HYDROCARBONS & AROMATIC COMPOUNDS

C1 ALKANES

Methods of Preparation of Alkanes and Cycloalkanes

1. Hydrogenation of alkanes and alkynes:
   (i) General Reactions:

   \[
   \text{CH}_3\text{CH} = \text{CH}_2 + \text{H} \xrightarrow{\text{Ni, Pt, or Pd}, \text{Solvent Pressure}} \text{CH}_3\text{CH}_2\text{CH}_3
   \]

   The reaction is usually carried out in the presence of solvent \( \text{C}_2\text{H}_5\text{OH} \).

   Specified Examples:

   (a) \( \text{CH}_3\text{CH} = \text{CH}_2 + \text{H} \xrightarrow{\text{Ni}, 200-300^\circ\text{C}} \text{CH}_3\text{CH}_2\text{CH}_3 \)

   [Any reduction that is carried out in this manner is called as Sabatier-Sanderen’s reduction]

   (b) \( \text{CH}_3 - \text{CH} - \text{HC} = \text{CH}_2 + \text{H}_2 \xrightarrow{\text{Raney Ni/Pd/Pt}, 25^\circ\text{C} (\text{C}_2\text{H}_5\text{OH}, 50 \text{ atm})} \text{CH}_3 - \text{CH} - \text{CH}_2 + \text{C}_3\text{H}_5 \)

   (c) \( \text{C}_3\text{H}_6 + \text{H}_2 \xrightarrow{\text{Pd, C}_2\text{H}_5\text{OH}(25^\circ\text{C}, 1 \text{ atm})} \text{C}_3\text{H}_8 \)

   Limitation:
   This method cannot be used for the preparation of methane.

2. Reduction of Alkyl Halides:

   (a) Hydrolysis of Grignard reagent:

   \[
   \text{R} - \text{X} + \text{Mg} \xrightarrow{\text{dry ether}} \text{R} - \text{MgX} \xrightarrow{\text{H}_2\text{O}} \text{R} - \text{H} + \text{MgX} \xrightarrow{\text{OH}} \text{X}
   \]

   Examples:

   \[
   \text{CH}_3\text{CH}_2 - \text{CH} - \text{CH}_3 \xrightarrow{\text{Mg}, \text{dry ether}} \text{CH}_3 - \text{CH}_2\text{CH} - \text{CH}_3 \xrightarrow{\text{H}_2\text{O}} \text{CH}_3 - \text{CH}_2 - \text{CH} - \text{CH}_3
   \]

   sec-Butyl bromide

   sec-Butyl magnesium bromide

   n-Butane
(b) Reduction by metal and acid

\[ R - X + Zn + H^+ \rightarrow R - H + Zn^{2+} + X^- \]

Example:

\[ \text{CH}_3\text{CH}_2\text{CH}_3 + \text{Zn}, \text{H}^+ \rightarrow \text{CH}_3\text{CH}_2\text{CH}_3 \]

sec-Butyl bromide \hspace{1cm} n-Butane

(c) \[ 4R - X + \text{LiAlH}_4 \rightarrow 4R - H + \text{LiX} + \text{AlX}_3 \quad [X \neq F] \]

\[ R - X + \text{H}^+ \rightarrow RH + \text{H}^- \quad [\text{H}^- \text{comes from LiAlH}_4] \]

\( \text{LiAlH}_4 \) can reduces 1° and 2° alkylhalide

(d) \[ R - X + n(\text{- C}_4\text{H}_9)_3\text{SnH} \rightarrow RH + (n - \text{- C}_4\text{H}_9)_3\text{SnX} \]

\( \text{Tributyl tin hydride} \)

[It can reduce 1°, 2° and 3° alkyl halide].

3. Coupling of alkyl halides with organomettalic compounds – (Corey-house alkane synthesis)

\[ \text{R} - \text{X} + 2\text{Li} \rightarrow \text{R} - \text{Li} \]

\[ \begin{array}{c}
\text{CuX} \\
\text{Ether} \\
\text{LiX}
\end{array} \rightarrow \text{R} - \text{CuLi} \]

may be 1°, 2° or 3°

Lithium dialkyl copperate

\[ \text{R'}X \text{ (should be 1°)} \]

\[ \text{R} - \text{R'} + \text{R} - \text{Cu} + \text{LiX} \]

[This method is used to prepare higher alkanes]. This method is particularly suitable for preparation of unsymmetrical alkanes].

\[ \text{CH}_3\text{CH}_2\text{Cl} + 2\text{Li} \rightarrow \text{CH}_3\text{CH}_2\text{Li} + \text{LiCl} \]

Ethyl chloride \hspace{1cm} Ethyl Lithium

Lithium dialkyl copperate

\[ \text{CH}_3\text{CH}_2\text{Br} \]

\[ \text{LiBr} + \text{CH}_3\text{CH}_2\text{Cu} + \text{CH}_3\text{CH}_2 - \text{CH}_2(\text{CH}_3)_2\text{CH}_2 \]

n-heptane

4. By reduction of alcohols, aldehydes, ketones, carboxylic acid

\[ \text{R} - \text{CH}_2\text{OH} \rightarrow \text{R} - \text{CH}_3 + \text{H}_2\text{O} + \text{I}_2 \]

\[ \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CH}_3 + \text{H}_2\text{O} + 2\text{I}_2 \]

5. By wurtz reaction :

\[ \text{R} - \text{X} + 2\text{Na} \rightarrow \text{R} - \text{X} \rightarrow \text{R} - \text{R} + 2\text{NaX} \]
Example:

\[ 2Na + 2CH_3CH_2CH_2Cl \rightarrow \text{ether} \rightarrow CH_3CH_2CHCH_2CH_3 + 2NaCl \]

[This method is useful for the preparation of symmetrical alkanes]

6. Decarboxylation (The process of eliminating \( \text{CO}_2 \) from carboxylic acid is called as decarboxylation)

\[
\text{RCOO}_\text{Na} + \text{NaOH(CaO)} \xrightarrow{\Delta} R - H + \text{Na}_2\text{CO}_3
\]

\[
\text{CH}_3\text{COONa} + \text{NaOH(CaO)} \xrightarrow{\Delta} \text{CH}_4 + \text{Na}_2\text{CO}_3
\]

[The alkane formed in this way always contain one carbon atom less than the carboxylic acid].

7. Kolbe’s Electrolytic Method: A concentrated solution of the sodium or potassium salt of carboxylic acid is electrolysed.

\[
R_1\text{COOK} + R_2\text{COOK} + 2\text{H}_2\text{O} \rightarrow R_1 - R_2 + 2\text{CO}_2 + \text{H}_2 + 2\text{KOH}
\]

[If \( R_1 \) and \( R_2 \) are different then \( R_1 - R_1 \) and \( R_2 - R_2 \) are also obtained]

other side products are – alkenes, esters, alcohols.

Practice Problems:

1. By Wurtz reaction, a mixture of methyl iodide and ethyl iodide gives
   (a) propane (b) ethane  
   (c) butane (d) a mixture of the above three

2. Kolbe’s synthesis of sodium salt of butanoic acid gives
   (a) n-hexane  (b) isobutane  (c) n-butane  (d) propanone

3. \((\text{CH}_3)_3\text{C} - \text{MgCl}\) on reaction with \( \text{D}_2\text{O} \) produces
   (a) \((\text{CH}_3)_3\text{CD}\)  (b) \((\text{CH}_3)_3\text{OD}\)  (c) \((\text{CD})_3\text{CD}\)  (d) \((\text{CD})_3\text{OD}\)

4. Aq. solution of potassium acetate is electrolysed. Possible organic products are :
   (a) \(\text{CH}_3 - \text{CH}_3\)  (b) \(\text{CH}_3\text{COOCH}_3\)  
   (c) \(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3\)  (d) both (a) and (b) are correct

[Answers : (1) d (2) a (3) a (4) d]

C2 General Chemical properties of alkanes:

1. Halogenation:

\[
\text{C} + \text{H} + \text{X}_2 \xrightarrow{250-400^\circ\text{C}} \text{or light} \rightarrow \text{C} + \text{X} + \text{HX}
\]

Normally a mixture

Reactivity \(:\) \( \text{F}_2 > \text{Cl}_2 > \text{Br}_2 \) \( (\text{I}_2 \text{ does not react})\)

\( \text{H} : 3^\circ > 2^\circ > 1^\circ > \text{CH}_3 - \text{H} \)

Example:

\[
\begin{align*}
\text{CH}_3 - \text{CH} - \text{CH}_3 & \xrightarrow{\text{Cl}_2, 250-400^\circ\text{C}} \text{CH}_3 - \text{CH} - \text{CH}_2\text{Cl} + \text{CH}_3 - \text{C} - \text{CH}_3 \\
\text{Isobutane} & \quad (67 \%) \quad (33 \%)
\end{align*}
\]
Bromination:

1. Although both chlorination and bromination yield a mixture of isomers, the results given above shows that relative amounts of isomer differ markedly depending upon the halogen used.
2. Chlorination gives a mixture of isomers in which no one predominates. In bromination on contrast one isomer predominates to such an extent that as to be only product produced.

The factors determines the relative yields of isomeric products:

1. Probability Factor: This factor is based on the number of each kind of H-atom in the molecule. For example, in CH₃CH₂CH₂CH₃ there are six equivalent 1°H’s and four equivalent 2°H’s. The ratio of abstraction of 1°H are thus 6 to 4 or 3 to 2.
2. Reactivity of H*: The order of reactivity of H is 3° > 2° > 1°.
3. Reactivity of X*: The more reactive Cl is less selective and more influenced by the probability factor. The less reactive Br is more selective and less influenced by the probability factor, as summarised by the reactivity-selectivity principle. If the attacking species is more reactive then it will be less selective, and yields will be closer to those expected from the probability factor.
   — The rate of abstraction of hydrogen atoms is always found to follow the sequence 3° > 2° > 1°.
   — At room temperature are 5 : 3.8 : 1 using these values we can predict the ratio of isomeric chlorine products from a given alkane.
Example:

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 & \xrightarrow{\text{Cl}_2, \text{light}, 25^\circ\text{C}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{CH}_3\text{CH}_2\text{CHCH}_3 \\
\text{n-Butyl Chloride} & = \frac{\text{no. of 1}^0\text{H}}{\text{no. of 2}^0\text{H}} \times \text{reactivity of 1}^0\text{H} \\
\text{sec-Butyl Chloride} & = \frac{\text{no. of 2}^0\text{H}}{\text{reactivity of 2}^0\text{H}} \\
\frac{6}{4} & = \frac{3.8}{15.2} = 28\% \times 72\%
\end{align*}
\]

The same sequence of reactivity, 3\(^0\) > 2\(^0\) > 1\(^0\) is found in Bromination, but with enormously larger reactivity ratios. At 127\(^\circ\)C the relative rate per hydrogen atom are 1600 : 82 : 1. Here, difference in reactivity are so marked so as to outweigh probability factor. Hence bromination is selective product.

