)-but-2-ene
(trans-2-butene)

Chapter 2: Structure and Classification of Organic Compounds

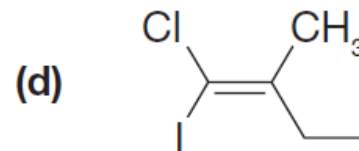
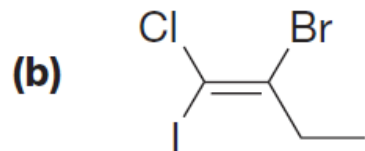
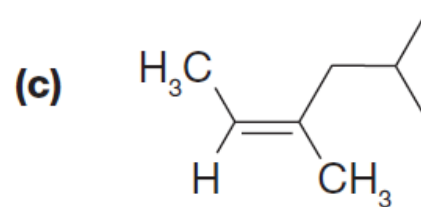
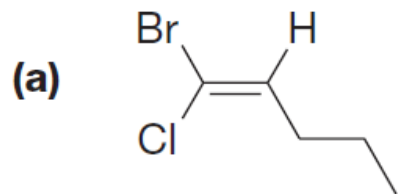
1. Aliphatic Hydrocarbons

1.4. Isomerism

1.4.2. Geometric Isomerism in Alkenes

C) The (E)–(Z) System for Alkene

- Practice Problem: Using the (E)–(Z) designation for the following:

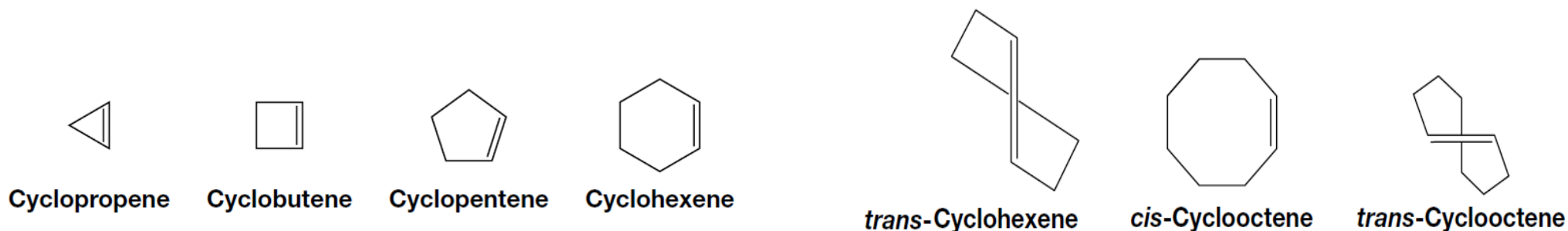


1. Aliphatic Hydrocarbons

1.4. Isomerism

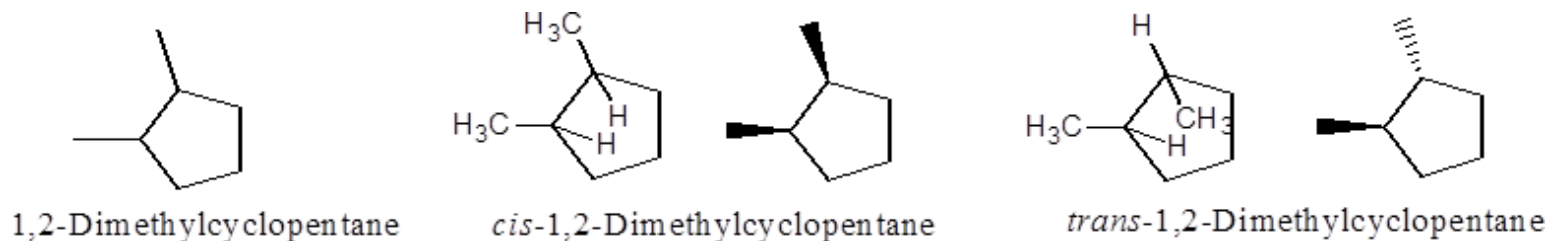
1.4.3. Geometric Isomerism in Cycloalkenes

- For very small rings (5 carbons or fewer), only the *cis* cycloalkene isomer is possible and a *trans* double bond cannot fit into these small rings.
- While *trans* double bonds are too strained to exist in small cycloalkenes, they become possible in larger rings.



■ *cis-trans* Isomerism in Cycloalkanes

cis-trans isomerism (sometimes called geometric isomerism) is one kind of stereoisomerism.

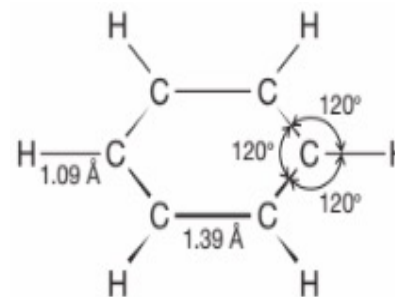
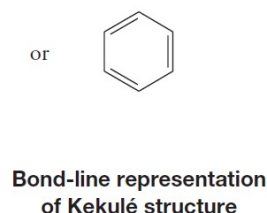
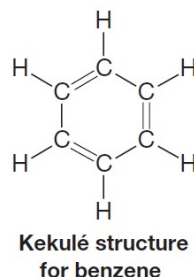
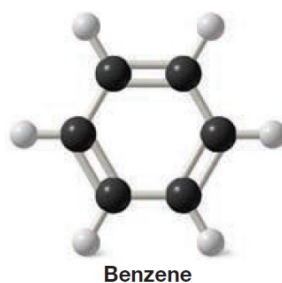


2. Aromatic Hydrocarbons

- The term "aromatic" referred to pleasant-smelling compounds from plants, many of which contained a benzene ring.
- Today, *aromaticity* is defined by electronic structure not odor.
- Aromatic compounds, are classified based on special stability from a *delocalized ring of π -electrons*, even if they have no scent.
- Aromatic compounds are a major class of unsaturated cyclic hydrocarbons, with *benzene* being the fundamental example.

