Principles of Organic Chemistry I
CHEM 244

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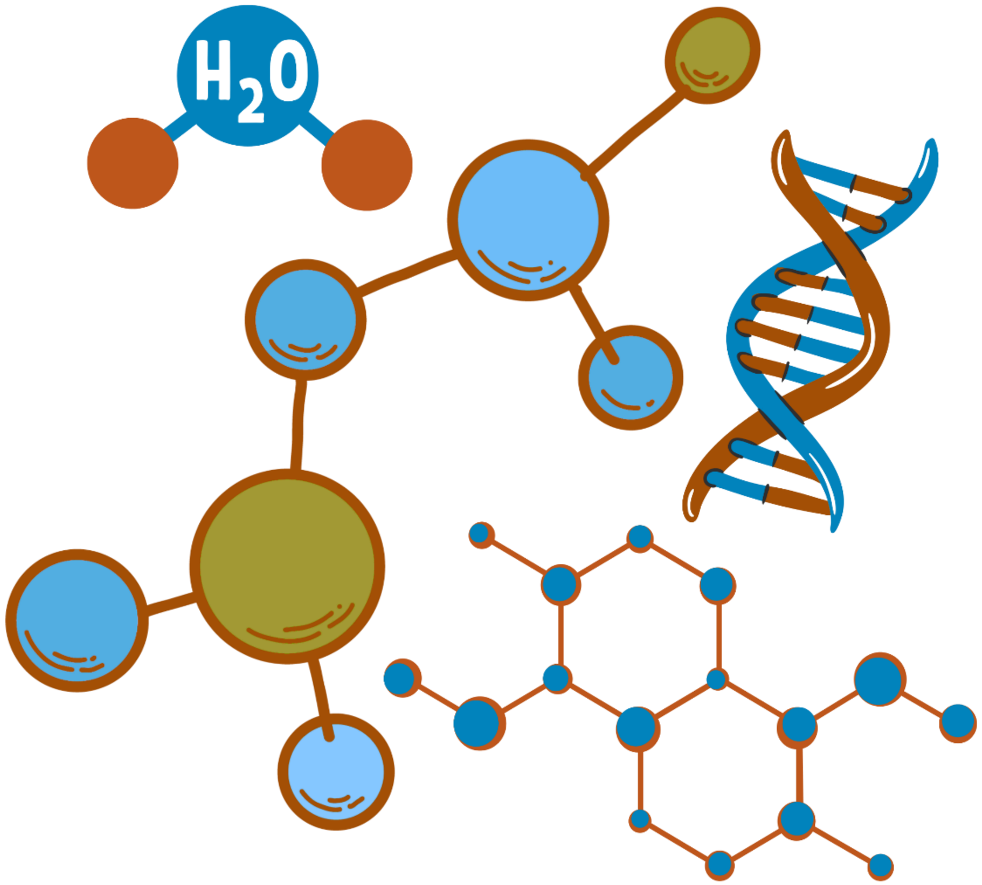
Chapter 2: Structure and Classification of Organic Compounds



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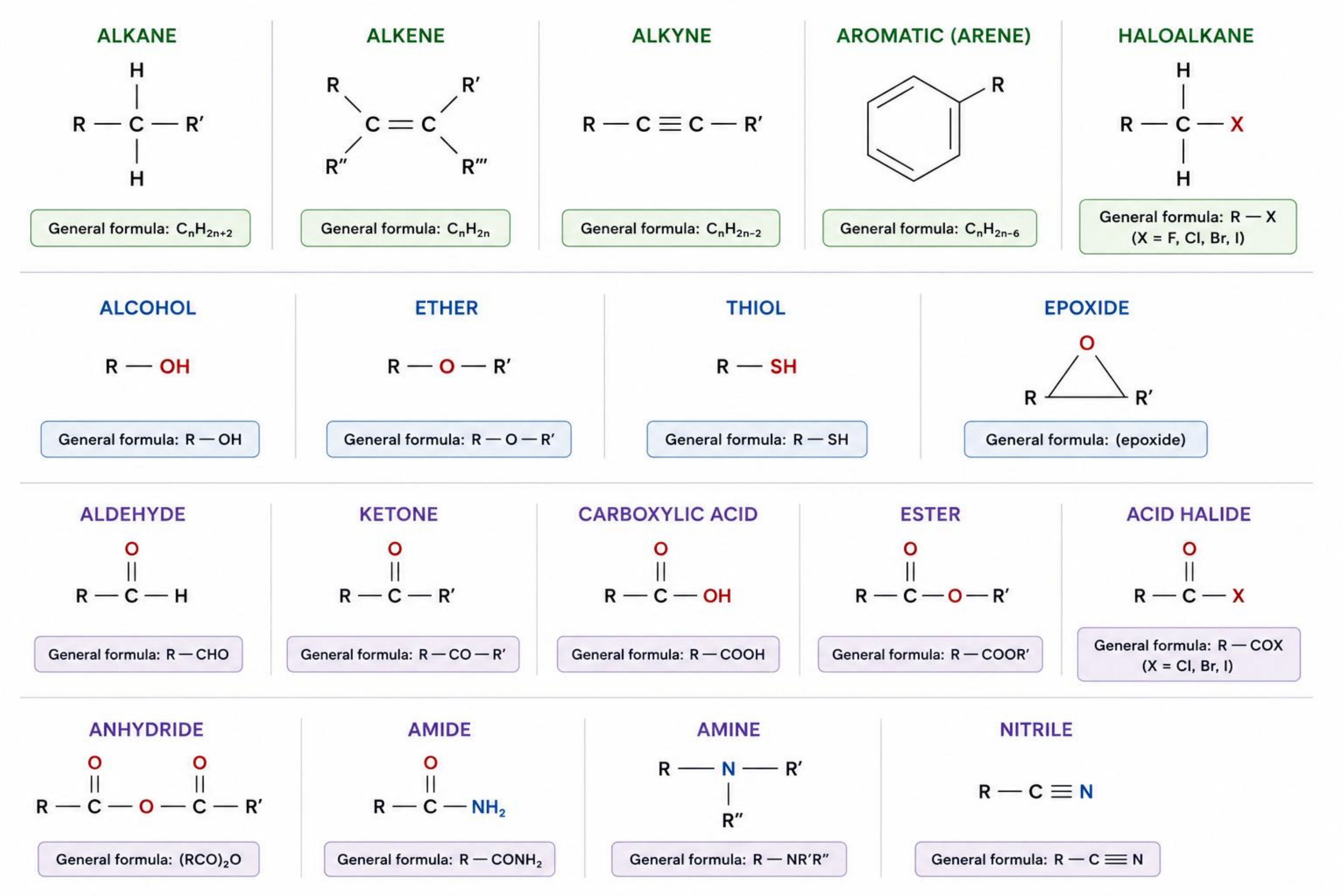
1. Functional Groups:



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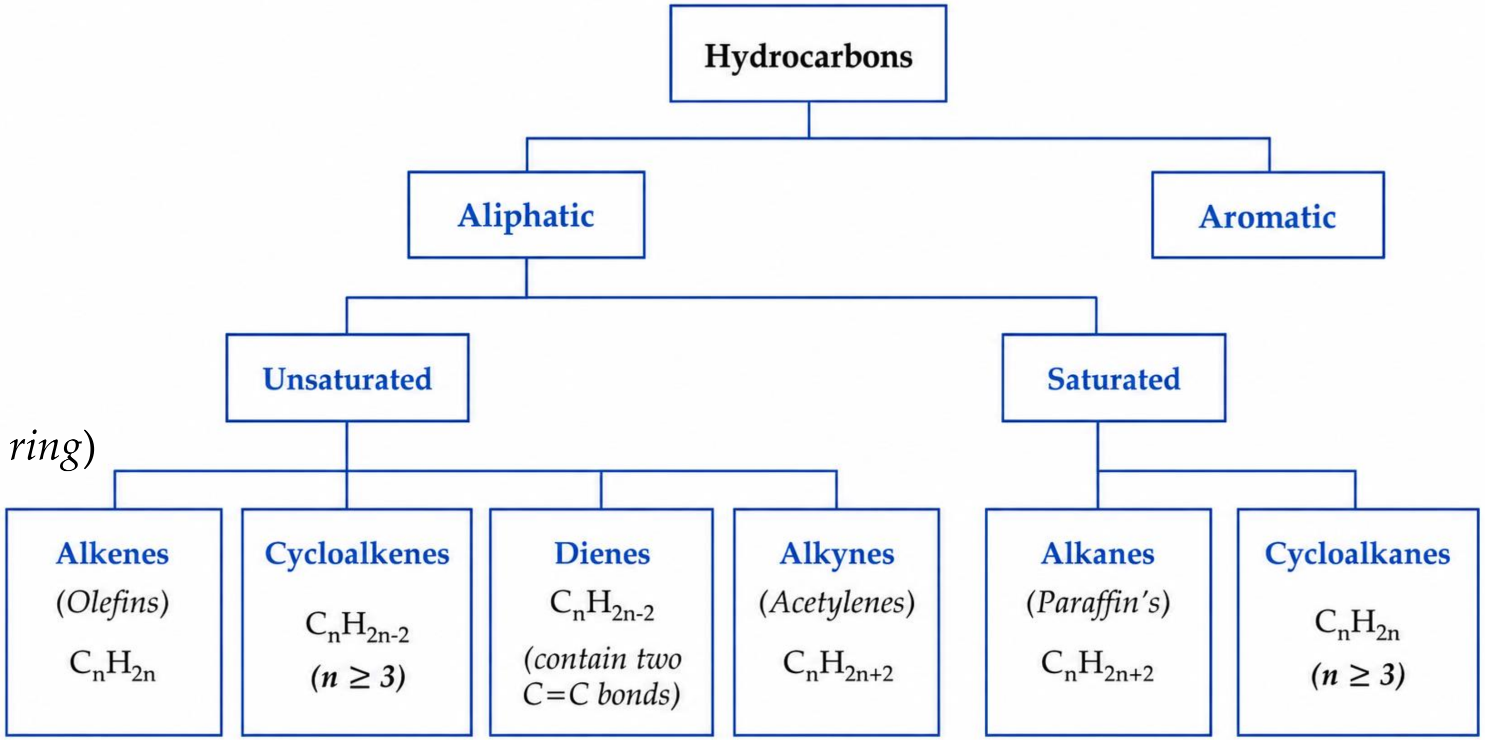
2. Aliphatic Hydrocarbons:

- **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*)
  - *Unsaturated hydrocarbons*
    - Alkenes; C_nH_{2n}
      (*contain carbon-carbon double bond)*
    - Dienes; C_nH_{2n-2}
      (*contain two carbon–carbon double bonds)*
    - Cycloalkenes; C_nH_{2n-2}
      (*contain a carbon–carbon double bond in a ring)*
    - Alkynes; $C_n H_{2n-2}$
      (*contain carbon-carbon triple bond)*



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2. Aliphatic Hydrocarbons

2.1. Alkanes and Cycloalkanes

- **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}

Name	Number of carbons	Molecular formula	Structural formula	Number of structural isomers
methane	1	CH_4	CH_4	1
ethane	2	C_2H_6	CH_3CH_3	1
propane	3	C_3H_8	$CH_3CH_2CH_3$	1
butane	4	C_4H_{10}	$CH_3CH_2CH_2CH_3$	2
pentane	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexane	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptane	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octane	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonane	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
decane	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

2. Aliphatic Hydrocarbons

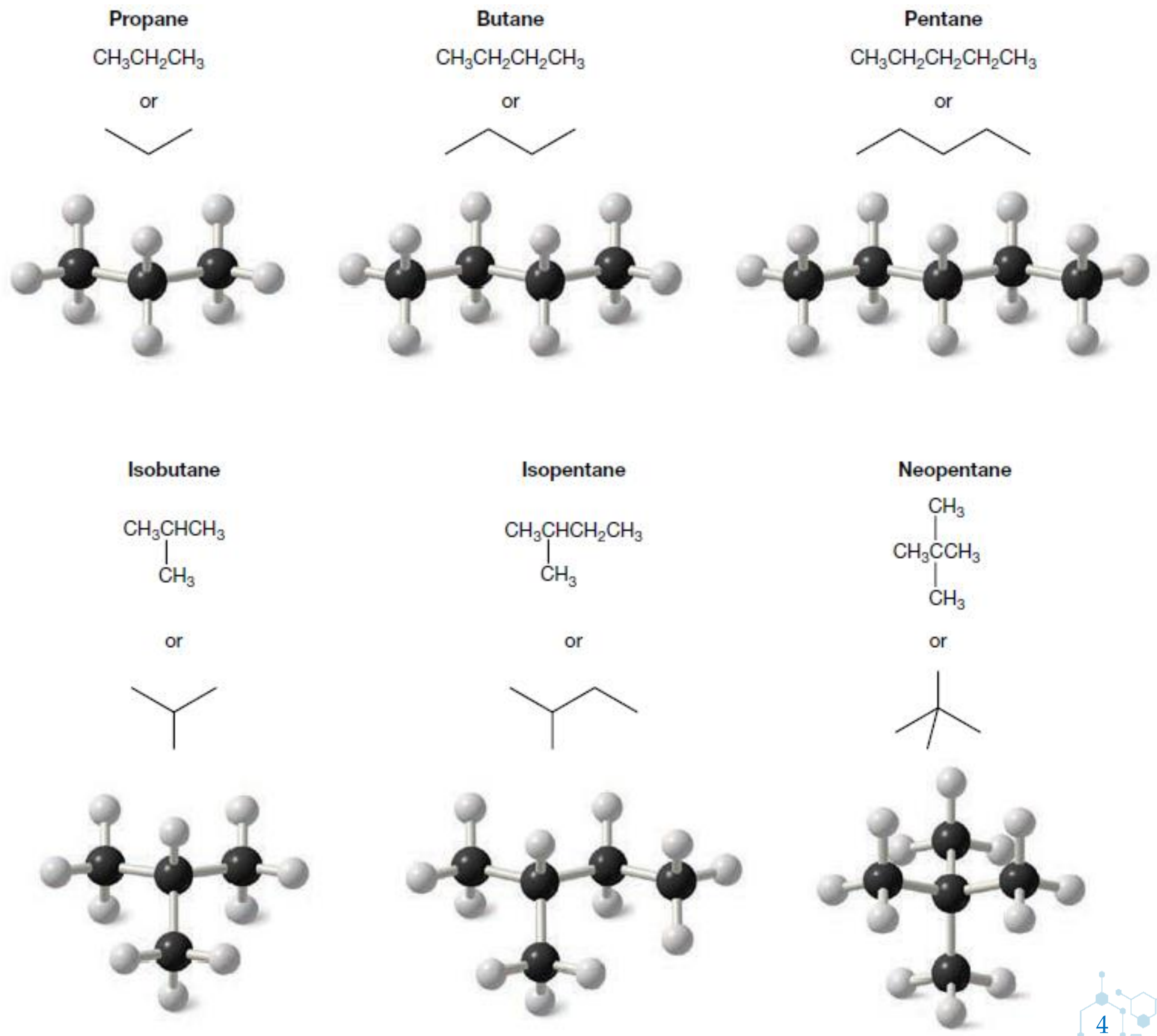
2.1. Alkanes and Cycloalkanes

2.1.1. Shapes of 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.



2. Aliphatic Hydrocarbons

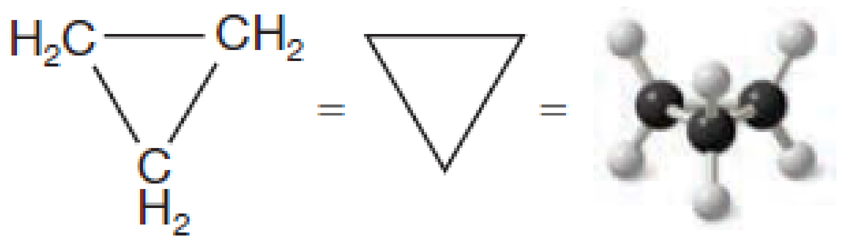
2.1. Alkanes and Cycloalkanes

2.1.2. Shapes of Cycloalkanes

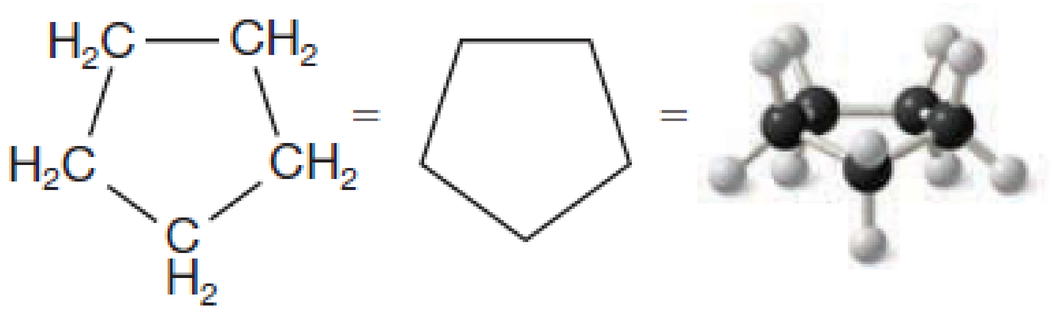
- **Carbon atoms in cycloalkanes are sp^3 hybridized, and their rings can adopt different shapes.**
- **Planar rings:**

  Cyclopropane has a planar, triangular structure. Its three carbon atoms lie in the same plane.
- **Branched-chain alkanes:**

  Larger cycloalkanes generally adopt non-planar (puckered) structures. Cyclopentane, for example, adopts a puckered shape.