In bromination of isobutane at 127\(^\circ\)C

\[
\begin{align*}
\text{Isobutyl bromide} & = \frac{\text{no. of 1}^0\text{H}}{\text{no. of 3}^0\text{H}} \times \text{reactivity of 1}^0\text{H} \\
\text{tert-butyl bromide} & = \frac{\text{no. of 3}^0\text{H}}{\text{reactivity of 3}^0\text{H}} \\
\frac{9}{1} & = \frac{1}{1600} = \frac{9}{1600}
\end{align*}
\]

Hence, tert-butyl bromide happens to be the exclusive product (over 99\%)

2. Combustion:

\[
\begin{align*}
\text{C}_n\text{H}_{2n+2} + \text{O}_2 & \xrightarrow{\text{flame}} n\text{CO}_2 + (n + 1)\text{H}_2\text{O} \\
\Delta H & = \text{enthalpy of combustion}
\end{align*}
\]

Pyrolysis: (Cracking)

3. Decomposition of a compound by heat alone is known as Pyrolysis

Pyrolysis of alkanes particularly when petroleum is concerned is known as cracking.

\[
\begin{align*}
\text{Alkane} & \xrightarrow{400-600^\circ\text{C}} \text{H}_2 + \text{smaller alkanes} + \text{alkenes}. \\
\text{with or without catalyst}
\end{align*}
\]

In thermal cracking alkanes are simply passed into a chamber to a high temperature. Large alkanes are converted into smaller alkanes, alkenes and some hydrogen.

Practice Problems:

1. The number of possible enantiomeric pairs that can be produced during mono chlorination of 2-methyl butane is

(a) 2 (b) 3 (c) 4 (d) 1

2. An alkane with molecular mass 72 formed only one substitution product. Suggest a structure for the alkane.

(a) \(\text{CH}_3\) \(\text{H}_3\text{C} - \text{C} - \text{CH}_3\) \(\text{CH}_3\) (b) \(\text{CH}_3\) \(\text{CH}_2\text{CH}_3\)

(c) \(\text{CH}_3\) \(\text{H}_3\text{C} - \text{CH}_2 - \text{CH}_2 - \text{CH}_3\) (d) \(\text{CH}_3\) \(\text{CH}_3\) \(\text{CH}_2\text{CH}_2 - \text{CH} - \text{CH}_3\)
3. \[ \text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{Mg}} \text{(A)} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{(B)} \xrightarrow{\text{Mg}} \text{OC}_2\text{H}_3\text{Br} \]

Thus A and B in the above reaction sequence are:

(a) (A) CH₃CH₂MgBr
    (B) CH₃CH₂

(b) (A) CH₃CH₂MgBr
    (B) CH₃CH₂CH₂CH₃

(c) (A) CH₃
    (B) CH₃CH₂CH₃

(d) (A) CH₃COOH
    (B) CH₃MgBr

4. \[ \text{C}_5\text{H}_{11} + \text{Cl}_2 \xrightarrow{\text{light}} \text{C}_5\text{H}_{11}\text{Cl} \xrightarrow{\text{Na/ether}} \text{(C)} \]

Only one structure of B is possible (A), (B) and (C) are:

(a) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\end{array}
\]

(b) \[
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3 \end{array}
\end{array}
\]

(c) both correct

(d) none is correct

[Answers : (1) a (2) a (3) a (4) a]

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**C3: ALKENES**

Methods of Preparation of Alkenes:

1. Dehydrohalogenation of Alkyl-Halide: 1,2 – Elimination

   \[
   \text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \text{Cl} + \text{KOH} \xrightarrow{\text{alc.}} \text{CH}_3 \text{CH}_2 \text{CH} = \text{CH}_2
   \]

Examples:

   \[
   \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} + \text{KOH} \xrightarrow{\text{alc.}} \text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2
   \]

   \[
   \text{Cl} \downarrow
   \text{CH}_3\text{CH}_2\text{CHCH}_3 + \text{KOH} \xrightarrow{\text{alc.}} \text{CH}_3\text{CH} = \text{CHCH}_3 + \text{CH}_2\text{CH}_2\text{CH} = \text{CH}_2
   \]

(cis or trans)

Discussion: Dehydrohalogenation means that there is an elimination of one hydrogen atom and one halogen atom. The reagent required is a base, whose function is to remove the hydrogen as a proton.

Mechanism – E₂ mechanism:

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Now if alkyl halide has more than one $\beta$, hydrogen atom then that hydrogen is removed which result in more substituted alkene, this is according to saytzeff’s rule.

More substituted alkene means that more no. of Alkyl groups are present around the double bond.

E$_2$ elimination reactions are characterised by the following:

1. Substrate contains a leaving group; an atom or group that leaves along with electron pair.
2. In position $\beta$ to the leaving group the substrate contain H-atom that can be abstracted by base.
3. Reaction is brought about by a base.

Typically strong bases like $\text{OH}^-$, $\text{RO}^-$ (alkoxide ion) derived from alcohol, $\text{C}_2\text{H}_5\text{O}^-$ (ethoxide ion), tert-butoxide ion ($\text{CH}_3\text{CO}^-$) etc.

Heterolytic bond dissociation energy: $\text{RF} > \text{RCI} > \text{RBr} > \text{RI}$

$\therefore$ Reactivity towards E$_2$: $\text{RI} > \text{RBr} > \text{RCI} > \text{RF}$

similarly reactivity order of $\text{R} - \text{X}$ is $3^0 > 2^0 > 1^0$

as more substituted alkene will form as the branching will increase.

Kinetics of E$_2$: Bimolecular.

Rate of the reaction $r = k \frac{[\text{RX}]}{[\text{Z}]}$
An exception to Saytzeff’s rule:

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{O}^- & + \text{CH}_3 - \text{CH}_2 - \text{C} - \text{Br} & \xrightarrow{75^\circ} & \text{CH}_3 - \text{CH}_2 - \text{C} - \text{CH}_3 \\
\text{CH}_3 & & \text{(CH}_3\text{)COH} & (72.5 \%) \\
\text{CH}_3 - \text{CH}_3 = \text{C} - \text{CH}_3 & & & (27.5 \%)
\end{align*}
\]

E\textsubscript{1} Mechanism: E\textsubscript{1} involves two steps for same process as it takes place in E\textsubscript{2}.

1. The substrate undergo heterolysis slowly to form halide ion and a carbocation.
2. In step (2) the carbocation readily looses a proton to the base and forms the alkene.

\[
\begin{align*}
\text{X} & \quad \text{slow} \\
\text{C} - \text{C} - & \quad \text{X} + \text{C} - \text{C} - \\
\text{H} & \quad \text{H} \\
\text{fast} & \\
\text{C} - \text{C} - & \quad \text{C} - \text{C} + \text{H} : \text{B}
\end{align*}
\]

Thus a carbocation may (a) combine with a nucleophile (b) can undergo rearrangement (c) eliminate a proton to form the alkene.

Kinetics of E\textsubscript{1} reaction:

\[ r = k [R \ X] \quad \text{[Unimolecular reaction]} \]

Order of reactivity of R — X for E\textsubscript{1}: \( 3^\circ > 2^\circ > 1^\circ \)

Thus because of rearrangement skeleton of carbon chain changes:

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{CHBr} - \text{CH}_3 & \xrightarrow{(\text{alc.})} \text{CH}_3 - \text{CH}_3, \text{CH}_3 \\
\text{CH}_3 & \xrightarrow{(\text{KOH})} \text{CH}_3 - \text{C} = \text{C} - \text{CH}_3 + \text{CH}_3 - \text{CH} - \text{C} = \text{CH}_2 \\
& \quad \text{CH}_3
\end{align*}
\]

Alkene that does not contain α-hydrogen in the presence of base can undergo E\textsubscript{1} elimination as follows:
Explanation:

\[
\begin{align*}
\text{CH}_3 - \text{C} - \text{CH}_2 - \text{Br} & \rightarrow \text{CH}_3 - \text{C} - \text{CH}_2 + \beta \rightarrow \text{CH}_3\text{C} = \text{CH} + \text{CH}_2 = \text{C} - \text{CH}_2 \\
\text{(chief product)}
\end{align*}
\]

**E<sub>2</sub> Vs E<sub>1</sub>**

- Reactivity of both mechanism increases with as we move from 1<sup>o</sup>, 2<sup>o</sup> to 3<sup>o</sup> substrate.
- But E<sub>2</sub> mechanism depends on concentration of base whereas E<sub>1</sub> mechanism is independent of the concentration of base.
- Stronger the base more E<sub>2</sub> is favoured
- 1<sup>o</sup> alkyl halide do not favour to form carbocation so they prefer E<sub>2</sub>.

2. **Dehydration of Alcohols**:

\[
\begin{align*}
\text{H} & - \text{C} - \text{H} \xrightarrow{\text{acid}} \text{H} = \text{C} - \text{H} + \text{H}_2\text{O}
\end{align*}
\]

**Ease of dehydration of alcohol 3<sup>o</sup> > 2<sup>o</sup> > 1<sup>o</sup>**

Examples:

\[
\begin{align*}
\text{H} & - \text{C} - \text{C} - \text{H} \xrightarrow{\text{acid}} \text{H} - \text{C} = \text{C} - \text{H} + \text{H}_2\text{O} \\
\text{Ethylene}
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} & \xrightarrow{\text{acid}} \text{CH}_3\text{C} = \text{CH} + \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \\
1\text{-Butene} & \text{ (major product)}
\end{align*}
\]

**Ease of dehydration of alcohols : 3<sup>o</sup> > 2<sup>o</sup> > 1<sup>o</sup>**

For secondary and tertiary alcohols the following mechanism is accepted:
Dehydration is acid-catalyzed: Acid transforms the poor leaving group (– OH) into the very good leaving group, –OH₂⁺

- As dehydration is acid catalysed as acid is hot consumed in the reaction. Acid used in step (1) is regenerated in step (3).

Dehydration is reversible: Unlike base promoted 1, 2-elimination, this elimination is reversible.

- As we shall study later that acid catalysed the hydration of alkenes to give alcohol.
- Thus each step is reversible.
- Under the condition of dehydration, the alkene being quite volatile is generally driven from the reaction mixture and thus equilibrium (3) is shifted in the right side.
- As a consequence the entire reaction is forced toward elimination.

Ease of dehydration of alcohol: 3° > 2° > 1°

- Rate of dehydration depends on step (2) and step (3) both.
- Where the structure of alkyl group permits the rearrangement of carbocation takes place.