2.1 Benzene: A Representative Aromatic Hydrocarbon

- Its structure is a six-membered ring with *delocalized electrons*, often depicted by the *Kekulé structure* with alternating single and double bonds.
- The molecule of benzene is *Planar* and that all of its carbon-carbon bonds are of equal length.
- Each carbon is *sp^2 hybridized* and the bond angles is 120° .
- The carbon-carbon bond lengths in benzene are $1.39 \text{ \AA}$, a value in between that for a carbon-carbon single bond between sp^2 hybridized atoms ($1.47 \text{ \AA}$) and that for a carbon-carbon double bond ($1.34 \text{ \AA}$).



2. Aromatic Hydrocarbons

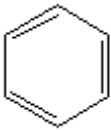
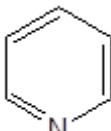
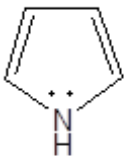
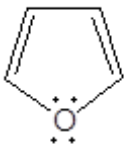
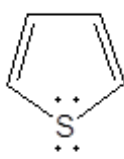
2.2. Aromatic Character (Aromaticity)

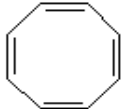
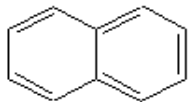
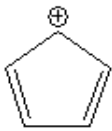
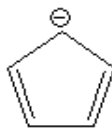
■ To be classified as aromatic, a compound must have:

1. Cyclic structure.
2. Cyclic structure contains what looks like a continuous system of alternating double and single bonds.
3. Aromatic compounds must be planar.
4. Fulfill Huckel rule:

The number of π electrons in the compound = $(4n + 2)$

Where ($n = 0, 1, 2, 3$, and so on).

					
	Benzene	Pyridine	Pyrrole	Furan	Thiophene
$4n+2=$	6	6	6	6	6
$n=$	1	1	1	1	1

					
$4n+2=$	8	10	2	2	4
$n=$	1.5	2	0	0	0.5
					
$4n+2=$	4	4	6	4	
$n=$	0.5	0.5	1	0.5	

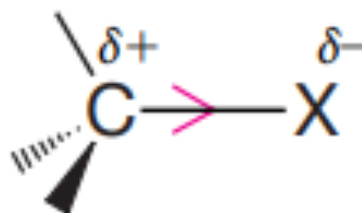
3. Functional Groups

3.1. Alkyl Halides (Haloalkanes)

- Alkyl halides (haloalkanes) are compounds in which a halogen atom (fluorine, chlorine, bromine, or iodine) replaces a hydrogen atom of an alkane.
- The generic formula for an alkyl halide is $R-X$, where X = fluorine, chlorine, bromine, or iodine.
- Examples;

CH_3Cl and CH_3CH_2Br are alkyl halides.

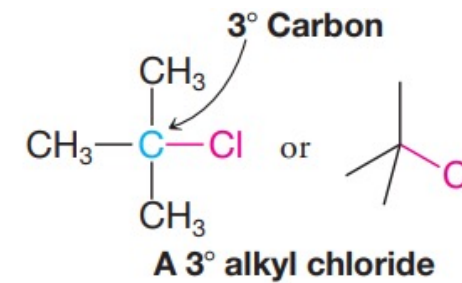
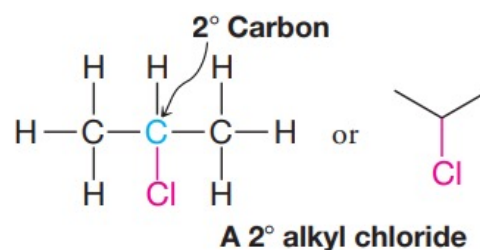
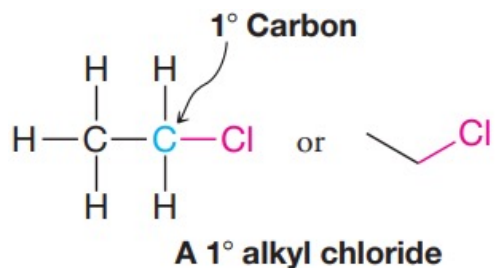
- An alkyl halide has a halogen atom bonded to an sp^3 -hybridized (tetrahedral) carbon atom.
- The carbon–halogen bond in an alkyl halide is polarized because the halogen is more electronegative than carbon. Therefore, the carbon atom has a partial positive charge ($\delta+$) and the halogen has a partial negative charge ($\delta-$).



3. Functional Groups

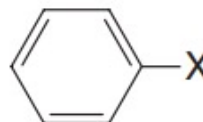
3.1. Alkyl Halides (Haloalkanes)

- Alkyl halides are classified as being **primary** (1°), **secondary** (2°), or **tertiary** (3°). This classification is based on the **carbon atom** to which the halogen is directly attached.
- For example: If the carbon atom that bears the halogen is directly attached to only one other carbon, the carbon atom is said to be a **primary carbon atom** and the alkyl halide is classified as a primary alkyl halide.
- Examples:



3.2. Aryl Halide

- An **aryl halide** is a compound with a halogen atom bonded to an aromatic ring.
- When the aromatic ring is specifically a benzene ring these compounds are called **phenyl halides**.