Cyclopentane

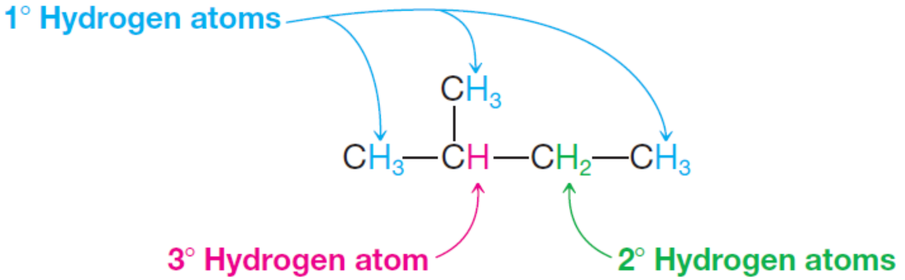


Cyclopropane

2. Aliphatic Hydrocarbons

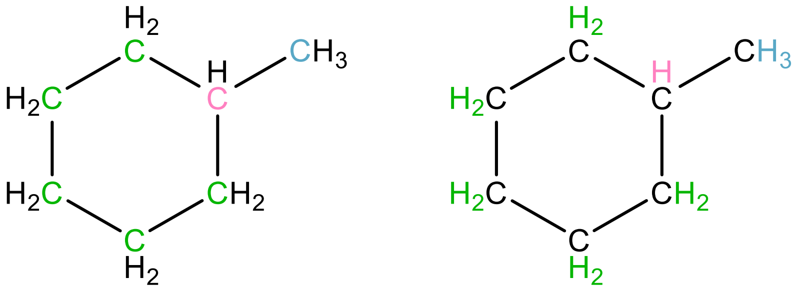
2.1. Alkanes and Cycloalkanes

2.1.3. How to classify carbon and hydrogen atoms



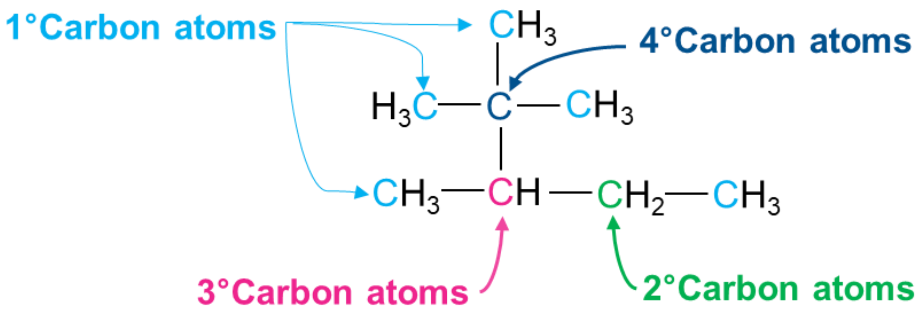
- A primary (1°) carbon is one that is bonded to only one other carbon.
- A secondary (2°) carbon is one that is bonded to two other carbons.
- A tertiary (3°) carbon is one that is bonded to three other carbons.
- The hydrogen atoms of an alkane are classified based on the carbon atom to which they are attached.

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



- In cycloalkanes, carbon and hydrogen atoms are classified in the same way based on the number of carbon atoms attached to the carbon atom.
- Examples:

  2-methylbutane and methylcyclohexane, have (1°), (2°), and (3°) carbon and hydrogen atoms. 2,2,3-trimethylpentane has (1°), (2°), (3°), and (4°) carbon atoms, but only (1°), (2°), and (3°) hydrogen atoms.



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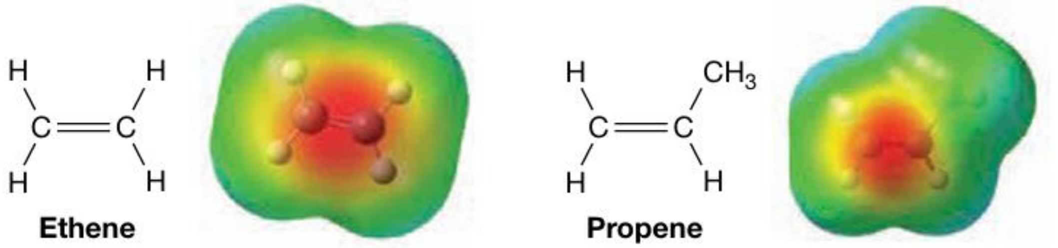
2. Aliphatic Hydrocarbons

2.2. Alkenes, Dienes, and Cycloalkenes

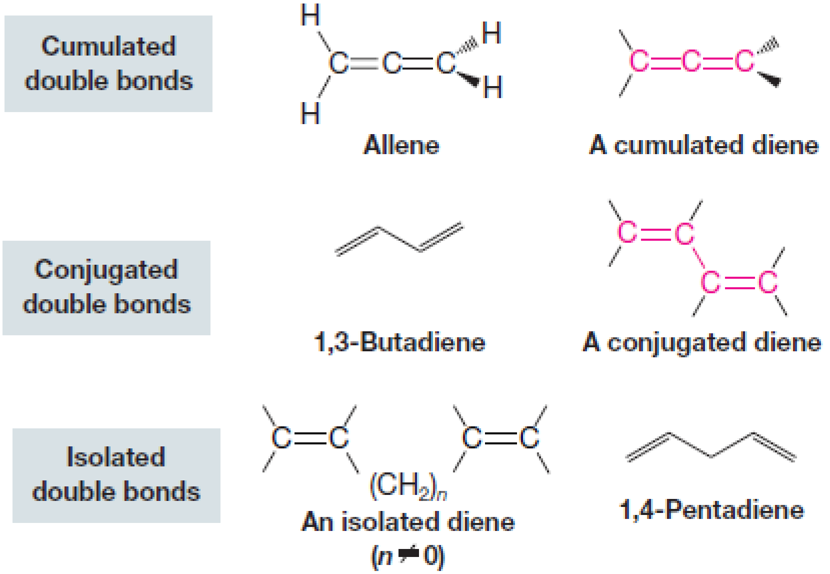
- Alkenes are hydrocarbons containing a carbon-carbon double bond, historically called olefins.
- General formula is C_nH_{2n}
- The simplest alkene, ethene (ethylene) (C_2H_4)



- Dienes are hydrocarbons containing two carbon–carbon double bonds (C=C).
- The general formula of acyclic dienes is C_nH_{2n-2}

2.2.1. How to Classify Dienes

1) Cumulated dienes: The double bonds share a common carbon atom.
2) Conjugated dienes: The double bonds are separated by one single bond.
3) Isolated dienes: The double bonds are separated by two or more single bonds.