Practice Problems:

1. Identify the possible number of products in the following reaction: \( \text{C}_6\text{H}_5\text{CH}_2\text{CH(Cl)C}_6\text{H}_5 \rightarrow \text{AlcKOH} \text{heat} \)

   (a) 1   (b) 2   (c) 3   (d) 4

   [Answers: (1) b]
**Chemical Properties of Alkene:**

(Addition Reactions)

1. **Addition of Hydrogen:** Catalytic hydrogenation

\[
\begin{align*}
\text{CH}_2\text{CH} = \text{CH}_2 & \quad \xrightarrow{\text{H}_2, \text{Ni}} \quad \text{CH}_3 - \text{CH}_2 - \text{CH}_3 \\
\text{1,2-Dibromoethane} & \quad \text{(Propylene bromide)}
\end{align*}
\]

2. **Addition of Halogens:**

\[
\begin{align*}
\text{CH}_2\text{CH} = \text{CH}_2 + \text{X}_2 & \quad \xrightarrow{\text{CCl}_4} \quad \text{CH}_2\text{CH} = \text{CH}_2 \\
\text{Propylene} & \quad \text{(Propylene bromide)}
\end{align*}
\]

3. **Addition of Hydrogen Halide:**

\[
\begin{align*}
\text{CH}_2\text{CH} = \text{CH}_2 & \quad \xrightarrow{\text{HX}, \text{HX} = \text{HCl}, \text{HBr}, \text{HI}} \quad \text{CH}_2\text{CH} = \text{CH}_2 \\
\text{1-Bromopropane} & \quad \text{(Isopropyl bromide)}
\end{align*}
\]
4. Addition of sulfuric acid:

\[ - \text{C} = \text{C}^- + \text{H}_2\text{SO}_4 \rightarrow - \text{C}^- \text{C}^- \text{OSO}_3\text{H} \]

5. Addition of dil-sulfuric acid:

\[ - \text{C} = \text{C}^- + \text{HOH} \rightarrow - \text{C}^- \text{C}^- \]

\[ \text{H} \quad \text{OH} \]

Example:

\[ \text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{H}_2\text{O}, \text{H}^+} \text{CH}_3 - \text{CH}^- \text{CH}_3 \]

Isopropyl alcohol (2-Propanal)

6. Halohydrin Formation:

\[ - \text{C} = \text{C}^- + \text{X}_2 + \text{H}_2\text{O} \rightarrow - \text{C}^- \text{C}^- + \text{HX}, \text{X}_2 = \text{Cl}_2, \text{Br}_2 \]

\[ \text{X} \quad \text{OH} \]

Example:

\[ \text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\text{Cl}_2, \text{H}_2\text{O}} \text{CH}_3 - \text{CH}^- \text{CH}_2 \]

Propylene (Propene) 1-Chloro-2-propanol (Propylene Chlorohydrin)

7. Dimerization:

Example:

\[ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \]

\[ \text{CH}_3 - \text{C} = \text{CH}_2 + \text{CH}_3 - \text{C} = \text{CH}_2 \xrightarrow{\text{acid}} \text{CH}_3 - \text{C} - \text{CH} = \text{C} - \text{CH}_3 \]

2, 4, 4-Trimethyl-2-pentene

\[ + \]

\[ \text{CH}_3 \quad \text{CH}_3 \]

\[ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{C} = \text{CH}_2 \]

\[ \text{CH}_3 \]

2, 4, 4-Trimethyl pentene
8. **Alkylation**:

\[ -C\equiv C- + R-H \xrightarrow{\text{acid}} -C-R \quad \text{H \quad R} \]

Example:

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 - C = CH_2 + CH_3 - C-H & \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3 - C - CH_2 - C - CH_3 \\
& \text{CH}_3 \quad \text{CH}_3
\end{align*}
\]

2, 2, 4, 4 - Tetramethylpentane

9. **Oxymercuration-demercuration**:

\[ C = C + \text{Hg} \,(\text{OAC})_2 + \text{H}_2\text{O} \xrightarrow{} -C-C- \xrightarrow{\text{NaBH}_4} -C-C- \]

\[
\begin{align*}
& \text{OH \quad HgOAc} \\
& \text{OH \quad H}
\end{align*}
\]

Markownikoff’s addition

Example:

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3 - C - CH = CH_2 & \xrightarrow{\text{Hg(OAC)_2, H}_2\text{O}} \text{NaBH}_4 \quad \text{CH}_3 - C - CH - CH_3 \\
& \text{CH}_3 \quad \text{OH} \quad \text{CH}_3
\end{align*}
\]

3, 3-Dimethyl-1-butene

3, 3-Dimethyl-2-butanol (no rearrangement takes place)

10. **Hydroboration-Oxidation**

\[ C = C \xrightarrow{(\text{BH})_2} \quad \text{H}_2\text{O}_2, \text{OH}^- \xrightarrow{} -C-C- + B(\text{OH})_3 \]

\[
\begin{align*}
& \text{H \quad B} \\
& \text{H \quad OH}
\end{align*}
\]

Anti Markownikoff’s addition

Examples:

\[
\begin{align*}
\text{CH}_3 & \\
\text{1-Methylcyclopentene} & \xrightarrow{(\text{BH})_2} \text{H}_2\text{O}_2, \text{OH}^- \quad \text{trans-2-Methyl-1-cyclopentanol}
\end{align*}
\]
11. **Addition of free radicals**

\[
\text{CH}_3 - C - CH = CH_2 + (\text{BH}_3) \rightarrow \text{H}_2\text{O}_2, \text{OH}^- \rightarrow \text{CH}_3 - C - \text{CH}_2 - \text{CH}_2 - \text{OH}
\]

3, 3-Dimethyl-1-butene 3, 3-Dimethyl-1-butanol

**Example:**

\[
\text{C}_6\text{H}_{14} + \text{BrCCl}_3 \rightarrow \text{BrCCl}_3, \text{BrCCl}_3
\]

1-octene Bromotrichloro methane 3-Bromo-1,1,1-trichloro propane

12. **Epoxidation:**

\[
\text{C} = \text{C} + \text{C}_6\text{H}_5\text{CO}_2\text{OH} \rightarrow \text{C} = \text{C} + \text{C}_6\text{H}_5\text{CO}_2\text{OH}
\]

Peroxybenzoic acid

13. **Hydroxylation:** Glycol formation

\[
\text{CH}_3 - C = C - H + \text{KMnO}_4 \rightarrow \text{CH}_3 - C = C - H + \text{HCO}_2\text{OH}
\]

14. **Halo-Genation:** Allylic Substitution

\[
\text{X}_2 (\text{low concentration}) \rightarrow \text{X} = \text{C} = \text{C} - \text{C} = \text{C} = \text{X}_2 = \text{Cl}_2, \text{Br}_2
\]

**Example:**

\[
\text{CH}_3\text{CH} = \text{CH}_2 \rightarrow \text{Cl} = \text{CH}_2\text{CH} = \text{CH}_2
\]

Allyl Chloride (3-Chloro-1-propene)
15. Cleavage Reactions (very important) used to determine structure.

Ozonolysis:

\[
\begin{align*}
\text{O}_{3} + \text{C}=\text{C} & \rightarrow \text{O} \ \ \ \ \ \text{H}_{2}\text{O}, \text{Zn} \\
\text{cyclohexene} & \rightarrow \text{3-Bromocyclohexene}
\end{align*}
\]

Example:

\[
\begin{align*}
\text{CH}_{3}\text{CH}_{2}\text{CH} & = \text{CH}_{2} \text{O}_{3} \rightarrow \text{CH}_{3}\text{CH}_{2}\text{CH} + \text{H} - \text{CH} \\
\text{CH}_{3} & = \text{C} = \text{CH}_{2} \text{O}_{3} \rightarrow \text{CH}_{3} - \text{C} = \text{O} + \text{O} = \text{C} - \text{H}
\end{align*}
\]

Substitution reactions at alylic positions:

SO\textsubscript{2}Cl\textsubscript{2} + CH\textsubscript{2} = CH – CH\textsubscript{3} \rightarrow CH\textsubscript{2} = CH– CH\textsubscript{2}Cl + SO\textsubscript{2} + HCl

Practice Problems:

1. A hydrocarbon containing 2 carbon atoms give Sabatier and Senderen’s reaction but does not give precipitate with ammonical silver nitrate solution. The hydrocarbon in question is
   (a) Ethane  (b) Acetylene  (c) Ethylene  (d) none of these

2. Which of the following is not correct about the reaction CH\textsubscript{2} = CH\textsubscript{2} + Br\textsubscript{2} \rightarrow CH\textsubscript{2}BrCH\textsubscript{2}Br?
   (a) The products formed are CH\textsubscript{2}BrCH\textsubscript{2}Br and CH\textsubscript{2}BrCH\textsubscript{2}I
   (b) The reaction follows polar mechanism
   (c) The reaction occurs readily in solution and is catalysed by inorganic halides
   (d) CH\textsubscript{2}ICH\textsubscript{2}I is formed only

3. 3-methyl-2-pentene on reaction with HOCl gives:
   \[
   \begin{align*}
   \text{Cl} & \text{ OH} \\
   (a) \text{CH}_{3} & = \text{CH} - \text{C} - \text{CH} - \text{CH}_{3}  & (b) \text{CH}_{3} & = \text{C} - \text{CH} - \text{CH}_{3} \\
   &  & \text{CH}_{3} & \text{CH}_{3}
   \end{align*}
   \]
4. Ozonolysis of \[
\begin{array}{c}
\text{(c) } \text{CH}_3-\text{CH} = \text{CH}-\text{CH} \equiv \text{CH} \\
\text{CH}_3 \\
\end{array}
\]
will give

(a) \[
\begin{array}{c}
\text{CH}_3-\text{CH} = \text{CH} \\
\end{array}
\]

(b) \[
\begin{array}{c}
\text{OC} - \text{CH} = \text{CH} - \text{CH} - \text{CO} \\
\text{CH}_2 \\
\text{CH}_2 \\
\text{CH}_2 \\
\end{array}
\]

(c) \[
\begin{array}{c}
\text{O} \\
\text{O} \\
\end{array}
\]

(d) None

5. Sample of 2, 3-dibromo-3-methyl pentane is heated with zinc dust. The resulting product is isolated and heated with HBr. Indicate which is the structure that represents the final organic product in the reaction

(a) \[
\begin{array}{c}
\text{BrCH}_2 - \text{CH} = \text{CH} - \text{CH} - \text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

(b) \[
\begin{array}{c}
\text{CH}_3 - \text{CH} = \text{CBr} - \text{CH} - \text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

(c) \[
\begin{array}{c}
\text{CH}_3 - \text{CH} = \text{CH} - \text{CH} - \text{CH}_3 \\
\text{Br} \\
\text{CH}_3 \\
\end{array}
\]

(d) \[
\begin{array}{c}
\text{CH}_3 = \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_3 \\
\text{CH}_3 \\
\end{array}
\]

6. \[
\begin{align*}
\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 & \xrightarrow{\text{H}_2/\text{Pt} \text{ equiv.}} \text{A} \xrightarrow{\text{O} / \text{H}_2 \text{O}} \text{A and B are} \\
\text{(a) } \text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}, (\text{CH}_3 \text{COOH} + \text{CO}_2) & \\
\text{(b) } \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3, \text{CH}_3 \text{COOH (2 mol)} & \\
\text{(c) } \text{CH}_3 - \text{CH} = \text{CH} = \text{CH}_3, \text{CH}_3 \text{CHO (2 mol)} & \\
\text{(d) } \text{CH}_3 - \text{CH} = \text{CH} = \text{CH}_3, (\text{CH}_3 \text{CH}_2 \text{CHO} + \text{HCHO}) & 
\end{align*}
\]

7. Identify the set of reagents / reaction conditions ‘X’ and ‘Y’ in the following set of transformations

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2 & \xrightarrow{\text{X}} \text{Product} \\
\text{Product} & \xrightarrow{\text{Y}} \text{CH}_3 - \text{CH} - \text{CH}_3 \\
\text{Br} & \\
\end{align*}
\]

(a) \[
\begin{align*}
\text{X} = \text{dilute aqueous NaOH, 20°C} & \\
\text{Y} = \text{HBr/acetic acid, 20°C} & \\
\end{align*}
\]

(b) \[
\begin{align*}
\text{X} = \text{concentrated alcoholic NaOH, 80°C} & \\
\text{Y} = \text{HBr / acetic acid, 20°C} & \\
\end{align*}
\]

(c) \[
\begin{align*}
\text{X} = \text{dilute aqueous NaOH, 20°C} & \\
\text{Y} = \text{Br}_2 / \text{CHCl}_3 / 0°C & \\
\end{align*}
\]

(d) \[
\begin{align*}
\text{X} = \text{concentrated alcoholic NaOH, 80°C} & \\
\text{Y} = \text{Br}_2 / \text{CHCl}_3 / 0°C & \\
\end{align*}
\]

[Answers : (1) c (2) d (3) d (4) b (5) b (6) b (7) b]
C5  **ALKynes** :  

**Electronic Structure of Triple Bond :**

- Acetylene is known to have a linear structure.
- $\text{C} \equiv \text{C} -$ distance of 1.20 Å is the shortest carbon – carbon bond length known.
- The carbon-hydrogen bond length of 1.06 Å is shorter than that in ethylene or in ethane. Thus it is stronger than either.
- The sp$^2$ – s $\sigma$-bonds are shorter than sp$^3$ – s $\sigma$-bonds. The trend also holds for the sp – s bonds in acetylene.
- Superimposed on the $\sigma$-electrons are two orthogonal $\pi$-electron system.