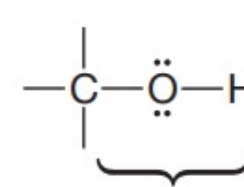


A phenyl halide or aryl halide

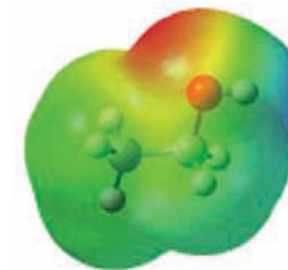
3. Functional Groups

3.3. Alcohols, Phenols and Thiols

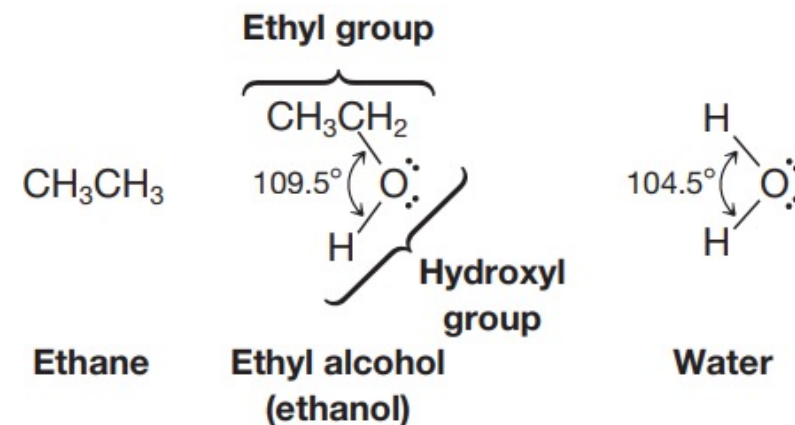
- **Methyl alcohol** (also called **methanol**) has the structural formula CH_3OH and is the simplest member of a family of organic compounds known as alcohols.
- The characteristic functional group of this family is the **hydroxyl** ($-\text{OH}$) **group** attached to an sp^3 -hybridized carbon atom.
- **Alcohols** may be viewed structurally in two ways:
 - (1) As alkyl derivatives of water.
 - (2) As hydroxyl derivatives of alkanes.
- **Ethyl alcohol**, for example, can be seen as an ethane molecule in which **one hydrogen** has been replaced by a **hydroxyl group** or as a water molecule in which **one hydrogen** has been replaced by an **ethyl group**.



This is the functional group of an alcohol.



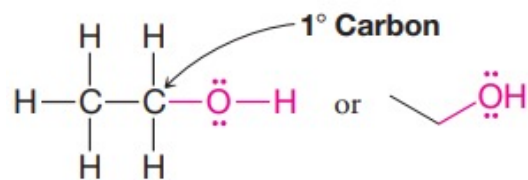
Ethanol



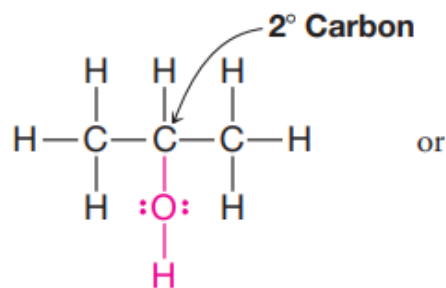
3. Functional Groups

3.3. Alcohols, Phenols and Thiols

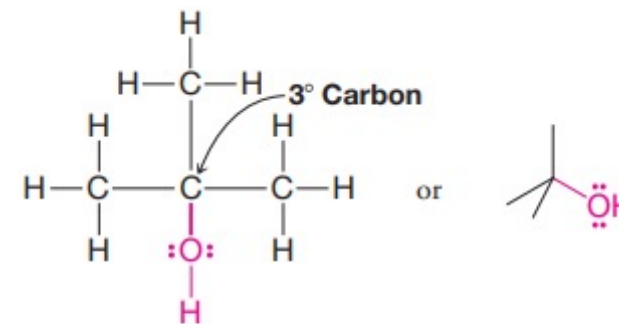
- Alcohols are classified into three groups: **primary** (1°), **secondary** (2°), and **tertiary** (3°) alcohols.
- This classification is based on the degree of substitution of the carbon to which the hydroxyl group is directly attached.
 - Primary alcohol;** If the carbon has only one other carbon attached to it.
 - Secondary alcohol;** If the carbon atom that bears the hydroxyl group also has two other carbon atoms.
 - Tertiary alcohol;** If the carbon atom that bears the hydroxyl group has three other carbons attached to it.