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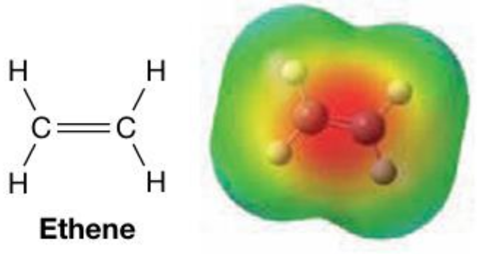
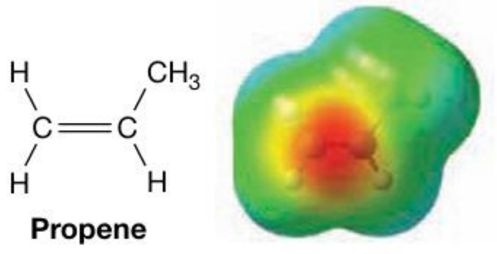
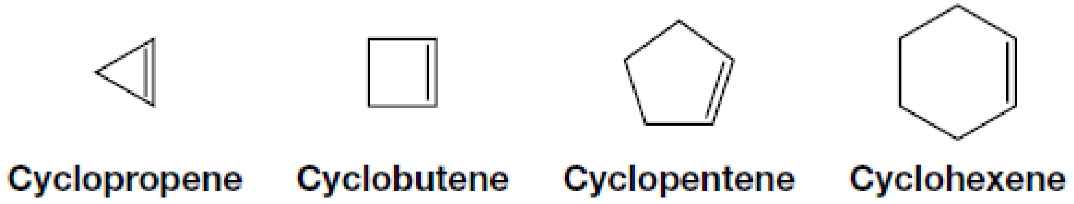
2. Aliphatic Hydrocarbons

2.2. Alkenes, Dienes, and Cycloalkenes

- Cycloalkenes are cyclic hydrocarbons containing a carbon–carbon double bond.
- General formula is C_nH_{2n-2}
- The simplest cycloalkenes, Cyclopropene (C_3H_4)

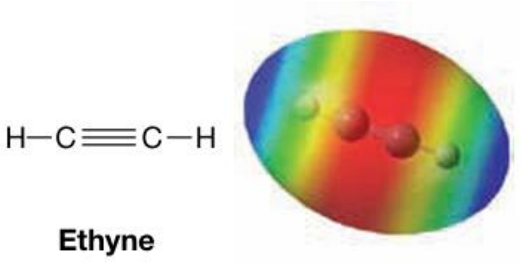






2.3. Alkynes

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



2. Aliphatic Hydrocarbons

2.4. Isomerism

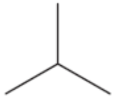
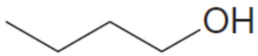
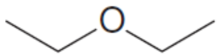
- **Isomers are different compounds with identical molecular formulas.**

Types of Isomerism

- **Structural Isomerism**
- **Geometrical Isomerism**

2.4.1. Structural or constitutional isomers

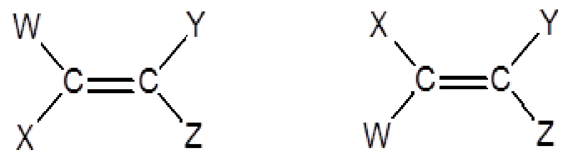
- **Structural isomers have the same molecular formula but different in the sequence of atoms bonded to each other.**
- **Examples:**

Molecular formula	***Constitutional isomers***		
C_4H_{10}	 **Butane**	and	 **2-Methylpropane**
$C_4H_{10}O$	 **1-Butanol**	and	 **Diethyl ether**

2. Aliphatic Hydrocarbons

2.4. Isomerism

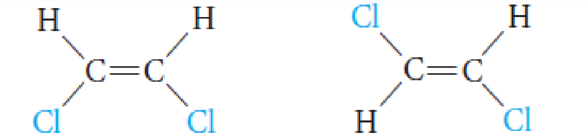
2.4.2. Geometric Isomerism in Alkenes



Geometric isomers

A) The (*cis*)–(*trans*) System for Alkene when W differs from X and Y from Z, Alkenes exist as 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.**

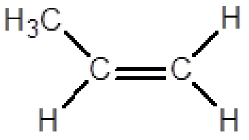


cis-1,2-dichloroethene
bp 60°C, mp −80°C

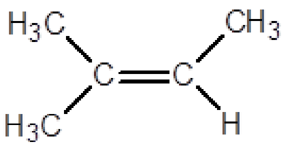
trans-1,2-dichloroethene
bp 47°C, mp −50°C

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

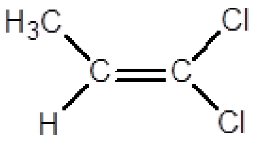
B) If (W = X or Y = Z), geometric isomerism is not possible.