Thus carbon-carbon "triple bond" is thus made up of one strong $\sigma$-bond and two weaker $\pi$-bonds. It has total strength of 198 kCal. It is stronger than the carbon-carbon double bond of ethylene and carbon-carbon single bond of ethane and is shorter than either.

2. **Acidity of Alkynes :** Very weak acids :  

- In our earlier consideration of acids we took acidity to be a measure of the tendency of a compound to loose the hydrogen ion.
- Appreciable acidity is shown by those compounds in which hydrogen is attached to rather electronegative atom like (F > O > N > C). The bond holding the hydrogen is polar, thus relatively positive hydrogen can separate as positive ion, and more electronegative atom can hold the negative charge effectively.
- In view of the electronegativity series F > O > N > C it is not surprising that HF > H$_2$O > NH$_3$ > CH$_4$.
- In organic chemistry we are frequently concerned with the acidities of compounds do not turn litmus red or neutralize aqueous bases. Yet they have tendency to loose proton H$^+$ to small extent.
- A triply bonded carbon behaved as it is more electronegative than carbon which is singly or double bonded. As a result the hydrogen bonded to terminal alkyne shows the hydrogen bonded to terminal alkyne shows appreciable acidity.

\[
\text{e.g.} \quad \text{CH} \equiv \text{CH} + \text{Na} \quad \rightarrow \quad \text{Na} + \frac{1}{2}\text{H}_2 + \text{CH} \equiv \text{C}^- \quad \text{sodium acetylide}
\]

\[
\begin{align*}
\text{CH} \equiv \text{CH} + \text{LiNH}_2 & \quad \rightarrow \quad \text{CH} \equiv \text{C}^- \text{Li}^- + \text{NH}_3 \\
\text{CH} \equiv \text{CH} & \text{ stronger } \text{ acid} \quad \text{base} \\
\end{align*}
\]

\[
\begin{align*}
\text{HOH} + \text{CH} \equiv \text{C}^- \text{Li}^- & \quad \rightarrow \quad \text{CH} \equiv \text{CH} + \text{LiOH} \\
\text{CH} \equiv \text{CH} \equiv \text{C}^- & \text{ stronger } \text{ acid} \quad \text{base} \\
\end{align*}
\]

Relative Acidities : H$_2$O > ROH > HC = CH > NH$_3$ > RH  

Relative Basicities : OH$^-$ < OR$^-$ < CH = C$^- < $NH$_3$ < R$^-$

If a terminal alkyne is treated with an alkyl magnesium halide or an alkyl lithium the alkane is displaced from its salt and the metal acetylide is obtained.
only terminal alkynes give these reaction:

\[ \text{CH}_3\text{C} \equiv \text{CH} + \text{AgNO}_3 \rightarrow \text{CH}_3\text{C} \equiv \text{C} \text{ Ag.} + \text{HNO}_3 \]

white precipitate

\[ \text{CH}_3\text{C} \equiv \text{CH} + \text{Cu}^{+} \rightarrow \text{CH}_3\text{C} \equiv \text{CCU (moist)} \]

Red (Ppt.)

C6. Method of Preparation of Alkynes:

Industrial method of preparation:

1. Acetylene is formed from the reaction of inorganic compound calcium carbide with water

\[ \text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{CH} \equiv \text{CH} \]

2. \(2\text{CH}_4 \xrightarrow{1500^\circ \text{C}} \text{CH} \equiv \text{CH} + 3\text{H}_2\)

3. Laboratory methods of preparation:

Dehydrohalogenation of gem or vicinal dihalite:

\[
\begin{align*}
\text{H} & \quad \text{X} & \quad \text{H} & \quad \text{H} & \quad \text{H} \\
\text{- C} & \quad \text{- C} & \quad \text{- C} & \quad \text{- C} & \quad \text{- C} \\
\text{H} & \quad \text{X} & \quad \text{X} & \quad \text{X} & \quad \text{X}
\end{align*}
\]

\[ \text{Alc. KOH} \rightarrow \text{NaNH}_2 \rightarrow \text{X} \]

gem-dihalid vic-dihalide vinyl halide

vinyl halide requires the stronger base sodamide NaNH\(_2\).

4. Dehalogenation of vic-tetrahalogen compounds:

\[ \text{Br} \quad \text{Br} \]

\[ \text{CH}_3 \quad \text{C} \quad \text{- C} \quad \text{- C} \quad \text{Br} \quad \text{Br} \]

\[ \xrightarrow{\text{C}_2\text{H}_5\text{OH} \text{ heat}} \text{CH} \quad \text{- C} \quad \text{- C} \quad \text{- CH}_3 \quad \text{ZnBr}_2 \]

2-Butyne

5. Alkyl substitution in acetylene (Method of preparation of higher alkynes):

\[ \text{R} \quad \text{- C} \quad \text{= CH} \quad \text{+ NaNH}_2 \rightarrow \text{R} \quad \text{- C} \quad \text{= CNa} \quad \text{+ NH}_3 \]

\[ \text{R} \quad \text{- C} \quad \text{= C} \quad \text{Na} \quad \text{+ CH}_2\text{CH}_2 \quad \text{- X} \rightarrow \text{R} \quad \text{- C} \quad \text{= C} \quad \text{- CH}_2\text{CH}_3 \quad \text{+ NaX} \]

\[ \text{HC} \quad \text{= CH} \quad \text{+ 2NaNH}_2 \rightarrow \text{NaC} \quad \text{= CNa} \quad \text{+ 2NH}_3 \]

\[ \xrightarrow{\text{2n - C}_3\text{H}_2\text{Br}} \]

C\(_2\)H\(_7\) - C \equiv C - C\(_3\)H\(_7\)

This method is good for synthesis of alkynes when applied to primary halides that do not have branches close to reaction centre. With secondary halide and even with primary halides that have branches closer to the reaction centre, elimination is usually the major reaction.
C7 Chemical Properties of Alkynes:

Addition reaction at the triple bond: \( \pi \)-electrons of alkyne add electrophiles in reactions similar to additions to alkenes. Alkynes can add two moles of reagent but are less reactive than alkenes.

1. Hydrogenation

\[
\text{CH}_3\text{C} \equiv \text{C} \text{-CH}_2\text{CH}_3 + 2\text{H}_2 \xrightleftharpoons{\text{Pt}} \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3
\]

\[
\text{CH}_3\text{C} \equiv \text{C} \text{-CH}_3 + \text{H}_2 \xrightarrow{\text{Lindlar's catalyst}} \text{CH}_3\text{C} \equiv \text{C} \text{-CH}_3
\]

\[
\text{Na, Liq. NH}_3 \quad \text{(cis)}
\]

\[
\text{CH}_3\text{C} \equiv \text{C} \text{-CH}_3
\]

\[
\text{(trans)}
\]

2. \( \text{HX (HCl, HBr, HI)} \)

\[
\text{CH}_3\text{C} \equiv \text{C} \rightarrow \text{CH}_3\text{C} \equiv \text{CH}_2 \rightarrow \text{CH}_3\text{C} = \text{CH}_3
\]

\[
\text{Br} 
\]

\[
\text{Br} \quad \text{(Markovnikov's addition)}
\]

3. Halogen (\( \text{Br}_2, \text{Cl}_2 \))

\[
\text{R} = \text{C} \equiv \text{C} - \text{H} + \text{X}_2 \rightarrow \text{R} = \text{C} = \text{C} - \text{H} 
\]

\[
\text{R} = \text{C} = \text{C} - \text{H} + \text{X}_2 
\]

\[
\text{R} = \text{C} = \text{C} - \text{H} \quad \text{(Markovnikov's addition)}
\]

4. Addition of water

\[
\text{CH}_3\text{C} \equiv \text{CH} + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4, \text{Hg}^2+} \text{CH}_3\text{C} - \text{CH}_2
\]

\[
\text{CH}_3\text{C} - \text{CH}_3
\]

Acetophenone
5. **Boron hydride**:

\[ R' - C \equiv C - H + R_2 BH \xrightarrow{H_2O_2, NaOH} R' CH_2CHO \]

Boron hydride

\[ R' - C \equiv C - CH_3 + R_2 BH \xrightarrow{H_2O_2, NaOH} R' CH_2C - CH_3 \]

6. **Ozonylysis**:

\[ CH_2CH_2C \equiv CCH_3 + O_3 \xrightarrow{} CH_3CH_2-C-C=CH_3 \]

\[ CH_3COOH + CH_3CH_2COOH \xleftarrow{H_2O_2} CH_3CH_2-C=C-C\]

**Exception**:

\[ HC \equiv CH \xrightarrow{O_2/H_2O_2} CHO + HCOOH \]

**Practice Problems**:

1. The end product of the following sequences is \( CaO + C \xrightarrow{Heat} A \xrightarrow{H_2O} B \xrightarrow{H_2SO_4, Hg^{2+}} C \)
   - (a) Ethanol
   - (c) Acetaldehyde
   - (b) Ethyl hydrogen sulphate
   - (d) Ethylene glycol

2. \( CH = C - COOH \xrightarrow{HgSO_4/H_2SO_4} \) product
   - (a) \( CH_3 = C - COOH \)
   - (b) \( OHC - CH_2 - COOH \)
   - (c) \( CH_2 = C - COOH \)
   - (d) \( OH - CH = CH - COOH \)

3. \( A \xrightarrow{H_2SO_4/H_2SO_4} B \)
   - (a) \( CH = CH \)
   - (c) \( CH_3 - C = C - CH_2 - CH_3 \)
   - (b) \( CH_3 - C = CH \)
   - (d) \( CH_3 - CH_2 - C = CH \)
4. \[ CH = CH \xrightarrow{HgSO_4, H_2SO_4} B \leftarrow \text{reaction } R \quad \text{A, B and reaction R are:} \]

(a) \( CH_3 - C - Cl, CH_3CHO, \)

(b) \( CH_3CN, CH_3CHO, \)

Rosenmund \((\text{Pd}/\text{BaSO}_4, \text{H}_2)\) Stephen \((\text{SnCl}/\text{HCl})\)

(c) \( CH = CH, CH_3CHO, \)

hydroboration oxidation

(d) all of above

[Answers: (1) c (2) b (3) a (4) d]

Aromatic Compounds:

Nomenclature of Benzene Derivatives:

Two systems are used in naming monosubstituted benzenes.

In certain compound benzene is the parent name and the substituent is simply indicated by prefix we have for example

![Fluorobenzene, Chlorobenzene, Bromobenzene, Nitrobenzene](image)

For other compound, the substituent and the benzene ring taken together may form a new parent name. Methylbenzene is usually called toluene, hydroxybenzene is almost always called phenol, and aminobenzene is almost always called aniline. These and other examples are indicated here.