Ethyl alcohol
(a 1° alcohol)



Isopropyl alcohol
(a 2° alcohol)

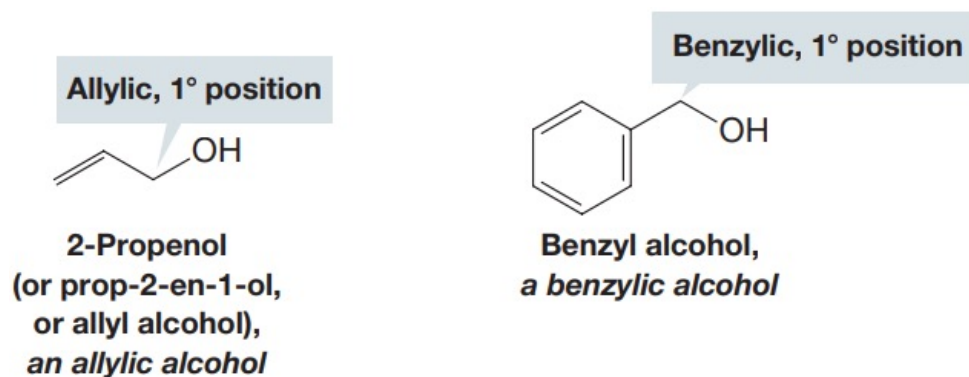


tert-Butyl alcohol
(a 3° alcohol)

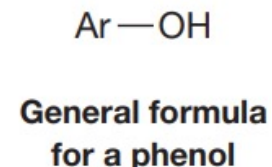
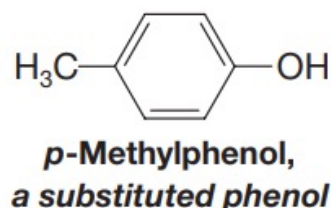
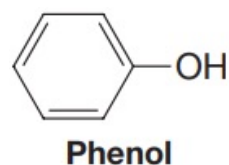
3. Functional Groups

3.3. Alcohols, Phenols and Thiols

- The **alcohol carbon** atom may also be a saturated carbon atom adjacent to an **alkenyl group**, in which case it is called **allylic**, or the **carbon atom** may be a saturated carbon atom that is attached to a **benzene ring** in which case it is called **benzylic**.



- When a hydroxyl group is bonded to a benzene ring the combination of the ring and the hydroxyl is called a **phenol**.
- Compounds that have a hydroxyl group attached directly to a benzene ring are called **phenols**.



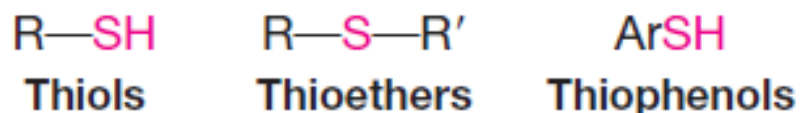
3. Functional Groups

3.3. Alcohols, Phenols and Thiols

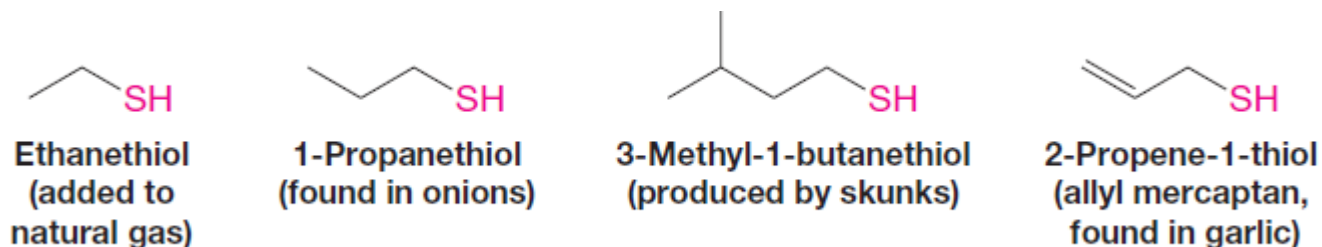
- **Thiol**, also called a **mercaptan**, is an organic compound in which a sulfur atom forms a single bond with a carbon atom.
- The functional group of thiols is the **sulfhydryl group** ($-SH$).
- General formula $R-SH$, where R is an organic fragment such as an alkyl or aryl group.
- Example; CH_3-SH , or methanethiol, is the simplest alkyl thiol.
- **Thiols** are sulfur analogs of alcohols, in which the oxygen atom is replaced by a sulfur atom.

Alcohol: $R-OH \rightarrow$ **Thiol:** $R-SH$

- **Thiols** are an organic chemical compound with similar characteristics of alcohol and phenols. However, it has a sulphur atom instead of an oxygen atom.



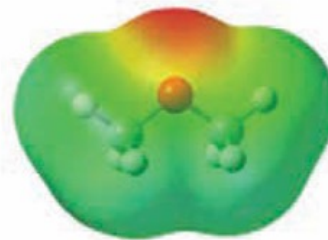
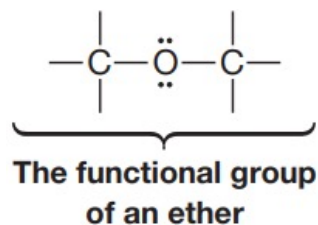
- Examples;



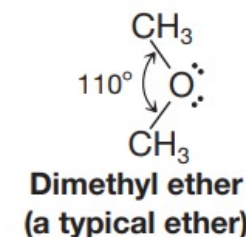
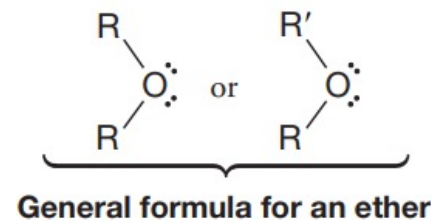
3. Functional Groups

3.4. Ethers and Epoxides

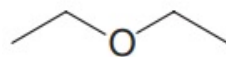
- **Ethers** have the general formula $R-O-R$ or $R-O-R'$, where R' may be an alkyl (or phenyl) group different from R .
- **Ethers** can be thought of as derivatives of water in which both **hydrogen atoms** have been replaced by **alkyl groups**.
- **Ethers** differ from alcohols in that the oxygen atom of an ether is bonded to two carbon atoms.