Propene



2-Methyl-2-butene



1,1-Dichloropropene

2. Aliphatic Hydrocarbons

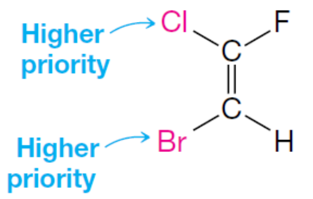
2.4. Isomerism

2.4.2. Geometric Isomerism in Alkenes

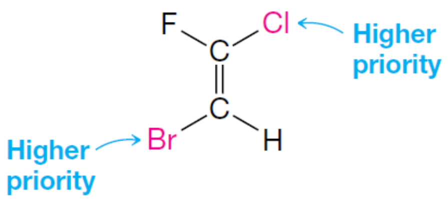
C) The (E)–(Z) System for Alkene

- **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.**



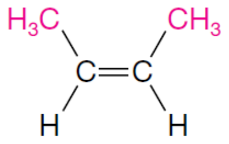
(*Z*)-2-Bromo-1-chloro-1-fluoroethene



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

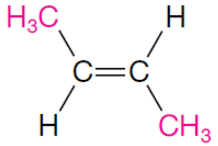
Cl > F

Br > H



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

CH_3 > H



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

2. Aliphatic Hydrocarbons

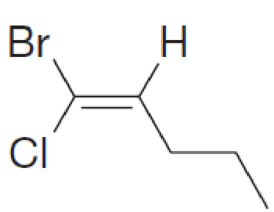
2.4. Isomerism

2.4.2. Geometric Isomerism in Alkenes

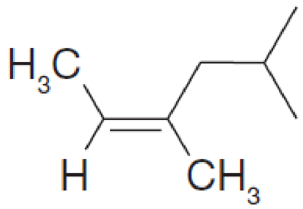
C) The (E)–(Z) System for Alkene

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

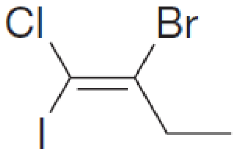
(a)



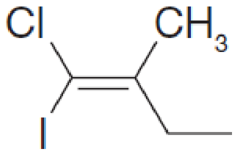
(c)



(b)



(d)



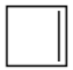
2. Aliphatic Hydrocarbons

2.4. Isomerism

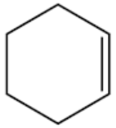
2.4.3. Geometric Isomerism in Cycloalkenes

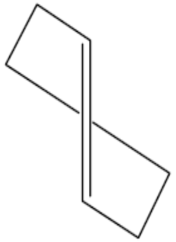
- **For very small rings (5 carbons or fewer), only the *cis* cycloalkene isomer is possible and a *trans* double bond cannot fit into these small rings.**
- **While *trans* double bonds are too strained to exist in small cycloalkenes, they become possible in larger rings.**

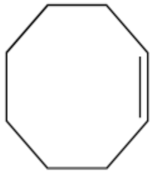

Cyclopropene

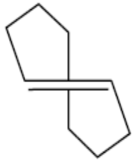

Cyclobutene


Cyclopentene


Cyclohexene

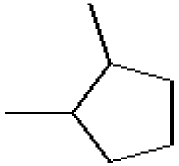

trans-Cyclohexene

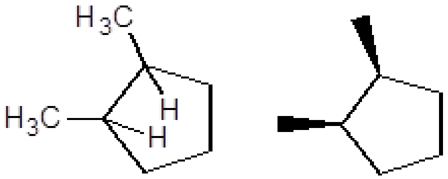

cis-Cyclooctene


trans-Cyclooctene

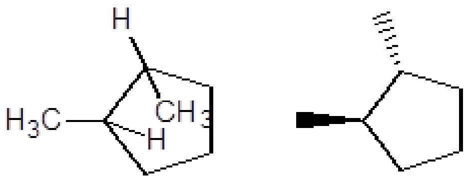
- ***cis-trans* Isomerism in Cycloalkanes**

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


1,2-Dimethylcyclopentane



cis-1,2-Dimethylcyclopentane



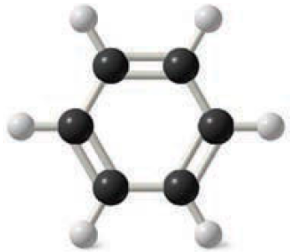
trans-1,2-Dimethylcyclopentane

3. Aromatic Hydrocarbons

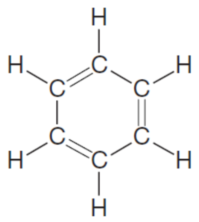
- The term "aromatic" referred to pleasant-smelling compounds from plants, many of which contained a benzene ring.
- Today, *aromaticity* is defined by electronic structure not odor.
- Aromatic compounds, are classified based on special stability from a *delocalized ring of π-electrons*, even if they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

3.1 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 Å, a value in between that for a carbon–carbon single bond between *sp*^{2} hybridized atoms (1.47 Å) and that for a carbon–carbon double bond (1.34 Å).