![Toluene, Phenol, Aniline, Benzene Sulfonic Acid, Benzoic Acid, Acetophenone, Anisole](image)

When two substituents are present their relative positions are indicated by the prefixes ortho, meta and para (abbreviated as o-, m- and p-) or by the use of numbers. For the dibromobenzene we have

![1,2-Dibromobenzene (o-dibromobenzene), 1,3-Dibromobenzene (m-dibromobenzene), 1,4-Dibromobenzene (p-dibromobenzene)](image)
The dimethylbenzenes are often called xlenes

\[
\begin{align*}
&\text{1,2-Dimethylbenzene} \\
&(\text{o-xylene})
\end{align*}
\]

**IMPORTANT:**

Numbers can be used for two or more substituents but ortho, meta, para must not be used for more than two substituents.

If more than two groups are present on the benzene ring, their positions must be indicated by numbers e.g.

\[
\begin{align*}
&\text{Cl} \\
&\text{Cl} \\
&\text{Cl}
\end{align*}
\]

1, 2, 4 - Trichlorobenzene

We notice that the benzene ring is numbered so as to give minimum possible numbers to the substituents. When more than two substituents are present and the substituents are different they are listed in alphabetical order. When the substituent is one that when taken together with the benzene ring gives a new base name, that substituent is assumed to be position 1 and the new parent name is used

\[
\begin{align*}
&\text{CO}_2\text{H} \\
&\text{NO}_2 \\
&\text{NO}_2
\end{align*}
\]

3, 5 - Dintrobenzoic acid

\[
\begin{align*}
&\text{SO}_2\text{H} \\
&\text{F} \\
&\text{F}
\end{align*}
\]

2, 4 - Diflourobenzene

Sulfonic acid

When C_6H_5 group is named as a substituent it is called phenyl group. A hydrocarbon composed of one saturated chain and one benzene ring is usually named as a derivative of the Larger Structural Unit.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{Butyl benzene} \\
\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{where as} \\
\end{align*}
\]

2-Phenylheptane

If the side chain is unsaturated, the compound may be named as a derivative of that chain, regardless of the ring size e.g.

\[
\begin{align*}
\text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3
\end{align*}
\]

2-Phenyl-2-butene

The phenyl group is abbreviated as C_6H_5^- or Ph^- . The name benzyl is the alternative name of the phenylmethyl group. It is sometimes abbreviated as BZ.
C9A Properties of Benzene:

Benzene does react with the Br₂ but only in the presence of Lewis acid catalyst such as ferric bromide FeBr₃.

Substitution: \[ C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr \] (observed)

Addition: \[ C_6H_6 + Br_2 \rightarrow C_6H_5Br_2 + C_6H_2Br_4 \] (not observed)

When benzene reacts with bromine only one monobromo benzene is observed or formed.

Kekule Structure for benzene:

\[ \ \bigcirc \quad \ \bigcirc \] or \[ \ \bigcirc \quad \ \bigcirc \quad \ \bigcirc \]

C9B Huckle Rule (4n + 2)π Electron Rule:

Huckle's rule is concerned with the compounds containing one planar ring in which each atom has a p-orbital as in benzene ring. His calculations shows that planar monocyclic ring containing \( (4n + 2) \) π electrons where \( n = 0, 1, 2, 3... \) (i.e. rings containing 2, 6, 10, 14 etc......π electrons) have closed shells of delocalized electrons should be aromatic with substantial resonance energies.

\[ \therefore \quad \ \bigcirc \ \text{Benzene has 6 π electrons so it is a Huckle number & is aromatic.} \]

\[ \ \bigcirc \ \text{8 π electrons, not a Huckle number so it is not aromatic although it contain} \]

\[ \ \text{alternate single & double bonds.} \]

Aromatic Ions: (Also known as non-benzoic aromatic ions)
Aromatic Compounds: are defined as those in which $\pi$-electrons are delocalized over the entire ring and that is stabilized by delocalization of the $\pi$-electron.

The stability of benzene: Benzene shows unusual behaviour by undergoing substitution reaction then addition reaction. On the basis of Kekule Structure we should expect it to undergo addition reaction. But it is more stable than the Kekule Structure suggests. How?

**Resonance Energy:** Heat of hydrogenation of benzene using Kekule structure suggests that,

$$\Delta H^\circ = 3 \times (-120) = -360 \text{ kJ/mol}$$

[If one mole of $H_2$ adds to double bond then $-120$kJ/mol of energy is released as here 3 mol of $H_2$ are added so energy released is $3 \times (-120)$]. But actual amount of heat released is $-208$ kJ/mol. So the difference in actual heat released and that calculated from kekule structure is $152$ kJ/mol. This energy is called as Resonance Energy.

**Resonance Explanation of Benzene:** It is found that carbon-carbon bond length in benzene is same. They have a bond order between single and double bond.

**Heterocyclic Aromatic Compounds:**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Hybridisation</th>
<th>Bond Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyridine</td>
<td>sp' hybridised</td>
<td>6π-electron</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>sp' hybridised</td>
<td></td>
</tr>
<tr>
<td>Furan</td>
<td>sp' hybridised</td>
<td></td>
</tr>
<tr>
<td>Thiophene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Its lone pair is not involved as already cyclic delocalization in the ring is present. In all these structures one lone pair is involved in cyclic delocalization to give it aromatic structure.

C10A Electrophilic Aromatic Substitution Reaction:

**General Reaction:**

Aromatic hydrocarbons are known as arenes. Arenes are designated as Ar-H just as Alkanes.

$$\text{Ar-H} + \text{E} \rightarrow \text{Ar-E} + \text{HA}$$
The most characteristic reaction of benzoid arenes are substitution reaction that occur when they react with electrophilic reagents. The reactions are of general type as shown above.

Electrophilic aromatic substitutions allow the direct introduction of wide variety of groups onto an aromatic ring. They are listed as follows:

General mechanism of Electrophilic Aromatic Substitution:

Step – 1 (Rate determining step)

Step – 2

(The proton is removed by any of the base present e.g. by the anion derived from the electrophile)

1. Halogenation of Benzene:
Benzene does not react with the bromine or chlorine unless a lewis acid is present in the mixture.
Anhydrous AlCl$_3$ can also be used as Lewis acid along with FeCl$_3$, FeBr$_3$, FeCl$_3$ or FeBr$_3$ are generated in the mixture by adding iron to it. The iron then react with halogen to produce the ferric halide.

**Mechanism**

**Step – 1**  
\[ \text{Br} - \text{Br} \xrightarrow{\text{FeBr}_3} \text{Br}^+ + \text{FeBr}_4^{-} \]

**Step – 2**

\[
\begin{align*}
\text{Br}^+ & \xrightarrow{\text{slow}} \text{Br}^- \\
\text{H} & \xrightarrow{\text{Br}} \text{H} \\
\text{Br}^- & \xrightarrow{\text{H}} \text{Br} \\
\text{Br}^+ & \xrightarrow{\text{FeBr}_3} \text{Br}^- + \text{FeBr}_4^{-} + \text{HBr}
\end{align*}
\]

(Arenium ion)

Chlorination of benzene can be done in presence of FeCl$_3$ in the same way as shown above. Flourination of benzene requires special condition as it react so rapidly with benzene. Iodination also requires special technique as iodine is so unreactive, the reaction has to be carried out in the presence of the strong oxidizing agent like nitric acid HNO$_3$.

2. **Nitration of Benzene**

Benzene reacts slowly with hot concentrated nitric acid to yield nitrobenzene. The reaction is much faster if it reacts with mixture of nitric acid and sulfuric acid concentrated.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{I} + \text{HNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow{50-55^\circ \text{C}} \text{C}_6\text{H}_5\text{NO}_2 + \text{H}_2\text{O} + \text{HSO}_4^-
\end{align*}
\]

Concentrated sulfuric acid increases the rate by increasing the concentration of electrophile i.e, NO$_2^+$ (nitronium ion)

**Mechanism**

**Step – 1**  
\[
\text{HO}_2\text{S} - \text{O} - \text{H} + \text{H} - \text{O} - \text{NO}_2 \xrightarrow{} \text{HSO}_4^- + \text{HONO}_2^+ \\
(\text{Stronger acid})
\]

**Step – 2**

\[
\begin{align*}
\text{H} & \xrightarrow{\text{O}} \text{H} \\
\text{O} & \xrightarrow{\text{N}} \text{H}_2 + \text{N}_2 \text{O}
\end{align*}
\]

**Step – 3**

\[
\begin{align*}
\text{C}_6\text{H}_5\text{O} + \text{NO}_2^- & \xrightarrow{} \text{C}_6\text{H}_5\text{NO}_2^- + \text{H} \\
\text{so on...} & \xrightarrow{\text{Arenium ion}}
\end{align*}
\]
3. Sulphonations of Benzene:

Benzene reacts with fuming sulfuric acid at room temperature to produce benzene sulfonic acid. Fuming sulfuric acid is the sulfuric acid that contain added SO₃. Sulphonation can also take place with concentrated sulfuric acid alone but that takes place slowly.

\[
\begin{align*}
\text{Benzene sulphonylating} & \\
\text{acid} & \\
\end{align*}
\]

In either reaction electrophile appears to be sulfur trioxide SO₃.

Mechanism:

**Sulphonation of Benzene:**

**Step – 1:**

\[
2\text{H}_2\text{SO}_4 \rightleftharpoons \text{SO}_3 + \text{H}_2\text{O}^+ + \text{HSO}_4^-
\]

**Step – 2:**

**Step – 3:**

(Benzene sulphonate ion)

**Step – 4:**

As all the steps are in equilibrium so overall reaction is also in equilibrium.

The position of equiliberia can be influenced by using concentrated sulfuric acid or fuming sulfuric acid. Under these conditions equiliberia positions lies more towards the right.
4. **Friedel-Crafts Alkylation**:

\[
\ce{C} + \ce{R-X} \rightarrow \ce{C} + \ce{HX}
\]

**Mechanism**:

**Step – 1**:

\[
\ce{CH_3CH=CH - Cl + AlCl_3 \rightleftharpoons AlCl_3^+ + 'CHCH_3}
\]

**Step – 2**:

\[
\ce{CHCH_3} \rightleftharpoons \ce{CHCH_3} \rightleftharpoons \ce{HCHCH_3} \rightleftharpoons \ce{HCHCH_3}
\]

**Step – 3**:

\[
\ce{HCHCH_3} \xrightarrow{\text{HF}} \ce{HCl + AlCl_3 + C6H5CH3}
\]

Isopropyl benzene (cumene)

Cyclohexyl benzene

\[
\ce{C} + \ce{CH3CH = CH_2 \xrightarrow{0^\circ \text{C}, \text{HF}} C6H_5CH3}
\]

\[
\ce{C} + \ce{CH3CH = CH_2 \xrightarrow{60^\circ \text{C}, BF_3} C6H_5CH3 + H_2O}
\]

5. **Friedel Craft Acylation**: The \( \ce{C-O} \) group is called acyl group. Two common acyl groups are the acetyl group and Benzoyl group.

\[
\ce{CH_3-C-O} \quad \ce{C6H_5-C-O}
\]

Acetyl group  Benzoyle group
Acyl chloride are also obtained from by treating carboxylic acids with thionyl chloride (SOCl$_2$) or phosphorous pentachloride (PCl$_5$)

$$\text{CH}_3-\text{C}-\text{OH} + \text{SOCl}_2 \xrightarrow{80^\circ \text{C}} \text{CH}_3\text{COCl} + \text{SO}_2 + \text{HCl}$$

Friedel craft acylation can also be done in the presence of acetic anhydride e.g.