Dimethyl ether



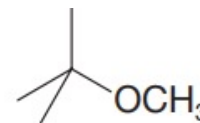
- Examples;



Diethyl ether



Allyl methyl ether



tert-Butyl methyl ether

- **Ethers are classified as**

- **Symmetrical ethers;**

When the organic groups attached to the oxygen are **identical**.

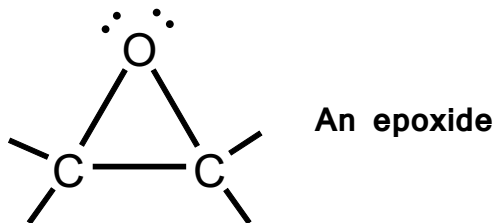
- **Unsymmetrical ethers (*mixed ethers*);**

When the organic groups attached to the oxygen are **different**.

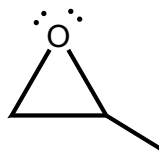
3. Functional Groups

3.4. Ethers and Epoxides

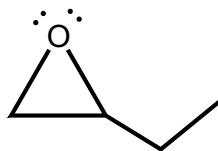
- **Epoxides** are cyclic ethers with three-membered rings.
- The three-membered ring contains one oxygen atom and two carbon atoms.
- General structure of **epoxides**;
- Simplest **epoxides**;



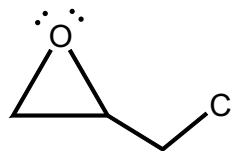
- Examples;



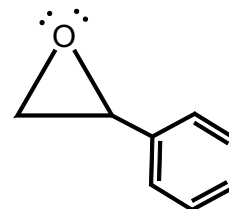
2-methyloxirane



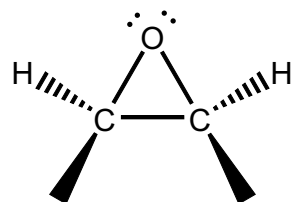
2-ethyloxirane



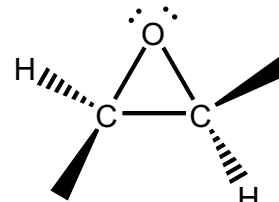
2-(chloromethyl)oxirane



2-phenyloxirane



cis-2,3-Dimethyloxirane



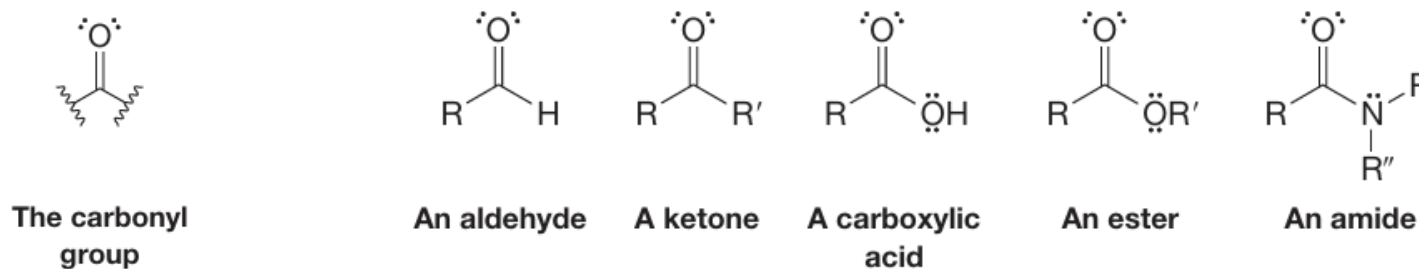
Trans-2,3-Dimethyloxirane

3. Functional Groups

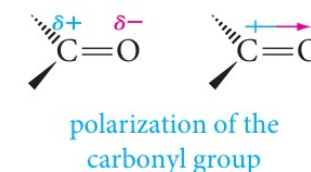
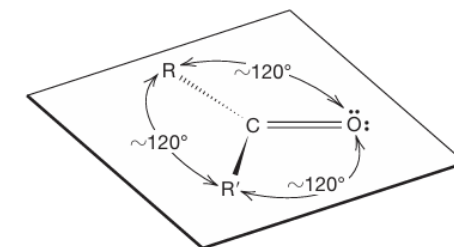
3.5. Containing Carbonyl Group:

Structure of the Carbonyl Group

- Carbonyl compounds are a broad group of compounds that includes **aldehydes**, **ketones**, **carboxylic acids**, **esters**, and **amides**.



- The **carbonyl carbon atom** is **sp^2 hybridized**; thus, it and the three atoms attached to it lie in the same plane.
- The bond angles between the three attached atoms are a **trigonal planar** structure; they are approximately **120°** .
- The carbon–oxygen double bond consists of two electrons in a **σ bond** and two electrons in a **π bond**.
- Oxygen is much more electronegative than carbon. Therefore, the electrons in the C=O bond are attracted to the oxygen, producing a **highly polarized** bond.



