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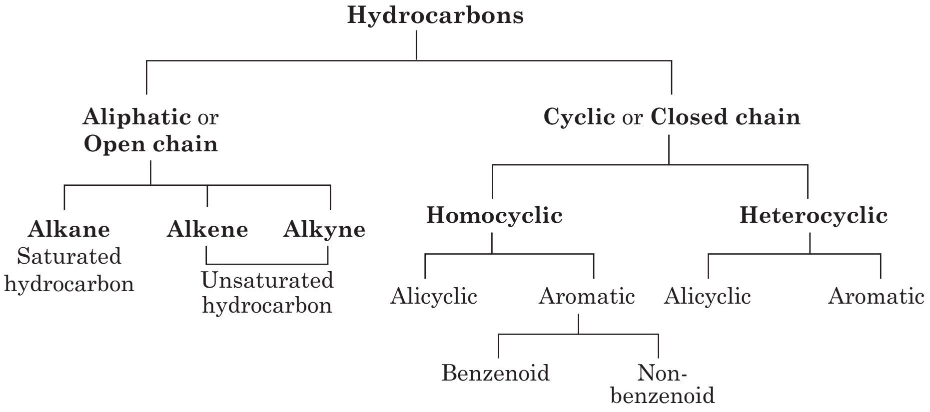
Hydrocarbons

Hydrocarbons means compounds essentially containing carbon and hydrogen. These are considered as the parental compounds of all organic substances. They may contain only single bonds or double/triple bonds.

Only single bond containing hydrocarbons are called **saturated hydrocarbons** while those having multiple bond(s) ($=$ or $\equiv$ bond) are known as **unsaturated hydrocarbons.**

Classification of Hydrocarbons

These hydrocarbons are mainly obtained from petroleum and their broad outline classification is given below.



Alkanes

These are the simplest organic compounds made up of carbon and hydrogen. Chemically, these have very low reactivity and that's why also known as **Paraffins** (Latin, *Parum affinis* = Little affinity). The general formula of alkane series is C_nH_{2n+2} and the first member is CH_4 (methane).

Each carbon in alkanes is ***sp*^{3}-hybridised** with **bond angle 109°28′** and C—C bond dissociation energy in 83 kcal/mol. The main sources of alkanes are **natural gas** and **petroleum.**

IN THIS CHAPTER ....

- Classification of Hydrocarbons
- Alkanes
- Alkenes
- Alkynes
- Aromaticity
- Benzene

Nomenclature

In chapter 13 you have already read the nomenclature of alkane. Still to recap, the names of initial alkanes (till C-atom 10) are methane, ethane … decane. The names of some important alkanes having carbon more than 10 are tabulated below.

IUPAC Name of Higher Alkanes

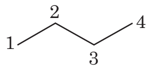
Molecular formula	Name	Molecular formula	Name
$C_{11}H_{24}$	Undecane	$C_{31}H_{64}$	Hentriacontanes
$C_{12}H_{26}$	Dodecane	$C_{40}H_{82}$	Tetracontanes
$C_{20}H_{42}$	Icosane (Eicosane)	$C_{50}H_{102}$	Pentacontanes
$C_{21}H_{44}$	Henicosane	$C_{90}H_{182}$	Nonacontanes
$C_{22}H_{46}$	Docosane	$C_{100}H_{202}$	Hectane
$C_{30}H_{62}$	Triacontanes		

Isomerism

Alkanes exhibit mainly structural, isomerism i.e. chain and conformational, e.g.

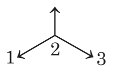
C_4H_{10} have two chain isomers as

I.



Butane

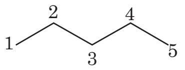
II.



iso-butane
or 2-methyl propane

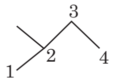
and C_5H_{12} have three chain isomers as,

I.



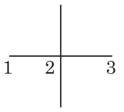
Pentane

II.



iso-pentane

III.



neo-pentane

Methods of Preparation

Following methods are used for the preparation of alkanes

1. By the Reduction of Different Compounds

Different reagents are used to reduce different compounds to produce alkanes, description of which is given below.

(i) **Reduction of alcohols, carboxylic acids their derivatives and alkyl halides** is carried out by heating them with red P + HI but the yield is very less. e.g.

$$CH_3COOH + 6HI \xrightarrow[425\text{ K}]{\text{Red P}} CH_3—CH_3 + 2H_2O + 3I_2$$

$$CH_3CH_2OH + 2HI \xrightarrow[425\text{ K}]{\text{Red P}} CH_3—CH_3 + H_2O + I_2$$

$$C_2H_5I + HI \xrightarrow{\text{Red P}} C_2H_6 + I_2$$

Here, red P is used to remove iodine as volatile PI_3, otherwise the reaction becomes reversible.

$$2P + 3I_2 \longrightarrow 2PI_3$$

(ii) **For reducing carbonyl compounds** like aldehydes and ketones the reagents used are

(a) **Red P + HI/Δ as,**

$$>C{=}O + 6HI \xrightarrow[425\text{ K}]{\text{Red P}} >CH_2 + H_2O + 3I_2$$

(b) **Zn-Hg/conc. HCl** (Clemmensen reduction) ,

$$>C{=}O + 4[H] \xrightarrow[\text{conc. HCl}]{\text{Zn-Hg}} >CH_2 + H_2O$$

(c) **Hydrazine followed by $C_2H_5O^-Na^+$ at 180°C** (Wolf-Kishner reduction).

$$>C{=}O + NH_2NH_2 \xrightarrow[-H_2O]{} >C{=}N—NH_2$$

$$\xrightarrow[-N_2]{C_2H_5ONa} >CH_2$$

Among above reactions Wolf-Kishner reduction is a specific method for reducing $>C{=}O$ group into $>CH_2$ group. N_2 is released in the process.

For reduction the generalised reducing agents can also be used. These can be (a) **metal + proton donor** and (b) **complex hydrides**.

I. Metal + Proton Donor

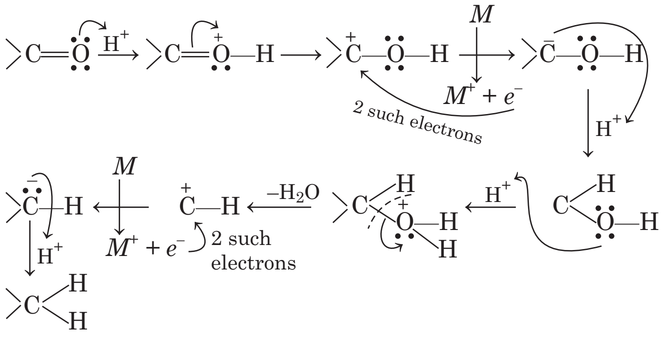
Among metal + proton donor, the metal works as electron donor and the complete process looks like

$$\boxed{>C{=}O + M \text{ with } H^+ \longrightarrow >C{<}^{H}_{H} + H_2O}$$

Here, M = metal; H^+ = any protic agent

Mechanism

The stepwise mechanism of reaction is shown below.



The metal used can be Na, Zn or amalgams etc., like Zn/HCl, Sn/HCl, Zn / CH_3COOH, Zn—Cu couple with CH_3OH, Na with ethanol etc., e.g.

- Alkyl halides also get reduced in a similar fashion as

$$RX + 2[H] \xrightarrow[H_2O]{\text{Zn-Cu}} \underset{\text{Alkane}}{R—H} + HX$$

- The order of reactivity of alkyl halides is $RI > RBr > RCl > RF$.

II. Complex Hydrides

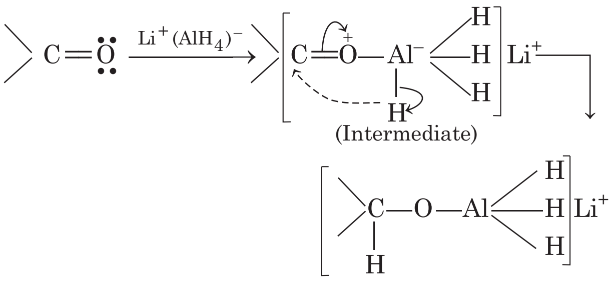
Among the complex hydrides, **LAH** (Lithium aluminium hydride, $LiAlH_4$) is the best reagent and others include $NaBH_4$, $NaAlH_4$, Ph_3SnH etc.

The equation of reduction with complex hydride looks like

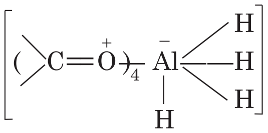
$$>C=O + 4[H] \xrightarrow{LiAlH_4} >CH_2 + H_2O$$

Mechanism

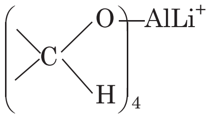
The steps in mechanism of complete reaction are given below



LAH is a strong reducing agent because it reduces four molecules at a time, thus the intermediate formed looks like :

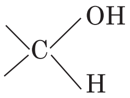


Li⁺ and finally results to



The final intermediate on acid hydrolysis with HCl

yields 4 molecules of



along with $AlCl_3$ and LiCl.

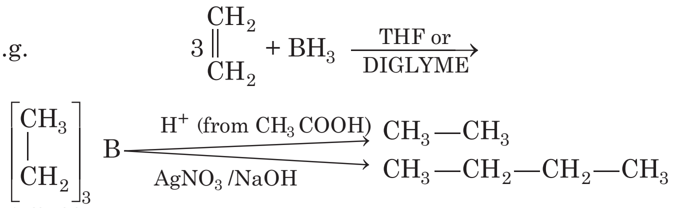
Note When reducing agent is $LiAlH_4$, tertiary halides give mainly alkenes.

Reduction with Boron Hydrides (Hydroboration)

- Alkenes on reduction with B_2H_6 or BH_3 in the presence of Lewis bases like THF (tetrahydrofuran) or DIGLYME (diethylene glycol methyl ether) form alkanes having longer chains.

  These Lewis bases convert dimeric B_2H_6 to BH_3 by forming acid-base complex.

e.g.



Trialkyl borane

Initially trialkyl boranes are obtained which on treatment with any protic agent or $AgNO_3$/NaOH give alkanes.

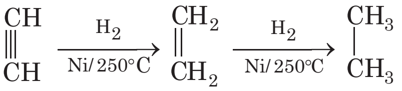
Here, $AgNO_3$/NaOH is called coupling reagent that's why this reaction is also called **coupling reaction.** It also sometimes called **hydroboration reaction.**

The reaction looks like anti-Markownikoff addition but infact, it is Markownikoff addition. Here, the difference lies only in BH_3, the H of BH_3 plays the role of (–) ve partner while boron plays the role of (+) ve partner.

2. Hydrogenation or Catalytic Reduction

The precise meaning of hydrogenation is addition of hydrogen .The best catalyst used for hydrogenation is **Raney Ni**. It is an alloy containing equal amounts of Ni and Al digested with NaOH. The catalyst is very effective over normal Ni which works at 200-300°C, as **Raney Ni** can work even at room temperature.

Other catalysts commonly used are Pd, Pt etc., which require a temperature between 200-300°C. The reduction of unsaturated hydrocarbons with Ni at temperatures between 200-300°C is called **Sabatier- Sanderens reaction.** The equation of this reaction looks like



$$CH\equiv CH \xrightarrow[Ni/250^\circ C]{H_2} CH_2=CH_2 \xrightarrow[Ni/250^\circ C]{H_2} CH_3-CH_3$$

3. Decarboxylation

Elimination of CO_2 from any carboxylic acid is called decarboxylation. Hot **soda lime** (NaOH/CaO) is frequently used reagent for this purpose. However, various other reagents may also be used. The equation of reaction is given below

$$R\boxed{COO^-Na^+ + NaO}H / CaO \xrightarrow{\Delta} RH + Na_2CO_3$$

Here, alkanes so produced, contains one carbon atom less than the original acid.

The reaction takes place by free radical mechanism and involves the formation of several byproducts like *lower alkanes, hydrogen, alkenes, esters* alongwith the main alkanes.

The removal of these products is usually difficult. Thus, this reaction is not very useful. An example is

$$C_2H_5COONa \xrightarrow{NaOH\ (CaO)} \underset{(44\%)}{C_2H_6} + \underset{(20\%)}{CH_4} + \underset{(33\%)}{H_2}$$
$$+ \text{ unsaturated compounds}$$

The reason of using CaO alongwith NaOH is that it keeps the NaOH (hygroscopic) dry.

4. Kolbe's Electrolytic Method or Kolbe's Decarboxylation

This method is used to create a new C—C linkage and to prepare alkenes and alkynes as well. The reaction looks like

$$\begin{array}{l} CH_3COO^-K^+ \\ CH_3COO^-K^+ \end{array} \xrightleftharpoons{\text{Electrolysis}} \underbrace{\begin{array}{c} CH_3 \\ | \\ CH_3 \end{array} + CO_2\uparrow}_{\text{At anode}} + \underbrace{H_2\uparrow + K^+OH^-}_{\text{At cathode}}$$

Mechanism (free radical)

$$2CH_3CO\overset{-}{O}\overset{+}{Na} \xrightleftharpoons{\text{Electrolysis}} 2CH_3COO\overset{\bullet\bullet}{{}^{\ominus}} + 2Na^{\oplus}$$

At anode (oxidation)

$$2CH_3COO^{\ominus} \longrightarrow 2e^{\ominus} + 2CH_3CO\dot{O} \longrightarrow 2CH_3^{\bullet} + 2CO_2\uparrow$$
$$\longrightarrow \underset{\text{Ethane}}{CH_3—CH_3}$$

At cathode (reduction) Reduction of H_2O takes place since reduction potential of it is greater than that of $Na^{\oplus}$.

$$2H_2O + 2e^{\ominus} \longrightarrow 2\overset{-}{O}H + H_2\uparrow$$

Because of the generation of OH^- ions, the solution becomes alkaline.

Note CH_4 cannot be prepared by this method. This method is not suitable for alkanes having odd number of carbon atoms, as in such cases a mixture of hydrocarbons is formed which is difficult to separate.

In Kolbe's decarboxylation reaction if n is the number of carbon atoms in sodium or potassium carboxylate, the number of carbon atoms in alkane formed will be $(n - 1)$ while during reduction processes the number of carbon atoms in alkane formed and that in parent compound is same.

5. From Grignard's Reagent

Grignard's reagent on treatment with compounds like H_2O, ROH, acids etc., i.e. protic agents forms alkane as shown below

$$RMgX + HOH \longrightarrow RH + Mg(OH)X$$
$$RMgX + R'OH \longrightarrow RH + Mg(OR')X$$
$$RMgX + R'COOH \longrightarrow RH + Mg(OOCR')X$$
$$RMgX + R'C{\equiv}CH \longrightarrow RH + Mg(C{\equiv}CR')X$$

Notify that in each of the above equation RH type of alkane is formed.

6. Wurtz Reaction

When alkyl halides are treated with sodium metal in dry ether, it results in the formation of an alkane having double the number of carbons as that are present in parent halide. This reaction is called Wurtz reaction.

$$R\boxed{X + 2Na + X}R \xrightarrow{\text{Dry ether}} R—R + 2NaX$$

A single symmetrical alkane is obtained as the product if a single alkyl halide is used. However, if more than one alkyl halides are used, the product is non-separable mixture of alkanes, so it is more suitable for the synthesis of symmetrical alkanes. e.g.

$$CH_3X + 2Na + C_2H_5X \xrightarrow[-NaX]{\text{Ether}} CH_3—CH_3 + CH_3—C_2H_5$$
$$+ C_2H_5—C_2H_5$$

A small percentage of alkene is also obtained during this reaction.

Mechanism

The mechanism of this reaction may be free radical or ionic but normally free radical is preferred, which takes place as,

$$R—X + Na^{\bullet} \longrightarrow R^{\bullet} + NaX$$
$$R^{\bullet} + R^{\bullet} \longrightarrow R—R$$

Moreover, free radicals have a property to disproportionate, i.e.

$$R^{\bullet} + R^{\bullet} \longrightarrow \text{Saturated hydrocarbon} + \text{Unsaturated hydrocarbon}$$

This can be best understood by the following example

$$CH_3CH_2X + Na \longrightarrow CH_3CH_2^{\bullet} + Na^+X^-$$
$$2CH_3CH_2^{\bullet} \longrightarrow CH_3CH_2CH_2CH_3$$

$$CH_3CH_2^{\bullet} + CH_3CH_2^{\bullet} \xrightarrow{\text{Disproportionation}} CH_3CH_3 + CH_2{=}CH_2$$

Remember CH_4 cannot be prepared by this reaction. This method cannot be used to convert 3°alkyl halides to alkanes as in such cases alkenes are obtained instead of alkanes as the major product.

So, we can say that the yield of major product is not very good in such cases when we take more than 1 alkyl halide. To overcome this problem Corey-House synthesis was developed in 1960s.

7. Corey-House Synthesis

This method was developed in 1960 to synthesise mixed alkanes. The method proceeds as,

$$RBr + 2Li \xrightarrow{\text{Ether}} RLi + LiBr$$
$$2RLi + CuI \longrightarrow \underset{\substack{\text{Lithium dialkyl} \\ \text{cuperate}}}{Li(R)_2Cu} + LiI$$
$$Li(R)_2Cu + R'Br \longrightarrow R'—R + RCu + LiBr$$

Notify that the alkane formed here is $R — R'$ type, i.e. asymmetric. So, this is a good method to prepare unsymmetrical alkanes from alkyl halides.

Remember Dialkyl zinc also gives similar type of reaction but specifically for 3°alkyl halides. So, the main product in this reaction is quaternary alkane.

$$(CH_3)_2Zn + (CH_3)_3CCl \longrightarrow (CH_3)_4C + CH_3ZnCl$$

8. Frankland Reaction

Another similar method for preparing alkanes is Frankland method in which Zn is used in the place of Na. Here, rest of the things remain absolutely same as the Wurtz reaction. The reaction looks like :

$$R\boxed{X + Zn + X}R \xrightarrow[\text{ether}]{\text{Dry}} R—R + ZnX_2$$

9. Other Methods of Preparation

(i) **From carbides** CH_4 is prepared by reacting carbides, i.e. Al_4C_3 and Be_2C with water. Hence, these carbides are also called **methanides.**

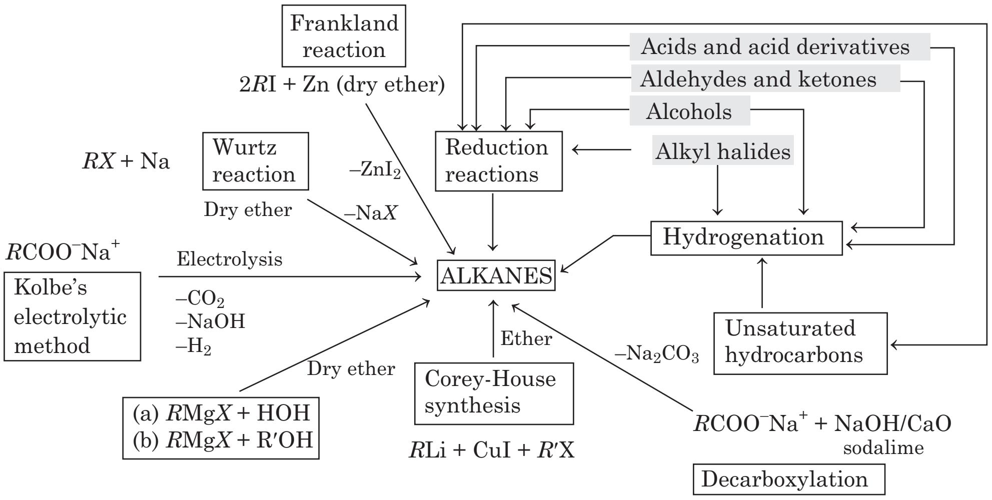
$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$

$$Be_2C + 4H_2O \longrightarrow 2Be(OH)_2 + CH_4$$

(ii) **Synthesis from constituents** Lower alkanes are also prepared by

$$C + 2H_2 \xrightarrow[\text{1473 K}]{\text{Electric arc}} CH_4$$

Summary of the methods described above is shown in the following flow chart.



Flow chart showing methods of preparation of alkanes

Physical Properties of Alkanes

- First four alkanes are gases, next 13 are colourless liquids and rest higher ones are waxy solids.
- These are insoluble in polar solvents like water but are soluble in non-polar solvents like alcohol, ether, benzene etc. Their solubility diminishes with increase in molecular weight.
- As the number of carbon atoms increases, the boiling points of alkane increases because van der Waals' forces increases. However, branching results in decrease in boiling point due to decreased surface area. This reduced area in turn results in weaker van der Waals' forces.
- Melting point also increases with increase in molecular weights but **alkanes with even number of carbon atoms have higher melting point** than the preceding and succeeding members, due to their well packed structures.
- The dipole moment of all alkanes, whether straight or branched chain is **zero**. However, when one H-atom is replaced by another atom or group, i.e. substituent, the resultant molecule will now possess some dipole moment.
- The densities of alkanes increases with increase in molecular mass. However, these become constant at about 0.8 g cm^{-3}. It shows that all the alkanes are lighter than water.

Chemical Properties of Alkanes

Important chemical properties of alkanes are discussed below

1. Halogenation

This is the process of replacement of one or more hydrogens of an alkane by halogens. The complete equation of reaction is given below

$$CH_4 + Cl_2 \xrightarrow[-HCl]{h\nu \text{ or } 473\text{-}523 \text{ K}} CH_3Cl + CH_2Cl_2 + CHCl_3 + CCl_4$$

Mechanism

This reaction follows free radical mechanism and involves the following steps

***Step* I** Initiation step – single

$$X-X \xrightarrow{\text{UV or } \Delta} \underset{\text{Free radicals}}{X^{\bullet}+X^{\bullet}}$$

***Step* II** Propagation steps – multiple

$$R-\mathrm{H}+X^{\bullet} \longrightarrow R^{\bullet}+\mathrm{H}X$$

$$R^{\bullet}+X-X \longrightarrow RX+X^{\bullet}$$

***Step* III** Termination steps – multiple

$$X^{\bullet}+X^{\bullet} \longrightarrow X_2$$

$$R^{\bullet}+X^{\bullet} \longrightarrow RX$$

$$R^{\bullet}+R^{\bullet} \longrightarrow R-R$$

Important Facts Regarding this Reaction

- For this reaction the order of reactivity of alkanes is $I_2 > Br_2 > Cl_2 > F_2$.
  - (i) Cl_2 reacts under UV light/diffused sun light/300-400°.
  - (ii) Br_2 reacts less vigorously and prefers site of its selection.
  - (iii) With I_2, reaction is reversible and carried out in the presence of oxidising agent like HIO_3, HgO, etc.
  - (iv) F_2 reacts with explosion.
- This reaction mainly given by those compounds which at least have one hydrogen atom present on sp^3-hybrid C-atom.
- Reactivity of sp^3-hybrid C-atom is as follows *tert*-benzyl carbon > *sec*-benzyl carbon > *p*-benzyl carbon > *t*-allylic carbon > *s*-allylic carbon > *p*-allylic carbon > *t*-alkyl carbon > *s*-alkyl carbon > *p*-alkyl carbon > CH_4.
- A chlorine free radical is so reactive that it makes primary, secondary and tertiary radicals with almost equal ease.
- Since, the reaction takes place by free radical mechanism, **free radical inhibitors like oxygen** inhibit the reaction while **free radical accelerator** such as benzoyl peroxide $(C_6H_5COO)_2$, tetraethyl lead $Pb(C_2H_5)_4$ etc., accelerate the reaction.
- The number of monohalogenation products obtained from any alkane depends upon the number of different types of hydrogens it contains. e.g. Butane contains two types of hydrogen, so it gives two monohalogenated product on mono halogenation.

$$\underset{n\text{- butane}}{CH_3CH_2CH_2CH_3} \xrightarrow{Cl_2/h\nu} \underset{\text{1-chlorobutane}}{CH_3CH_2CH_2CH_2-Cl} + \underset{\text{2-chlorobutane}}{CH_3-CHCl-CH_2-CH_3}$$

- **Yield of halogenation** The yield of halogenation depends upon the reactivity of H. The relative order of reactivity of H for chlorination is

$$\underset{(3^\circ\,\mathrm{H})}{5} > \underset{(2^\circ\,\mathrm{H})}{3.8} > \underset{(1^\circ\,\mathrm{H})}{1}$$

For bromination the order is

$$\underset{(3^\circ\mathrm{H})}{1600} > \underset{(2^\circ\mathrm{H})}{82} > \underset{(1^\circ\mathrm{H})}{1}$$

From the reactivity, the yield is calculated as,

$$\%\text{ yield} = \frac{\text{Number of H atom} \times \text{relative reactivity of H} \times 100}{(\text{Number of } 1^\circ\text{H} \times \text{their reactivity} + \text{Number of } 2^\circ\text{H} \times \text{their reactivity} + \text{Number of } 3^\circ\text{H} \times \text{their reactivity})}$$

2. Nitration

Higher alkanes, i.e. those having more than five carbon atoms can be nitrated when heated with fuming HNO_3. This reaction is called **liquid phase nitration.** e.g.

$$C_6H_{14}+HNO_3 \longrightarrow C_6H_{13}NO_2+H_2O$$

For nitration of lower alkanes, a technique called **vapour phase nitration** is used. In this a mixture of the lower hydrocarbons and nitric acid vapours is passed through the silica tube at highly elevated temperature of 400-500°C. The reaction also involves cleavage of C—C linkage alongwith C—H linkage, resulting to a mixture of nitroalkanes as

$$C_2H_6+HONO_2 \longrightarrow C_2H_5NO_2+CH_3NO_2+H_2O$$

Nitration just like halogenation also follows free radical mechanism.

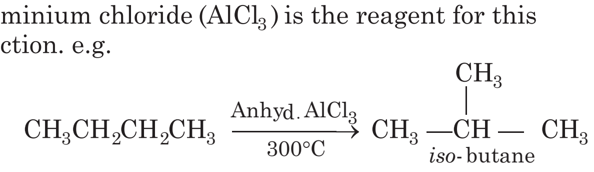
3. Sulphonation

Sulphonation is normally given by alkanes with minimum 6C-atoms onwards, i.e. hexane onwards. Lower alkanes except those having tertiary hydrogen atom can't get sulphonated. It is done by fuming H_2SO_4 as,

$$\underset{\substack{iso\text{- butane}\\ \text{(contains one } 3^\circ\text{C)}}}{(CH_3)_3CH} + \underset{\text{Oleum}}{H_2S_2O_7} \longrightarrow \underset{\substack{t\text{- butylsulphonic}\\ \text{acid}}}{(CH_3)_3CSO_3H} + H_2O$$

4. Isomerisation

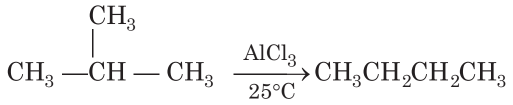
This reaction is a result of molecular rearrangement involving 1,2-hydride or methyl shift. Anhydrous aluminium chloride $(AlCl_3)$ is the reagent for this reaction. e.g.



$$CH_3CH_2CH_2CH_3 \xrightarrow[300^\circ C]{\text{Anhyd. }AlCl_3} \underset{iso\text{- butane}}{CH_3-\overset{\overset{\displaystyle CH_3}{|}}{CH}-CH_3}$$

This reaction does not occur unless a trace of water is present (to form HCl from $AlCl_3$) together with a trace of alkyl halide or an alkene.