Mechanism:

**Step – 1:**

$$\text{R - C - Cl} : + \text{AlCl}_3 \rightarrow \text{R - C - Cl}^- \cdot \text{AlCl}_3$$

**Step – 2:**

$$\text{R - C - Cl}^- \cdot \text{AlCl}_3 \rightarrow \text{R - C} \equiv \text{O} \leftrightarrow \text{R - C} \equiv \text{O} : + \text{AlCl}_3$$

An Acylium ion (a resonance hybrid)

**Step – 3:**

$$\text{Acenium ion} \leftrightarrow \text{Resonating Structure}$$

**Step – 4:**

$$\text{R - C} \equiv \text{O} + \text{AlCl}_3 \rightarrow \text{R - C} \equiv \text{O} + \text{HCl} + \text{AlCl}_3$$
Step – 5:

\[
\begin{array}{c}
\text{C} \quad + \quad \text{AlCl}_3 \\
\text{O} \\
\text{O} \quad + \quad \text{AlCl}_3 \\
\end{array}
\]

Treating this complex with water liberates the ketone

Step – 6:

\[
\begin{array}{c}
\text{C} \quad + \quad \text{AlCl}_3 \\
\text{C} \\
3\text{H}_2\text{O} \\
\text{C} \\
\text{C} \quad + \quad \text{Al(OH)}_3 \\
3\text{HCl} \\
\text{C} \\
\text{C} \\
\end{array}
\]

Limitations of Friedel-Craft’s Reactions:

1. When the carbocation formed from an alkyl halide, alkene or alcohol can rearrange to more stable carbocation, thus major product obtained from the reaction is usually the one from the more stable carbocation. When benzene is alkylated with butyl bromide then sec-butyl benzene is the major product as 1°-carbocation undergoes rearrangement.

\[
\begin{array}{c}
\text{C} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{Br} \\
\text{AlCl}_3 \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}^+ \\
\text{rearrangement} \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH} = \text{CHCH}_3 \\
\end{array}
\]

(64 - 68 %) (32 - 36 %)

2. Friedel-Craft’s reaction usually give poor yields when powerful electron-withdrawing groups are present on the aromatic ring or when the ring bears an –NH$_2$, –NHR or –NR$_2$ group. This applies to both alkylation and acylation.

\[
\begin{array}{c}
\text{NO}_2 \\
\text{O} \\
\text{O} \\
\text{CF}_3 \\
\text{SO}_2\text{H} \\
\text{NH}_2 \\
\text{H} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\text{C} \\
\end{array}
\]

These usually give poor yields in Friedel-Craft reaction

3. The amino groups –NH$_2$, –NHR and –NR$_2$ are changed into powerful electron withdrawing groups by Lewis acid used to catalyze Friedel-Craft’s reaction.

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H} \\
\text{AlCl}_3 \\
\end{array}
\]

Does not undergo a Friedel Craft reaction
4. Aryl and vinyl halides cannot be used as the halide component because they do not form carbocations readily.

6. Clemmensen Reduction:
Rearrangements of the carbon chain do not occur in Friedel-Craft’s acylation. The acylium ion is more stabilized by resonance is more stable than any other carbocation. Thus there is no driving force for rearrangement. Thus there is possible of formation of n-alkyl benzene. The ketone group can be reduced to – CH₂ – group in the presence of HCl & Zn(Hg).

7. The effect of Electron-Releasing and Electron - withdrawing groups:
Groups which activate the benzene ring towards the electrophilic substitution, whereas other groups deactivate the ring. Group which activate the ring means that the group increases the relative rate of reaction. We mean that aromatic compound with an activating group reacts faster in electrophilic substitution than benzene.

The General mechanism is shown as follows:

If Q → is electron with drawing it destablises the transition state so is the arenium ion so reaction is slower.
If Q → is electron releasing it stablizes the transition state so the reaction is faster.

8. Effect of substituents on Reactivity and Orientation:
Substituent groups can be divided into two classes according to their influence on the reactivity of the ring.
Activating group increase the reactivity towards the electrophile than benzene. Deactivating group decreases the reactivity than benzene.

**Effect of substituent on Electrophilic Aromatic Substitution:**

**Ortho-Para director Strongly Activating**

- $\text{NH}_2$, $\text{NHR}$, $\text{NR}_2$
- $\text{OH}$, $\text{O}^-$
- $\text{NHCOR}$
- $\text{OCH}_3$, $\text{COR}$

**Meta director**

- $\text{C} = \text{N}$
- $\text{SO}_3$H
- $\text{CO}_2$H, $\text{COR}$
- $\text{CHO}$, $\text{COR}$

**Moderately Activating**

- $\text{CO}_2$H, $\text{COR}$
- $\text{CHO}$, $\text{COR}$

**Strongly Deactivating**

- $\text{NO}_2$, $\text{NR}_3$, $\text{CF}_3$, $\text{CCl}_3$

**Weakly Activating**

- $\text{F}$, $\text{Cl}$, $\text{Br}$, $\text{I}$

9. **Meta-directing group**: All meta directing groups are having either a full positive charge or partial positive change. As a typical example let us consider the trifluoromethyl groups.

We can understand how the trifluoromethyl group affects the orientation in electrophilic aromatic substitution if we examine the resonance structures of the arenium ion that would be formed when the electrophile attacks at the ortho, meta and para positions of the trifluoro methyl benzene.
As we see from the resonance structures for the arenium ion arising from the ortho and para attack that one contributing structure is highly unstable relative to all others because the positive charge is located on the ring carbon that bears the electron withdrawing group. We see no such resonance structure in arenium ion arising from meta attack. This means that arenium ion formed by meta attack should be most stable of the three.

\[
\begin{align*}
\text{CF}_3 & \quad \text{HNO}_3 & \quad \text{H}_2\text{SO}_4 \\
\text{O} & \quad \text{NO}_3 \\
(\sim 100\%) & 
\end{align*}
\]

10. Ortho-Para Directing Groups:

Except for the alkyl and phenyl substituents, all of the ortho-para directing groups are of following general type:

- At least one non-bonding electron pair

The electron donating resonance effect applies with decreasing strength in the following order:

- \(\text{NH}_3, \text{NR}_3 > \text{OH} > \text{Cl} > \text{X}\)

Ortho-Attack:

Para Attack:

In meta attack the relative stable contributor resonating structure does not form.
1. The highest boiling point is expected for
   (a) iso-octane  
   (b) n-octane 
   (c) 2, 2, 3, 3-tetramethyl butane 
   (d) n-butane

2. Ethane can be prepared by
   (a) heating sodalime with sodium acetate 
   (b) electrolysis of sodium succinate 
   (c) electrolysis of sodium acetate 
   (d) all the above

3. Which of the following substances is used as antiknock compound
   (a) TEL  
   (b) lead tetra chloride 
   (c) lead acetate 
   (d) \( C_2H_5PbCl \)

4. Most of hydrocarbons from petroleum are obtained by
   (a) fractional distillation 
   (b) fractional crystallisation  
   (c) vapourisation  
   (d) isomerisation

5. The compressed gas available in cooking gas cylinder is a mixture of 
   (a) \( C_6H_6 + C_6H_5CH_3 \)  
   (b) \( C_2H_2 + C_2H_4 \)  
   (c) \( C_2H_6 + CH_4 \)  
   (d) \( C_4H_{10} + C_3H_4 \)

6. The reaction conditions leading to best yields of \( C_2H_5Cl \) are 
   (a) \( C_2H_6(\text{excess}) + Cl_2 \xrightarrow{UV\text{light}} \)  
   (b) \( C_2H_6 + Cl_2 \xrightarrow{\text{Dark-room temp.}} \)  
   (c) \( C_2H_2 + Cl_2(\text{excess}) \xrightarrow{UV\text{light}} \)  
   (d) \( C_2H_4 + Cl_2 \xrightarrow{UV\text{light}} \)

7. Paraffin wax is 
   (a) ester  
   (b) alcohol  
   (c) unsaturated hydrocarbons  
   (d) saturated hydrocarbons

8. The most stable conformation of n-butane is 
   (a) skew boat  
   (b) gauche  
   (c) staggered anti  
   (d) eclipsed

9. Which of the following reactions is expected to readily give a hydrocarbon product in good yield
   (a) \( (CH_3)_3C - Cl \xrightarrow{C_2H_5OH} \)  
   (b) RCOOK \( \xrightarrow{\text{Electrolysis}} \)  
   (c) \( CH_3 - CH_2 \xrightarrow{Cl_2, hv} \)  
   (d) \( RCOOAg \xrightarrow{Br_2} \)

10. Coal-tar is a main source of 
    (a) aromatic compounds  
    (b) alicyclic compounds 
    (c) aliphatic compounds  
    (d) heterocyclic compounds

11. Which one of the following would be most reactive towards nitration 
    (a) benzene  
    (b) nitrobenzene  
    (c) toluene  
    (d) chlorobenzene

12. Which of the following is meta directing group 
    (a) \(-COOH\)  
    (b) \(-OH\)  
    (c) \(-NH_2\)  
    (d) \(-Cl\)

13. Nitration of benzene is 
    (a) nucleophilic substitution  
    (b) nucleophilic addition 
    (c) electrophilic substitution  
    (d) electrophilic addition

14. The function of anhydrous aluminium chloride in the Friedel-Crafts reaction is 
    (a) to absorb water  
    (b) to absorb hydrochloric acid 
    (c) to produce an electrophile 
    (d) to produce nucleophile

15. The reaction, \( C_6H_6 + CH_3Cl \xrightarrow{\mathrm{KCl}_{\text{anhyd.}}} C_2H_5CH_3 + HCl \) is 
    (a) Friedel-Crafts reaction  
    (b) Wurtz-Fittig reaction 
    (c) Kolbe reaction 
    (d) Rosenmund reaction

16. Toluene may be oxidised to benzaldehyde by the use of 
    (a) \( \text{KMnO}_4 + H_2\text{SO}_4 \)  
    (b) \( \text{K}_2\text{Cr}_2O_7 + H_2\text{SO}_4 \) 
    (c) \( \text{CrO}_2\text{Cl}_2 \)  
    (d) all of these
17. The oxidation of toluene to benzaldehyde with chromyl chloride in carbon tetrachloride is called
(a) Sandmeyer’s reaction
(b) Perkin’s reaction
(c) Fittig reaction
(d) Etard’s reaction

18. In Raschig’s process for the preparation of chlorobenzene the reactant are
(a) \( \text{C}_6\text{H}_6 \) and \( \text{Cl}_2 \)
(b) \( \text{C}_6\text{H}_5\text{OH} \) and \( \text{PCl}_5 \)
(c) \( \text{C}_6\text{H}_6 + \text{HCl} + \text{O}_2 \)
(d) \( \text{C}_6\text{H}_5\text{OH} \) and \( \text{HCl} \)

19. Chlorobenzene when condensed with chloral in the presence of conc. \( \text{H}_2\text{SO}_4 \) yields :
(a) Gammexane (b) DDT
(c) TNB (d) \( \text{C}_6\text{Cl}_6 \)

20. Which one of the following compounds would undergo nitration with greatest ease
(a) benzene (b) phenol
(c) nitrobenzene (d) benzoic acid

21. The direct iodination of benzene is not possible because
(a) \( \text{I}_2 \) is an oxidising agent
(b) resulting \( \text{C}_6\text{H}_5\text{I} \) is reduced to \( \text{C}_6\text{H}_6 \) by \( \text{HI} \)
(c) \( \text{HI} \) is unstable
(d) the ring gets deactivated