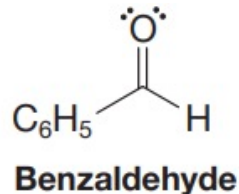
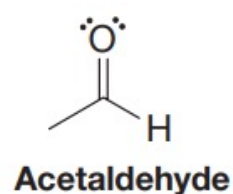
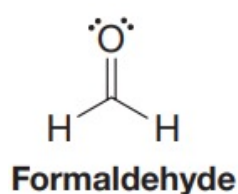
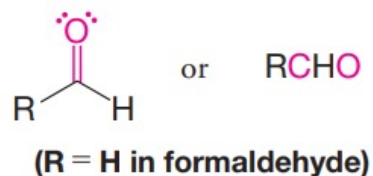
3. Functional Groups

3.5. Containing Carbonyl Group:

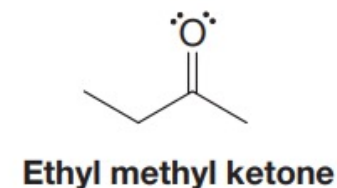
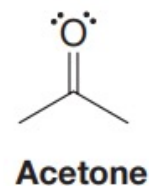
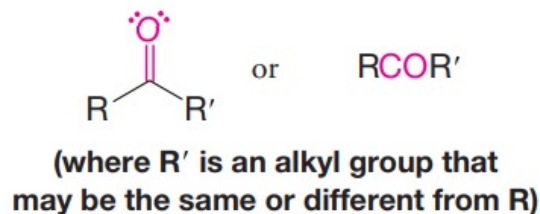
3.5.1. Aldehydes and Ketones

- The carbonyl group of an **aldehyde** is bonded to one **hydrogen atom** and **one carbon atom** (except for formaldehyde, which is the only aldehyde bearing two hydrogen atoms).
- The carbonyl group of a **ketone** is bonded to **two carbon atoms**.

ALDEHYDES



KETONES



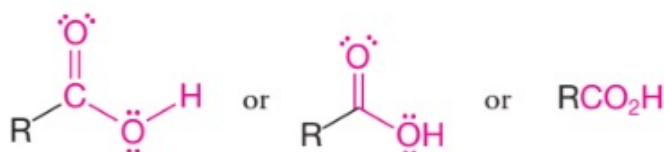
3. Functional Groups

3.5. Containing Carbonyl Group:

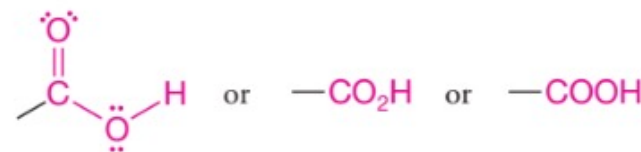
3.5.2. Carboxylic Acids and their derivatives

A) Carboxylic Acids

- Carboxylic acids have a **carbonyl group** bonded to a **hydroxyl group**, and they have the general formula, **RCOOH**.
- The functional group (abbreviated **-CO₂H** or **-COOH**) is called the **carboxyl group** (carbonyl + hydroxyl)

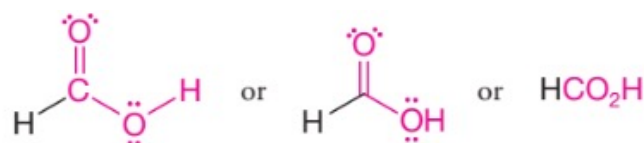


A carboxylic acid

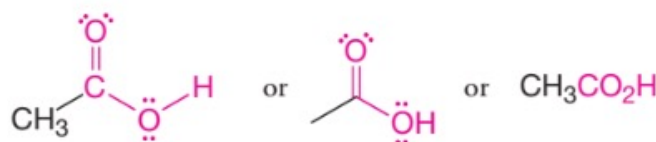


The carboxyl group

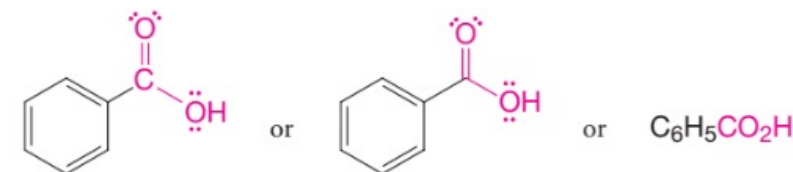
- Examples: **formic acid**, **acetic acid**, and **benzoic acid**.
 - Formic acid** is an irritating liquid produced by ants.
 - Acetic acid**, the substance responsible for the sour taste of vinegar.



Formic acid



Acetic acid



Benzoic acid

Chapter 2: Structure and Classification of Organic Compounds

3. Functional Groups

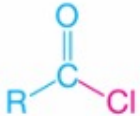
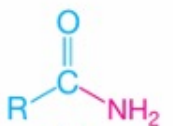
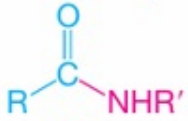
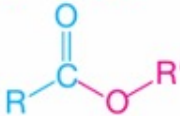
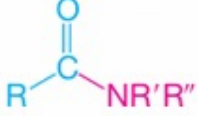
3.5. Containing Carbonyl Group:

3.5.2. Carboxylic Acids and their derivatives

Carboxylic Acids derivatives

- Esters, Acid Anhydrides, Acyl chlorides and amides all contain a **carbonyl group** that is bonded to an **oxygen** or **nitrogen** atom.

