2.3 Introduction to the Common Functional Groups in Organic Chemistry: Their Typical properties, Preparations and Reactions.

A. Alkanes

Physical Properties

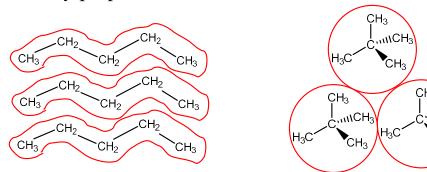
- Methane, ethane, propane, and butane are gases at room temperature.
- The unbranched alkanes pentane (C_5H_{12}) through heptadecane $(C_{17}H_{36})$ are liquids.
- Higher homologs are solids.
- The boiling points of unbranched alkanes increase with the number of carbons.

Name	Number of carbons	Molecular formula	Condensed structure	bp (°C)
Methane	1	CH ₄	CH ₄	-164
Ethane	2	C_2H_6	CH ₃ CH ₃	-88.6
Propane	3	C_3H_8	CH ₃ CH ₂ CH ₃	-42.1
Butane	4	C_4H_{10}	CH ₃ (CH ₂) ₂ CH ₃	-0.60
Pentane	5	C_5H_{12}	CH ₃ (CH ₂) ₃ CH ₃	36.1
Hexane	6	C_6H_{14}	CH ₃ (CH ₂) ₄ CH ₃	68.9
Heptane	7	C7H16	CH ₃ (CH ₂) ₅ CH ₃	98.4
Octane	8	C ₈ H ₁₈	CH ₃ (CH ₂) ₆ CH ₃	125.7

Solubility

- Alkanes are insoluble in water because the polar water molecules are not attracted to the non-polar alkane molecules.
- Alkanes are soluble in non-polar solvents such as Carbon Tetrachloride, CCl₄.
- Branched alkanes have lower boiling points than their unbranched isomers.

- Pentane molecules have more van der Waals attraction than the other.
 - > Straight chain pentane molecules have more surface area available for contact between them than the spherical 2,2-dimethylpropane.



Preparations of Alkanes

1. Catalytic hydrogenation of alkenes or alkynes.

$$H_2C=CH_2 + H_2 \xrightarrow{Pt} H_3C-CH_3$$

2. Thermal Decarboxylation of a Carboxylate Salt

$$H_3C-CH_2-COOH$$
 + NaOH $-Heat$ H_3C-CH_3 + CO_2

3. Grignard reagents

Organic compounds in which a metal atom is directly linked to carbon atom are known as organometallic compound.

Alkyl magnesium halide (R-MgX) are also called Grignard reagents or organometallic compounds.

• hydrolyzing of Grignard reagent (react it with water) gives alkane.

$$R-Mg-X$$
 \longrightarrow $R + MgXOH$

$$H_3C-Br + Mg \longrightarrow H_3C-Mg-Br$$

$$H_3C-Mg-Br \longrightarrow CH_4 + MgBrOH$$

Reactions of Alkanes

- Alkanes are sometimes referred to as paraffins, meaning "little affinity".
- They show little chemical affinity for other substances and are chemically inert to most laboratory reagent.
- Alkanes react with halogens in the presence of heat or light.

B. Alkenes

Physical properties of alkenes

- Alkenes are also referred to as "olefins". The word means fat dissolving since fats are relatively non-polar as alkenes are.
- The boiling points and solubilities of alkenes are very similar to the alkanes.
- The b.p and m.p of alkenes increase with increasing molecular weight but show some variations that depend on the shape of the molecule.
- Isomeric alkenes show different b.p and m.p depending on the position of the double bond.

Preparation of Alkenes

1. Dehydrogenation of Alkanes

High temperature dehydrogenation of alkenes produce alkenes.

CH₃CH₃
$$750^{\circ}$$
C H_2 C=CH₂ + H₂

CH₃CH₂CH₃ 750° C H_2 C=CHCH₃ + H₂

2. Dehalogenation of Vicinyl di-halides

A vicinyldihalide is an alkyl halide that has two atoms of halogen attached to adjacent carbons in the molecule.

$$CH_3$$
— CH — CH_2 + $2NaI$ acetone CH_3 — CH — CH_2 + $2NaCl$ + I_2

3. Dehydrohalogenation of an alkyl halide

4. Dehydration of an Alcohol

In the dehydration of alcohols, the H and OH are lost from adjacent carbons. An acid catalyst is necessary.

$$-\overset{|}{C}-\overset{|}{C}-\overset{H^{+}}{C} \longrightarrow C=C + H_{2}O$$

$$CH_3CH_2OH$$
 H_2SO_4 $H_2C=CH_2 + H_2O$ heat

$$\begin{array}{c|c} OH & \underline{H_2SO_4} \\ \hline & \text{heat} \end{array} \qquad + \ \underline{H_2C}$$

Reactions of Alkenes

Alkenes are electron-rich species. The characteristic reaction of alkenes is addition to the double bond according to the general equation.

$$A-B + C=C \longrightarrow A-C-C-B$$

1. Hydrogenation

$$(CH_3)_2C = CHCH_3 + H_2 \xrightarrow{Pt} (CH_3)_2CHCH_2CH_3$$

$$H_3C$$
 CH_3
 H_3C
 CH_3
 H_3C
 CH_3
 H_3C
 CH_3

2. Addition of Halogens

Latin vicinalis, means "neighboring."