22. According to Huckel rule, the number of pi electrons in naphthalene is
(a) 6 (b) 10
(c) 14 (d) 16

23. Which of the following compounds react slower than benzene in electrophilic substitution :
(a) \[
\begin{array}{c}
\text{NO}_2 \\
\text{OH}
\end{array}
\]
(b) \[
\begin{array}{c}
\text{NH}_2 \\
\text{CH}_3
\end{array}
\]
(c) \[
\begin{array}{c}
\text{OH} \\
\text{CH}_3
\end{array}
\]
(d) all correct

24. \[
\begin{array}{c}
\text{X} \xrightarrow{\text{Cl}_2} \text{Benzotrichloride} \xrightarrow{\text{hydrolysis}} \text{Y} \\
\text{X} \text{ and } \text{Y} \text{ respectively are}
\end{array}
\]
(a) benzene and benzoic acid
(b) benzene and benzaldehyde
(c) toluene and benzoic acid
(d) toluene and benzaldehyde

25. When nitrobenzene is treated with \( \text{Br}_2 \) in presence of \( \text{FeBr}_3 \), the major product formed is m-bromonitro benzene. Statements which are related to obtain the m-isomer are
(a) the electron density on meta carbon is more than that on ortho and para positions
(b) loss of aromaticity when \( \text{Br}^+ \) attacks at the ortho and para positions and not at meta position
(c) easier loss of \( \text{H}^+ \) to regain aromaticity from the meta position than from ortho and para position
(d) none of these

26. The C — H bond distance is the longest in
(a) \( \text{C}_2\text{H}_2 \) (b) \( \text{C}_2\text{H}_4 \)
(c) \( \text{C}_2\text{H}_6 \) (d) \( \text{C}_2\text{H}_2\text{Br}_2 \)

27. During Wurtz reaction, which of the following is sometimes also obtained because decomposition of free radicals
(a) Alkynes (b) Alkenes
(c) \( \text{CO}_2 \) (d) Alkyl Alkenes

28. \[
\begin{array}{c}
\text{CH}_3\text{CHCH}_2\text{Cl}
\end{array}
\]
hydrocarbon \( \text{(X)} \) \( \text{X} \) is
(a) \[
\begin{array}{c}
\text{CH}_3\text{CHCH}_3
\end{array}
\]
(b) \[
\begin{array}{c}
\text{CH}_3\text{CHCH}_3
\end{array}
\]
(c) \[
\begin{array}{c}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3
\end{array}
\]
(d) all correct
29. Increasing order of the following for $S_n$ reaction:

(a) $I < II < III$  
(b) $III < II < I$  
(c) $II < III < I$  
(d) $I < III < II$

30. The correct sequence of activating power of a group in benzene is:

(a) $-\text{NH}_2 > -\text{NHCOCH}_3 > -\text{CH}_3$
(b) $-\text{NH}_2 > -\text{NHCOCH}_3 < -\text{CH}_3$
(c) $-\text{NH}_2 > -\text{NHCOCH}_3 < -\text{CH}_3$
(d) $-\text{NH}_2 < -\text{NHCOCH}_3 > -\text{CH}_3$

31. Consider the following aryl alkyl ketones

Friedel-Crafts acylation can be used to obtain:

(a) I, II and III  
(b) I and II  
(c) II and III  
(d) I and III

32. $C_9H_{14}$ (A)

(a)  
(b)  
(c)  
(d)  

33. $A(C_4H_8) \xrightarrow{\text{H}_2/\text{Pt}} B(C_4H_8) \xrightarrow{O_3/\text{H}_2\text{O}/\text{Zn}}$

$C \xrightarrow{\text{HCN}} D$

D has chiral carbon and can be hydrolysed to lactic acid. Hence A is

(a) $\text{CH}_3 - \text{HC} = \text{CH} - \text{CH}_3$
(b) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

34. Carbanion (A) loses a leaving group to form alkene

which is correct statement:

(a) It is $E_1$ Carbanion type  
(b) It is $E_2$ type  
(c) It is $E_1$ type  
(d) none

35. $\text{A} + \text{CH}_3\text{MgBr} \xrightarrow{\text{H}_2\text{O}} \text{A}$

$\text{B} \xrightarrow{\text{O}_3/\text{H}_2\text{O}/\text{Zn}} \text{C}$

A, B and C are:

(a)  
(b)  
(c)  
(d)  

---

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36. \[ \text{CH}_3\text{CH}_2\text{Br} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CH}_2\text{NH}_2 \] (true)

hence \[ \begin{array}{c}
\text{Br} + \text{NH}_3 \rightarrow A
\end{array} \]

A is:

(a) \[ \begin{array}{c}
\text{NH}_2
\end{array} \]

(b) \[ \begin{array}{c}
\text{NH}
\end{array} \]

(c) 

(d) none

37. With alcoholic potash \( \text{C}_2\text{H}_5\text{Cl} \) \((\text{A})\) gives \( \text{C}_2\text{H}_6 \) \((\text{B})\) which reacts with ammonical cuprous chloride. Identify A.

(a) 1-Butyne  (b) But-2-yne  
(c) Butene  (d) But-2-ene

38. Butyne on reaction with hot alkaline \( \text{KMnO}_4 \) gives:

(a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{COOH} \)

(b) \( \text{CH}_3\text{CH}_2\text{COOH} \)

(c) \( \text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_2 \)

(d) \( \text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH} \)

39. Propene \( \text{CH} = \text{CH}_2 \) can be converted into propanol-1 by oxidation. Indicate which set of reagents amongst the following is ideal to bring the above conversions

(a) \( \text{O}_3 / \text{Zn dust} \)

(b) \( \text{B}_2\text{H}_6 \) and alkaline \( \text{H}_2\text{O}_2 \)

(c) alkaline \( \text{KMnO}_4 \)

(d) \( \text{OsO}_4 \) followed by \( \text{NaHSO}_3 / \text{alcohol} \)

40. The intermediate during the addition of \( \text{HCl} \) to propene in the presence of peroxide is

(a) \( \text{CH}_3 \text{CHClCH}_2\text{Cl} \)

(b) \( \text{CH}_3 \text{CH}_2\text{CHCH}_3 \)

(c) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \)

(d) \( \text{CH}_3\text{CH}_2\text{CH}_2 \text{CH}_2 \)
The structure of compound A is passed through ammonical Cu with KNH molecular formula C\textsubscript{4}H\textsubscript{10}. Compounds A and B both yield hexane when they are treated with excess hydrogen in the presence of a platinum catalyst. Under these conditions C absorb only one molar equivalent of hydrogen and gives a product with the formula C\textsubscript{4}H\textsubscript{12}. When A is oxidised with hot basic potassium permanganate and the resulting solution acidified, the only organic product that can be isolated is CH\textsubscript{2}(CH\textsubscript{3})\textsubscript{3}CO\textsubscript{2}H. Similar oxidation of B gives only CH\textsubscript{2}CH\textsubscript{2}CO\textsubscript{2}H, and similar treatment of C gives only HO\textsubscript{2}C(CH\textsubscript{3})\textsubscript{2}CO\textsubscript{2}H.

5. The structure of compound B is
(a) CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Br
(b) CH\textsubscript{3}CH\textsubscript{2}CH = CH\textsubscript{2}
(c) CH\textsubscript{3}CH\textsubscript{2}CHBrCH\textsubscript{2}Br
(d) CH\textsubscript{3}CH\textsubscript{2}CH = CH

6. The structure of compound C is
(a) CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Br
(b) CH\textsubscript{3}CH\textsubscript{2}CH = CH\textsubscript{2}
(c) CH\textsubscript{3}CH\textsubscript{2}CHBrCH\textsubscript{2}Br
(d) CH\textsubscript{3}CH\textsubscript{2}CH = CH

7. The structure of compound D is
(a) CH\textsubscript{3}CH\textsubscript{2}CH\textsubscript{2}CH\textsubscript{2}Br
(b) CH\textsubscript{3}CH\textsubscript{2}CH = CH\textsubscript{2}
(c) CH\textsubscript{3}CH\textsubscript{2}CHBrCH\textsubscript{2}Br
(d) CH\textsubscript{3}CH\textsubscript{2}CH = CH

EXERCISE BASED ON NEW PATTERN

MATCHING-MATCH TYPE

Matching-1

<table>
<thead>
<tr>
<th>Column - A</th>
<th>Column - B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>C\textsubscript{2}H\textsubscript{5}OH \xrightarrow{443k} C\textsubscript{2}H\textsubscript{4}</td>
</tr>
<tr>
<td>(B)</td>
<td>Hydogenation of carbon</td>
</tr>
<tr>
<td>(C)</td>
<td>n-heptane \xrightarrow{670k} Cu tube</td>
</tr>
<tr>
<td>(D)</td>
<td>Decane \xrightarrow{773K}</td>
</tr>
</tbody>
</table>

Matching-2

<table>
<thead>
<tr>
<th>Column - A</th>
<th>Column - B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Dehydrolahogenation</td>
</tr>
<tr>
<td>(B)</td>
<td>nCH\textsubscript{4} = CH\textsubscript{2}</td>
</tr>
<tr>
<td>(C)</td>
<td>Ozonylysis</td>
</tr>
<tr>
<td>(D)</td>
<td>Mustard gas</td>
</tr>
</tbody>
</table>

Matching-3

<table>
<thead>
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<th>Column - A</th>
<th>Column - B</th>
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</thead>
<tbody>
<tr>
<td>(A)</td>
<td>Acetylene tetrachloride</td>
</tr>
<tr>
<td>(B)</td>
<td>Baeyer’s reagent</td>
</tr>
<tr>
<td>(C)</td>
<td>Geometrical isomerism</td>
</tr>
<tr>
<td>(D)</td>
<td>Lewisite</td>
</tr>
</tbody>
</table>

MULTIPLE CORRECT CHOICE TYPE

1. Only two mono-chloro derivatives are possible for
(a) ethene (b) propane (c) n-Butane (d) Iso-butane
2. \( x \overset{\text{KOH(alc)}}{\longrightarrow} CH_2CH = CH_2 \), the compound X are
   (a) 1-propanol
   (b) 1-Bromopropane
   (c) 2-Bromopropane
   (d) 3-Bromo-1-propene

3. Which of the following statements are false
   (a) Boiling point of cis-2-butene is less than that of trans-2-butene
   (b) unsaturated hydrocarbons have higher octane number than saturated
   (c) chemical name of antinoc compound AK-33x is cyclopentadiethylmanganese carbonyl
   (d) quality of Gasoline is measured in term of cetane number

4. Which of the compound have only one type of hybridised carbon?
   (a) \( CH_2 = CH - CH = CH_2 \)
   (b) \( CH = C - CH = CH \)
   (c) \( CH_2CH_2CH_2CH_3 \)
   (d) \( CH_3 - C = C - CH_3 \)

5. Which of the following statements are true?
   (a) an activating group is an electron releasing group
   (b) an activating group, activates all positions of benzene ring
   (c) the effect of any group-whether activating or deactivating is the strongest at O- and p-positions of benzene ring.
   (d) an activating group, activates only O- and p-positions in the benzene ring.

Assertion-Reason Type
Each question contains STATEMENT-1 (Assertion) and STATEMENT-2 (Reason). Each question has 4 choices (A), (B), (C) and (D) out of which ONLY ONE is correct.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

1. STATEMENT-1: Addition of bromine to but-1-ene gives two optical isomers
   STATEMENT-2: Two product contains one asymmetric carbon atom

2. STATEMENT-1: 1-Butene an reaction with HBr in the presence of peroxide produces 1-Bromobutane
   STATEMENT-2: It involves the formation of a primary free radical.