Carboxylic acid derivatives

Structure	Name	Structure	Name
	Acyl (or acid) chloride		} Amide
	Acid anhydride		
	Ester		

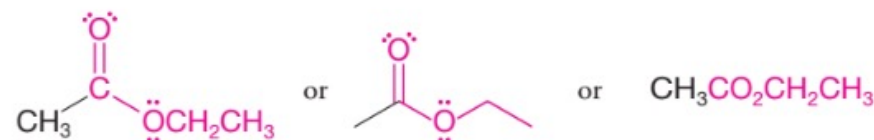
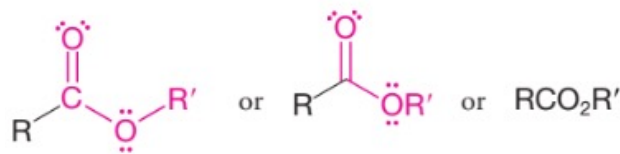
3. Functional Groups

3.5. Containing Carbonyl Group:

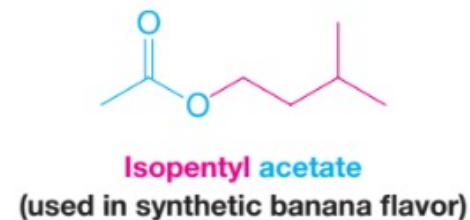
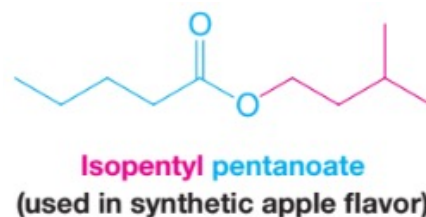
3.5.2. Carboxylic Acids and their derivatives

B) Esters

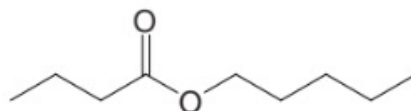
- **Esters** have the general formula $\text{RCO}_2\text{R}'$ (or RCOOR'), where a **carbonyl group** is bonded to an **alkoxyl** ($-\text{OR}$) group.



- **Esters** usually have pleasant odors, some resembling those of fruits, and are used in the manufacture of synthetic flavors.



- Your body makes esters from long-chain carboxylic acids called “**fatty acids**” by combining them with glycerol.



Pentyl butanoate smells like apricots and pears.

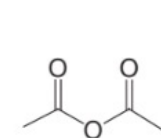
3. Functional Groups

3.5. Containing Carbonyl Group:

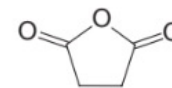
3.5.2. Carboxylic Acids and their derivatives

C) Acid Anhydrides

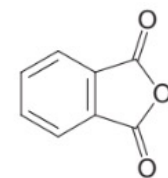
- Acid Anhydrides are named by dropping the word **acid** from the name of the carboxylic acid and then adding the word **anhydride**.



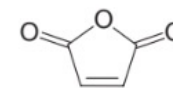
Acetic anhydride
(ethanoic anhydride)
mp -73 °C



Succinic anhydride
mp 121 °C



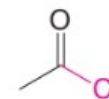
Phthalic anhydride
mp 131 °C



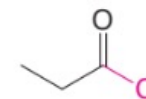
Maleic anhydride
mp 53 °C

D) Acyl chlorides

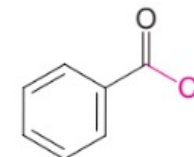
- Acyl chlorides are also called **acid chlorides**.
- Acyl chlorides and carboxylic anhydrides have boiling points in the same range as esters of comparable molecular weight.



Acetyl chloride
(ethanoyl chloride)
mp -112 °C; bp 51 °C



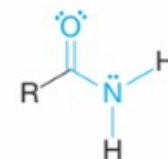
Propanoyl chloride
mp -94 °C; bp 80 °C



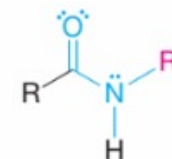
Benzoyl chloride
mp -1 °C; bp 197 °C

E) Amides

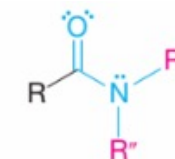
- Amides have the formulas RCONH_2 , RCONHR' , or $\text{RCONR}'\text{R}''$ where a carbonyl group is bonded to a nitrogen atom bearing hydrogen and/or alkyl groups.



An unsubstituted amide



An N-substituted amide



An N,N-disubstituted amide

General formulas for amides

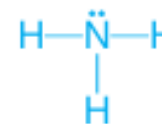
Chapter 2: Structure and Classification of Organic Compounds

3. Functional Groups

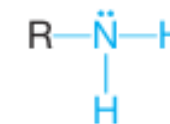
3.6. Containing Nitrogen:

3.6.1. Amines

- Amines may be considered as organic derivatives of ammonia.

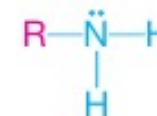


Ammonia

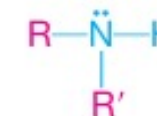


An amine

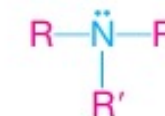
- Amines are classified as primary, secondary, or tertiary amines. This classification is based on the number of organic groups that are attached to the nitrogen atom.



A primary (1°) amine

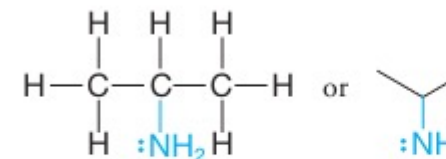


A secondary (2°) amine

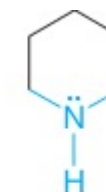


A tertiary (3°) amine

- Example;** Isopropyl amine is a primary amine because only one organic group is attached to the nitrogen atom.