The reverse of this reaction is visible with $AlCl_3$ only at 25°C. Its equation is shown below



$$CH_3-\underset{}{\overset{CH_3}{\overset{|}{C}H}}-CH_3 \xrightarrow[25°C]{AlCl_3} CH_3CH_2CH_2CH_3$$

5. Oxidation

This can be complete or partial. Complete oxidation is called **combustion** which is shown by following generalised equation as,

$$C_nH_{2n+2} + \left(\frac{3n+1}{2}\right)O_2 \xrightarrow{\text{Flame}} nCO_2 + (n+1)H_2O + \text{Heat}$$

Like $CH_4 + 2O_2 \xrightarrow{\text{Flame}} CO_2 + 2H_2O$

When alkanes are burnt **in insufficient supply of oxygen**, CO and carbon black are obtained.

$$C_nH_{2n+2} + O_2 \longrightarrow \underset{\substack{\text{Carbon}\\ \text{black}}}{C} + 2H_2O$$

1° and 2° alkanes are usually not affected by oxidising agents like $KMnO_4$ and $K_2Cr_2O_7$. However, alkanes having 3° hydrogen are oxidised by these oxidising agent to give corresponding alcohols.

$$(CH_3)_3CH + [O] \xrightarrow[\text{Alc.}]{KMnO_4} (CH_3)_3COH$$

Lower alkanes undergo **restricted oxidation** in the presence of metallic catalysts such as Cu at high temperature and pressure to form alcohols, aldehydes, ketones and acids, e.g.

$$\text{(i)}\ \underset{9}{2CH_4} + \underset{:\ \ 1}{2\,[O]} \xrightarrow[\text{100 atm/200°C}]{\text{Cu- tube}} \underset{\text{Methyl alcohol}}{2CH_3OH}$$

$$\text{(ii)}\ CH_4 + O_2 \xrightarrow[277°C]{Mo_2O_3} \underset{\text{Formaldehyde}}{HCHO} + H_2O$$

$$\text{(iii)}\ HCH_3 + \frac{3}{2}O_2 \xrightarrow[\text{or } Ag_2O]{(CH_3COO)_2Mn} \underset{\text{Formic acid}}{HCOOH} + H_2O$$

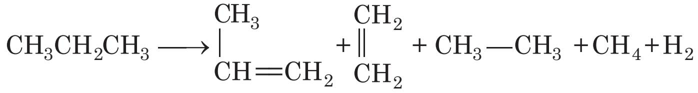
Methane or ethane with oxygen at high pressure and comparatively low temperatures are oxidised as

$$\begin{tikzcd}
CH_4 \arrow[r, "{[O]}"] & CH_3OH \arrow[r, "{[O]}", "-H_2O"'] & HCHO \arrow[r, "{[O]}"] & HCOOH \arrow[d, "{[O]}"] \\
 & & & H_2O + CO_2
\end{tikzcd}$$

This oxidation is called **controlled oxidation.**

6. Pyrolysis (Greek, Pyro = fire, Lysis = loosening)

It is **thermal breakage** of organic molecules. When the process is applied to higher alkanes, it is called **cracking** (a word given by petroleum industry). The reaction product is in the form of a mixture containing alkanes, alkenes and other compounds.



$$CH_3CH_2CH_3 \longrightarrow \overset{CH_3}{\overset{|}{CH}}{=}CH_2 + \overset{CH_2}{\overset{\|}{CH_2}} + CH_3-CH_3 + CH_4 + H_2$$

The process generally requires temperatures in the range 500 - 800°C. Some catalysts like **finely divided silica-alumina** can also be used. Then the process is called **catalytic cracking.** A free radical mechanism is favoured for pyrolysis.

7. Aromatisation

It is also called as **reforming onwards.**

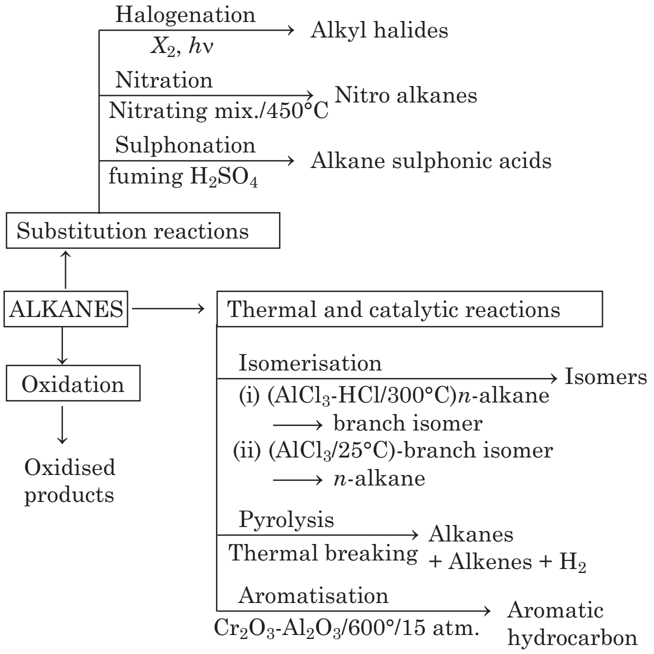
It is applicable to alkanes from hexane to decane, e.g.

$$\text{Hexane} \xrightarrow{\text{Aromatisation}} \text{Benzene}$$

$$\text{Heptane} \xrightarrow{\text{Aromatisation}} \text{Toluene, etc.}$$

The reaction conditions for aromatisation is the presence of Al_2O_3 or Cr_2O_3 or V_2O_5 and 770 K temperature and high pressure.

Summary of Reactions of Alkanes



Conformations or Conformers

Different infinite arrangements of atoms that can be converted into one another by rotation about single bonds are called conformations or conformers. These conformers are also termed as **rotamers** and conformational isomerism as **rotamerisms**.

Conformations of Ethane

In ethane molecule (CH_3-CH_3), the two carbon atoms are bonded by a single covalent bond. If one of the carbon atoms (methyl group) is kept fixed and the other is rotated about the C—C bond, an large number of arrangements of the hydrogen atoms attached to one carbon atom with respect to other are possible. These large number of different arrangements are infact called **conformations of ethane.** Out of these two major ones are as follows

(i) **Eclipsed conformation** In this conformation, the hydrogens of one carbon atom are directly behind those of the other. Consequently, **the repulsion in these atoms is maximum**.

(ii) **Staggered conformation** In this arrangement, the hydrogens of the two carbon atoms are staggered with respect to one another. As a result, these are **at maximum distance apart** and **have minimum repulsion between them**.

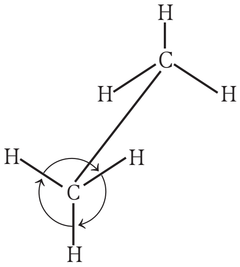
All the possible conformation between these confirmations are called **skew conformation.**

Representation of Conformations

These conformations can be represented in two simple ways as shown below

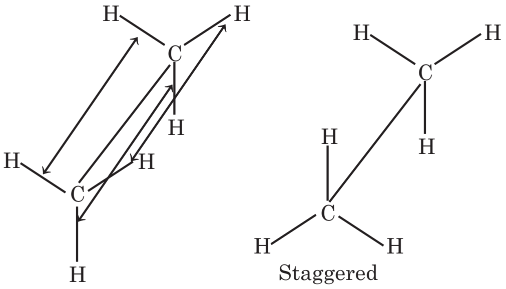
1. Saw Horse Projections

In this projection carbon-carbon bond is viewed from an oblique angle and indicate spatial arrangements by showing all the C—H bonds as shown in figure, below



Saw Horse projection showing rotation around C—C single bond in ethane

Saw Horse projections of ethane conformations are represented in the figure below.



Eclipsed conformation

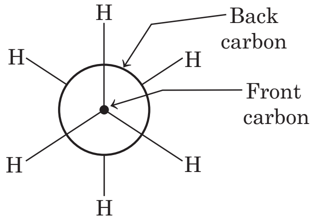
Staggered conformation

Saw Horse projections of eclipsed and staggered conformations of ethane

2. Newmann Projection

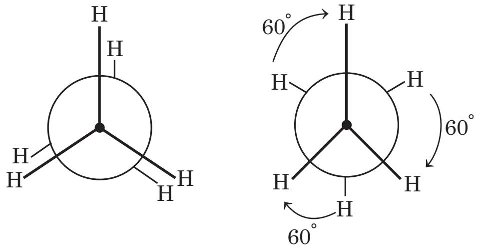
In this method, the two carbon atoms forming the σ-bond are represented by one point and one circle present one behind the other.

The C—H bonds of the front carbon are depicted from the centre of the point while C—H bonds of the back carbon are drawn from the circumference of the circle.



Newmann projections of ethane

The Newmann projections for staggered and eclipsed conformations of ethane are shown in figure below.



Eclipsed conformation Staggered conformation

Newmann projections of eclipsed and staggered conformations of ethane

It is clear that when the eclipsed conformation is rotated through an angle of 60°, it changes to staggered conformation and *vice-versa*.

Relative Stabilities of the Conformations of Ethane

The two major conformations of ethane differ in their relative stabilities. The staggered conformation has minimum repulsions between the H-atoms attached tetrahedrally to the two carbon atoms.

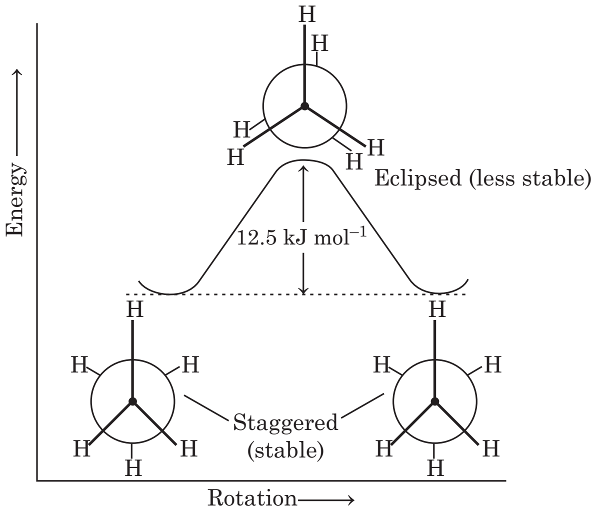
On the other hand, the eclipsed conformation has maximum force of repulsion between H-atoms. Therefore, **the staggered conformation is more stable than the eclipsed conformation.**

The difference in the energy contents of the staggered and eclipsed conformations is 12.5kJ mol^{-1}. This small barrier to rotation is also called **torsional barrier of the single bond**.

However, this energy difference is not large enough to prevent rotation Even at ordinary temperatures the molecules have thermal or kinetic energy to overcome this energy barrier.

Therefore, the two conformations of ethane go on changing from one form to another thus consequently, *it is not possible to isolate the different conformations of ethane*.

For these conformations the variation of energy *versus* rotation about the C—C bond has been shown in the following figure.



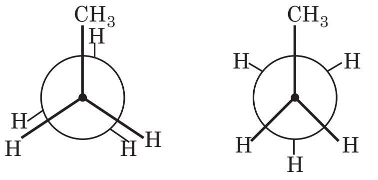
The variation of energy *versus* rotation about C—C bond

Remember The dihedral angle between the C—H bonds on adjacent carbons in staggered and eclipsed conformations of ethane are 180° and 0° respectively.

Conformations of Propane

The next higher member in alkane series, i.e. propane ($CH_3CH_2CH_3$) also has two extreme conformations, i.e. **eclipsed conformation** and **staggered conformation.**

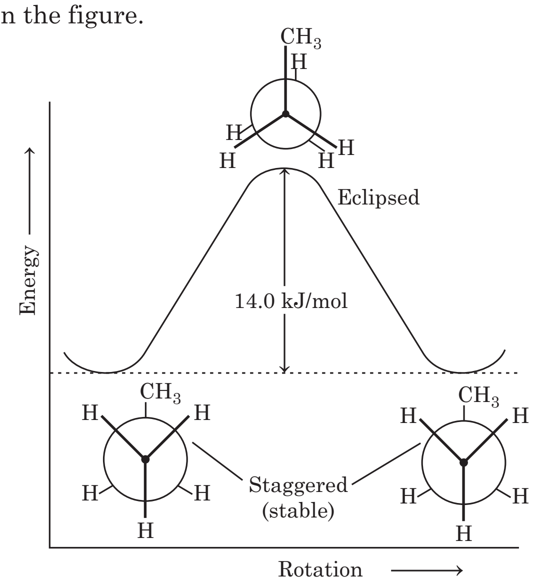
In figure given below only Newmann projections are shown for simplicity. However, the energy barrier in propane is 14 kJ mol^{-1}, which is slightly higher than that in ethane.



Eclipsed propane Staggered propane

Newmann projections of propane

The variation of energy *versus* rotation about C— C bond is shown in the figure.



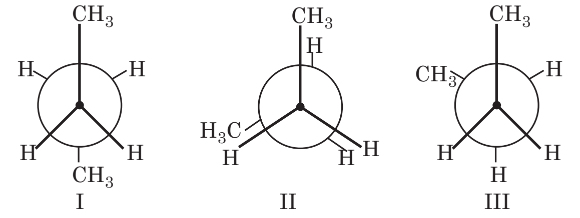
The variation of energy *versus* rotation about C—C bond in propane.

Conformations of Butane

As the alkane molecule becomes larger, the conformation situation becomes more complex. In butane ($CH_3CH_2CH_2CH_3$), all the staggered as well as eclipsed conformations will not have same stability and energy because of different types of interaction between C—C (of methyl) and C—H bonds.

The lowest energy conformation will be the one, in which the two methyl groups are as far apart as possible, i.e. 180° away from each other. The staggered conformation here is also called **anti conformation** (marked I below).

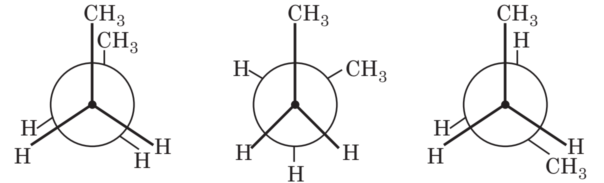
Other conformations can be obtained by rotating one of the C_2 or C_3 carbon atoms roughly at an **angle of 60°** as shown below.



I Anti

II Eclipsed

III Skew or *gauche*



IV Fully eclipsed

V Skew or *gauche* (same as III)

VI Eclipsed (same as II)

Different conformations of butane

As it is clear from the above Newmann projections, the *gauche* or skew conformations (III and V) are also staggered.

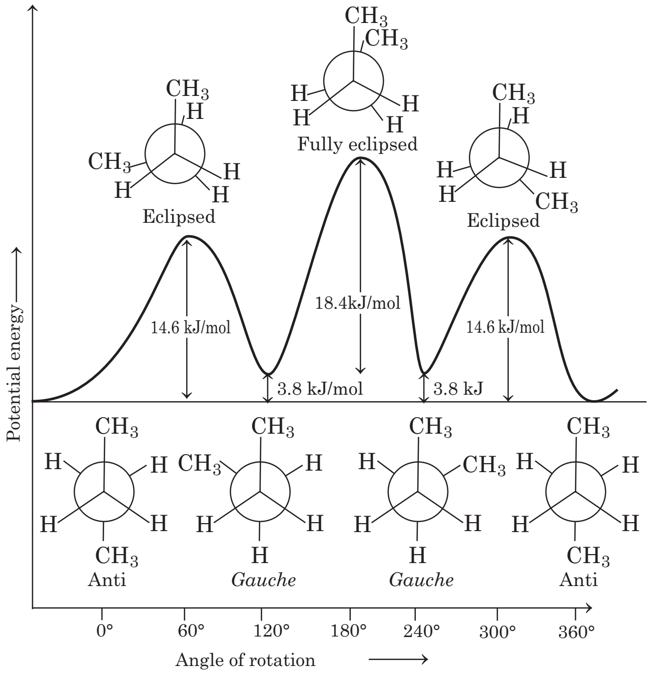
However, in these conformations, the methyl groups are so close that these repel each other. This repulsion causes *gauche* conformations to have about 3.8 kJ mol^{-1} more energy than anti conformation. The conformations II and VI are eclipsed conformations. These are unstable because of repulsions. They have 14.6 kJ mol^{-1} energy and are less stable than other anti conformations.

The conformation IV is also eclipsed and it is least stable having energy 18.4 kJ mol^{-1} more than anti conformation. This is because of repulsion between methyl-methyl groups which are very close to each other. It is called *fully eclipsed conformation*.

So, the order of stability of these conformations is

Anti > Skew or *Gauche* > Eclipsed > Fully eclipsed

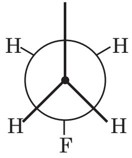
The energy differences between various conformations is shown in the figure given below.



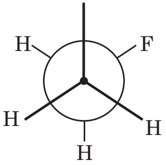
Energy change during rotation about $C_2 – C_3$ bond of *n*-butane

It is clearly visible from the above figure the dihedral angles between the two methyl groups in *gauche* and anti confirmations are 60° and 180° respectively.

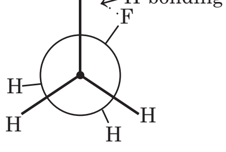
Remember If there exist a possibility of H-bonding or any other such interaction then gauche form may become more stable than anti (staggered) due to H-bonding as shown below.



Less stable



Less stable



Most stable

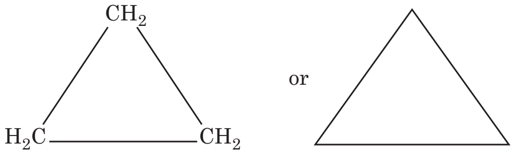
Steric Strain and Stability of Cycloalkanes

Energy profiles of cycloalkanes are quite different from those of aliphatic alkanes. It is related to their changed bond angles and related steric strains. These strains are seen more in smaller cycles.

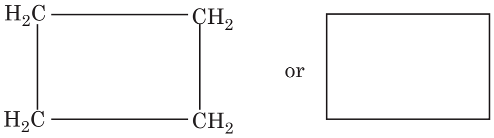
A brief description related to energy profile of these cycloalkane is given below.

Cyclopropane and Cyclobutane

Cyclopropane and cyclobutane are planar molecules having bond angles of 60° and 90° respectively.



Cyclopropane (bond angle = 60°)



Cyclobutane (bond angle = 90°)

The bond angles in these molecules are quite different from the normal tetrahedral bond angle of 109.5°, which is a normal angle for sp^3-hybridised carbon atoms.

As a result of deviation from normal bond angle, there is a considerable strain in the molecules of these compounds.

Therefore, these cyclo compounds are quite reactive. Obviously, cyclopropane with a bond angle of 60° is more strained and reactive than cyclobutane (bond angle 90°).

Cyclopentane and Cyclohexane

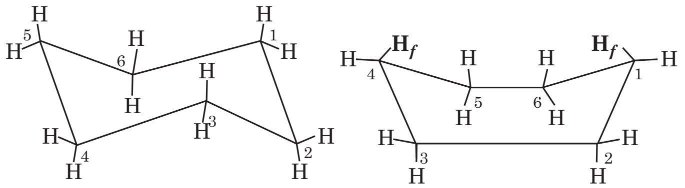
In cyclopentane, the bond angle is 108° which is quite close to normal tetrahedral angle. Therefore, cyclopentane has very less strain and is, therefore, stable.

Similarly, the bond angle in cyclohexane ring is 120° and is expected to be quite reactive and strained. But in actual practice cyclohexane is quite stable.

Conformations of Cyclohexane

The stability of cyclohexane indicates that the molecule avoids strain by assuming conformation in which all the bond angles between carbon atoms are close to tetrahedral angle of 109.5°.

Therefore, cyclohexane adopts a non-planar structure. The two important conformations for cyclohexane are the **chair form** and the **boat form** as shown in the figure below.



Chair conformation

Boat conformation

These structures are also called **puckered ring structures**. The names of these forms are due to resemblance of their shapes with chair and boat respectively.

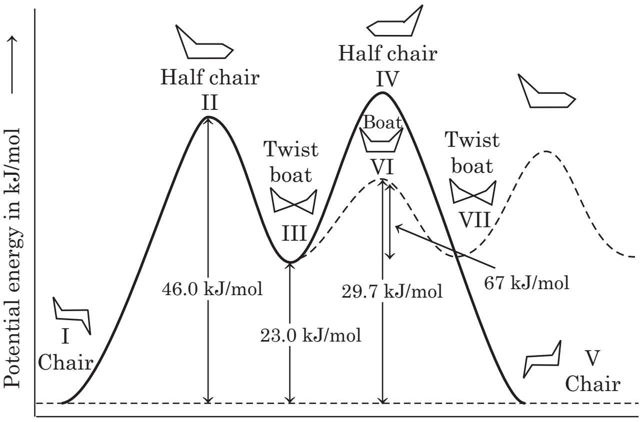
Stabilities of the Conformations of Cyclohexane

The chair conformation of cyclohexane is more stable than the boat conformation due to the following reasons

- In chair conformation, the adjacent hydrogen atoms on all the neighbouring carbon atoms are quite staggered and the force of repulsion in between them is the minimum.

  However, in the boat conformation, the adjacent hydrogen atoms on $C_2—C_3$ and $C_5—C_6$ atoms are eclipsed.
- The two hydrogen atoms bonded to the C_1 and C_4 atoms in boat conformation are quite close (distance = 183 pm) and repel each other. These are called **flag pole hydrogens.** These hydrogens are shown as H_f in the figure. Therefore, the energy of the boat conformation is more than that of chair conformation.

The energy of the boat conformation of cyclohexane is about **44 kJ mol^{-1}** more than that chair conformation. Therefore, cyclohexane exists mainly in the chair form.



Relative potential energies of the various conformations of cyclohexane

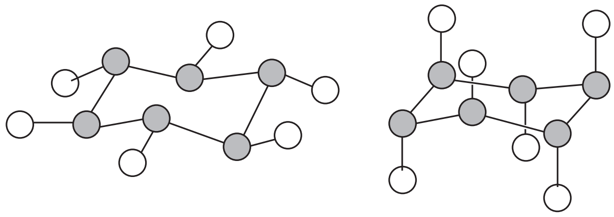
Axial and Equatorial Bonds

Let us return to the model of the chair conformation of cyclohexane. Consider that the carbon atoms lie roughly in a plane. If we look at the molecule in this way, we see that the hydrogen atoms occupy two kinds of position

(i) six hydrogens lie in the plane, while

(ii) six hydrogens lie above or below the plane. The bonds holding the hydrogens that are in the plane of the ring lie in a belt about the "equator" of the ring, and are called **equatorial bonds**.

The bonds holding the hydrogen atoms that are above and below the plane are pointed along an axis perpendicular to the plane and are called **axial bonds**. In the chair conformation each carbon atom has one equatorial bond and one axial bond. These both the bond types are shown in the figure given below.

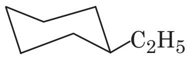


Equatorial bonds

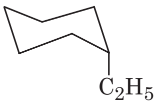
Axial bonds

Chair cyclohexane : equatorial and axial bonds

Remember The structure of cyclohexane in which two or more bulkier groups ocupy equatorial positions is more stable, than the one in which these occupy axial position, i.e.



(More stable)



(Less stable)

Example 1. *Which of these factors does not govern the stability of a conformation in acyclic compounds ?*

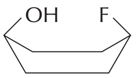
(a) Electrostatic forces of interaction **(JEE Main 2019)**

(b) Torsional strain

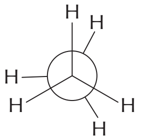
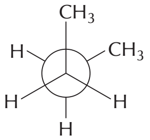
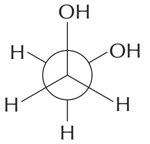
(c) Angle strain

(d) Steric interactions

Sol. (c) The four types of strains *viz*., (a) electrostatic force of attraction, (b) torsional strain, (c) angle strain, (d) steric stain, are responsible for the stability or energy barriers of conformers. In cyclic compounds, all types of strains may be present.

Compound	**Type of strains/forces**
	a + c
	a + b + c
	a + b + c + d

In a a cyclic or open-chain compounds, angle strain (c) is absent. e.g.

Compound	Types of strains/forces
	a
	$a+b$
	$a+b+d$

Alkenes

These constitute the first series of unsaturated hydrocarbons with a π-bond. These are characterised by the presence of a double bond between two adjacent carbons $\left(>C=C<\right)$. Their general formula is C_nH_{2n}. These are also called olefins (Latin, *oleum*= oil, *ficar* = to make) as their lower members form oily products on halogenation. Their main source is petroleum.

Alkenes are named by adding suffix 'ene' in the root word. These exhibit chain, position, ring-chain and geometrical isomerism. The carbon atoms of the double bond are sp^2-hybridised. The bond energy of C═C bond is **681 kJ mol^{-1}**. Also, more the number of alkyl groups attached to the double bonded carbon atoms, greater is the stability of the alkene.

Methods of Preparation

Important methods of preparation of alkenes are as follows

1. Dehydrohalogenation

Alkyl halides when treated with alcoholic KOH/Δ gives alkenes as,

$$CH_3CH_2Br \xrightarrow[\Delta]{\text{Alc. KOH}} CH_2{=}CH_2 + KBr + H_2O$$

The other reagents which can be used for E2 reactions that occur in primary alkyl halides with β-carbon is 1° or 2° are high concentrations of **NaH / Δ**, **$NaNH_2$** or **KNH_2**/ Δ and **sodium** or **potassium alkoxides** and for E1 reactions that occur in tertiary alkyl halides, secondary alkyl halides with β-carbon is 3° or 4° and primary alkyl halides whose β-carbon is 3° or 4° at room temperatures are **R_3N / NaOH**.

Features

Important facts about dehydrohalogenation reaction of alkyl halides are as follows

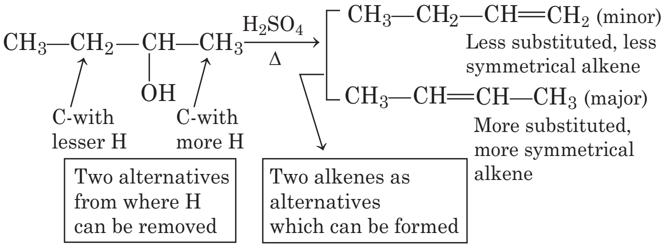
- Ease of dehydrohalogenation is 3° > 2° > 1° for alkyl halides.
- In most of the cases **Saytzeff rule** is followed : This rule was given by **A.M. Zaitsev** of university of Kazan (Russia).
- The rule originally was stated as "*in elimination reactions, when alternatives are available, then the* H-*atom will be removed from that* C-*atom containing lesser number of hydrogens*".
- This simply indicates that the C-atom which is already poor in hydrogen atoms, becomes more poor.
- Two different expressions of this rule were also developed later on, which are

  In elimination reactions **"when alternatives are available".**

  (i) More substituted alkene will be preferred.

  (ii) More stable, i.e. symmetrical alkene will be preferred.

  All the 3 statements of this rule can be visualised in following figure.



2. Dehydration of Alcohols

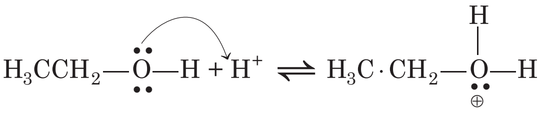
Alcohols when treated with concentrated sulphuric acid at 170°C, alkene is obtained as shown in equation below.

$$CH_3CH_2OH \xrightarrow[170^\circ C]{H_2SO_4} CH_2{=}CH_2 + H_2O$$

Mechanism

***Step* I Generation of protonated alcohol**.

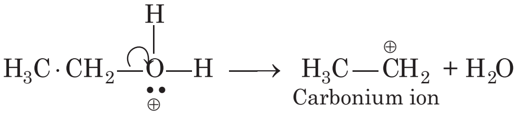
$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$



$$H_3CCH_2{-}\ddot{\underset{\cdot\cdot}{O}}{-}H + H^+ \rightleftharpoons H_3C\cdot CH_2{-}\underset{\oplus}{\overset{H}{\overset{|}{O}}}{-}H$$

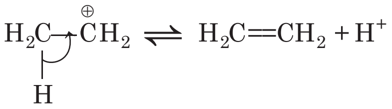
Protonated alcohol

***Step* II Generation of carbonium ion**



$$H_3C\cdot CH_2{-}\underset{\oplus}{\overset{H}{\overset{|}{O}}}{-}H \longrightarrow H_3C{-}\overset{\oplus}{C}H_2 + H_2O$$

***Step* III Removal of proton**

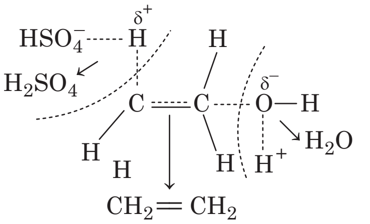


$$\underset{H}{\underset{|}{H_2C}}{-}\overset{\oplus}{C}H_2 \rightleftharpoons H_2C{=}CH_2 + H^+$$

Features

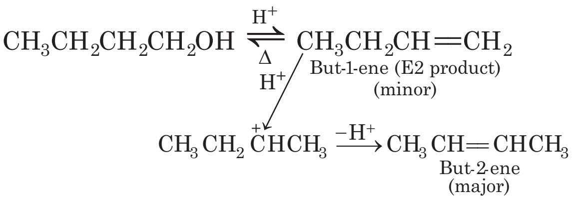
Important facts related to dehydration are as

- 1° alcohols follow E2 mechanism while 3° alcohols follow E1 mechanism, 2° alcohols may follow either E2 or E1 mechanism however, E1 is preferred.
- Infact above mechanism also proceeds through the formation of following transition state, i.e. E2 mechanism.
- Ease of dehydration is $3° > 2° > 1°$ because of the involvement of carbocation intermediate.
- The reaction is also possible with Al_2O_3 350°C, P_2O_5, H_3PO_4, $POCl_3$ in pyridine.