3. STATEMENT-1: Photobromination of 2-methyl propane give a mixture of 1-Bromo-2-methyl propane and 2-Bromo-2-methyl propane in the ratio 9:1
   STATEMENT-2: Abstraction of \( 1^0, 2^0, 3^0 \) H of alkanes by photobromination is 1:82:1600.

4. STATEMENT-1: n-Pentane is relatively more stable than isopentane
   STATEMENT-2: Methane can't be prepared by Wurtz's reaction

5. STATEMENT-1: Oxidation of methyl benzene and Ethyl-benzene with KMnO\(_4\) produce benzoic acid.
   STATEMENT-2: Both methyl benzene and ethyl benzene are more reactive than benzene

6. STATEMENT-1: Reaction of tert-Butyl chloride with Na gives 2, 3, 4-tetramethylbutane
   STATEMENT-2: Methane can't be prepared by Wurtz's reaction

7. STATEMENT-1: Ozonolysis involves cleavage of (C = C) bond and put oxygen at breaking part to give ozonide.
   STATEMENT-2: Ozonolysis is applicable to determine the structure of alkene

8. STATEMENT-1: Iodination of alkane is carried out by heating alkane with iodine in presence of iodic acid.
   STATEMENT-2: Iodic acid is an oxidising agent.
1. Write the structural formula and IUPAC names of the different alkanes formed when a mixture of 1-bromopropane and 2-bromopropane is reacted with sodium in presence of ether.

2. An alkane with molecular mass 72 formed only one substitution product. Suggest a structure for the alkane.

3. Give reason why chlorination of ethane of ethyl chloride is more practicable than the chlorination of n-pentane to 1-chloropentane.

4. Complete the following reactions:

(i) CH₂CH₂Br + Mg → (A) + MgBr₂
(ii) CH₃Br + Na → (A) + NaBr
(iii) CH₃COOH + NaOH → (A) + Na₂CO₃
(iv) CH₃CH₂CH₂CH₂CH₂CH₃ + CrO₃/Al₂O₃ → (A)

5. The relative reactivity of 1° : 2° : 3° hydrogens to chlorination is 1 : 3.8 : 5. Calculate the percentages of all the monochlorinated products obtained from 2-methylbutane.

6. What are the major products of monobromination of

(a) decalin
(b) 
(c)

7. Singlet methylene ( : CH₂) is formed by decomposition of diazomethane (CH₂N₂). It can be inserted between the C — H bonds in an alkane. What are different products of random insertion of methylene singlet in n-pentane?

8. Acetylene is acidic but it does not react with NaOH or KOH. Give reason.

9. Compound (A) contains only carbon and hydrogen. It decolourises bromine in CCl₄ solution and reacts slowly with concentrated H₂SO₄. Compound A reacts with HBr to form (B). (B) reacts with NaOH to form (C). On oxidising (C) gives hexanone-3. Write the structural formulae of (A), (B) and (C) and explain the reactions involved.

10. How will you synthesis the following?

(i) 1, 5-Hexadiene from propene
(ii) Allene from propene
(iii) 1, 3-Butadiene from 1-butene
(iv) Hexachloro ethane from calcium carbide

11. A hydrocarbon, C₇H₁₄, neither decolourised bromine in carbon tetrachloride nor reacted with HBr. When heated to 200°C with hydrogen in presence of a nickle catalyst, a new hydrocarbon, C₇H₁₆, was formed. What was the original hydrocarbon?

12. Complete the following equations:

(i) CH₂ = CH₂ + H₂ → (A) + (B) → (C)
(ii) CH₃COOH + H₂SO₄ → (A) + (B)
(iii) CH₃CH = CH₂ + H₂ → (A)
(iv) H₂C = CH₂ + H₂ → (A) → (B)
(v) C₆H₅CH = CH₂ + Hg(OAc)₂ → (A) + NaBH₄ + NaOH
(vi) CH₂ = CH₂ + BH₃/THF → (A)
(vii) CH₃COOH + Br₂ → (A) + (B)
(viii) C₆H₅CH₂CH(Cl)C₆H₅ + Al₂KOH → (A)
(ix) CH₂ = CH₂ + Br₂CCI₃ → (A)
(x) (CH₃)₂C + CH₂ + isobutane → (A)

13. Deduce the structures of the compounds which yield the following products on reductive ozonolysis

(a)

15. C₅H₉Br(A) has one element of unsaturation. A does not react with KMnO₄ and Br₂. A on reaction with alcoholic KOH forms (B), C₅H₈, which does react with KMnO₄ and Br₂. Ozonolysis of (B) forms (C), C₅H₈O₂. Identify A, B, C and explain reactions.

16. Ozonolysis of natural rubber yields chiefly the compound

What does this tell us about structure of rubber?

17. Tetrachloroethene (Cl₂C = CCl₂) is non-reactive towards Cl₂ but addition of AlCl₃ makes it reactive. Explain.

18. Identify A, B... in following reactions

(a)

(b)

(c)

(d)

Ozone of natural rubber yields chiefly the compound

What does this tell us about structure of rubber?

19. (a) Show with equations how the following compounds are prepared (equations need not to be balanced) 1-Propanol from 2-Propanol (in three steps)

(b) Fill in the blanks with appropriate words:
Acetylene is treated with excess sodium in liquid ammonia. The product is reacted with excess methyl iodide. The final product is

20. (a) Complete the following equations:

(i) Me₂CO → Me₂CH₂

(ii) EtCH = CH₂ → B₂H₆ → AgNO₃ → NaOH

(b) Arrange the following carbonium ions in order of increasing stability, and give your reasons.

21. (a) What alkenes could you expect from the following compounds? Give the experimental conditions:

(i) Me₂CCl;

(ii) Me₂C(OH)CMe₃;

(b) Formulate the reactions between but-1-ene, in the presence of a small amount of benzoyl peroxide, and (i) CCl₄;

(ii) CBrCl₃. Give your reasons.

22. (a) Discuss the mechanisms of the following reactions:

CCl₃CH = CH₂ + HOBr → CCl₃CHBrCH₂OH

(b) Compound A(C, 87.1%; H, 12.8%), on catalytic reduction, gives B(C, 81.4%, H, 15.9%). Ozonolysis of A gives acetic acid, acetone, and pyruvic acid (MeCOCO₂H). What are A and B?

23. (a) Complete the following equations:

iso Pr Br → Pr H

(b) Eth₂CHBrMe → EtOK → 1-ene + 2-ene + 2-ene

(c) Arrange EtOH, CF₃CH₂OH, and CCl₃CH₂OH in order of increasing
strength as acids and give your reasons.

24. (a) Convert (i) n-C\textsubscript{4}H\textsubscript{9}OH into MeC≡CMe; (ii) n-PrOH into cis-hex-2-ene.
(b) An olefin was treated with O\textsubscript{3} and the resulting product on hydrolysis gave 2-pentanone and acetaldehyde. What is the structure of the original olefin? Write equations for the reactions involved.
(c) 36.4 g of 1, 2, 2 tetrachloropropane was heated with zinc dust and the product was bubbled through ammon. AgNO\textsubscript{3}. What is the wt. of the ppt. obtained? Give equations for the reactions involved.

25. (a) An alkyl halide, X, of formula C\textsubscript{8}H\textsubscript{14}Cl on treatment with protassium tertiary butoxide gives two isomeric alkenes Y and Z (C\textsubscript{6}H\textsubscript{12}). Both alkenes on hydrogenation give 2, 3-dimethyl butane. Predict the structures of X, Y, and Z.
(b) Give the structures of the major organic products from 3-ethyl, 2-pentanone under each of the following reaction conditions.
(a) HBr in the presence of peroxide
(b) Br\textsubscript{2}/H\textsubscript{2}O
(c) Hg (OAc)\textsubscript{2}/H\textsubscript{2}O; NaBH\textsubscript{4}

**FINAL STEP EXERCISE**

(SUBJECTIVE)

1. How will you synthesise?
   (a) Vinyl chloride from acetylene
   (b) Chloroprene from acetylene
   (c) Vinyl acetate from ethyl alcohol

2. C\textsubscript{5}H\textsubscript{10} represents three isomeric alkenes A\textsubscript{1}, A\textsubscript{2} and A\textsubscript{3}. Each of hydrogenation gives 2-methylbutane. A\textsubscript{1} and A\textsubscript{3} on oxymercuration-demercuration give the same 3\textsuperscript{o} alcohol. A\textsubscript{2} and A\textsubscript{3} on hydroboration oxidation give different 1\textsuperscript{o} alcohol. Assign structures to A\textsubscript{1}, A\textsubscript{2} and A\textsubscript{3} and explain the reaction.

3. Limonene (A) is a naturally occurring C\textsubscript{10}H\textsubscript{16} hydrocarbon that causes the odour of lemons (a “circus” smell). When treated with excess hydrogen in the presence of platinum catalyst, it takes up two equivalents of hydrogen. When treated with ozone, followed by zinc in acetic acid, it forms one mol of formaldehyde (C) and one mol of the tricarbonyl compound (B) shown below.

Propose a suitable structure for Limonene if it has a one six membered ring.

4. Explain mechanism.

5. Explain the formation of from 2, 7 dimethyl 2, 6 octa-di-ene in presence of conc. H\textsubscript{2}SO\textsubscript{4}.

6. Identify A, B, C, D, E, F.

7. Compound X consumes five mol of H\textsubscript{2} to form

Identify X.
8. Compound (A) with M.W. 108 contained 88.89% C and 11.11% H. It gave a white precipitate with ammonical silver nitrate. Complete hydrogenation of (A) gave another compound (B) with molecular weight 112. Oxidation of (A) gave an acid with equivalent weight 128. Decarboxylation of this acid gave cyclohexane. Give structures of (A) and (B) and write the equation of the reactions involved.

9. An organic compound A of m.f. C\textsubscript{2}H\textsubscript{4} was treated with an acid in presence of liquid benzene to give a compound B. Cl\textsubscript{2} gas was bubbled through a solution of B and was irradiated. This yielded C. Elemental analysis of C confirmed the presence of only one halogen atom. C was dissolved in C\textsubscript{2}H\textsubscript{5}OH and a few NaOH pellets were added. This reaction gave a compound D. D when treated with Br\textsubscript{2}/CCl\textsubscript{4} gave a colourless liquid and the colourless liquid on treatment with NaN\textsubscript{3}/liq. NH\textsubscript{3} gave E. Identify A to E.

10. Identify A to F.

11. (a) One mole of a hydrocarbons (A) reacts with one mole of bromine giving a dibromo compound C\textsubscript{5}H\textsubscript{10}Br\textsubscript{2}. Substance (A) on treatment with cold dilute alkaline potassium permanganate solution forms a compound C\textsubscript{5}H\textsubscript{12}O\textsubscript{2}. On ozonolysis (A) gives equimolar quantities of propanone and ethanol. Deduce the structural formula of (A).

12. Complete the following equations:

\[
\begin{align*}
\text{CH}_3\text{COCCH}_3 & \xrightarrow{\text{NaNH}_2} ? \xrightarrow{\text{C}_2\text{H}_2} ? \xrightarrow{\text{H}^+} \\
(\text{CH}_3)_2\text{C(OH)C} & \xrightarrow{\text{H}_2/Pd} \xrightarrow{\text{Al}_2\text{O}_3/} 400^\circ\text{C}?
\end{align*}
\]