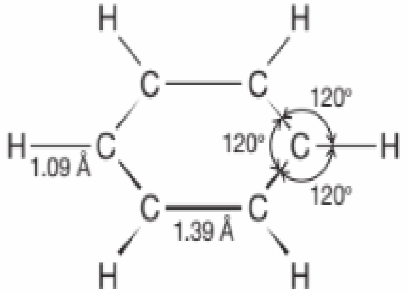
Benzene



Kekulé structure for benzene

or

Bond-line representation of Kekulé structure



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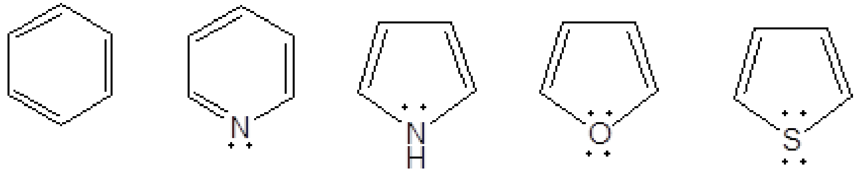
3. Aromatic Hydrocarbons

3.2. Aromatic Character (Aromaticity)

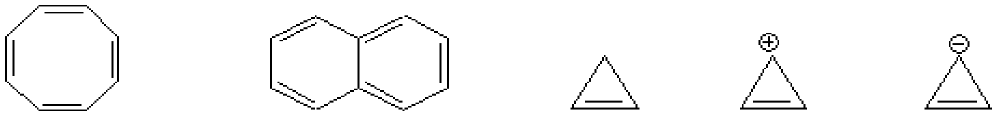
- **To be classified as aromatic, a compound must have:**

  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:**

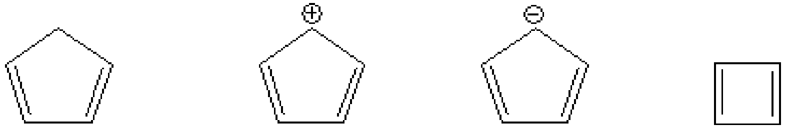
The number of π electrons in the compound = ($4n + 2$) **Where (n = 0,1, 2, 3, and so on).**



	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

جامعة الملك سعود
King Saud University
COLLEGE OF SCIENCES
CHEMISTRY DEPARTMENT

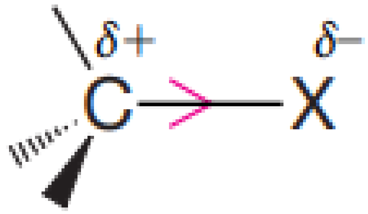
4. Organic Halogen Compounds

4.1. 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 (δ+) and the halogen has a partial negative charge (δ–).

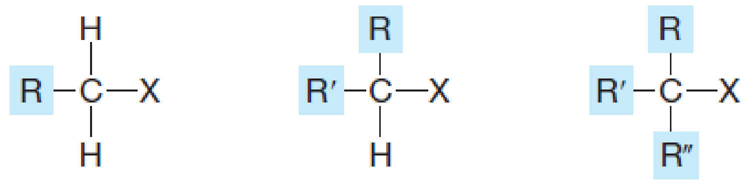


4. Organic Halogen Compounds

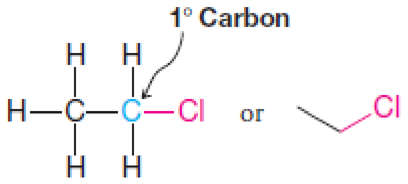
4.1. Alkyl Halides (Haloalkanes)

4.1.1. How to Classify Alkyl Halides

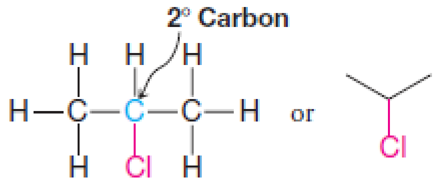
- Alkyl halides are classified as primary (1°), secondary (2°), or tertiary (3°) according to the number of carbon groups (R) directly bonded to the carbon bearing the halogen atom.



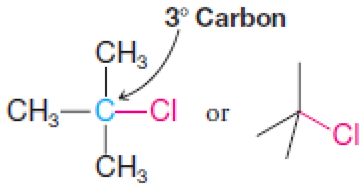
Primary (1°) Secondary (2°) Tertiary (3°)



1° alkyl chloride



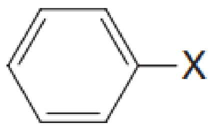
2° alkyl chloride



3° alkyl chloride

4.2. Aryl Halide (Haloarenes)

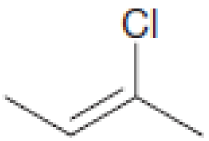
- An aryl halide is a compound with a halogen atom bonded to an aromatic ring.
- When the aromatic ring is specifically a benzene ring these compounds are called phenyl halides.



A phenyl halide or aryl halide

4.3. Alkenyl Halide (Haloalkenes)

- An alkenyl halide is a compound with a halogen atom bonded directly to an alkene carbon.
- The halogen atom is attached to an sp^2-hybridized carbon of the C=C double bond.
- Also called vinyl halides when the halogen is attached to a vinyl group (CH_2=CH–X).



An alkenyl chloride