Product Yield *vs* E2 Mechanism

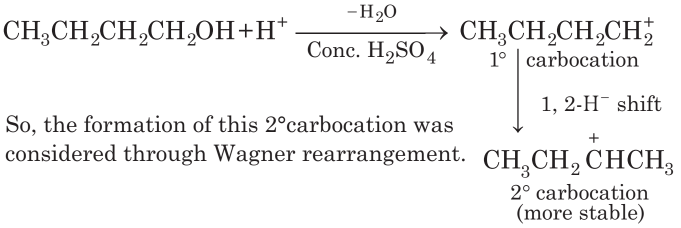
Although, primary alcohols follow E2 mechanism but it is found that the yield of product is very less. The reason is the presence of H^+ ion in the reaction which works as an electrophile for alkene formed and responsible for modification or reversibility of reaction as seen in following example of butan-1-ol.



Major product (but-2-ene) formed after reaction modificationdue to H^+.

Previously, it was throught that is due to **retropinacol** or **Wagner** rearrangement.

The rearrangement in open chain compounds in which shifting of $C_6H_5^-$ (Ph^-), CH_3^-, H^- takes place to give more stable carbocation and also the more stable product, is called retropinacol or Wagner rearrangement. Shifting of groups in this takes place in the following sequence $C_6H_5^- < CH_3^- < H^-$. An example of such rearrangement is



$$CH_3CH_2CH_2CH_2OH + H^+ \xrightarrow[\text{Conc. } H_2SO_4]{-H_2O} \underset{1° \text{ carbocation}}{CH_3CH_2CH_2\overset{+}{C}H_2} \xrightarrow{1,\,2\text{-}H^- \text{ shift}} \underset{\substack{2° \text{ carbocation} \\ \text{(more stable)}}}{CH_3CH_2\overset{+}{C}HCH_3}$$

So, the formation of this 2°carbocation was considered through Wagner rearrangement.

However, now it is clear that formation of this carbonium ion in the reaction is due to the attack of H^+ on But-1-ene formed *via* transition state formation, i.e.

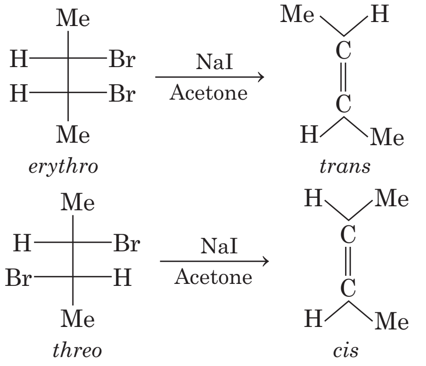
$$CH_3CH_2CH=CH_2 \xrightarrow{H^+} CH_3CH_2\overset{+}{C}HCH_3$$

3. Dehalogenation

When heated with a dehalogenating agent like zinc dust. Only *vicinal* dihalides (in which the halogen atoms are attached to two successive C-atoms) give alkenes while *geminal* dihalides (in which the halogen atoms are attached to the same C-atoms) give alkynes. The equation of reaction is given below.

$$\underset{vic\text{-dihalide}}{BrCH_2—CH_2Br} + Zn \xrightarrow{C_2H_5OH} CH_2=CH_2 + ZnBr_2$$

Other reagents that can be used for dehalogenation are **NaI in acetone** and **Na in dry ether** (like Wurtz reaction). In the case of Na in dry ether elimination is associated with coupling and it is useful only for elimination from *gem*-dihalides. The elimination is **stereo-selective,** i.e. *anti* predominantly.



erythro *trans*

threo *cis*

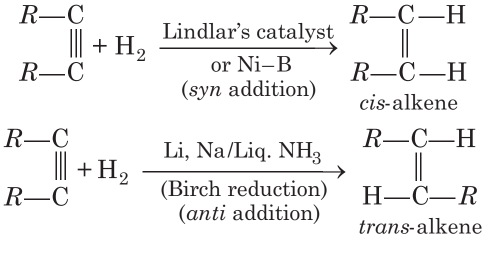
If sodium metal is used in place of zinc, the higher alkenes can be obtained.

4. Controlled Hydrogenation

Alkynes on hydrogenation with **Lindlar's catalyst** or **nickel boride** (P-2 catalyst) or with Na or Li in liquid ammonia, give alkenes.

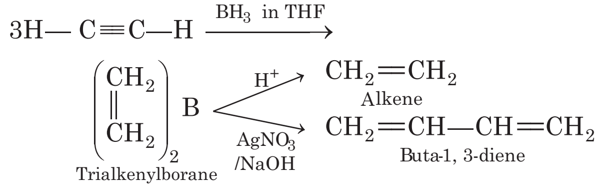
Lindlar's catalyst is Pd *poisoned with* $\mathbf{BaSO_4}$ *or* $\mathbf{CaCO_3}$ *in quinoline or xylene.* The addition is stereo-selective and *syn* in the case of Lindlar's catalyst or nickel boride (P-2 catalyst). However, *anti*-addition is seen in the case of Na or Li in liquid NH_3 **Birch reduction**.

The *syn* and *anti* additions can be seen as,



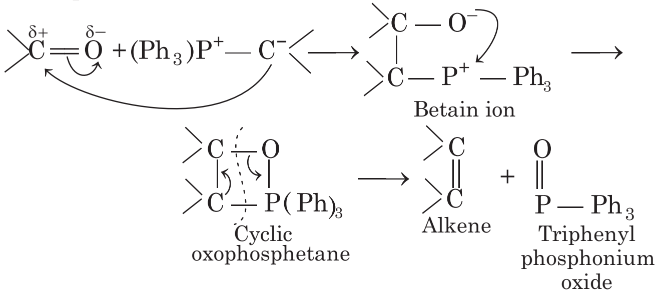
5. Hydroboration

Hydroboration of alkynes gives alkenes and conjugated dienes. The equation of these reactions is shown below.



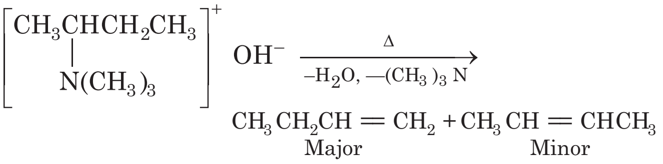
6. Wittig Reaction

In the Wittig reaction there is nucleophilic addition of triphenylphosphonium (ylide) ion to aldehyde or ketone which produces alkene

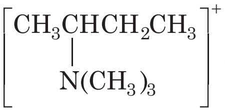


7. Pyrolysis of Quaternary Ammonium Compounds

The opposite results to Zaitsev rule were obtained by **Hofmann** while working on β-elimination in quaternary ammonium hydroxides as



$$\left[\begin{array}{l}CH_3CHCH_2CH_3\\ \quad\;|\\ \quad N(CH_3)_3\end{array}\right]^+ OH^- \xrightarrow[-H_2O,\ -(CH_3)_3N]{\Delta} \underset{\text{Major}}{CH_3CH_2CH=CH_2} + \underset{\text{Minor}}{CH_3CH=CHCH_3}$$



$$\left[\begin{array}{l}CH_3CHCH_2CH_3\\ \quad\;|\\ \quad N(CH_3)_3\end{array}\right]^+$$

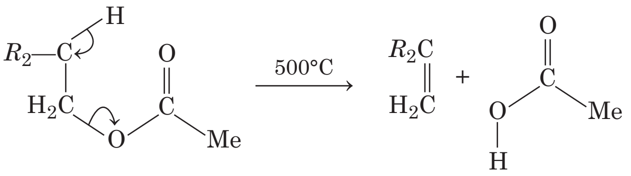
X^- also gives the similar results.

He explained the difference in results on the basis of presence of bulky $N(CH_3)_3$ group in the compound. This group destabilises transition state in second case. The findings of Hofmann are considered as **Hofmann rule.**

8. By Pyrolysis of Esters

Esters on thermal decomposition give alkenes.

The equation of complete reaction is given below.

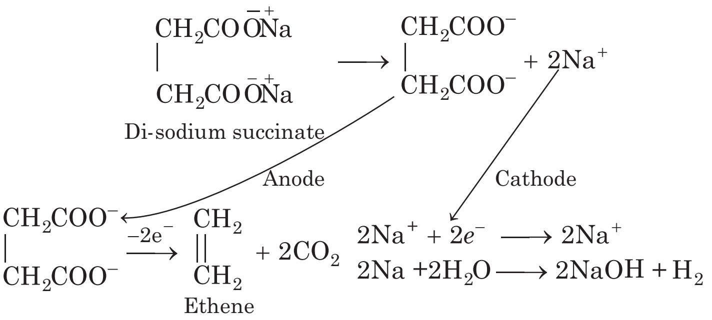


Pyrolysis of alkanes also gives alkenes in the product mixture.

9. Kolbe's Electrolytic Method

Electrolysis of sodium or potassium salts of dicarboxylic acid, e.g. $\begin{array}{l}CH_2COO^-K^+\\ |\\ CH_2COO^-K^+\end{array}$ (potassium succinate) produces alkene, $\begin{array}{c}CH_2\\ ||\\ CH_2\end{array}$

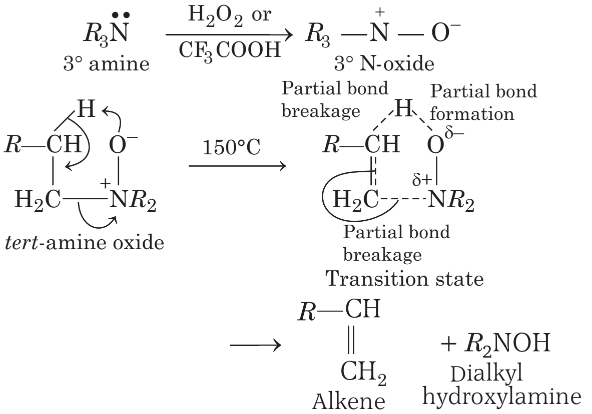
The complete equation is given below



The method is an extension of **Kolbe's method** for the preparation of alkanes.

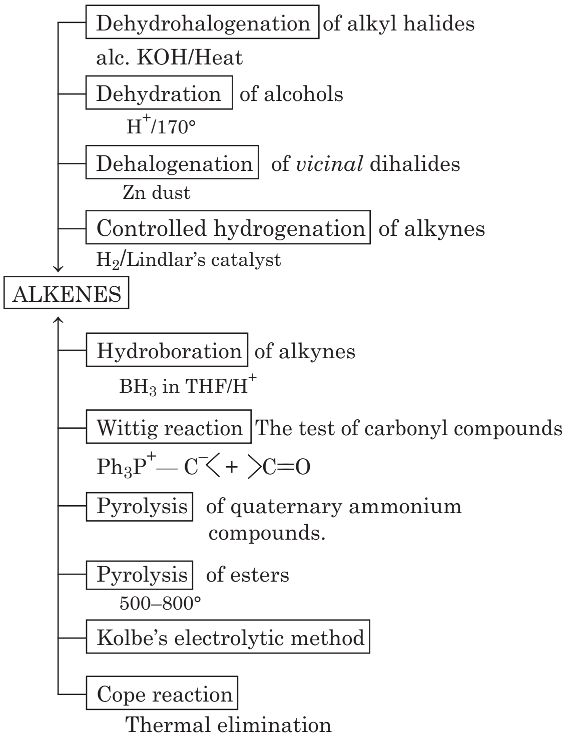
10. Cope Reaction

When a 3° amine oxide containing atleast one β-hydrogen is heated at 150°C, it decomposes to form an alkene and a derivative of hydroxylamine.



This reaction may also be carried out in dimethyl sulphoxide or THF at room temperature.

Summary of preparation methods of alkenes is given below.



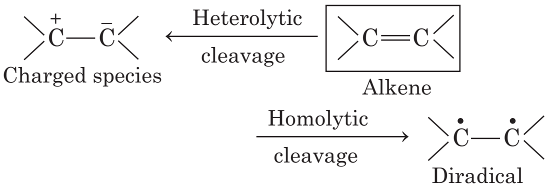
Flow chart showing methods of preparation of alkenes

Physical Properties

- First three alkenes are gases, next 14 are liquids and rest are solids.
- All alkenes are colourless and odourless except ethene which has pleasent odour.
- All alkenes are lighter than water and their density gradually increases with rise in molecular mass.
- Alkenes also show same trend of boiling and melting points as alkanes but geometrical isomers behave differently like *cis*-alkenes have higher boiling point as compared to their *trans*-isomers. However, melting point is higher in case of *trans*-isomers.
- In general, *trans*-form has almost zero dipole moment and thus, exhibits weaker intermolecular attractions.
- Alkenes are insoluble in water but soluble in non-polar solvents like benzene, ether, CCl_4 etc.
- The stability of alkenes is estimated on the basis of **number of hypercojugative structures** that can be formed.
- The more hyperconjugative structures the more stable is the alkene.
- **Heat of hydrogenation** is also an index of stability. The lower the heat of hydrogenation of an alkene, the more stable is the alkene.

Chemical Properties

Alkenes generally undergo **electrophilic addition** reactions because of the presence of a double bond. The double bond contains a strong σ and a weaker π-bond) π electrons of this bond are easily polarisable being loosely held. These electrophilic addition reactions involve cleavage of a π-bond and formation of two new σ-bonds. The cleavage may be homolytic or heterolytic as shown below.



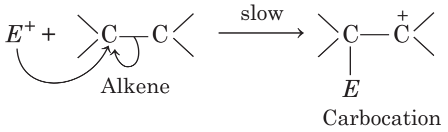
In polar solvents, at low temperature addition proceeds by ionic mechanism , whereas in the presence of light or non-polar solvents at high temperature, the addition occurs by free radical mechanism.

The steps involved in ionic mechanism are as follows

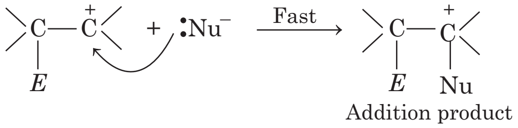
***Step* I** Ionisation of reagent to generate electrophile and nucleophile

$$E\text{—}Nu \longrightarrow E^+ + :Nu^-$$

***Step* II** Attack of electrophile on alkene



***Step* III** Attack of nucleophile to give addition product.



Since, electrophile attacks first, the reactions are called electrophilic addition reactions.

Stereoselective and Stereospecific Additions

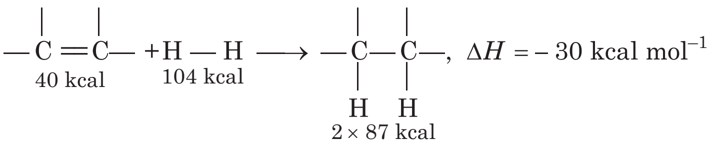
From the stereochemistry point of view, electrophilic addition reactions can be **stereoselective** (i.e. one stereoisomer predominates over the other) or **stereospecific** (i.e. a single product is formed from both the geometrical isomers). Stereoselective reactions usually proceed through *syn* and *anti* addition. So, while going for stereoselective reactions always remember

(i) *cis* alkene + *anti* addition ⟶ Racemic mixture
(ii) *trans* alkene + *anti* addition ⟶ *meso* form
(iii) *cis* alkene + *syn* addition ⟶ *meso* form
(iv) *trans* alkene + *syn* addition ⟶ Racemic mixture

1. Addition of Hydrogen or Hydrogenation

This reaction involves the breaking of a π-bond (about 40 kcal) and a H—H bond (104 kcal), alongwith the formation of two C—H bonds (average value 87 kcal).

The net result is the evolution of about 30 kcal of heat, which is called **heat of hydrogenation**.



$$—\underset{40\text{ kcal}}{C=C}— + \underset{104\text{ kcal}}{H—H} \longrightarrow —\underset{2\times 87\text{ kcal}}{\underset{H\ \ H}{C—C}}—, \quad \Delta H = -30\text{ kcal mol}^{-1}$$

For most of the alkenes, the heat of hydrogenation is approximately 30 kcal.

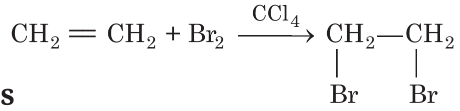
Features

- **Wilkinson catalyst, $RhCl[(C_6H_5)_3P)_3]_3$** is one of the best catalysts for hydrogenation. Other good catalysts are Raney Ni, Na in liquid NH_3 etc.
- **Birch reagent,** i.e. Na in liquid NH_3 with C_2H_5OH or CH_3OH works only on terminal double bonds in aliphatic alkenes.

  In this reagent, Na works as electron donor which liquid NH_3/alcohols work as proton donors.

2. **Addition of Halogens** (Halogenation)

Alkenes (and also alkynes) form addition products with Cl_2 and Br_2. Bromine water is decolourised by unsaturated hydrocarbons hence, it is also used as **test of unsaturation**.



$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2}—\underset{Br}{CH_2}$$

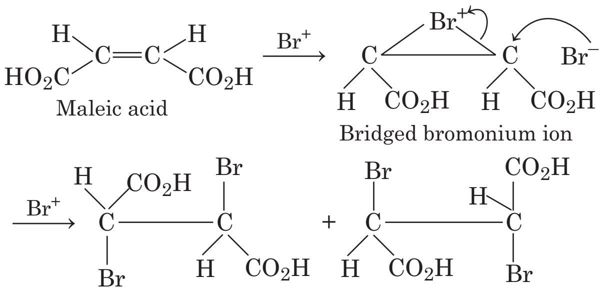
Features

- The reaction is *stereo-selective* and predominantly *anti* addition occurs, i.e. Br atoms are added on the opposite side of the plane of the molecule.
- Relative rates of reaction of alkene with Br_2 / CH_3OH are in order of ethene
  < 1-butene < *trans*-2-butene < 2-methyl-1-butene
  < 2,3-dimethyl-2-butene.

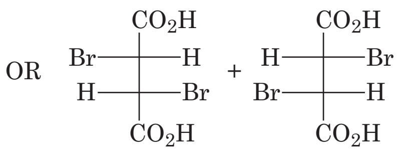
Mechanism

The reaction proceeds through the formation of a bridged bromonium ion which is more stable than carbocation followed by attack by the bromide ion.

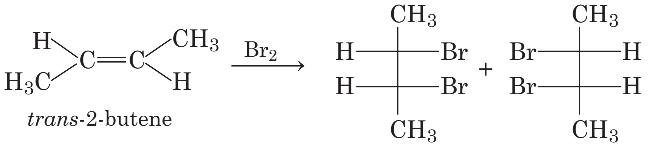
$$Br_2 \rightleftharpoons Br^+ + Br^-$$



(±)
Racemic mixture



The attack occurs because the positively charged bromine is very electronegative and readily accepts an electron pair. With *trans*-2-butene, product of Br_2 addition is optically inactive due to the formation of symmetric *meso* compound.



Identical (*meso*)

3. **Reaction with Hydrogen Halides**

The addition of **halogen acids** is frequently carried out by passing dry gaseous halogen acids in moderately polar solvent. In the case of asymmetric alkenes, reaction occur as per **Markownikoff rule.** Here, ionic mechanism is followed.

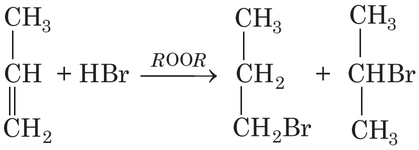
The only exception is addition of HBr in the presence of organic peroxide (Kharasch effect) where free radical mechanism is followed.

The order of stability of carbocations is

$$3° > 2° > 1° > \overset{\oplus}{C}H_3.$$

This rule and its working mechanism is already discussed in last chapter.

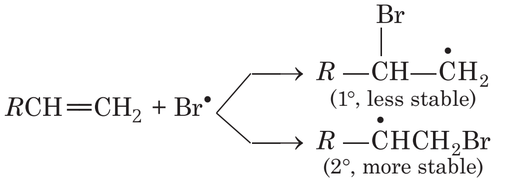
The above rule is not followed if HBr is added to an asymmetrical alkene in the presence of *R*OO*R* (peroxide) as



$$CH_3CH=CH_2 + HBr \xrightarrow{ROOR} \underset{\text{Major}}{CH_3CH_2CH_2Br} + \underset{\text{Minor}}{CH_3CHBrCH_3}$$

The main responsible factor here is organic peroxide which dissociates into free radicals and modifies the electrophilic addition to free radical addition

$$ROOR \longrightarrow 2RO^\bullet$$
$$RO^\bullet + HBr \longrightarrow R—OH + Br^\bullet$$



Now, here as the 2° free radical is more stable thus it is responsible for major product formation.

$$R—\dot{C}HCH_2Br + HBr \longrightarrow RCH_2CH_2Br + Br^\bullet$$

This modified case of HBr addition in the presence of peroxide is called Kharasch effect and considered as an example of anti-Markownikoff addition as it follows an opposite course to that suggested by Markownikoff. The rule is also applicable on alkynes.

HF, HCl and HI does not give such modified reaction because

- The bonds between halogen and hydrogen is very strong in HF and HCl that's why $RO^{\bullet}$, free radical is unable to break them homolytically. Thus, reaction procedure is not modified.
- In the case of HI, although $RO^{\bullet}$ free radical produces homolytic cleavage but $I^{\bullet}$, free radical formed has more tendency to form I_2 as compared to form free radical of carbon.

4. **Reaction with Water** (Hydration)

A water molecule is added when alkene it treated with dil. H_2SO_4, or subjected to hydroboration or oxymercuration-demercuration reaction.

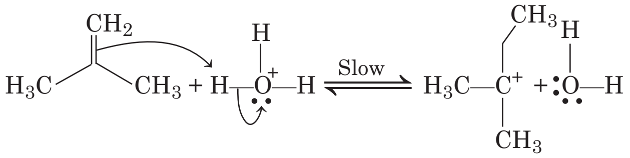
(i) **With dil. H_2SO_4** The reaction takes place as

$$CH_2 = CH_2 \xrightarrow{\text{Dil. } H_2SO_4} CH_3 - CH_2HSO_4 \xrightarrow[\text{Warm}]{H_2O} CH_3CH_2OH$$

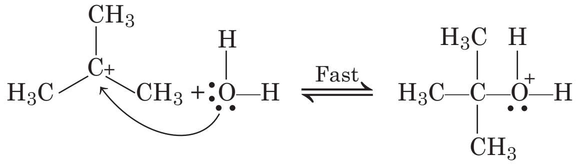
The reaction follows Markownikoff's addition.

Mechanism

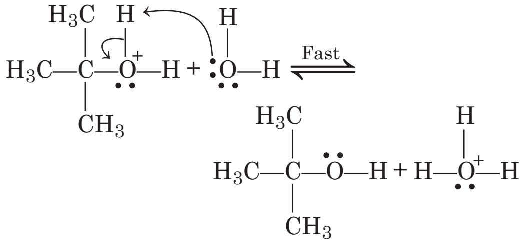
***Step* I** The alkene accepts a proton to form more stable 3° carbocation.



***Step* II** The carbocation reacts with a molecule of water to form a protonated alcohol.



***Step* III** The transfer of proton to a molecule of water leads to the product as.



(ii) In hydroboration when trialkyl borane reacts with H_2O_2, alcohols are produced as

$$CH_2{=}CH_2 + BH_3 \longrightarrow (CH_3CH_2)_3B \xrightarrow{H_2O_2} 3CH_3CH_2OH + H_3BO_3$$

This reaction involves following two steps

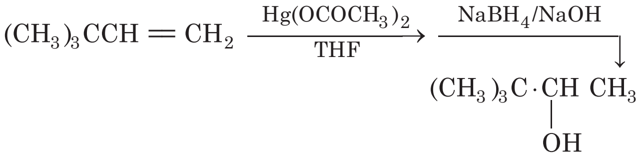
(a) *syn* addition of borane to double bond.

(b) oxidative hydrolysis to get alcohol.

(iii) **Oxymercuration-demercuration** Mercuric acetate (in THF) followed by reduction with $NaBH_4$ /NaOH can also be used for the purpose. The reaction is called **oxymercuration- demercuration reaction** and proceeds through cyclic transition state formation involving mercury metal.

It is contrary to hydration with H_2SO_4 where carbonium ion is produced.

Remember If the carbonium ion is intermediate then there always exists a possibility of rearrangement for stability sake while such a possibility is not seen in the case of **oxymercuration demercuration**. This simply means in this reaction the addition is exactly localised. The equation of reaction is shown below,



$$(CH_3)_3CCH = CH_2 \xrightarrow[\text{THF}]{Hg(OCOCH_3)_2} \xrightarrow{NaBH_4/NaOH} (CH_3)_3C\cdot\underset{\displaystyle OH}{\underset{|}{CH}}\,CH_3$$

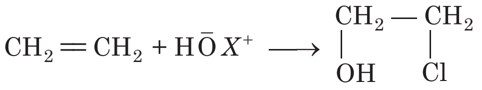
In this reaction, mercury diacetate first adds across the double bond in an oxymercuration step. Water then displaces the mercury acetate group.

5. **Reaction with Hypohalous Acid** (HOX)

The hypohalous acid breaks as OH^- and X^+ and **it is the halonium ion (X^+)** which initiate the attacks on π-bond. The products are halohydrins.

These halohydrins are the compounds containing —OH and —X groups at successive C-atoms.

Reaction is **stereo-selective** (*anti*-addition is seen) and its equation is given below.



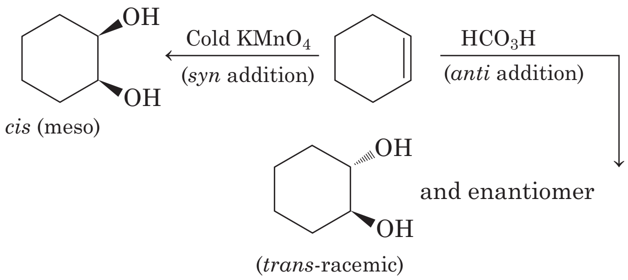
$$CH_2 = CH_2 + H\bar{O}X^+ \longrightarrow \underset{\displaystyle OH}{\underset{|}{CH_2}} - \underset{\displaystyle Cl}{\underset{|}{CH_2}}$$

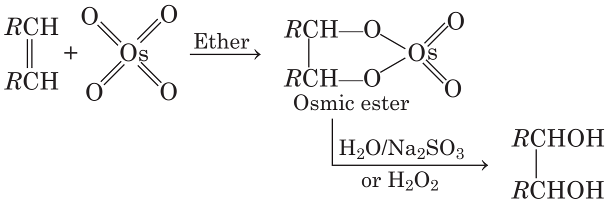
Markownikoff's rule is followed in the case of unsymmetrical alkenes.

The order of reactivity of different X_2/ H_2O is $Cl_2 / H_2O > Br_2 / H_2O > I_2 / H_2O$.

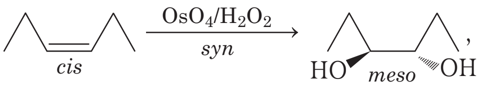
6. **Hydroxylation** (Insertion of — OH Group)

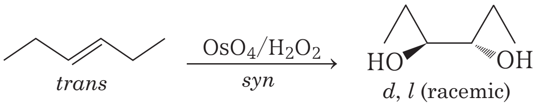
- Hydroxylation with **Baeyer's reagent** ($KMnO_4$/NaOH or $KMnO_4$ cold or $KMnO_4$) and OsO_4 is *syn*-addition (stereo-selective) while with peroxyacids it is an *anti*-addition.
- Infact with peroxy acids oxiranes are produced in the beginning and peroxyformic acid (HCOOOH) is strong enough to break them into glycols. That means with rest peroxyacids oxiranes are the last product.