$$\begin{array}{ccc} \text{CH}_3\text{CH=CH}_2 & \xrightarrow{\text{Br}_2} & \text{H}_3\text{C-CH-CH}_2 \\ & \text{CHCI}_3 & \text{Br} & \text{Br} \end{array}$$

• anti-stereochemistry-two new groups are added to opposite sides of the original pi bond

$$\bigcirc$$
 + Br_2 \longrightarrow \bigcirc Br_2

3. Addition of Hydrogen Halide (HX)

$$C = C + \delta^{+}H - X^{\delta^{-}} \longrightarrow H - C - C - X$$
Alkene Hydrogen halide Alkyl halide
$$CH_{3}CH_{2}CH = CH_{2} + HBr \longrightarrow CH_{3}CH_{2}CHCH_{3} + CH_{3}CH_{2}CH_{2}CH_{2}$$

$$Br = Br = Br$$
2-Bromobutane (80%) 1-Bromobutane (20%)

The major product is determined by Markovnikov's rule

Markovnikov's rule states that when an unsymmetrically substituted alkene reacts with a hydrogen halide, the hydrogen adds to the carbon that has the greater number of hydrogens, and the halogen adds to the carbon having fewer hydrogens.

$$CH_3$$
 + HCl \longrightarrow CH_3

- In the presence of peroxide (ROOR) the hydrobromination follows *Anti Markovnikovaddition* .
- Only HBr addition occurs by this pathway.

Ex. Write the structure of the major organic product formed in the reaction of HCl with the following

a) 2-methyl-butene

c) cis-2-Butene

b) 2-methyl-2-butene

d) сн₃-сн**=**⟨___⟩

4. Addition of water (Hydration)

$$C = C + HOH \xrightarrow{H^+} H - C - C - OH$$
Alkene Water Alcohol

The reaction follows Markovnikov's rule.

$$H_2O$$
 H_2SO_4
 OH

5. Hydroboration-Oxidation of Alkenes

A two steps reaction

$$C=C$$
 + R_2B-H \longrightarrow $H-C-C-BR_2$

Alkene Boron hydride Organoborane

 $H-C-C-BR_2$ $\xrightarrow{3H_2O_2}$ $H-C-C-OH$ + $2ROH$ + $B(OH)_4$

• borane-tetrahydrofuran complex (H₃B-THF)-common hydroborating agent

6. Conversion of Alkenes to Vicinal Halohydrins

$$C = C + X_2 + H_2O \longrightarrow HO - C - C - X + HX$$
Alkene Halogen Water Halohydrin Hydrogen halide

$$H_2C=CH_2 + Br_2 \xrightarrow{H_2O} HOCH_2CH_2Br$$
2-Bromoethanol (70%)

7. Epoxidation of Alkenes

Epoxides are easy to prepare via the reaction of an alkene with a peroxy acid.

$$C = C + RCOOH \longrightarrow C - C + RCOH$$
Alkene Peroxy acid Epoxide Carboxylic acid

$$H_2C = CH(CH_2)_9CH_3 + CH_3COOH \longrightarrow H_2C - CH(CH_2)_9CH_3 + CH_3COH$$

$$\begin{array}{c} O \\ + CH_3COOH \longrightarrow \\ \hline \end{array} \begin{array}{c} O \\ + CH_3COH \end{array}$$

7. Ozonolysis of Alkenes

Ozone is a powerful electrophile and undergoes a remarkable reaction with alkenes in which both the σ and π components of the carbon-carbon double bond are cleaved to give a product referred to as an **ozonide**.

$$C = C + O_3 \longrightarrow C \bigcirc C$$
Alkene Ozone Ozonide

Ozonides undergo hydrolysis in water, giving carbonyl compounds.

The two-stage reaction sequence is called **ozonolysis**

The two-stage reaction sequence is called **ozonolysis** and is represented by the general equation

$$\begin{array}{c} R \\ R'' \end{array} \xrightarrow{\begin{array}{c} 1. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} R \\ R'' \end{array} \xrightarrow{\begin{array}{c} 1. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_3CH_2CH_2CH_2CCH_2 \end{array} \xrightarrow{\begin{array}{c} 1. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_3CH_2CH_2CH_2CCH_3 \end{array} + \begin{array}{c} O \\ HCH_2 \end{array} \xrightarrow{\begin{array}{c} 1. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_3 \end{array} \xrightarrow{\begin{array}{c} O \\ R'' \end{array}} \begin{array}{c} O \\ CH_3CH_2CH_2CH_2CCH_3 \end{array} + \begin{array}{c} O \\ HCH_2 \end{array} \xrightarrow{\begin{array}{c} 1. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ 2. H_2O, Zn \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array}} \begin{array}{c} O \\ CH_2 \end{array} \xrightarrow{\begin{array}{c} 0. O_3 \\ CH_2 \end{array} \xrightarrow{\begin{array}$$

8. Hydroxylation

• addition of two OH groups to each of the two double bonded carbon

9. Oxidative cleavage of an alkene using hot alkaline KMnO₄

Acidic KMnO₄ also causes double bond cleavage like ozone.