Isopropylamine
(a 1° amine)



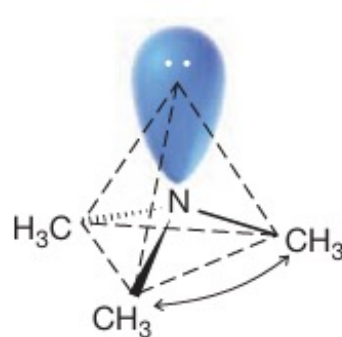
Piperidine
(a cyclic 2° amine)

3. Functional Groups

3.6. Containing Nitrogen:

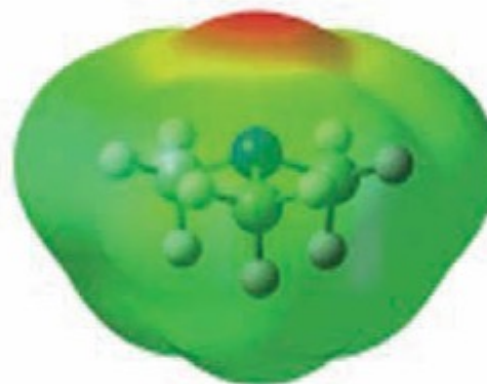
3.6.1. Amines

- **Amines** are like ammonia in having a **trigonal pyramidal** shape.
- The **C–N–C** bond angles of trimethylamine are **108.7°**,
a value very close to the **H–C–H** bond angles of methane.
- The nitrogen atom of an amine can be considered to be **sp^3** hybridized with the unshared electron pair occupying one orbital. This means that the **unshared pair** is relatively **exposed**, and as we shall see this is important because it is **involved** in almost all of the **reactions of amines**.



Bond angle = 108.7°

Trimethylamine

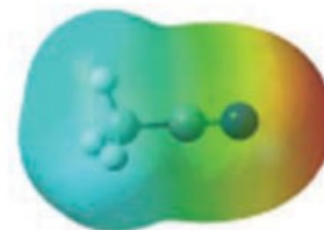
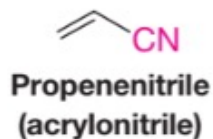


3. Functional Groups

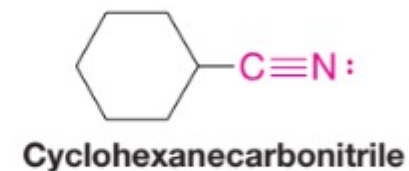
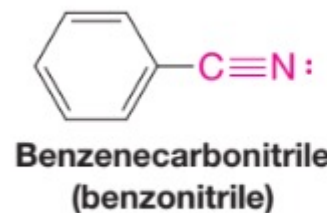
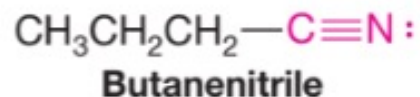
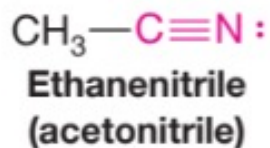
3.6. Containing Nitrogen:

3.6.2. Nitriles

- A nitrile has the formula $R-C\equiv N:$ (or $R-CN$).
- The carbon and the nitrogen of a nitrile are *sp* hybridized.
- Carboxylic acids can be converted to nitriles and vice versa.



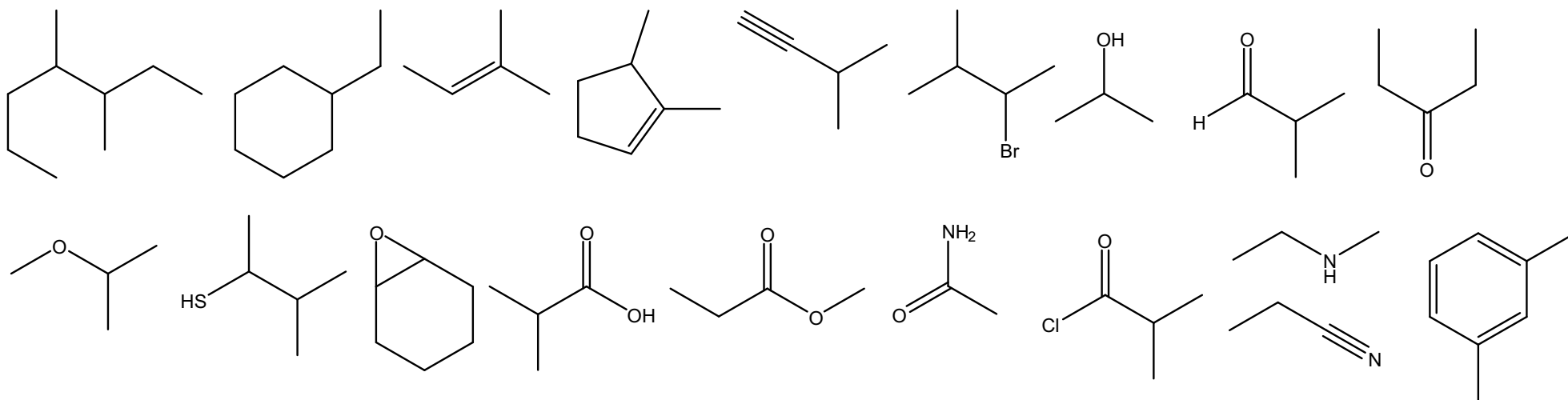
Acetonitrile



Chapter 2: Structure and Classification of Organic Compounds

4. Practice Problems

1) Classify the following compounds based on their functional groups:



2) Classify the following alkyl halide, alcohol, amine, and amide as primary (1°), secondary (2°), or tertiary (3°):