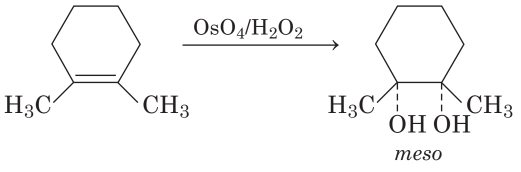




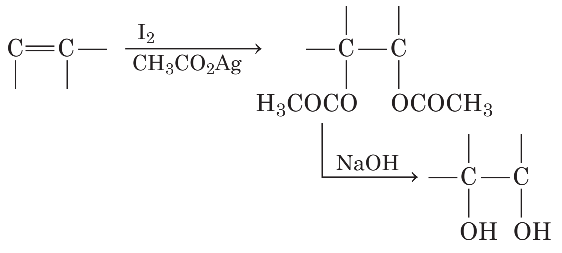
Like $KMnO_4$, in this case also, addition is *syn*.





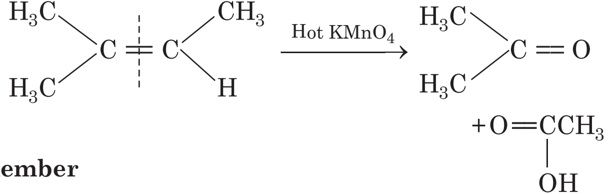


- I_2 with silver acetate can also be used as hydroxylating agent and in this case also the addition is of *syn* type.



7. **Oxidation by Hot or Acidic $KMnO_4$**

With hot or acidic $KMnO_4$, complete cleavage occurs at $\rangle C{=}C\langle$ bond resulting to acids or ketone as,



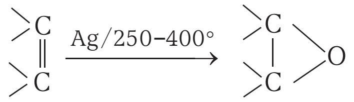
Remember

(i) During oxidation of alkene with hot $KMnO_4$.
- Both the C—C bonds are oxidised.
- All the C—H bonds are oxidised.

(ii) If HCOOH is formed in the above cleavage, it is further oxidised to CO_2.

7. **Catalytic Oxidation**

This reaction produces cyclic ethers as,



8. **Wacker's Process**

In this process alkene is oxidised by treating it with Pd and $CuCl_2$ at 50°C, e.g.

$$\underset{\text{Ethene}}{H_2C=CH_2} + PdCl_2 + H_2O \xrightarrow{50°C} \underset{\text{Acetaldehyde}}{CH_3CHO} + Pd + 2HCl$$

$PdCl_2$ is produced by the reaction of Pd and $CuCl_2$ as,

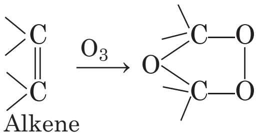
$$\left[\begin{array}{r} Pd + 2CuCl_2 \longrightarrow PdCl_2 + Cu_2Cl_2 \\ Cu_2Cl_2 + 2HCl + 1/2\,[O]_2 \longrightarrow 2CuCl_2 + H_2O \end{array}\right]$$

With propene, acetone is formed.

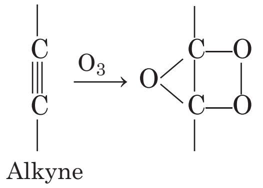
$$\underset{\text{Propene}}{CH_3CH=CH_2} + PdCl_2 + H_2O \longrightarrow \underset{\text{Acetone}}{CH_3COCH_3} + Pd + 2HCl$$

10. **Ozonolysis**

Ozonolysis is oxidation with O_3, i.e. ozonide formation followed by its hydrolysis. In ozonide formation two bonds between carbon atoms are used as,



Similarly,



Features

The normal products of this reaction are carbonyl compounds which are formed if hydrolysis is carried out in the presence of mild reducing agents like Zn / CH_3COOH. This cancels out the oxidising tendency of H_2O_2 formed as the by product of this reaction.

Other hydrolysis may be of oxidative or reductive type

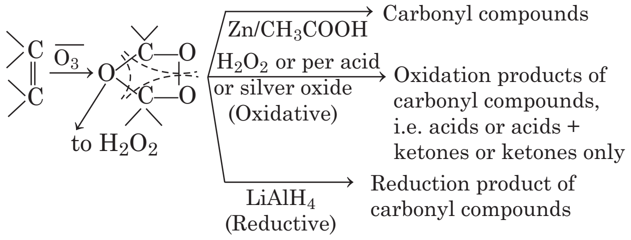
(i) The **oxidative type** hydrolysis results in oxidation products of carbonyl compounds, i.e. acids.

It occurs in the presence of oxidising agents like silver oxide or peroxy acids.

- H_2O_2 produced may also auto-oxidise the products.
- Among the carbonyl compounds, ketones are not easily oxidised. Thus, we may get either only **acids** or **acid + ketones** or only **ketones** as the product of *oxidative hydrolysis*.

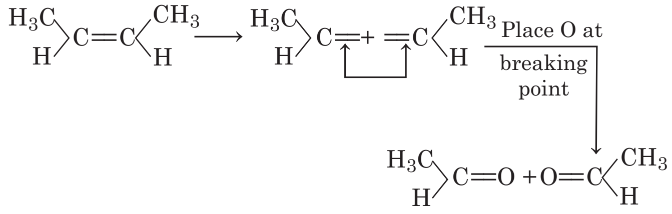
(ii) The hydrolysis may be **reductive type** also with reagents like $LiAlH_4$ (strong reducing agents) and results to primary and secondary alcohols.

These are the reduction products of carbonyl compounds.

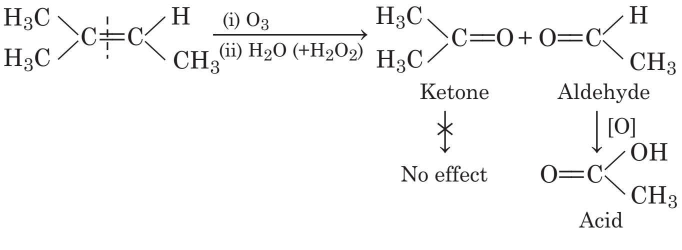


Tips to Solve Questions Related to Ozonolysis

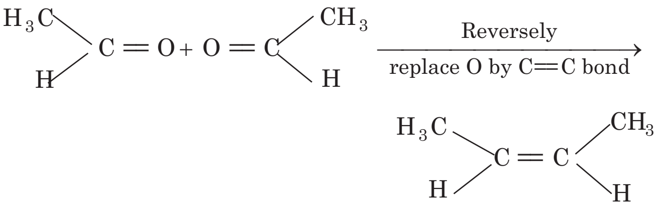
- To determine product by ozonolysis of alkenes, break C=C bond and place oxygen at breaking point



- If the ozonide is hydrolysed without any reagent, H_2O_2 is formed as a by product. Under these conditions (or H_2O_2 is added from outside), aldehydes are converted into carboxylic acids, but ketones remain unaffected.



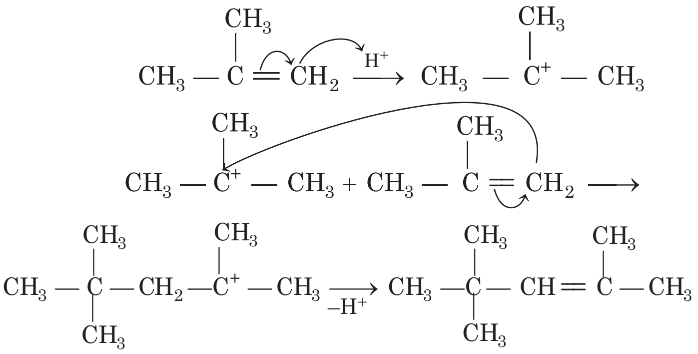
- To decide the structure of alkene from ozonolysis products, bring the products together in such a way that their O atoms come face to face. Then replace these-O atoms by C=C bond. Thus,



11. Dimerisation

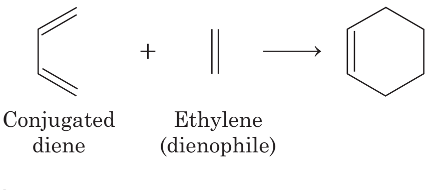
Alkylated alkenes show dimerisation like processes in the presence of protonating agents at elevated temperatures. The reaction proceeds through carbonium ion formation. This ion on further addition eliminates H^+ to yield dimerised alkene.

Due to the presence of H^+ in the reaction yield of product is low. Thus, equatirial procedure of dimerisation looks like



12. Diels-Alder Reaction

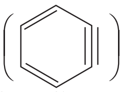
This reaction is also called **cycloaddition** as a new cycle is generated in this reaction. Basically in the reaction a conjugated diene is attacked by an olefin which is called **dienophile.** The equation of reaction is given below.

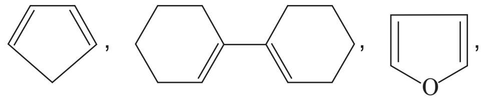


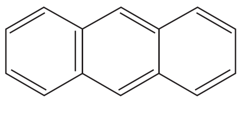
Features

No other conditions are specified but it is seen that

(i) Attachment of *electron attracting groups* in dienophile or *electron releasing groups* in conjugated diene increases the rate of reaction.

(ii) Besides olefins, **alkynes**, **benzyne**  and **allenes** $(>C{=}C{=}C<)$ can be used as dienophiles.

(iii) 

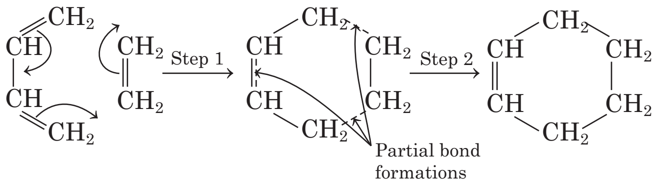
 can be used as conjugated dienes

(iv) *Benzene*, *naphthalene* and *phenanthrene* are quite unreactive and as such are not used in this reaction.

(v) The reaction is strictly **stereospecific**, i.e. orientation of groups does not change from reactants to products.

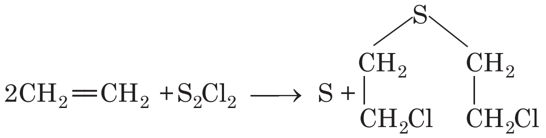
Mechanism

The mechanism of this reaction can be shown by following steps,



13. Reaction With S_2Cl_2

Ethylene on reaction with disulphur dichloride (S_2Cl_2) forms mustard gas which is highly poisonous and used in chemical warfare.

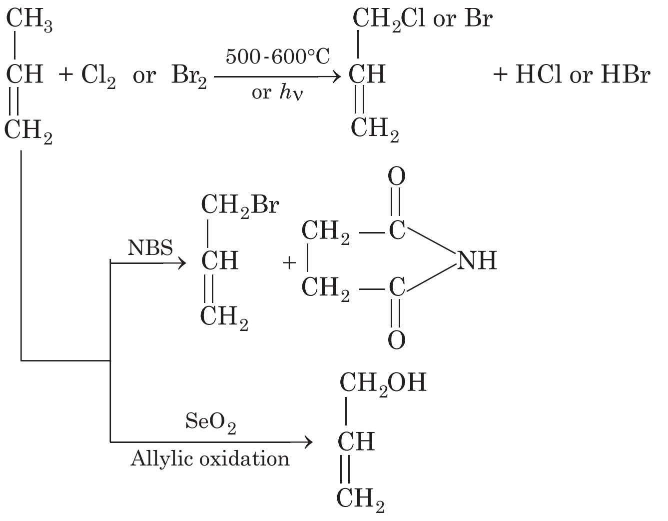


$$2CH_2{=}CH_2 + S_2Cl_2 \longrightarrow S + \underset{\text{Mustard gas}}{S(CH_2CH_2Cl)_2}$$

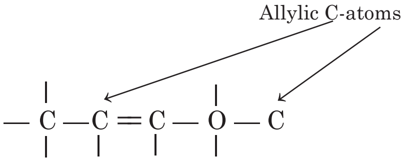
Mustard gas

14. Allylic Substitution and Allylic Oxidation

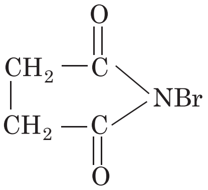
It is the only substitution reaction shown by alkenes. The possibility of this reaction aligned with hyperconjugation. The reaction looks like



The C-atoms present alternate to carbon-carbon double bond are called **allylic C–atoms**, i.e.



NBS is called N–bromo succinimide with the structure

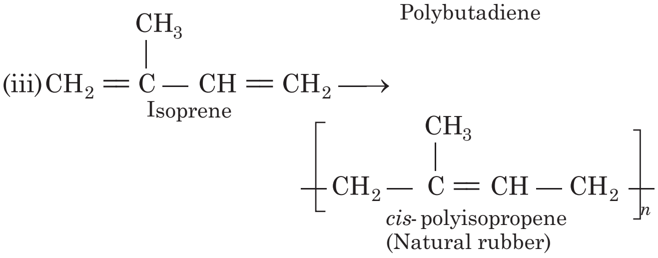


16. Polymerisation

When a large number of monomers combine to give a molecule bearing high molecular mass, called the polymer, the process is called polymerisation. The polymerisation in alkenes is shown below.

(i) $\underset{\text{Ethene}}{n\,CH_2 = CH_2} \longrightarrow \underset{\text{Polyethene}}{\left[CH_2 - CH_2\right]_n}$

(ii) $\underset{\text{Butadiene}}{CH_2 = CH - CH = CH_2} \longrightarrow \underset{\text{Polybutadiene}}{\left[CH_2 - CH = CH - CH_2\right]_n}$



(iii) $\underset{\text{Isoprene}}{CH_2 = C(CH_3) - CH = CH_2} \longrightarrow \left[CH_2 - C(CH_3) = CH - CH_2\right]_n$

cis- polyisopropene
(Natural rubber)

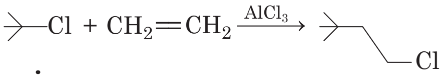
17. Combustion

The equation of generalised combustion reaction for alkenes is given below

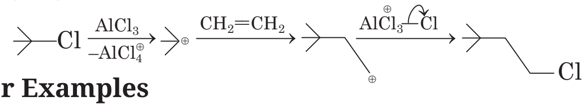
$$C_nH_{2n} + \frac{3n}{2}\,O_2 \longrightarrow nCO_2 + nH_2O + \text{Heat}$$

18. Friedel- Crafts' Reaction

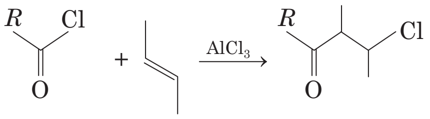
This reaction was earlier restricted to aromatic systems only. But now this can be used for the alkylation and acylation of alkenes.



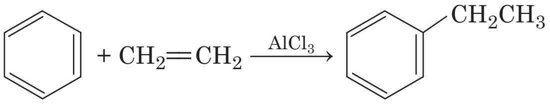
Mechanism



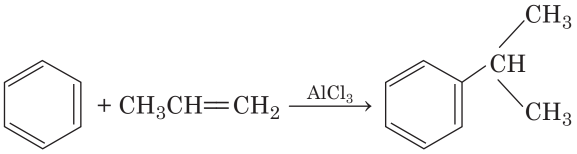
Other Examples



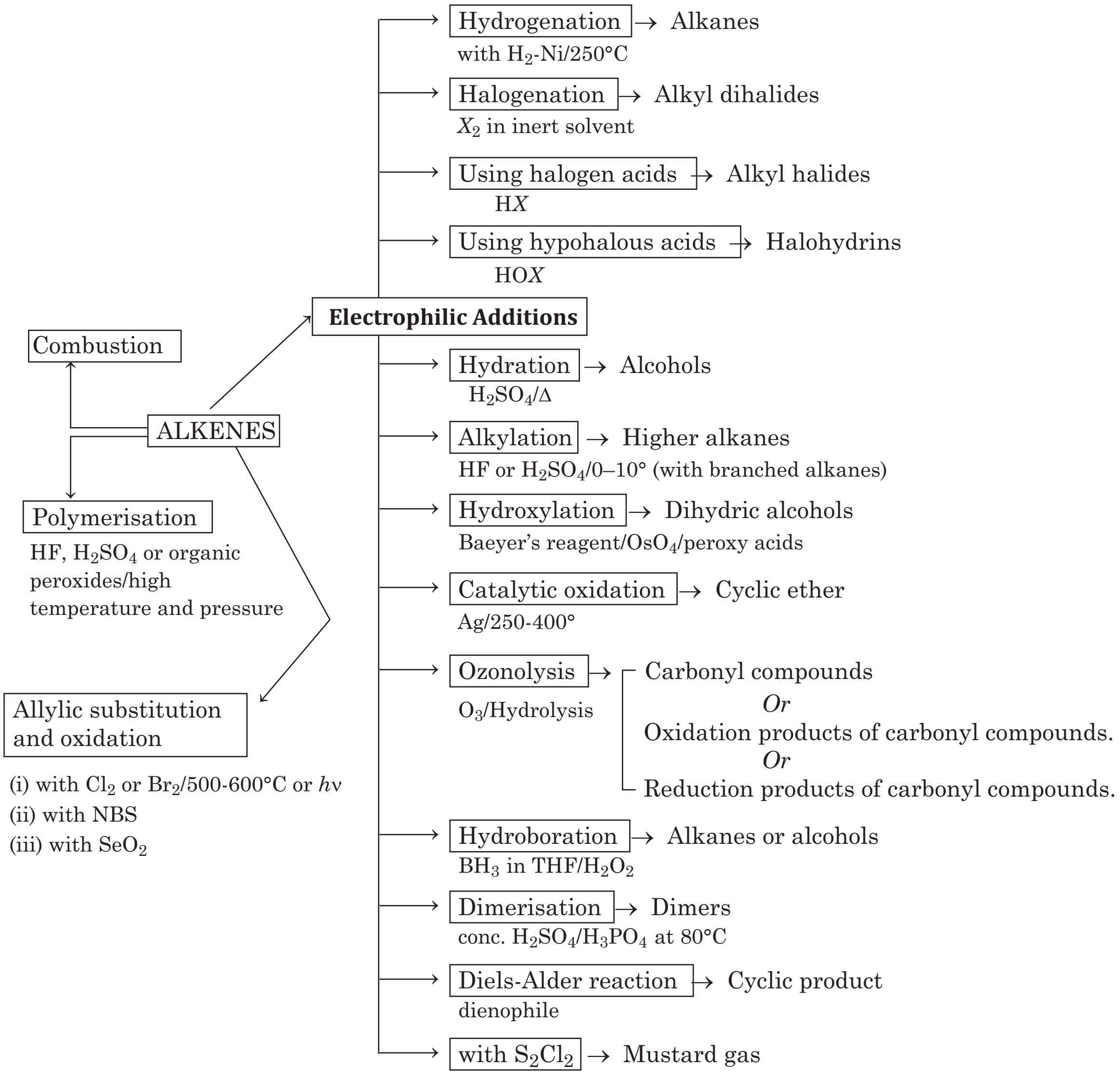
Even alkenes can be added to benzene ring also under similar conditions. e.g.



Similarly,



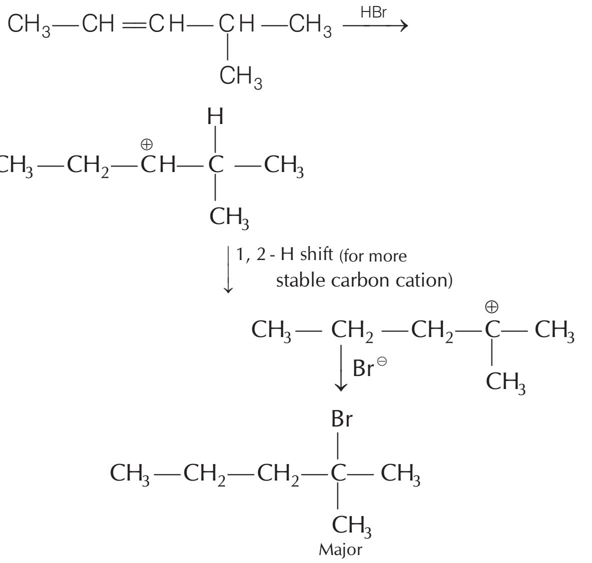
The chemical properties of alkenes can be summerised as following flow chart



Example 2. *The major product formed in the following reaction is* $CH_3CH{=}CHCH(CH_3)_2 \xrightarrow{HBr}$ ***(JEE Main 2020)***

(a) $CH_3CH(Br)CH_2CH(CH_3)_2$
(b) $CH_3CH_2CH(Br)CH(CH_3)_2$
(c) $Br(CH_2)_3CH(CH_3)_2$
(d) $CH_3CH_2CH_2C(Br)(CH_3)_2$

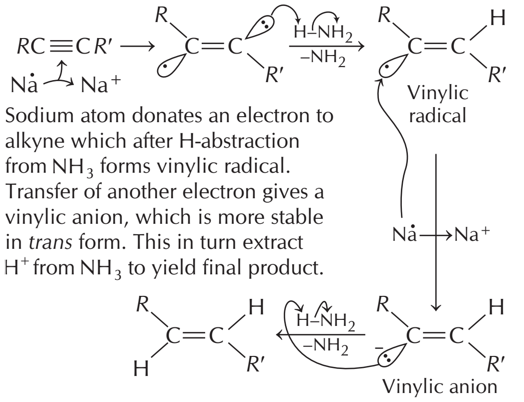
Sol. (*d*)



Example 3. *The trans-alkenes are formed by the reduction of alkynes with* ***(JEE Main 2018)***

(a) H_2-Pd/C, $BaSO_4$ (b) $NaBH_4$ (c) Na/liq. NH_3 (d) Sn-HCl

Sol. (*c*) Sodium metal in liquid ammonia reduces alkynes with anti stereochemistry to give *trans* alkenes. The reduction is selectively *anti* since the vinyl radical formed during reduction is more stable in *trans* configuration.



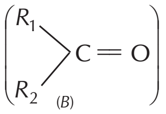
Sodium atom donates an electron to alkyne which after H-abstraction from NH_3 forms vinylic radical. Transfer of another electron gives a vinylic anion, which is more stable in *trans* form. This in turn extract H^+ from NH_3 to yield final product.

Example 4. *Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of* ***(AIEEE 2011)***

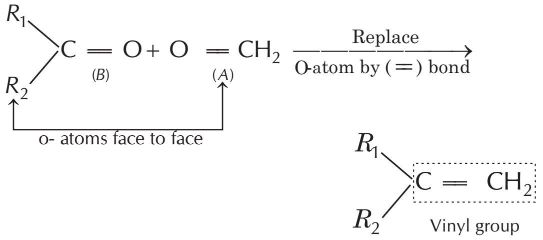
(a) two ethylenic double bonds
(b) a vinyl group
(c) an *iso* propyl group
(d) an acetylenic triple bond

Sol. (*b*) Alkenes give carbonyl compounds on ozonolysis.

$$\text{Alkene} \xrightarrow{O_3/Zn/H_2O} \underset{(A)}{HCHO} + \text{other carbonyl compound}$$



In order to determine alkene, place carbonyl compounds with their O-atom face to face. Replace O-atom by a double bond.



Alkynes

General formula of alkyne is C_nH_{2n-2}. These hydrocarbon have total 3 bonds two π-bonds and one σ-bond between two C-atoms.

These are named by adding suffix 'yne' to the root word. These exhibit chain and functional isomerism.

Methods of Preparation

General methods of preparation of alkynes are as follows

1. By Hydrolysis of Metal Carbides

The metal carbides of group II elements give alkynes on treatment with H_2O. Metal carbides are the only ionic compounds of carbon.

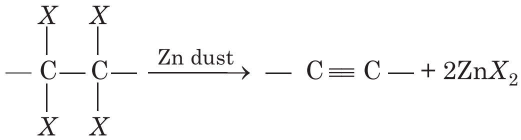
Magnesium form two types of carbides, thus, gives two alkynes.

$$\text{(i)} \left.\begin{matrix} MgC_2 \\ CaC_2 \\ SrC_2 \\ BaC_2 \end{matrix}\right\} + 2H_2O \longrightarrow C_2H_2 + \text{Metal hydroxide } [M(OH)_2]$$

$$\text{(ii)}\ Mg_2C_3 + 4H_2O \longrightarrow CH_3C{\equiv}CH + 2Mg(OH)_2$$

2. Dehalogenation

Dehalogenation of tetrahalides with Zn dust also produce alkynes:

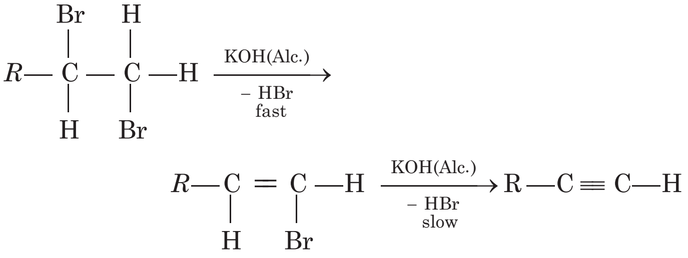


$$-\overset{X}{\underset{X}{C}}-\overset{X}{\underset{X}{C}}- \xrightarrow{\text{Zn dust}} -C\equiv C- + 2ZnX_2$$

In case of trihalides Ag is used.

$$CH\boxed{X_3 + 6Ag + X_3}CH \xrightarrow{\Delta} CH\equiv CH + 6AgX$$

3. Dehydrohalogenation of 1,2-Dihalides

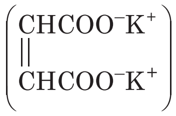


$$R-\underset{\text{H}}{\overset{\text{Br}}{\text{C}}}-\underset{\text{Br}}{\overset{\text{H}}{\text{C}}}-\text{H}\xrightarrow[\text{– HBr, fast}]{\text{KOH(Alc.)}}$$

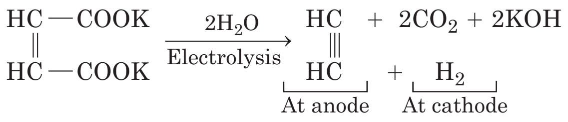
$$R-\underset{\text{H}}{\text{C}}=\underset{\text{Br}}{\text{C}}-\text{H}\xrightarrow[\text{– HBr, slow}]{\text{KOH(Alc.)}}\text{R}-\text{C}\equiv\text{C}-\text{H}$$

Here, we can also use sodamide ($NaNH_2$) instead of alcoholic KOH. With sodamide alkyne is produced directly.

4. Kolbe's Electrolytic Method



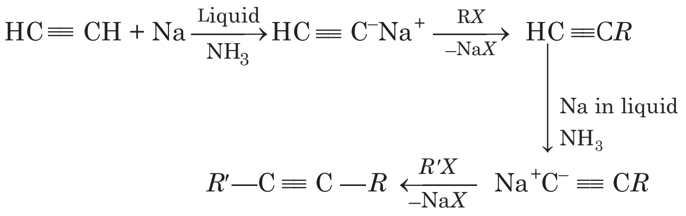
Electrolysis of potassium fumerate $\begin{pmatrix}\text{CHCOO}^-\text{K}^+\\ \|\\ \text{CHCOO}^-\text{K}^+\end{pmatrix}$ produces acetylene with the liberation of CO_2 and H_2 at anode and cathode respectively.



$$\begin{array}{l}\text{HC}-\text{COOK}\\ \|\\ \text{HC}-\text{COOK}\end{array}\xrightarrow[\text{Electrolysis}]{2\text{H}_2\text{O}}\underbrace{\begin{array}{c}\text{HC}\\ |||\\ \text{HC}\end{array}}_{\text{At anode}}+2\text{CO}_2+2\text{KOH}+\underbrace{\text{H}_2}_{\text{At cathode}}$$

5. From Sodium Acetylide

This reaction is particularly used to prepare higher alkynes from lower alkynes. Acetylides are the basic salts of acidic alkynes. These on reaction with alkyl halides.



$$\text{HC}\equiv\text{CH}+\text{Na}\xrightarrow[\text{NH}_3]{\text{Liquid}}\text{HC}\equiv\text{C}^-\text{Na}^+\xrightarrow[-\text{Na}X]{RX}\text{HC}\equiv\text{C}R$$

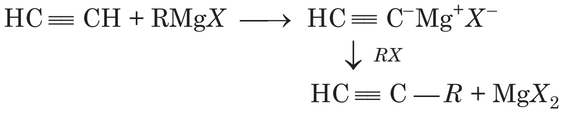
$$\text{HC}\equiv\text{C}R\xrightarrow{\text{Na in liquid NH}_3}\text{Na}^+\text{C}^-\equiv\text{C}R$$

$$R'-\text{C}\equiv\text{C}-R\xleftarrow[-\text{Na}X]{R'X}\text{Na}^+\text{C}^-\equiv\text{C}R$$

The acidic alkynes are those alkynes in which triply bonded C-atom contain atleast one replaceable H. The examples of such alkynes are acetylene and all terminal alkynes.

6. From Grignard's Reagent

Grignard reagents also help in preparing higher alkynes from lower alkynes as



$$\text{HC}\equiv\text{CH}+\text{RMg}X\longrightarrow\text{HC}\equiv\text{C}^-\text{Mg}^+X^-$$

$$\text{HC}\equiv\text{C}^-\text{Mg}^+X^-\xrightarrow{RX}\text{HC}\equiv\text{C}-R+\text{Mg}X_2$$

7. Other Methods (For Acetylene Only)

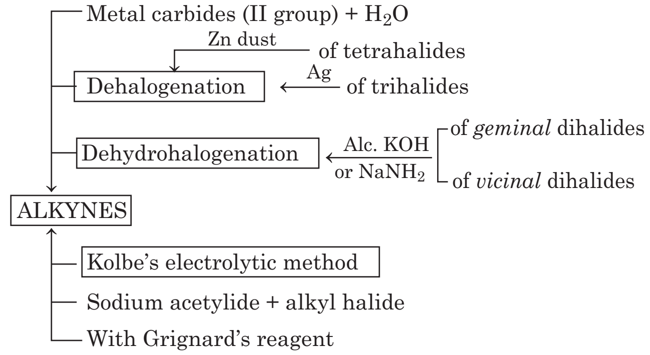
(i) By passing an electric discharge through graphite electrodes in the atmosphere of hydrogen.

$$\underset{\text{(Graphite)}}{2\text{C}}+\text{H}_2\xrightarrow{1200°\text{C}}\text{CH}\equiv\text{CH}$$

(ii) By the controlled oxidation of methane as

$$3\text{CH}_4+3\text{O}_2\xrightarrow{1500°\text{C}}\text{CH}\equiv\text{CH}+\text{CO}+5\text{H}_2\text{O}$$

The methods of preparation of alkynes can be summarised as



Flow chart showing general methods of preparation of alkynes

Physical Properties

- First three members of alkynes are gases, next eight are liquids and higher alkynes are solids.
- All alkynes are colourless and odourless except acetylene which has garlic odour.
- Melting and boiling points and densities of alkynes are slightly higher than that of corresponding alkenes and alkanes. These properties generally increases with increase in molecular mass.
- These are lighter than water and also insoluble in it. However, these are soluble in non-polar solvents like benzene, ether etc.

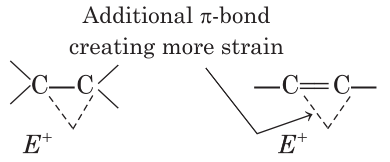
Chemical Properties

Chemical properties of alkynes are discussed below

1. Electrophilic Addition Reactions

As far as electrophilic additions are concerned, alkenes are more reactive than alkynes. The reason is more strained or less stable cyclic intermediate in the case of alkynes.

This additional strain is due to the presence of additional π-bond in alkynes as shown below.



Less strained, **more stable** cyclic intermediate of **alkenes**

More strained, **less stable** cyclic intermediate of **alkynes**

Following electrophilic additions are easily shown by alkynes

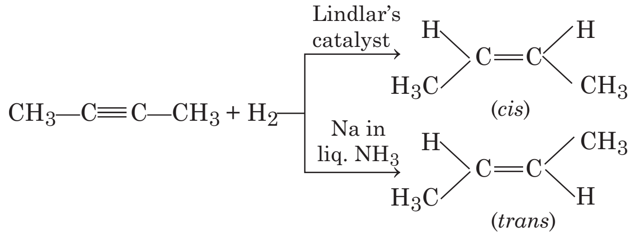
(i) **Hydrogenation** Simplest hydrogenations in alkynes are given below

$$CH_3-C\equiv CH + 2H_2 \xrightarrow{\text{Ni or Pt or Pd}} CH_3CH_2CH_3$$

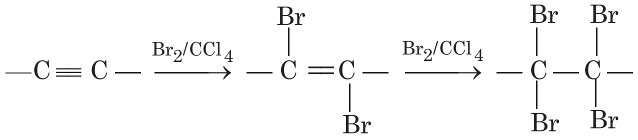
$$CH_3-C\equiv CH + H_2 \xrightarrow{\text{Lindlar's catalyst}} CH_3-CH=CH_2$$

For hydrogenation also see alkene (Chemical properties;) and alkanes (Methods of preparation).

2-butyne when reduced with Lindlar's catalyst gives nearly 100% *cis*-isomer while with Na in liquid ammonia gives nearly 100% *trans*-isomer.

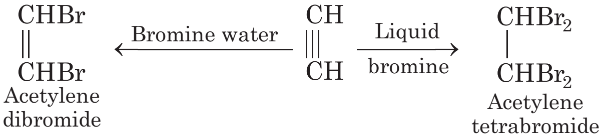


(ii) **Halogenation** With Br_2 water it is considered as test of unsaturation in alkynes also. This halogenation in alkynes is shown below.



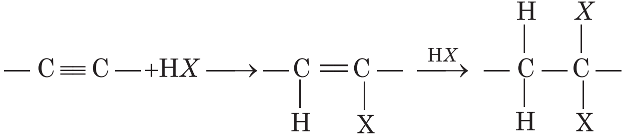
$$-C\equiv C- \xrightarrow{Br_2/CCl_4} -\overset{Br}{C}=\underset{Br}{C}- \xrightarrow{Br_2/CCl_4} -\overset{Br}{\underset{Br}{C}}-\overset{Br}{\underset{Br}{C}}-$$

Liquid bromine yields tetrabromo derivative while bromine water or Br_2/CCl_4 forms dibromo derivative.



$$\underset{\text{Acetylene dibromide}}{CHBr=CHBr} \xleftarrow{\text{Bromine water}} CH\equiv CH \xrightarrow[\text{bromine}]{\text{Liquid}} \underset{\text{Acetylene tetrabromide}}{CHBr_2-CHBr_2}$$

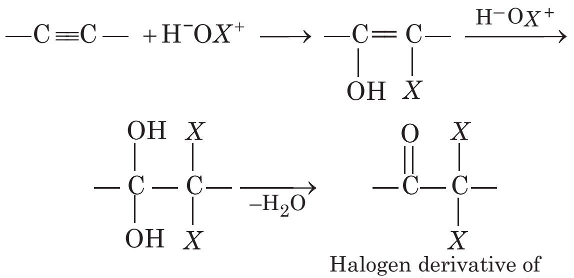
(iii) **Addition of halogen acids** As per Markownikoff addition it gives *Geminal* dihalides.



$$-C\equiv C-+HX \longrightarrow -\underset{H}{C}=\underset{X}{C}- \xrightarrow{HX} -\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-$$

(*Gem*-dihalide)

(iv) **Addition of hypohalous acids** The halohydrin formed initially which is converted into halogen derivative of carbonyl compound as shown below.

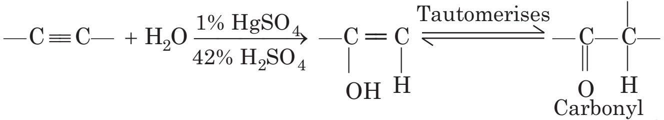


$$-C\equiv C- + H^-OX^+ \longrightarrow -\underset{OH}{C}=\underset{X}{C}- \xrightarrow{H^-OX^+}$$

$$-\overset{OH}{\underset{OH}{C}}-\overset{X}{\underset{X}{C}}- \xrightarrow[-H_2O]{} -\overset{O}{\overset{\|}{C}}-\overset{X}{\underset{X}{C}}-$$

Halogen derivative of carbonyl compound

(v) **Hydration** Hydration occurs in the presence of 1% $HgSO_4$ and 42% H_2SO_4 as,

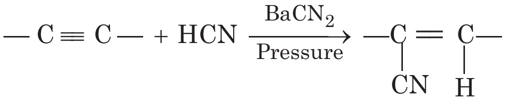


$$-C\equiv C- + H_2O \xrightarrow[42\%\ H_2SO_4]{1\%\ HgSO_4} -\underset{OH}{C}=\underset{H}{C} \xrightleftharpoons{\text{Tautomerises}} -\underset{O}{\overset{}{C}}-\overset{H}{\underset{H}{C}}-$$

Carbonyl compound

Among the alkynes **only acetylene gives aldehydes**, rest all the alkynes gives ketones as the final product of this reaction.

(vi) **Addition of HCN** Addition of HCN occurs in the presence of $BaCN_2$ under pressure as,



$$-C\equiv C- + HCN \xrightarrow[\text{Pressure}]{BaCN_2} -\underset{CN}{C}=\underset{H}{C}-$$

Acetylene gives vinyl cyanide (acrylonitrile)

$$HC\equiv CH + HCN \xrightarrow[\text{Pressure}]{BaCN_2} \underset{\text{Acrylonitrile}}{CH_2=CH-CN}$$

After addition of one mole further reaction is difficult as π-bond of $-C\equiv N$ cojugates with $>C=C<$ bond carbides.

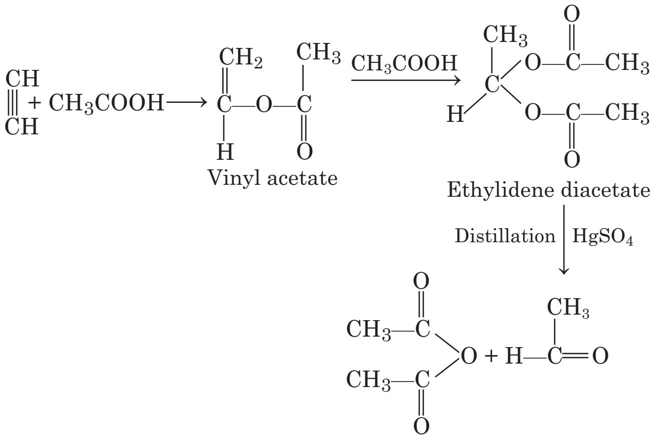
2. Some Addition Reactions Given by Acetylene Only

Only acetylene $(CH\equiv CH)$ undergoes some more addition reactions

(i) **Addition of alcohols** Ethers are produced as,

$$HC\equiv CH + ROH \xrightarrow[\substack{120\text{-}180^\circ \\ \text{high pressure}}]{KOH\text{ or }CH_3O^-K^+} \underset{\text{Alkyl vinyl ether}}{CH_2=CH-OR}$$

(ii) **Addition of CH_3COOH** It is a very useful reaction used in the preparation of acetic anhydride. Ethylidene diacetate is produced in the beginning, which on distillation in the presence of $HgSO_4$, gives acetaldehyde and acetic anhydride as

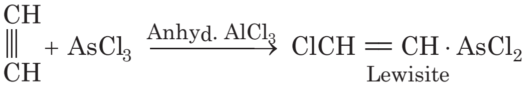


Vinyl acetate

Ethylidene diacetate

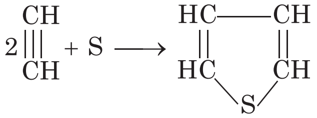
Vinyl acetate is used in the manufacture of synthetic rubber and plastic.

(iii) **Addition of arsenic trichloride** Reaction occur in the presence of $AlCl_3$ (anhydrous) to yield **lewisite** a poisonous gas. This gas was used as a chemical weapon in World War II



$$\begin{matrix}\text{CH}\\ |||\\ \text{CH}\end{matrix} + \text{AsCl}_3 \xrightarrow{\text{Anhyd. AlCl}_3} \underset{\text{Lewisite}}{\text{ClCH}=\text{CH}\cdot\text{AsCl}_2}$$

(iv) **Addition of sulphur** When acetylene is passed over heated iron pyrites (FeS_2) at 300°C, it combines with sulphur of iron pyrites to form **thiophene** as

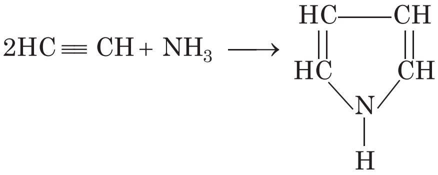


Thiophene

(v) **Addition of N_2** When an electric spark is passed through a mixture of acetylene and nitrogen, HCN is produced as

$$\text{HC}\equiv\text{CH} + \text{N}_2 \xrightarrow[\text{spark}]{\text{Electric}} 2\text{H}-\text{C}\equiv\text{N}$$

(vi) **Addition of NH_3** At high temperatures, NH_3 combines with acetylene to form **pyrrole** as,

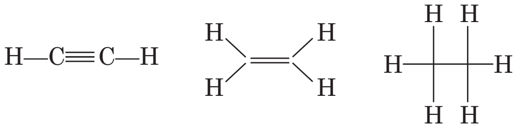


Pyrrole

2. Reactions due to Acidic Character of Alkynes

- Acetylene and terminal alkynes $\left[\begin{matrix}\text{CH}\\ |||\\ \text{CH}\end{matrix} \text{ and } \begin{matrix}\text{C}R\\ |||\\ \text{CH}\end{matrix}\right]$ are acidic in nature.
- The acidic nature of alkynes is due to *sp*-hybridisation present in them because of which the electrons of C—H bond are held more strongly towards C-nucleus.
- Alkynes like R—C≡C—R are non-acidic as these lack replaceable hydrogens in them.

The pK_a values for ethyne, ethene and ethane illustrate this point.



pK_a = 25 pK_a = 44 pK_a = 50

Due to the presence of this acidic H-atom, acetylene and terminal alkynes exhibit the following reactions.

(i) **Reaction with Na in liquid NH_3** The reaction with Na in liquid NH_3 is considered as test of acidity. H_2 is released in the reaction as

$$\text{H}-\text{C}\equiv\text{C}-R + \text{Na} \xrightarrow[\text{NH}_3]{\text{In liquid}} \text{Na}^+\text{C}^-\equiv\text{C}-R + \frac{1}{2}\text{H}_2\uparrow$$

(ii) **Reaction with Tollen's reagent** With Tollen's reagent i.e. ammoniacal $AgNO_3$, a **white precipitate**, of silver salt is obtained.

The reaction is used as a test to differentiate between acidics alkynes with rest of the alkynes.

$$\text{H}-\text{C}\equiv\text{C}-\text{H} + 2\text{AgNO}_3 + 2\text{NH}_4\text{OH} \longrightarrow \underset{\substack{\text{Silver acetylide}\\ \text{(white ppt.)}}}{\text{Ag}-\text{C}\equiv\text{C}-\text{Ag}} + 2\text{NH}_4\text{NO}_3 + 2\text{H}_2\text{O}$$

(iii) **Fehling's solution** Terminal alkynes with Fehling's solution give red precipitate of their copper salts.

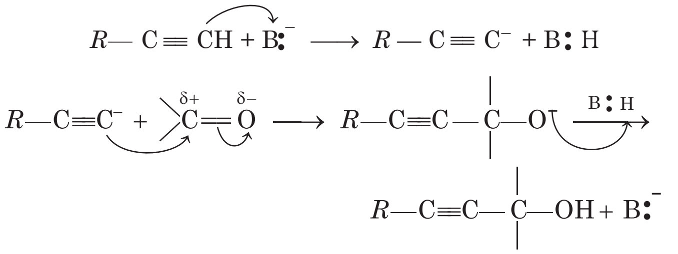
$$\text{H}-\text{C}\equiv\text{C}-\text{H} + \text{Cu}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \longrightarrow \underset{\substack{\text{Copper acetylide}\\ \text{(Red ppt.)}}}{\text{Cu}-\text{C}\equiv\text{C}-\text{Cu}} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$$

$$R-\text{C}\equiv\text{C}-\text{H} + \text{Cu}_2\text{Cl}_2 + 2\text{NH}_4\text{OH} \longrightarrow \underset{\text{Copper alkynide}}{R-\text{C}\equiv\text{C}-\text{Cu}} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}$$

These both the reactions are helpful in detecting the position of triple bond (interstitial or terminal).

3. Ethinylation

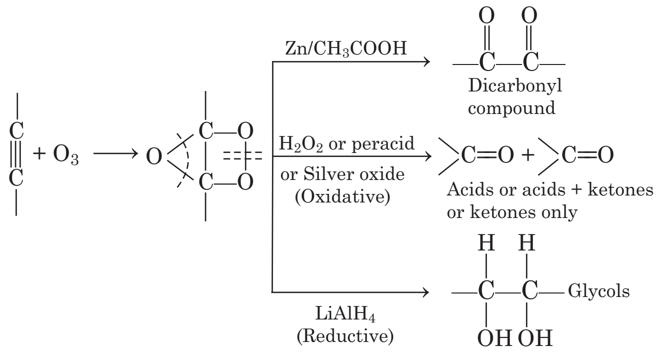
In this reaction terminal alkynes work as nucleophile, thus add to $>\text{C}=\text{O}$ group through nucleophilic addition, in the presence of base. Summerised mechanism of the reaction is given below.



Here, $\text{B}\mathbf{:}^-$ is a base. The reaction is seen as a modification of **aldol condensation.**

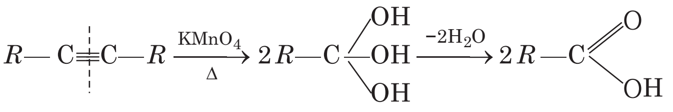
4. Ozonolysis

The ozonolysis in the case of alkynes gives following results

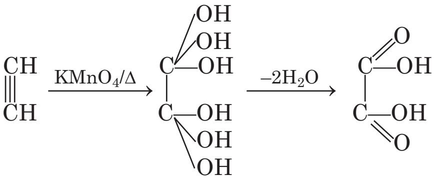


5. Oxidation with $KMnO_4$

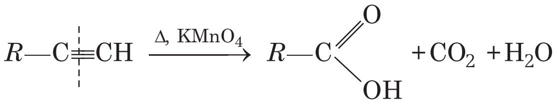
Oxidation with hot $KMnO_4$ oxidises both C—C and C—H linkages.Thus, produces carboxylic acids as,



CH≡CH under these conditions gives oxalic acid as,



Rest of acidic alkynes produce CO_2 also along with acid as



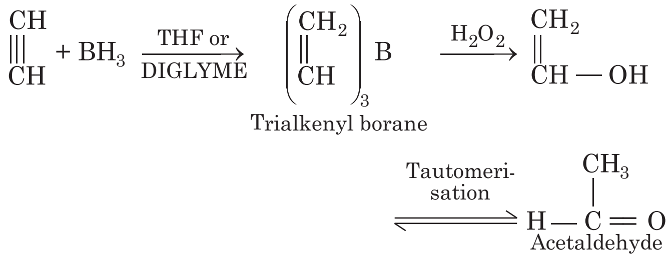
6. Combustion

Alkynes on combustion in the presence of air give CO_2 and H_2O like other hydrocarbons. The generalised equation for the reaction is as follows

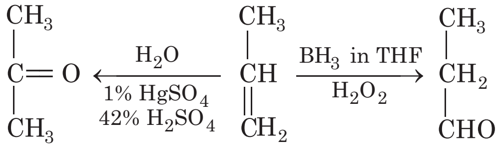
$$C_nH_{2n-2}+\left(\frac{3n-1}{2}\right)O_2 \longrightarrow nCO_2+(n-1)H_2O$$

7. Hydroboration-Oxidation

Hydroboration oxidation of alkyne give carbonyl compounds as

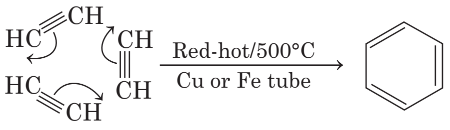


Contrary to hydration in this reaction all alkynes give aldehydes. The comparison of both the reactions is given below.



8. Polymerisation

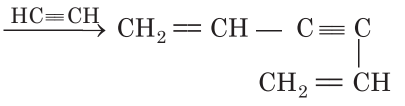
(i) In the polymerisation reactions of alkynes, aromatic compounds are produced. The reaction takes place when their vapours are passed through red hot Cu or Fe tube as



(ii) When acetylene is passed through cuprous chloride solution containing NH_4Cl, linear polymerisation occurs resulting to monovinyl and divinyl acetylene. The equation of reaction looks lilke

$$2HC\equiv CH \xrightarrow[NH_4Cl]{Cu_2Cl_2} CH_2=CH-C\equiv CH$$

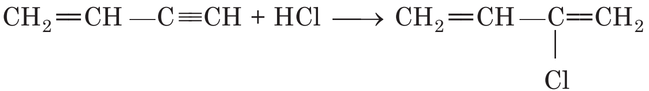
Monovinyl acetylene



$$\xrightarrow{HC\equiv CH} CH_2=CH-C\equiv C-CH=CH_2$$

Divinyl acetylene

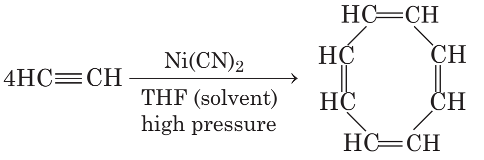
Monovinyl acetylene is used for the synthesis of **chloroprene,** the constituent of **neoprene the synthetic rubber** as



$$CH_2=CH-C\equiv CH + HCl \longrightarrow CH_2=CH-C(Cl)=CH_2$$

Chloroprene

(iii) In the presence of $Ni(CN)_2$ and under high pressure, acetylene dissolves in THF and polymerises to give cyclooctatetraene as



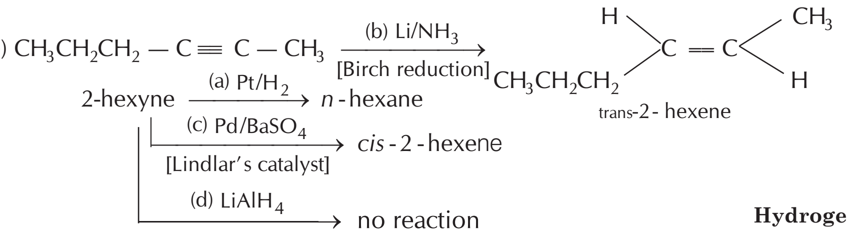
Cyclooctatetraene

(iv) When acetylene is heated in the presence of spongy copper or its oxides, a cork like substance is produced which is called **cuprene.** It is used in the manufacture of linoleum.

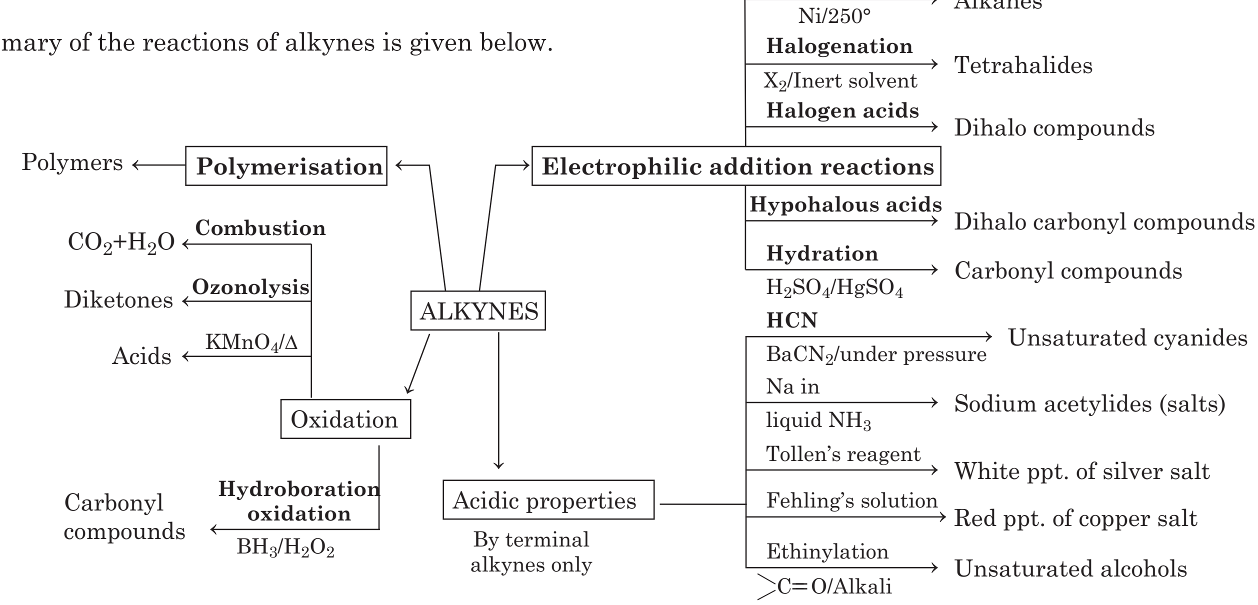
Example 5. *2-hexyne gives trans-2-hexene on treatment with* ***(AIEEE 2012)***

(a) Pt/H_2
(b) Li/NH_3
(c) $Pd/BaSO_4$
(d) $LiAlH_4$

Sol. (*b*)



Summary of the reactions of alkynes is given below.



Flow chart showing reactions of alkynes

Aromatic Hydrocarbons

Aromatic hydrocarbons are specialised cyclic compounds which are known for their characteristic unique smell (*Aroma* = fragrance).

The group is also called **arenes.** Although the name aromatic was given for their pleasant odour, but today, it is used for a class of compounds having a characteristic stability despite containing double bonds..

Aromaticity

A compound can be considered as aromatic if it follows following three conditions

(i) It must be cyclic and planar.
(ii) It must have the conjugated system of double bond.
(iii) It must follow Huckel rule.

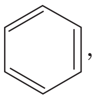
Huckel Rule

This rule states that an aromatic compound must contain $(4n+2)$ number of π electrons where, n = integer 0, 1, 2, 3 etc. Examples

(i) In  number of π-electrons = 2.

$(4n+2)=2$ and

$n=0$, thus Huckel rule is followed.

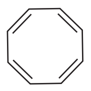
(ii) In , number of π-electron = 6.

$(4n+2)=6$ and

$n=1$, thus Huckel rule is followed.

Non-Aromatic Compounds

Those compounds which do not follow the above three rules are called **non-aromatic compounds**. These compounds may be cyclic and may have conjugated system but they do not follow Huckel rule.

For example,  (cyclooctatetraene) is cyclic and have conjugated system. However, it does not follow Huckel rule and its plane is also distorted, that's why it is non-aromatic compounds.

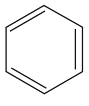
Anti-Aromatic Compounds

Compounds which are monocyclic and contain $(4n)$ π-electrons are much more reactive than expected. These are even more reactive than their acyclic analogues.

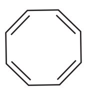
This decreased stability in $(4n)$ molecules has been called anti-aromaticity (Breslow, 1967) and such compuonds as *anti-aromatic* for example, cyclobutadiene.

Annulenes

The name annulene has been proposed as a general name for monocyclic compounds having alternating single and double bonds, i.e. having conjugated system of bonds. Their ring size is indicated with in brackets as a number before annulene as,



Benzene or [6] annulene
(aromatic)



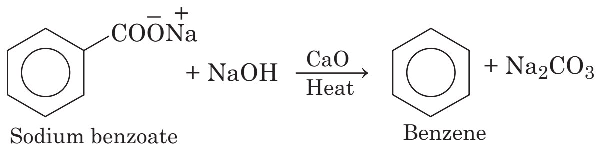
Cyclooctatetraene or
[8] annulene (non-aromatic)

Benzene

Methods of preparation of benzene are discussed below

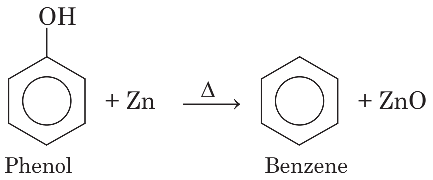
1. Decarboxylation

It is prepared by heating the mixture of sodium benzoate and sodalime.



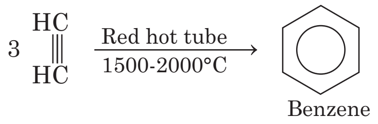
2. Dehydroxylation

Benzene is obtained by dehydroxylation of phenol with red hot zinc powder.



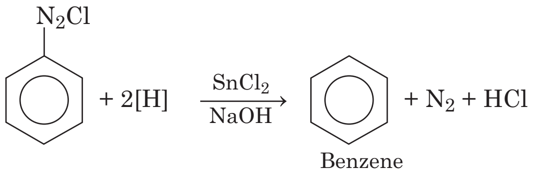
3. Polymerisation of Acetylene

When acetylene is passed through a red hot metallic tube, cyclic polymerisation takes place and benzene is formed.



4. Reduction of Benzene Diazonium Chloride

Benzene diazonium chloride is reduced to benzene by $SnCl_2$ and NaOH or absolute ethyl alcohol or hypophosphorous acid (H_3PO_2) as,

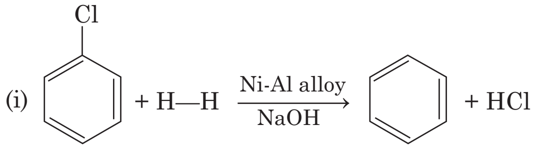


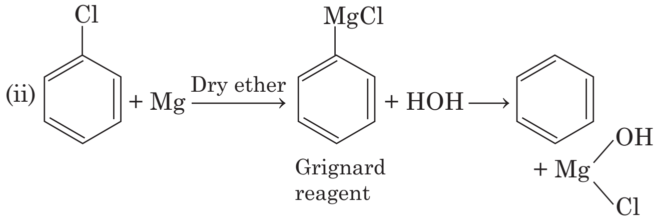
5. From Chlorobenzene

Benzene is prepared from chlorobenzene by following two method

(i) Hydrogenation

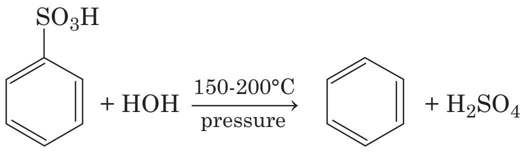
(ii) Grignard reagent formation followed by hydrolysis. Equations of both of these reactions is given below.





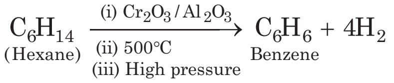
6. From Benzene sulphonic acid

Benzene sulphonic acid on hydrolysis under pressure gives benzene as



7. Aromatisation

Hexane to decane on aromatisation in the presence of Cr and Al oxides at high temperature and pressure give benzene and its homologues. The equation of reaction is given below



$$\underset{\text{(Hexane)}}{C_6H_{14}} \xrightarrow[\substack{\text{(ii) 500°C} \\ \text{(iii) High pressure}}]{\text{(i) } Cr_2O_3/Al_2O_3} \underset{\text{Benzene}}{C_6H_6} + 4H_2$$

8. Distillation

Benzene and its homologues are prepared by the destructive distillation of wood.

In the process following fractions are obtained at different temperatures

(i) **Light oil** Below 200°C-contains BTX (Benzene, toluene and xylene) as its chief components.

(ii) **Middle oil** 200-240°C-contains phenols, cresols and naphthalene.

(iii) **Heavy oil** 245-280°C-contains cresols and naphthalene.

(iv) **Anthracene oil** (green oil) 280-405°C-contains anthracene, phenanthrene and carbazole.

(v) **Pitch** The residue containing 5 and 6 membered fused rings and tar oils.

Benzene is obtained from light oil fraction through following steps

Light oil fraction

Washed ↓ ***Step* 1.** (i) H_2SO_4 (basic impurity remover)
(ii) NaOH (acidic impurity remover)

Light oil fraction without impurities

↓ ***Step* 2.** Washed water, dried and distilled

110°C fraction (contains benzene, toluene and thiophene)

↓ ***Step* 3.** Refractioned

Almost pure benzene between 80-82°C with traces of thiophene

↓ ***Step* 4.** H_2 /400°C
Ni under pressure

Pure benzene + H_2S

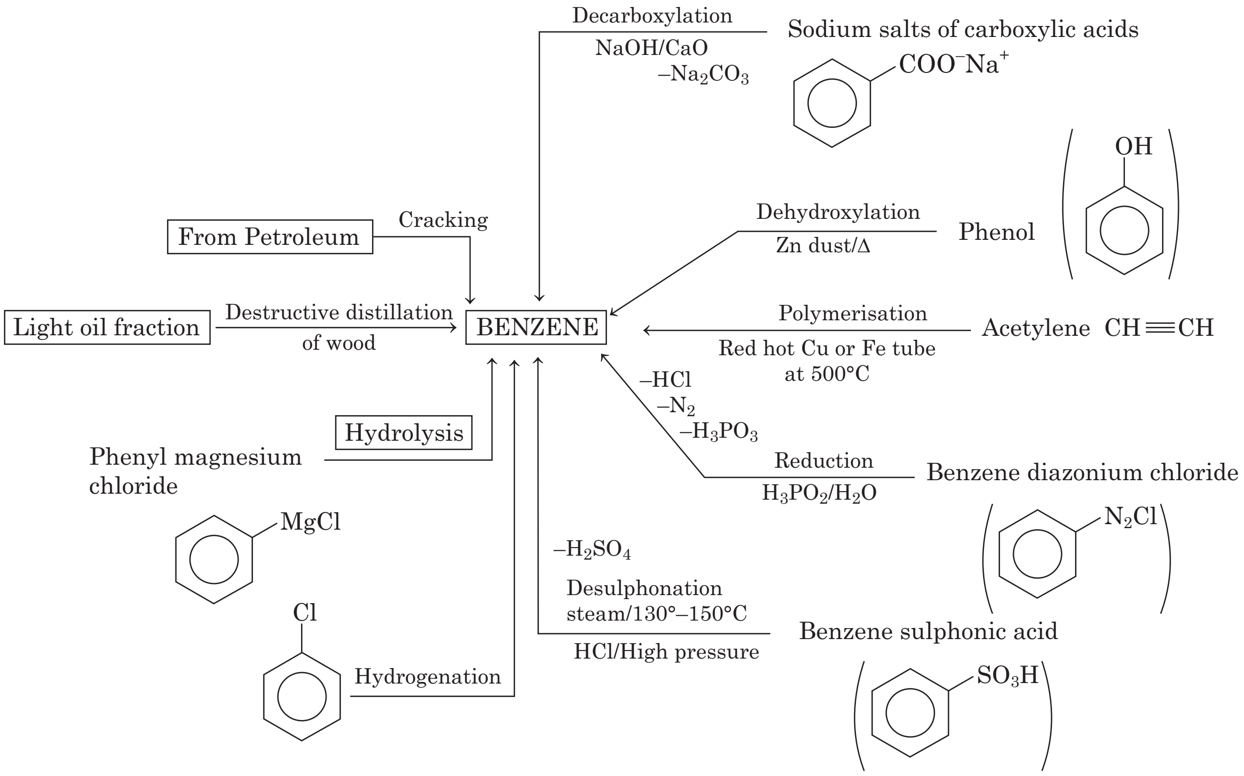
9. **Cracking of Petroleum**

From petroleum, benzene is obtained through aromatisation or platforming of C_6 — C_{10} fraction of petroleum naphtha at high temperature and high pressure as

$$\text{Hexane} \xrightarrow[\text{500°C 15 atm}]{\text{Pt, Al}_2\text{O}_3} \text{Benzene}\,;\ \text{Heptane} \xrightarrow[\text{500°C, 15 atm}]{\text{Pt, Al}_2\text{O}_3} \text{Toluene}$$

The reaction is the modified form of aromatisation reaction of alkanes.

Summary of the methods of preparation of benzene is given below.



Flow chart showing methods of preparation of benzene

Physical Properties of Benzene

- Benzene is a colourless inflammable liquid, b.p. 80.1°C, m.p. 5.5°C, insoluble in water, miscible with alcohol, ether and chloroform.
- The compound itself is a good solvent. It burns with a luminous sooty flame and its vapours are highly toxic. It is lighter than water.
- Inhalation of benzene causes toxic effects in our body and it is also carcinogenic in nature.

Chemical Properties of Benzene

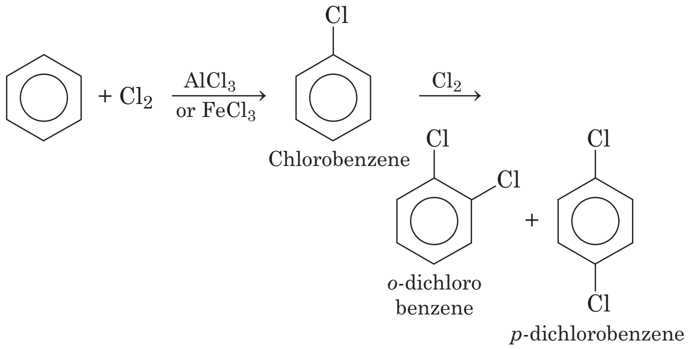
Important chemical reactions exhibited by benzene are given below.

Electrophilic Substitutions

Most of the reactions given by benzene are electrophilic substitution. Major one among these are given below.

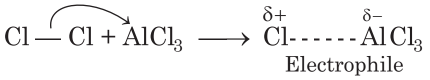
1. Halogenation

Benzene undergo chlorination when it is treated with chlorine in the presence of catalyst aluminium chloride or ferric chloride and in the absence of light.



This reaction undergo the following mechanism

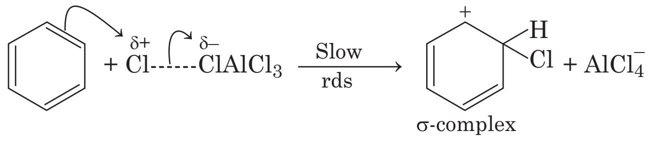
***Step* I** Generation of an electrophile

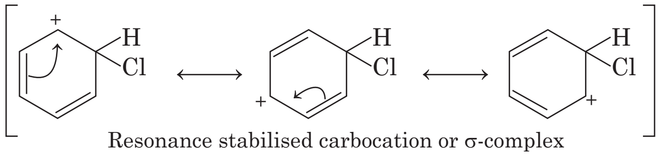


$$Cl-Cl + AlCl_3 \longrightarrow \overset{\delta+}{Cl}\text{------}\overset{\delta-}{Al}Cl_3$$

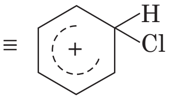
Electrophile

***Step* II** Formation of σ-complex or carbocation intermediate.





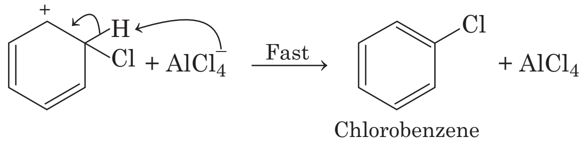
Resonance stabilised carbocation or σ-complex



Resonance hybrid

This step is the rate determining step.

***Step* III** Loss of a proton from the carbocation intermediate.

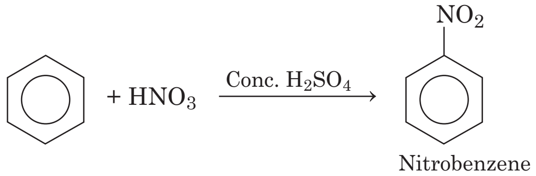


This step is fast and hence, does not affect the rate of the reaction.

2. Nitration

Benzene undergoes nitration when treated with conc. HNO_3 in the presence of conc. sulphuric acid.

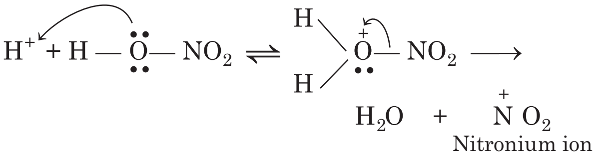
The mixture of conc. HNO_3 and conc. sulphuric acid is called **nitrating mixture**.



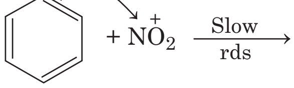
The steps involved in this reaction are as follows

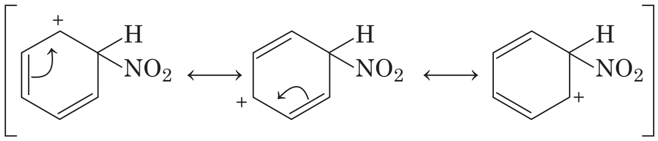
***Step* I** Generation of an electrophile, i.e. NO_2^+ (nitronium ion).

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

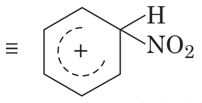


***Step* II** Formation of σ-complex or carbocation intermediate.



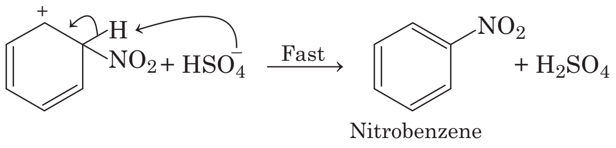


Resonance stabilised carbocation or the σ-complex



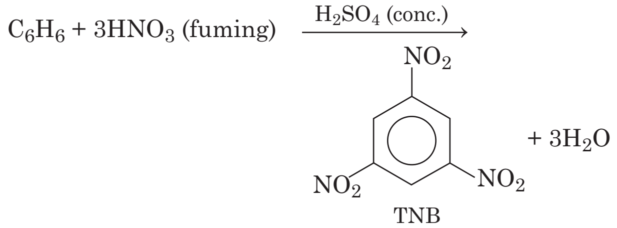
Resonance hybrid

***Step* III** Loss of a proton from the carbocation intermediate.



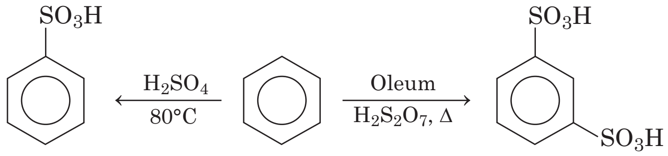
This step is fast and hence does not affect the rate of the reaction.

On heating benzene with fuming nitric acid and conc H_2SO_4, 1,3,5-trinitrobenzene (TNB) is formed.



3. Sulphonation

Benzene forms benzene sulphonic acid with hot conc. H_2SO_4. On the other hand with fuming H_2SO_4 or oleum at high temperature, *m*-benzene disulphonic acid is formed.



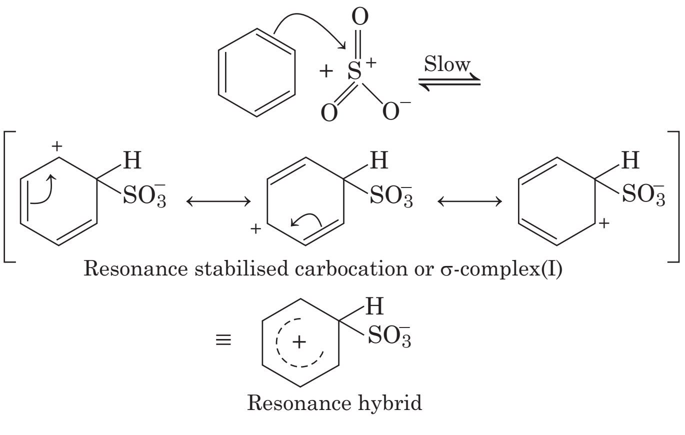
For sulphonation the attacking species is SO_3 or $\overset{+}{S}O_3H$.

This reaction involves the following mechanism

***Step* I** Generation of an electrophile, i.e. sulphur trioxide (SO_3).

$$2H_2SO_4 \rightleftharpoons SO_3 + HSO_4^- + H_3O^+$$

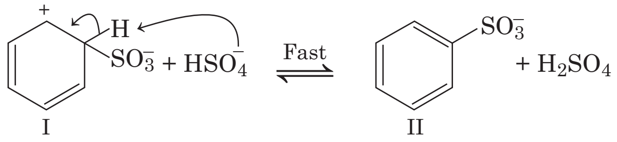
***Step* II** Formation of σ-complex or carbocation intermediate.



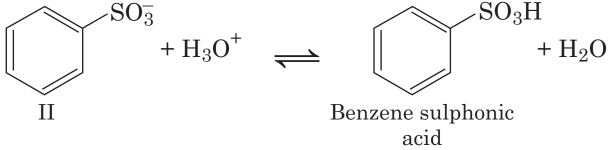
Resonance stabilised carbocation or σ-complex(I)

Resonance hybrid

***Step* III** Loss of a proton from the carbocation.



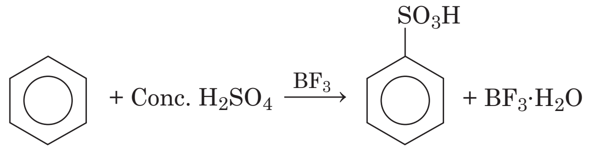
***Step* IV** Addition of proton to the benzenesulphonic acid anion (II) gives the final product.



Benzene sulphonic acid

This equilibrium lies far to the left since sulphonic acid is a strong acid. It may be pointed out here *that unlike other electrophilic aromatic substitution reactions, sulphonation is reversible.*

Sulphonation can also be carried out at room temperaure in the presence of BF_3 as the catalyst.



4. Friedel-Crafts' Alkylation, Acylation or Carbonylation

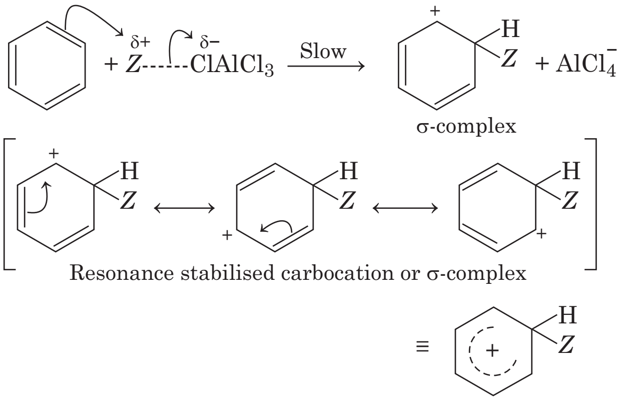
These are most common alkylation, acylation or carboxylation reactions. The lewis acids that can be used for these reactions are $AlCl_3$, $FeCl_3$, $SnCl_2$, $SnCl_4$, BF_3, HF etc. These reactions involve the following step

***Step* I** Generation of an electrophile

$$Z—Cl + AlCl_3 \longrightarrow \overset{\delta+}{Z}------\overset{\delta-}{Cl}Al\,Cl_3$$

Electrophile

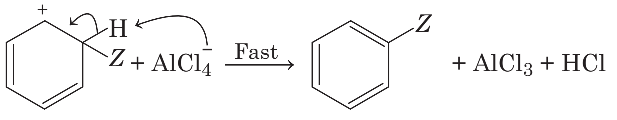
***Step* II** Formation of σ-complex or carbocation intermediate.



Resonance stabilised carbocation or σ-complex

Resonance hybrid

***Step* III** Loss of a proton from the carbocation intermediate.

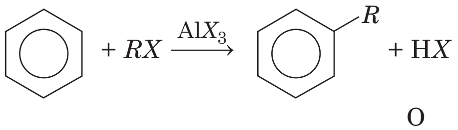


Alkyl benzene

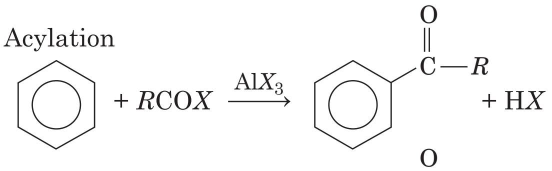
(This step is fast and hence does not affect the rate of the reaction) (where, $Z = -R$, —COR or COX)

Equations of all the three reactions are shown below

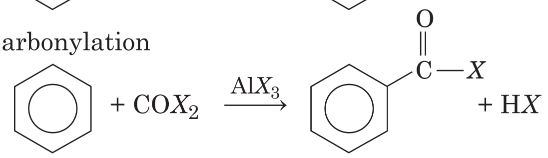
Alkylation



Acylation



Carbonylation



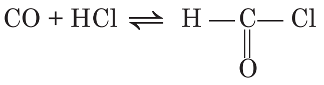
5. Formylation

It is simply the introduction of —CHO group into the the benzene ring.

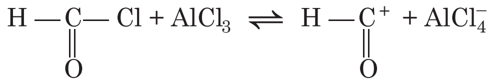
Formylation can be done *via* following two reactions.

(i) Gatterman-Koch synthesis

In this reaction the attacking electrophile is $\overset{\overset{\displaystyle O}{\|}}{C^{+}}—H$, which is produced as

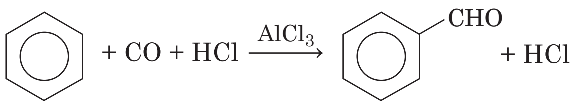


$$CO + HCl \rightleftharpoons H—\underset{\underset{\displaystyle O}{\|}}{C}—Cl$$



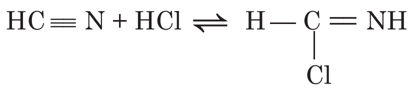
$$H—\underset{\underset{\displaystyle O}{\|}}{C}—Cl + AlCl_3 \rightleftharpoons H—\underset{\underset{\displaystyle O}{\|}}{C^{+}} + AlCl_4^-$$

The equation of complete reaction is shown below.

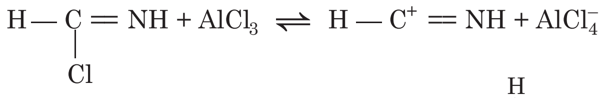


(ii) Gattermann Synthesis

(a) In this reaction the attacking electrophile is $\overset{+}{C}H = NH$, which is produced as

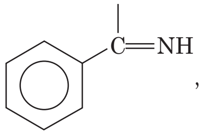


$$HC \equiv N + HCl \rightleftharpoons H—\underset{\underset{\displaystyle Cl}{|}}{C} = NH$$



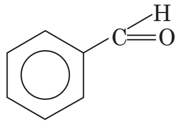
$$H—\underset{\underset{\displaystyle Cl}{|}}{C} = NH + AlCl_3 \rightleftharpoons H—C^{+} = NH + AlCl_4^-$$

(b) The product formed initially is



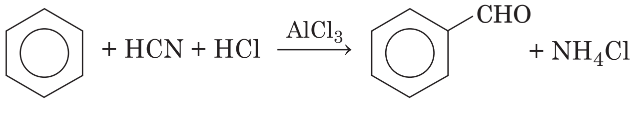
,

which on hydrolysis gave



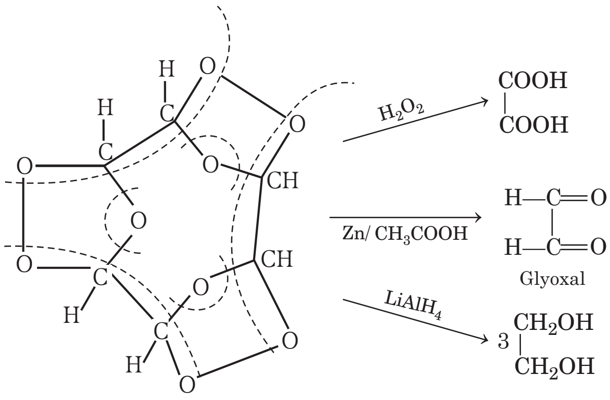
and NH_3.

The equation of complete reaction is shown below.



6. Ozonolysis

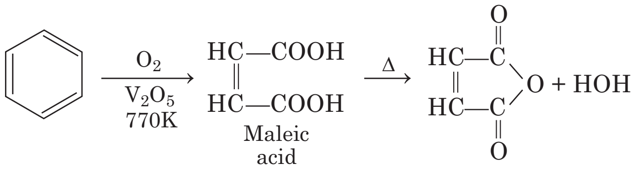
The ozonide formed and its hydrolysis in this reaction looks like



7. Vapour Phase Oxidation

The recation is earried rut at 770 K.

Maleic acid $\left(\begin{array}{c}CHCOOH\\ \|\\ CHCOOH\end{array}\right)$ is first produced in the reaction which looses water at such a high temperature and converted into anhydride. The equation of complete reaction in shown below

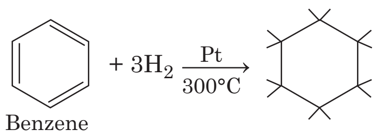


8. Addition Reactions

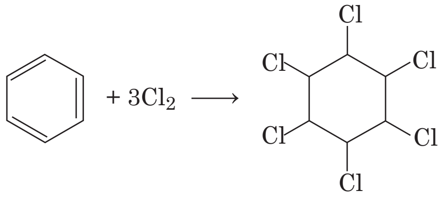
Benzene show following addition reactions also

(i) **Reduction or hydrogenation**

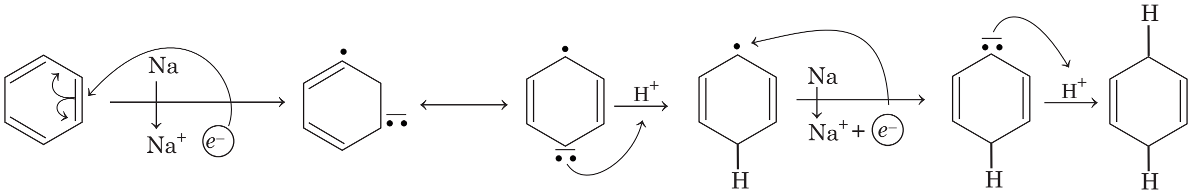
Benzene on reduction produce cyclohexane as,



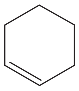
(ii) The product of halogenation is $C_6H_6Cl_6$ (Benzene hexachloride or BHC). It is also called **Lindane** or **Gammexane** or 666 and is used as insecticide.

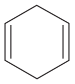
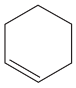


(c) Halogenation and hydrogenation operate through free radical mechanisms while in **Birch reduction** the metal used is of Ist group, i.e. Li, Na (mostly Na) and alcohol normally CH_3OH (or C_2H_5OH). Here metal works for electron donation and alcohol for proton donation as

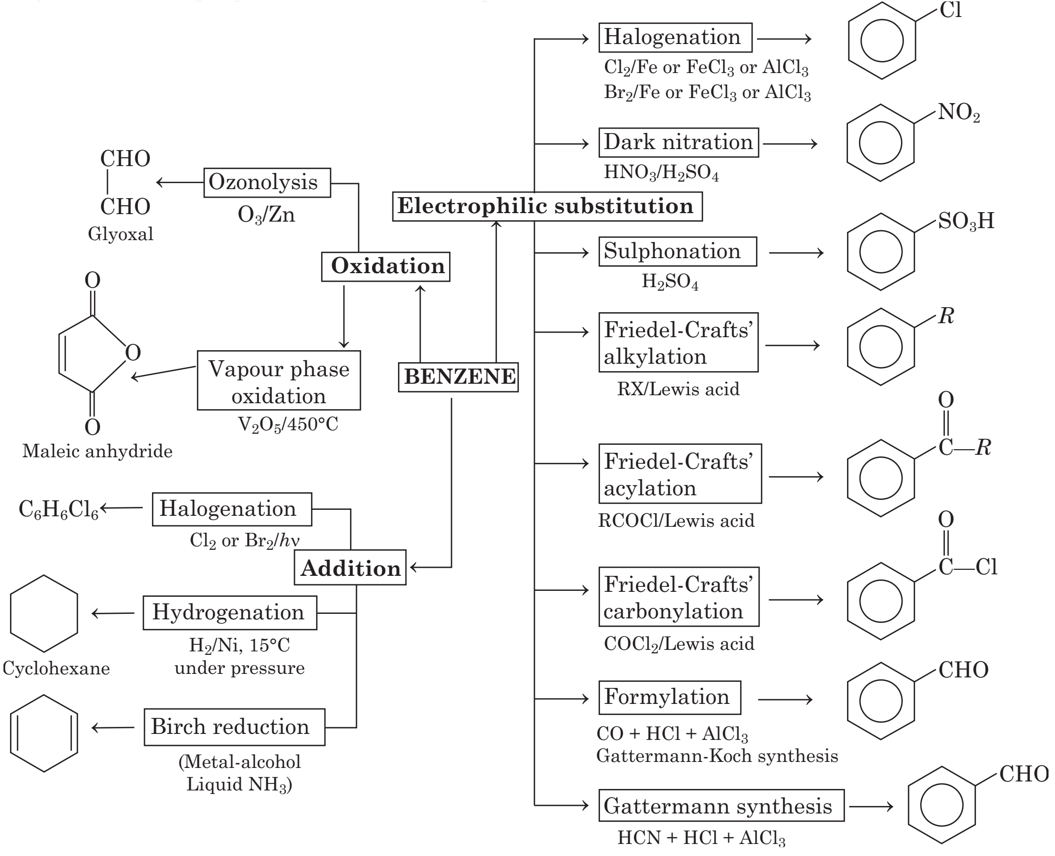


The H^+ is provided here by alcohol.

At high temperature even alcohol is not needed. NH_3 provides H^+ at high temperatures and the product at high temperatures is  .

The uniqueness of pathway here is that the addition is throughout 1,4-addition, i.e. initially  is formed which on further 1,4-addition gave  .

The summary of chemical properties of benzene is given below

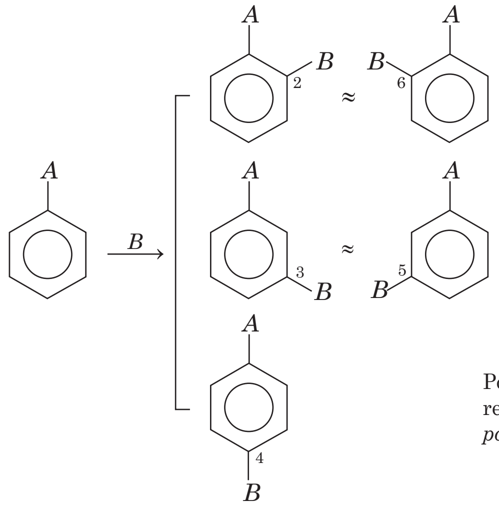


Flow chart showing chemical reactions of benzene

Directive Influence of Groups

All H-atoms of benzene ring are equivalent, thus in benzene only one monosubstitution product is possible.

For the second substituent following 3 positions are possible, i.e.



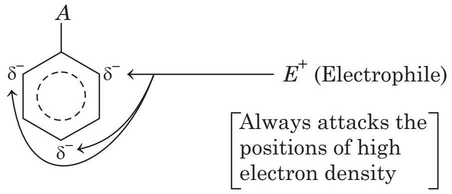
Positions numbered 2 and 6 are called *ortho* with respect to *A*

Position numbered 3 and 5 are called *meta* with respect to *A*

Position number 4 with respect to *A* is called *para* position

The speciality of di and further substitutions in benzene is that the group already present influences the entry of group to come in the first substituent (after monosubstitution) directs the next substituent as follows

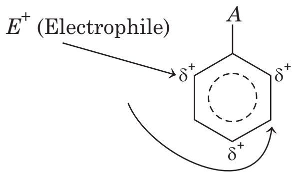
(i) if electron density at *ortho* and *para* position is increased due to first substituent, i.e.



Always attacks the positions of high electron density

A is *ortho* and *para* directing as electron density is highest at these positions

(ii) if electron density at *ortho* and *para* position is decreased due to first substituent, i.e.



A is *meta* directing as now electron density is maximum at these positions

The substituents which increase the electron density at the ring are called **ring activators** for further electrophilic substitution.

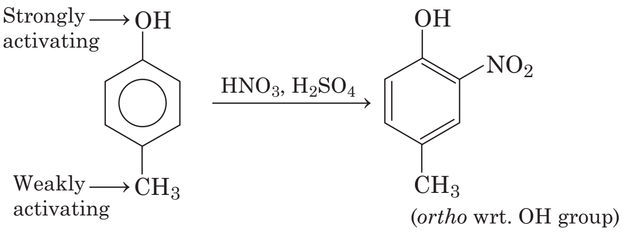
On the other hand the groups which decrease electron density on the ring are called **ring deactivators** for further electrophilic substitution. Thus, normally *ortho* and *para* directing groups are ring activators and ***meta* directing groups are ring deactivators**.

Halogens are present as exception because these are *ortho* and *para* directing but ring deactivators**.** The *ortho* and *para* directive influence of halogens is attributed to their ability of **donating lone pair** while their ring deactivation influence is attributed to their **high electronegativity**.

The various ring activator and deactivator groups in the order of their activity are given below

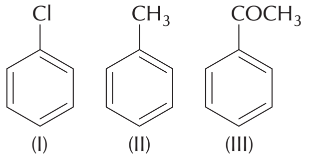
- ***o/p* directing and activating group**
  (i) strongly activating
  $—NH_2 > —NHR > —NR_2 > —OH > —O$
  (ii) moderately activating $—NHCOR > —OCOR$,
  (iii) weakly activating $—R > —Ar > —CH{=}CR_2$
  (iv) weakly deactivating $—F > —Cl > —Br > —I$
- ***m*-directing and deactivating**
  (i) moderately deactivating
  $—CHO > —COR > —COOR > —COOH$
  (ii) strongly deactivating
  $—CN < —SO_3 < \overset{+}{N}H_3 < \overset{+}{N}H_2R_2 < \overset{+}{N}HR_2 < \overset{+}{N}R_3 < —NO_2$
  most deactivating.

Remember that if two groups are present, the strongly activating groups generally win over the deactivating or weakly activating group., e.g.



(*ortho* wrt. OH group)

Example 6. *The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reaction is* ***(JEE Main 2019)***

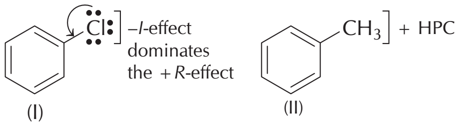


(a) III < I < II
(b) II < I < III
(c) III < II < I
(d) I < III < II

Sol. (a) In electrophilic aromatic substitution (ArS_E2) reaction, the aromatic (benzene nucleus here) compound (substrate) acts as a nucleophile which gets attacked by an electrophile in the rate determining step (rds).

Higher electron density on the nucleophile, i.e. benzene nucleus will fasten the rate of the reaction. Electron-donating groups (EDG) will increase electron density in benzene nucleus by any or both of their +*M* and hyperconjugative (HPC) effects.

Now, let us consider the given substrate.



As –*M* effect is more powerful than –*I* effect, the order of their reactivity, towards an electrophile will be

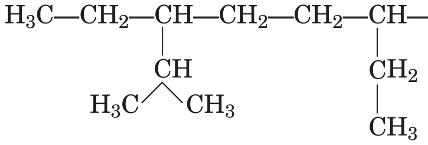
$$\underset{(-M)}{\text{III}} < \underset{(-I > +M)}{\text{I}} < \underset{(+\,\text{HPC})}{\text{II}}$$

Practice Exercise

ROUND I Topically Divided Problems

General Characteristics and Methods of Preparation of Alkanes

1. The correct IUPAC name of the following alkane is



(NCERT Exemplar)

(a) 3,6-diethyl-2-methyloctane
(b) 5-*iso*-propyl-3-ethyloctane
(c) 5-ethyl-5-*iso*-propyloctane
(d) 3-*iso*-propyl-6-ethyloctane

2. The compound with an isopropyl group is
(a) 2,2,3,3-tetramethylpentane
(b) 2,2-dimethylpentane
(c) 2,2,3-trimethylpentane
(d) 2-methylpentane

3. The number of primary, secondary, tertiary and quaternary carbons in *neo*-pentane are respectively,
(a) 4, 3, 2 and 1
(b) 5, 0, 0 and 1
(c) 4, 0, 0 and 1
(d) 4, 0, 1 and 1
(e) 4, 1, 0 and 0

4. Which of the following liberates methane on treatment with water?
(a) Silicon carbide
(b) Calcium carbide
(c) Beryllium carbide
(d) Magnesium carbide

5. Which of the following reactions of methane is incomplete combustion? *(NCERT Exemplar)*
(a) $2CH_4 + O_2 \xrightarrow{Cu/523\text{ K}/100\text{ atm}} 2CH_3OH$
(b) $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$
(c) $CH_4 + O_2 \longrightarrow C(s) + 2H_2O(l)$
(d) $CH_4 + 2O_2 \longrightarrow CO_2(g) + 2H_2O(l)$

6. Which of the following will not produce ethane?
(a) Reduction of CH_3COOH with HI and red P
(b) Reduction of CH_3COCH_3 with HI and red P
(c) Sodalime decarboxylation of sodium propionate
(d) Hydrogenation of ethane in the presence of Raney-Ni

7. Which of the following compounds cannot be prepared singly by the Wurtz reaction?
(a) C_2H_6
(b) $(CH_3)_2CHCH_3$
(c) $CH_3CH_2CH_2CH_3$
(d) All can be prepared

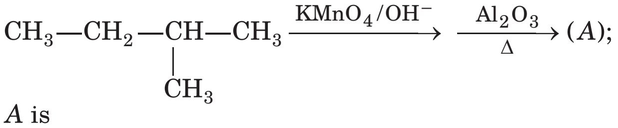
8. Both methane and ethane may be obtained by a suitable one-step reaction from
(a) CH_3I
(b) C_2H_5I
(c) CH_3OH
(d) C_2H_5OH

9. Which of the following can be used for the preparation of propane?
(a) $CH_3CH{=}CH_2 \xrightarrow[2.\ AgNO_3/NaOH]{1.\ B_2H_6}$
(b) $CH_3CH_2CH_2Cl \xrightarrow[2.\ H_2O_2]{1.\ Mg/ether}$
(c) $CH_3CH_2CH_2I \xrightarrow{HI/Red\ P,\ \Delta\ 150°C}$
(d) $CH_3CH_2COONa \xrightarrow[\Delta]{NaOH\ (CaO)}$

10. The compound with highest boiling point is *(JCECE)*
(a) *n*-hexane
(b) *n*-pentane
(c) 2,2-dimethylpropane
(d) 2-methylbutane

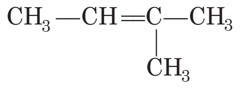
Physical and Chemical Properties of Alkanes

11. In the given sequence,

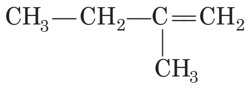


$$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3 \xrightarrow{KMnO_4/OH^-} \xrightarrow[\Delta]{Al_2O_3} (A);$$

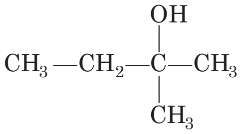
A is

(a) 

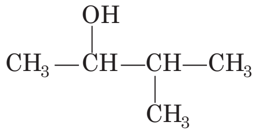
$CH_3-CH{=}\underset{\underset{\displaystyle CH_3}{|}}{C}-CH_3$

(b) 

$CH_3-CH_2-\underset{\underset{\displaystyle CH_3}{|}}{C}{=}CH_2$

(c) 

$CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_3$

(d) 

$CH_3-\overset{\overset{\displaystyle OH}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$

12. Arrange the halogens F_2, Cl_2, Br_2, I_2 in order of their increasing reactivity with alkanes *(NCERT Exemplar)*

(a) $I_2 < Br_2 < Cl_2 < F_2$ (b) $Br_2 < Cl_2 < F_2 < I_2$
(c) $F_2 < Cl_2 < Br_2 < I_2$ (d) $Br_2 < I_2 < Cl_2 < F_2$

13. An alkyl bromide, RBr of molecular weight 151 is the exclusive product of bromination of which hydrocarbon?

(a) Dodecane
(b) 2,2-dimethylpropane
(c) 2,2-dimethylhexane
(d) 2,2,3-trimethylheptane

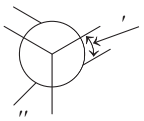
14. Several hydrocarbon radicals can be formed as intermediates during monochlorination of 2-methylpropane. Which of them is the most stable? *(NCERT Exemplar)*

(a) $(CH_3)_2\dot{C}CH_3$ (b) $(CH_3)_2CH\dot{C}H_2$
(c) $(CH_3)\dot{C}HCH_2CH_3$ (d) All are equally stable

15. The products obtained in the reaction of sodium with a mixture of 1-iodo-2-methylpropane and 2-iodopropane is/are *(NCERT Exemplar)*

(a) 2,5-dimethyl hexane (b) 2,3-dimethylbutane
(c) 2,4-dimethyl pentane (d) All of these

16. In the following skew conformation of ethane, H′ — C—C—H″ dihedral angle is



(JEE Main 2019)

(a) 58° (b) 149° (c) 151° (d) 120°

17. On mixing a certain alkane with chlorine and irradiating it with UV light, it forms one monochloro alkane. The alkane could be

(a) *neo*-pentane (b) propane
(c) pentane (d) *iso*-pentane

18. $CH_3CH_2CH_3 \xrightarrow{400\text{-}600°C} X + Y$

X and Y are

(a) hydrogen, methane
(b) methane, ethylene
(c) hydrogen, ethylene
(d) ethylene, ethane

19. Which of the following is Lindlar catalyst ? *(JEE Main 2021)*

(a) Zinc chloride and HCl
(b) Cold dilute solution of $KMnO_4$
(c) Sodium and liquid NH_3
(d) Partially deactivated palladised charcoal

20. When 1,1-dichloropropane and 2,2-dichloropropane are reacted separately with aqueous potassium hydroxide solution, compounds 'A' and 'B' are formed. Both 'A' and 'B' gave the same product 'C' on reduction using amalgamated zinc and HCl. Identify 'C'. *(EAMCET)*

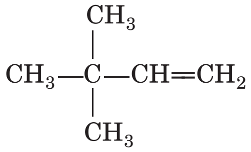
(a) propyl alcohol (b) isopropyl alcohol
(c) propyl chloride (d) propane

General Characteristics and Methods of Preparation of Alkene

21. The best method to prepare cyclohexene from cyclohexanol is by using

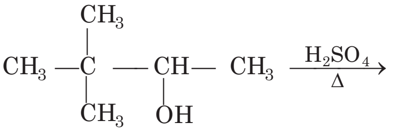
(a) conc. HCl + $ZnCl_2$ (b) conc. H_3PO_4
(c) HBr (d) conc. HCl

22. Which of the following reactions is not expected to give

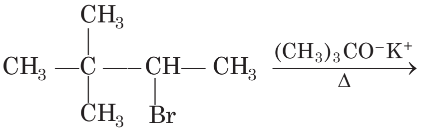


$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2$$

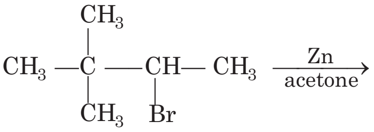
in yields of more than 50%?

(a) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{CH}-CH_3 \xrightarrow[\Delta]{H_2SO_4}$$

(b) 

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3 \xrightarrow[\Delta]{(CH_3)_3CO^-K^+}$$

(c) 

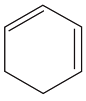
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{Br}{CH}-CH_3 \xrightarrow[\text{acetone}]{Zn}$$

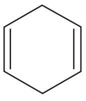
(d) None of the above

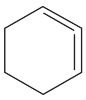
23. Allene (C_3H_4) contains

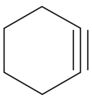
(a) one double bond, one triple bond and one single bond
(b) one triple and two double bonds
(c) two triple and one double bond
(d) two double and four single bonds

24. Which of the following compounds is the most stable ?

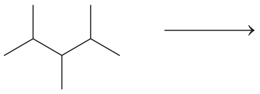
(a) 

(b) 

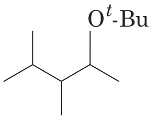
(c) 

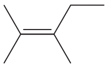
(d) 

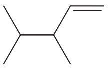
25. The major product in the following reaction is

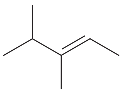


(JEE Main 2020)

(a) 

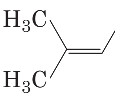
(b) 

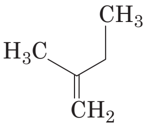
(c) 

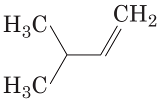
(d) 

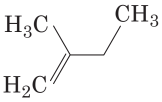
26. When neopentyl alcohol is heated with an acid, it slowly converted into an 85 : 15 mixture of alkenes *A* and *B*, respectively. What are these alkenes?

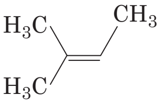
(JEE Main 2020)

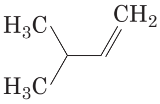
(a) 

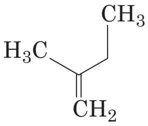
and 

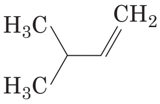
(b) 

and 

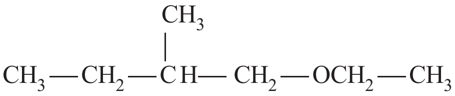
(c) 

and 

(d) 

and 

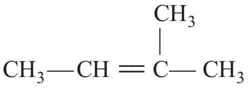
27. The major product [*B*] in the following reactions is



$$CH_3-CH_2-\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CH_2-OCH_2-CH_3$$

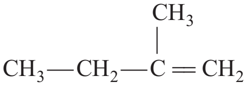
$$\xrightarrow[\text{Heat}]{\text{HI}}[A]\text{ alcohol}\xrightarrow[\Delta]{H_2SO_4}[B]$$

(JEE Main 2020)

(a) 

$CH_3-CH=\overset{CH_3}{\overset{|}{C}}-CH_3$

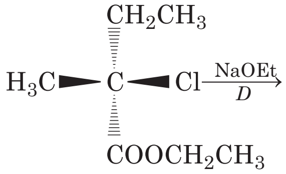
(b) $CH_2=CH_2$

(c) 

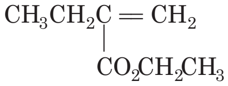
$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}=CH_2$

(d) $CH_3-CH_2-CH=CH-CH_3$

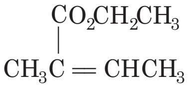
28. The major product of the following reaction is



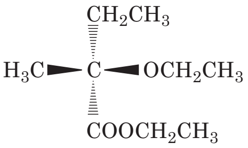
(JEE Main 2019)

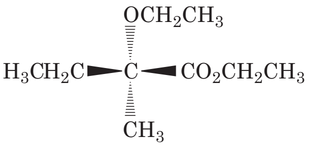
(a) 

$CH_3CH_2\underset{CO_2CH_2CH_3}{\underset{|}{C}}=CH_2$

(b) 

$CH_3\overset{CO_2CH_2CH_3}{\overset{|}{C}}=CHCH_3$

(c) 

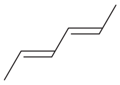
(d) 

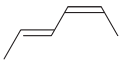
29. Elimination of bromine from 2-bromobutane results in the formation of

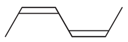
(a) predominantly 2-butyne
(b) predominantly 1-butene
(c) predominantly 2-butene
(d) equimolar mixture of 1 and 2-butene

Physical and Chemical Properties of Alkenes

30. The correct order of heat of combustion for following alkadienes is *(JEE Main 2020)*







(a) (*B*) < (*C*) < (*A*)
(b) (*A*) < (*B*) < (*C*)
(c) (*A*) < (*C*) < (*B*)
(d) (*C*) < (*B*) < (*A*)

31. Which one of the following has the smallest heat of hydrogenation per mole?

(a) 1-butene
(b) *trans*-but-2-ene
(c) *cis*-but-2-ene
(d) Buta-1,3-diene

32. The addition of HCl to 3,3,3-trichloropropene gives

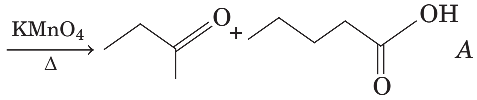
(a) $Cl_3CCH_2CH_2Cl$
(b) $Cl_3CCH_2CHCl_2$
(c) $Cl_2CHCH_2CHCl_2$
(d) $Cl_2CHCH(Cl)CH_2Cl$

33. Arrange the following hydrogen halides in the order of their decreasing reactivity with propene. ***(NCERT Exemplar)***

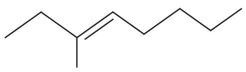
(a) HCl > HBr > HI	(b) HBr > HI > HCl
(c) HI > HBr > HCl	(d) HCl > HI > HBr

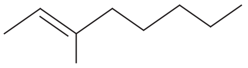
34. The addition of HBr to an alkene in the presence of peroxide is the example of

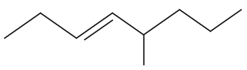
(a) electrophilic addition reaction
(b) nucleophilic addition reaction
(c) free radical addition reaction
(d) the formation of carbocation as an intermediate

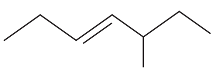
35. Alkene (A) 

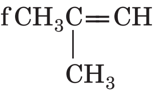
A is

(a) 

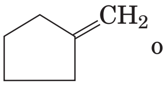
(b) 

(c) 

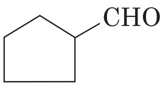
(d) 

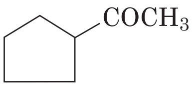
36. The treatment of 
$CH_3\underset{CH_3}{\underset{|}{C}}{=}CHCH_3$ with $NaIO_4$ or boiling $KMnO_4$ produces

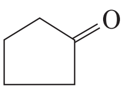
(a) $CH_3COCH_3 + CH_3COOH$
(b) $CH_3COCH_3 + CH_3CHO$
(c) $CH_3CHO + CO_2$
(d) CH_3COCH_3 only

37. 

on ozonolysis gives

(a) 

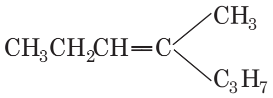
(b) 

(c) 

+ HCHO

(d) None of these

38. Propanal and pentan-3-one are ozonolysis product of an alkene. What is the structural formula of the alkene? ***(NCERT)***

(a) $CH_3CH_2CH{=}C(C_2H_5)_2$
(b) $CH_3CH{=}CHCH(C_2H_5)_2$
(c) $CH_3CH_2CH{=}CHCH_2C_3H_7$
(d) 
$CH_3CH_2CH{=}C\begin{array}{l}CH_3\\C_3H_7\end{array}$

39. An unsaturated hydrocarbon 'A' adds two molecules of H_2 and on reductive ozonolysis gives butane-1,4-dial, ethanol and propanone. Give the IUPAC name of A. ***(NCERT Exemplar)***

(a) 3-methylocta-2,6-diene
(b) 2-methylocta-2,5-diene
(c) 2-methylocta-2,6-diene
(d) 2-methylocta-3,5-diene

40. The alkene which on hydrogenation give 2-methyl butane is ***(NCERT)***

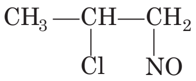
(a) 2-methylbut-1-ene
(b) 2-methylbut-2-ene
(c) 3-methylbut-1-ene
(d) All of the above

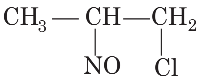
41. The reaction of propene with HOCl proceeds *via* the addition of

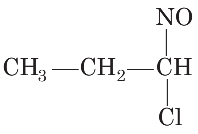
(a) Cl^+ and OH^- in a single step
(b) Cl^+ in the first step
(c) H^+ in the first step
(d) OH^- in the first step

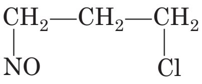
42. $CH_3{-}CH{=}CH_2 + NOCl \longrightarrow P$

Identify the adduct.

(a) 
$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{NO}{\underset{|}{CH_2}}$

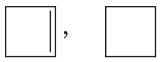
(b) 
$CH_3-\underset{NO}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

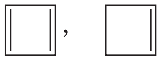
(c) 
$CH_3-CH_2-\overset{NO}{\overset{|}{\underset{Cl}{\underset{|}{CH}}}}$

(d) 
$\underset{NO}{\underset{|}{CH_2}}-CH_2-\underset{Cl}{\underset{|}{CH_2}}$

43. $A(C_4H_6)\xrightarrow[\text{1 mole}]{H_2,\ Ni} B\ (C_4H_8)\xrightarrow{O_3/H_2O/Zn} CH_3CHO.$

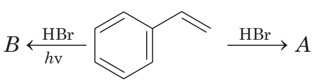
Thus, A and B are

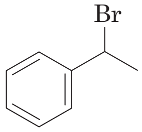
(a) 

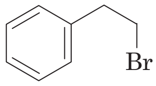
(b) 

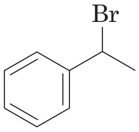
(c) $CH_3CH_2C \equiv CH, CH_3CH{=}CHCH_3$
(d) $CH_2{=}CH-CH{=}CH_2, CH_3CH{=}CH-CH_3$

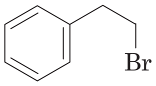
44. Observe the following and predict the nature of A and B

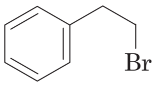


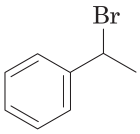
(a) A and B both are 

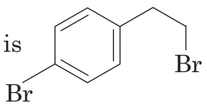
(b) A and B both are 

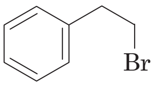
(c) A is 

and B is 

(d) A is 

and B is 

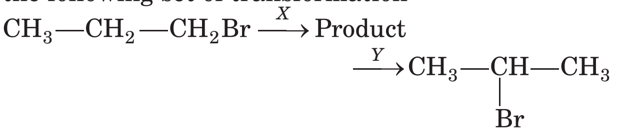
(e) A is 

and B is 

45. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because
(a) both are highly ionic
(b) one is oxidising and the other is reducing
(c) one of the steps is endothermic in both the cases
(d) all the steps are exothermic in both the cases

46. The intermedicate during the addition of HCl to propene in the presence of peroxide is
(a) $CH_3\overset{+}{C}HCH_2Cl$
(b) $CH_3\overset{+}{C}HCH_3$
(c) $CH_3CH_2\overset{\bullet}{C}H_2$
(d) $CH_3CH_2\overset{+}{C}H_2$

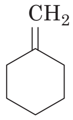
47. The set of reagent reaction conditions 'X' and 'Y' in the following set of transformation

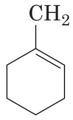


$$CH_3-CH_2-CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$$

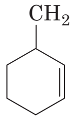
(a) X = dil. aqueous NaOH, 20°C ; Y = HBr / acetic acid, 20°C
(b) X = conc. alcoholic NaOH, 80°C; Y = HBr/acetic acid, 20°C
(c) X = dil. *aq.* NaOH, 20°C ; Y = $Br_2/CHCl_3$, 0°C
(d) X = conc. alcoholic NaOh, 80°C; Y = $Br_2/CHCl_3$, 0°C

48. In the reaction with HCl, an alkene reacts in accordance with the Markownikoff's rule to give a product 1- chloro -1 - methylcyclo hexane. The possible alkene is

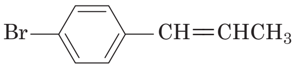
(a) 

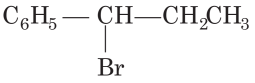
(b) 

(c) (a) and (b)

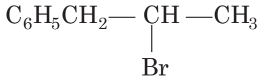
(d) 

49. The reaction of $C_6H_5CH{=}CHCH_3$ with HBr produces
(a) $C_6H_5CH_2CH_2CH_2Br$

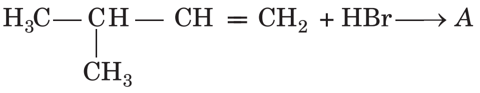
(b) 

(c) 

$C_6H_5-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_2CH_3$

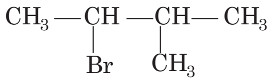
(d) 

$C_6H_5CH_2-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$

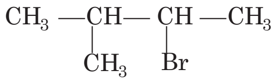
50. 

$$H_3C-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH=CH_2+HBr \longrightarrow A$$

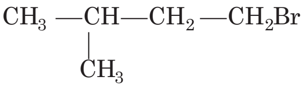
A (Predominantly) is

(a) 

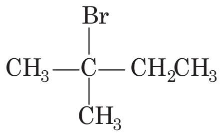
$CH_3-\underset{\underset{\displaystyle Br}{|}}{CH}-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_3$

(b) 

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\underset{\underset{\displaystyle Br}{|}}{CH}-CH_3$

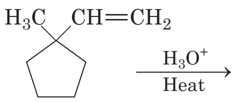
(c) 

$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-CH_2Br$

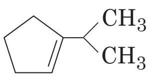
(d) 

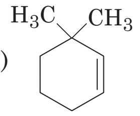
$CH_3-\overset{\overset{\displaystyle Br}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2CH_3$

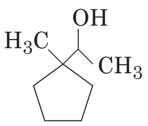
51. The major product in the following reaction is

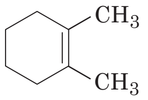


(JEE Main 2020)

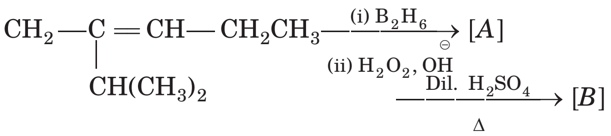
(a) 

(b) 

(c) 

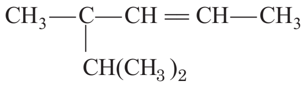
(d) 

52. The major product $[B]$ in the following sequence of reactions is

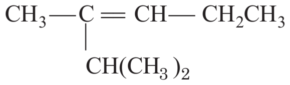


$$\underset{\displaystyle CH(CH_3)_2}{CH_2-\overset{}{C}}=CH-CH_2CH_3 \xrightarrow[\text{(ii) } H_2O_2,\ \overset{\ominus}{O}H]{\text{(i) } B_2H_6} [A] \xrightarrow[\Delta]{\text{Dil. } H_2SO_4} [B]$$

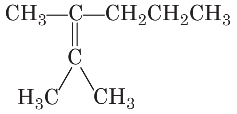
(JEE Main 2020)

(a) 

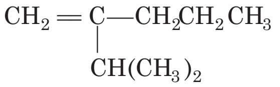
$CH_3-\underset{CH(CH_3)_2}{\underset{|}{C}}-CH=CH-CH_3$

(b) 

$CH_3-\underset{CH(CH_3)_2}{\underset{|}{C}}=CH-CH_2CH_3$

(c) 

$CH_3-\underset{\underset{H_3C\ \ CH_3}{\overset{\|}{C}}}{C}-CH_2CH_2CH_3$

(d) 

$CH_2=\underset{CH(CH_3)_2}{\underset{|}{C}}-CH_2CH_2CH_3$

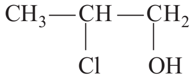
53. Which one of the following alkenes when treated with HCl yields majorly an anti Markownikoff product ? *(JEE Main 2019)*

(a) $Cl-CH=CH_2$
(b) $H_2N-CH=CH_2$
(c) $CH_3O-CH=CH_2$
(d) $F_3C-CH=CH_2$

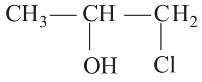
54. The major product of the following addition reaction is

$$H_3C-CH=CH_2 \xrightarrow{Cl_2/H_2O}$$

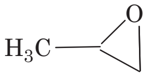
(JEE Main 2019)

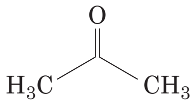
(a) 

$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

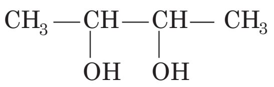
(b) 

$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

(c) 

(d) 

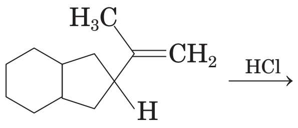
55. But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give *(JEE Main 2019)*

(a) 

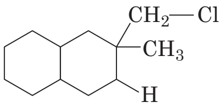
$CH_3-\underset{OH}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3$

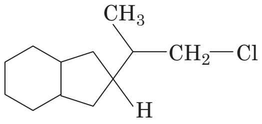
(b) one molecule of CH_3CHO and one molecule of CH_3COOH
(c) 2 molecules of CH_3COOH
(d) 2 molecules of CH_3CHO

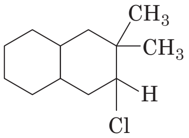
56. The major product of the following reaction is

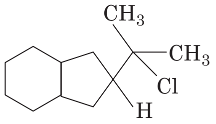


(JEE Main 2019)

(a) 

(b) 

(c) 

(d) 

57. 3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is *(JEE Main 2017)*

(a) six (b) zero (c) two (d) four

58. Ozonolysis of an organic compound A produces acetone and propionaldehyde in equimolar mixture. Identify A from the following compounds. *(AIEEE 2011)*

(a) 2-methyl-1-pentene (b) 1-pentene
(c) 2-pentene (d) 2-methyl-2-pentene

General Characteristics and Methods of Preparation of Alkynes

59. The number of possible alkynes with molecular formula C_5H_8 is

(a) 3 (b) 4 (c) 5 (d) 6

60. $CaC_2 + H_2O \longrightarrow A \xrightarrow{H_2SO_4/HgSO_4} B$

Identify A and B in the given reaction.

(a) C_2H_2 and CH_3CHO (b) CH_4 and $HCOOH$
(c) C_2H_4 and CH_3COOH (d) C_2H_2 and CH_3COOH

61. In the following reaction, what is X?

$$X \xrightarrow[H_2SO_4]{\text{Conc.}} Y \xrightarrow[\text{(ii) Alc. KOH}]{\text{(i) } Br_2} CH_3C\equiv CH$$

(a) $CH_3CH_2CH_3$ (b) $CH_3CH_2CH_2OH$
(c) $(CH_3)_2CHBr$ (d) CH_3CH_2Br

62. In the following sequence of reactions,

$$CH_3CH_2Br \xrightarrow{KOH(alc.)} X \xrightarrow{Br_2} Y \xrightarrow{KOH(alc.)} Z \text{ ; } Z \text{ is}$$

(a) $CH_2 = CH_2$ (b) CH_2BrCH_2Br

(c) $CH \equiv CH$ (d) CH_3CH_3

63. $R—CH_2— CCl_2—R \xrightarrow{Reagent} R—C \equiv C—R$

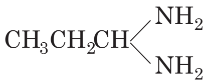
The reagent is

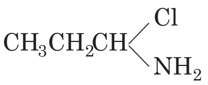
(a) Na (b) HCl in H_2O

(c) KOH in C_2H_5OH (d) Zn in alcohol

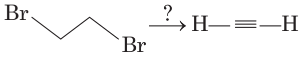
64. When $CH_3CH_2CHCl_2$ is treated with $NaNH_2$, the product formed is

(a) $CH_3—CH=CH_2$ (b) $CH_3—C \equiv CH$

(c) 
$CH_3CH_2CH(NH_2)_2$

(d) 
$CH_3CH_2CH(Cl)(NH_2)$

65. The reagents for the conversion



(a) alcoholic KOH

(b) alcoholic KOH followed by $NaNH_2$

(c) aqueous KOH followed by $NaNH_2$

(d) Zn/CH_3OH

66. Identify Z in the following reaction sequence:

$$CH_3CH_2CH_2OH \xrightarrow[160\text{-}180°C]{Conc.\ H_2SO_4} X \xrightarrow{Br_2} Y \xrightarrow[(ii)\ NaNH_2]{(i)\ Alc.\ KOH} Z$$

(a) $CH_3—CH(NH_2)—CH_2NH_2$

(b) $CH_3—CHOH—CH_2OH$

(c) $CH_3—C(OH)=CH_2$

(d) $CH_3—C \equiv CH$

67. 2, 3-dibromobutane can be converted into 2- butyne in a two step reaction using

(a) (i) HCl and (ii) NaH

(b) (i) Alc. KOH and (ii) $NaNH_2$

(c) (i) Na and (ii) NaOH

(d) Br_2 and (ii) NaH

68. 2 butanone is heated with PCl_5 and the product so obtained is heated with alcoholic KOH, the final product obtained is

(a) 1 - butyne (b) 2- butyne

(c) 1, 2-butadiene (d) 1, 3-butadiene

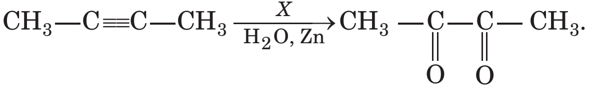
69. In the series,

$$C_2H_2 \xrightarrow{NaNH_2} X \xrightarrow{CH_3I} Y \xrightarrow[H_2SO_4,\ H_2O]{HgSO_4} Z,$$

the compound Z is

(a) $CH_3CH_2CH=CH_2$ (b) CH_3COCH_3

(c) CH_3CHO (d) $CH_3CH_2CH_2CHO$

70. 

$$CH_3—C \equiv C—CH_3 \xrightarrow[H_2O,\ Zn]{X} CH_3—\underset{\underset{O}{\|}}{C}—\underset{\underset{O}{\|}}{C}—CH_3.$$

In the given reaction, reagent X will be

(a) $KMnO_4$ (b) HIO_4 (c) O_3 (d) O_2

71. The reduction of 4-octyne with H_2 in the presence of $Pd/CaCO_3$ quinoline gives

(a) *trans*-4-octene

(b) *cis*-4-octene

(c) a mixture of *cis*-and *trans*-4-octene

(d) a completely reduced product C_8H_{18}

72. The product(s) obtained *via* oxymercuration ($HgSO_4 + H_2SO_4$) of but-1-yne would be

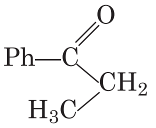
(a) $CH_3CH_2COCH_3$

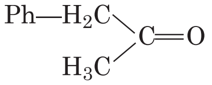
(b) $CH_3CH_2CH_2CHO$

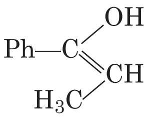
(c) $CH_3CH_2CHO + HCHO$

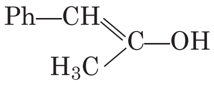
(d) $CH_3CH_2COOH + HCOOH$

73. $Ph—C \equiv C— CH_3 \xrightarrow{Hg^{2+}/H^+} A,$

(a) 

(b) 

(c) 

(d) 

74. The final product in the following sequence of reaction is

$$CH \equiv CH \xrightarrow{NaNH_2} A \xrightarrow{CH_3Br} B$$

(a) $CH_2 = CH — CH = CH_2$

(b) $HC \equiv C — CH_3$

(c) $CH_2 = CH — CH_3$

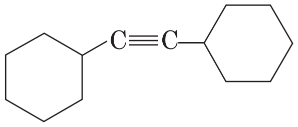
(d) $CH_3 — CH_2 — CH_3$

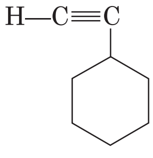
75. Acetylene and HCHO reacts in the presence of copper acetylide catalyst to form

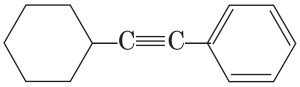
(a) 1-butyne-1, 4-diol (b) 2-butyne-1, 2-diol

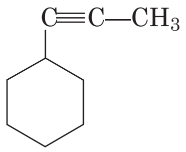
(c) 2-butyne-1, 4-diol (d) None of these

76. Which of the following form alkynide ?

(a) 

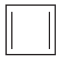
(b) 

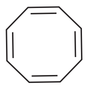
(c) 

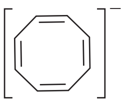
(d) 

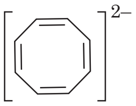
Aromatic Hydrocarbons Including Benzene

77. Which among the following is aromatic?

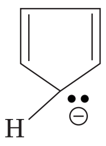
(a) 

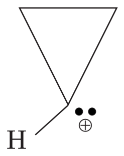
(b) 

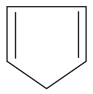
(c) 

(d) 

78. Which of the following species will be aromatic?

(a) 

(b) 

(c) 

(d) None of these

79. Which of the following annulenes is anti-aromatic?

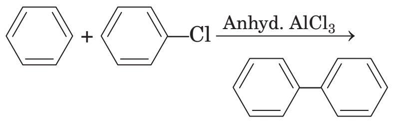
(a) Benzene

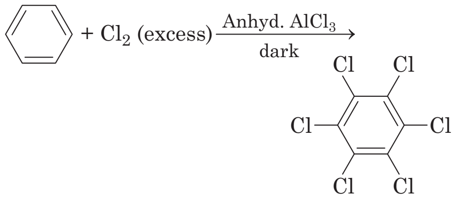
(b) Cyclobutadiene

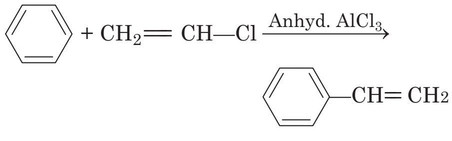
(c) Cyclodecapentene

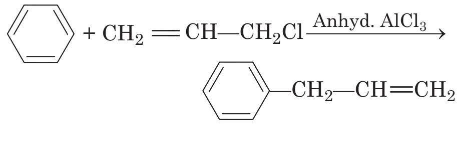
(d) Cyclooctatetraene

80. Consider the following reactions :

(A) 

(B) 

(C) 

(D) 

Which of these reactions are possible ? *(JEE Main 2020)*

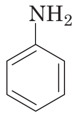
(a) (*B*) and (*D*)

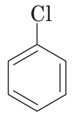
(b) (*A*) and (*D*)

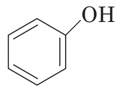
(c) (*B*), (*C*) and (*D*)

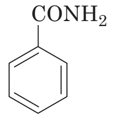
(d) (*A*) and (*B*)

81. Which of these will produce the highest yield in Friedel-Crafts' reaction? *(JEE Main 2020)*

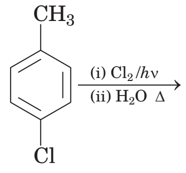
(a) 

(b) 

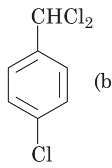
(c) 

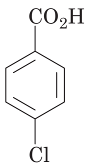
(d) 

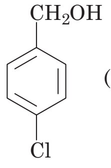
82. The major product of the following reaction is

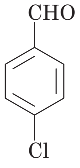


(JEE Main 2019)

(a) 

(b) 

(c) 

(d) 

83. Polysubstitutiion is a major drawback in *(JEE Main 2019)*

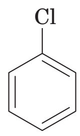
(a) Friedel-Crafts' alkylation

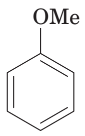
(b) Reimer-Tiemann reaction

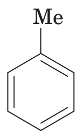
(c) Friedel-Crafts' acylation

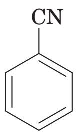
(d) Acetylation of aniline

84. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is *(JEE Main 2019)*


A


B


C


D

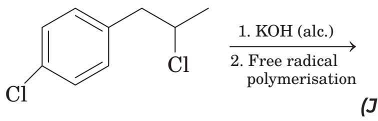
(a) $A < B < C < D$

(b) $B < C < A < D$

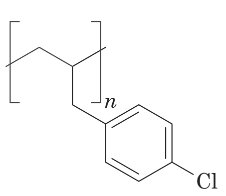
(c) $D < A < C < B$

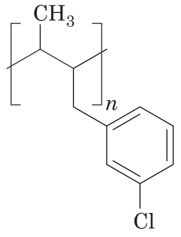
(d) $D < B < A < C$

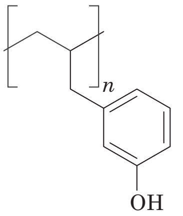
85. The major product of the following reaction is

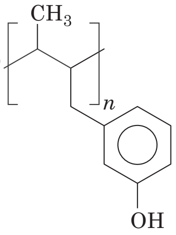


(JEE Main 2019)

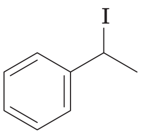
(a) 

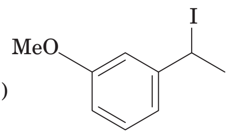
(b) 

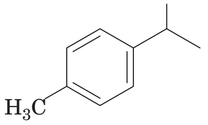
(c) 

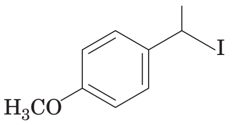
(d) 

86. Increasing rate of S_N1 reaction in the following compounds is *(JEE Main 2019)*

(*A*) 

(*B*) 

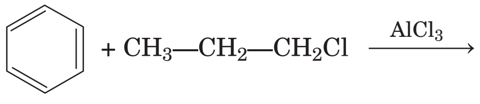
(*C*) 

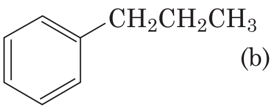
(*D*) 

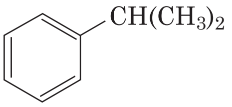
(a) (*A*) < (*B*) < (*C*) < (*D*) (b) (*B*) < (*A*) < (*C*) < (*D*)

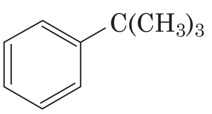
(c) (*A*) < (*B*) < (*D*) < (*C*) (d) (*B*) < (*A*) < (*D*) < (*C*)

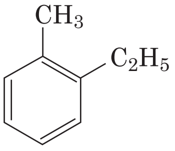
87. What will be the product obtained as a result of the following reaction and why? *(NCERT Exemplar)*



(a) 

(b) 

(c) 

(d) 

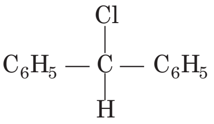
88. The treatment of benzene with benzoyl chloride in the presence of $AlCl_3$ gives

(a) benzaldehyde (b) benzophenone

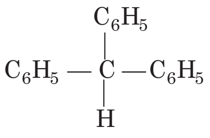
(c) diphenyl (d) cyclohexane

89. A Friedel-Crafts reaction of benzene with chloroform produces

(a) $C_6H_5CHCl_2$

(b) 

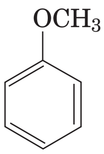
$C_6H_5-\overset{Cl}{\underset{H}{C}}-C_6H_5$

(c) 

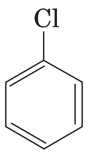
$C_6H_5-\overset{C_6H_5}{\underset{H}{C}}-C_6H_5$

(d) All of these

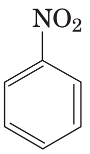
90. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile. *[NCERT Exemplar]*



I



II



III

(a) I > II > III

(b) I > III > II (c) II > I > III (d) II > III > I

91. Among the following, the compound that can be most readily sulphonated is

(a) benzene (b) nitrobenzene

(c) toluene (d) chlorobenzene

92. Nitrobenzene can be prepared from benzene by using a mixture of concentrated HNO_3 and concentrated H_2SO_4. In the nitrating mixture, HNO_3 acts as

(a) base (b) acid

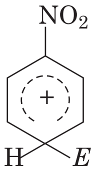
(c) reducing agent (d) catalyst

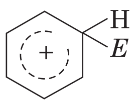
93. The reaction of toluene with chlorine in the presence of ferric chloride gives predominantly

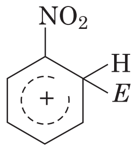
(a) benzoyl chloride (b) *m*-chlorotoluene

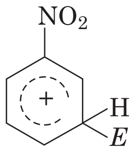
(c) benzyl chloride (d) *o*-and *p*-chlorotoluene

94. The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ-complex of the following, which σ-complex is of lowest energy?

(a) 

(b) 

(c) 

(d) 

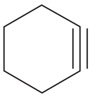
95. Arrange the following set of compounds in the order of their decreasing relative reactivity with an electrophile, E^+

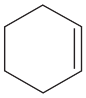
I. chlorobenzene
II. 2,4-dinitrochlorobenzene
III. *p*-nitrochlorobenzene
IV. toluene
V. *p*-$H_3C-C_6H_4-NO_2$, *(NCERT)*

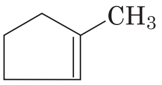
(a) I > II > III > IV > V (b) IV > V > I > III > II

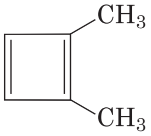
(c) V > IV > III > II > I (d) I > III > II > V > IV

96. Compound (*A*) on oxidation with $OsO_4/NaIO_4$ gives hexanedinal. Structure of compound (*A*) will be

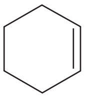
(a) 

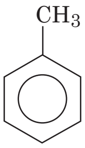
(b) 

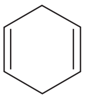
(c) 

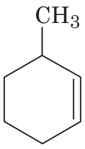
(d) 

97. Which one of the following on ozonolysis followed by oxidation will give adipic acid ?

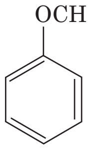
(a) 

(b) 

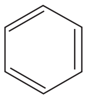
(c) 

(d) 

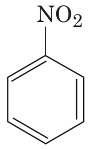
98. Among the following compounds (I – III) the correct order of reaction with electrophile is



I



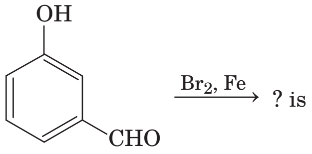
II

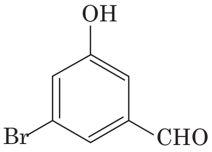


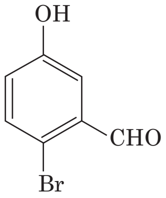
III

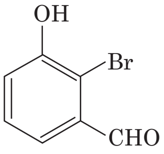
(a) II > III > I (b) III < I < II (c) I > II > III (d) I ≈ II > III

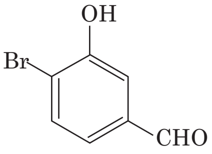
99. The product of the following reaction



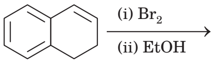
(a) 

(b) 

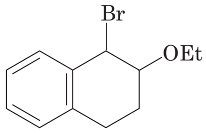
(c) 

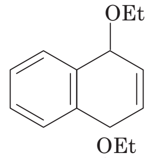
(d) 

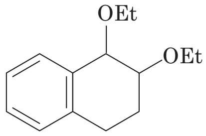
100. The major product of the following reaction is

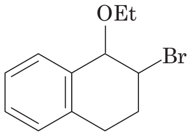


(JEE Main 2019)

(a) 

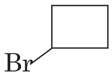
(b) 

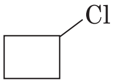
(c) 

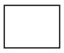
(d) 

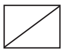
ROUND II Mixed Bag

1. What would be the product formed when 1-bromo-3-chloro cyclobutane reacts with two equivalents of metallic sodium in ether?

(a) 

(b) 

(c) 

(d) 

2. An alkene, C_8H_{18} is obtained as the only product on subjecting a primary alkyl halide to Wurtz reaction. On monobromination this alkane yields a single isomer of a tertiary bromide. The primary alkyl halide is *(NCERT Exemplar)*

(a) 1-chloro butane
(b) *iso*-butyl halide
(c) *iso*-pentyl halide
(d) *neo*-pentyl halide

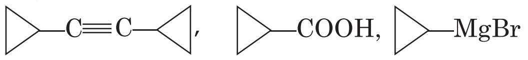
3. The relative reactivity of 1°, 2°, 3° hydrogen's towards chlorination is 1 : 3.8 : 5. The percentages of 2° monochlorinated products obtained from 2-methylbutane is *(NCERT Exemplar)*

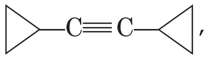
(a) 41.67 (b) 35.18
(c) 23.15 (d) 48.5

4. $C_8H_{10}(A) \xrightarrow{O_3/H_2O}$ acid (*B*)

$C_3H_5MgBr(C) \xrightarrow{CO_2,\ H_3O^+}$ acid *B*

Identify *A*, *B* and *C*.

(a) 

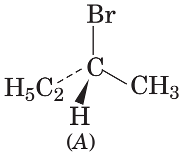
(b) 

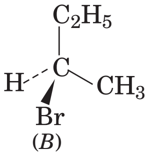
, $CH_3CH_2CH_2COOH$,
$CH_2{=}CH{-}CH_2MgBr$

(c) $CH_3-CH_2-CH_2-CH_3$, $CH_3CH_2CH_2COOH$,
$CH_2=CH-CH_2MgBr$

(d) $CH_3CH_2CH_2CH_3$, 

5. The addition of HBr to 1-butene gives a mixture of products *A, B* and *C*





$CH_3CH_2CH_2CH_2Br$
(*C*)

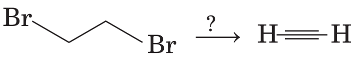
The mixture consists of *(NCERT Exemplar)*

(a) *A* and *B* as major and *C* as minor products
(b) *B* as major, *A* and *C* as minor products
(c) *B* as minor, *A* and *C* as major products
(d) *A* and *B* as minor and *C* as major products

6. Alkyne, C_7H_{12}, when reacted with alkaline $KMnO_4$ followed by acidification with HCl gives a mixture of $(CH_3)_2CHCOOH + CH_3CH_2COOH$. The alkyne C_7H_{12} is

(a) 3-hexyne
(b) 2-methyl-2-hexene
(c) 2-methyl-3-hexyne
(d) 3-methyl-2-hexyne

7. The reagent(s) for the following conversion,



is/are

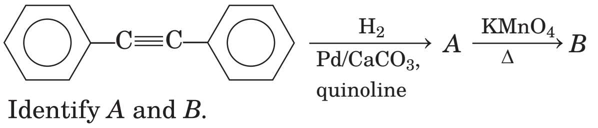
(a) alcoholic KOH
(b) alcoholic KOH followed by $NaNH_2$
(c) aqueous KOH followed by $NaNH_2$
(d) Zn / CH_3OH

8. $A \xleftarrow[\text{(ii) } H_2O_2,\ OH^-]{\text{(i) } BH_3,\ THF} CH_3C\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} B$

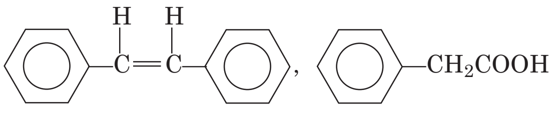
Identify *A* and *B*.

(a) CH_3CHO, CH_3COCH_3
(b) CH_3CH_2CHO, CH_3COCH_3
(c) $CH_3CH_2CHO, CH_3COCH_2CH_3$
(d) $HCHO, CH_3COCH_3$

9.



Identify *A* and *B*.

(a)


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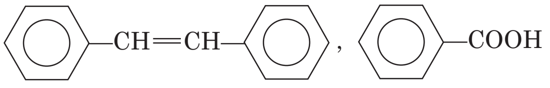

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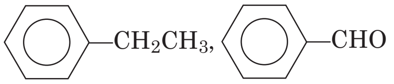

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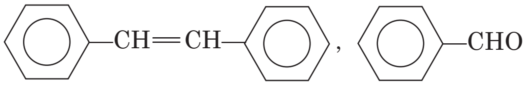


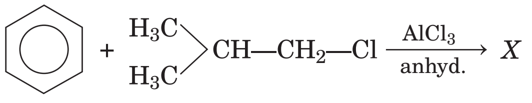
10. Propyne and propene can be distinguished by

(a) conc. H_2SO_4
(b) Br_2 in CCl_4
(c) alk. $KMnO_4$
(d) $AgNO_3$ in NH_3

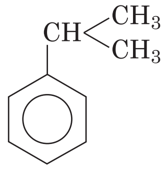
11. Arrange benzene, *n*-hexane and ethyne in the decreasing order of acidic behaviour. *(NCERT)*

(a) Ethyne > benzene > hexane
(b) Hexane > benzene > ethyne
(c) Ethyne > hexane > benzene
(d) Benzene > hexane > ethyne

12.



Identify the *X* in the above reaction

(a)


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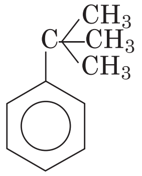

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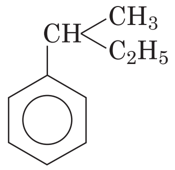

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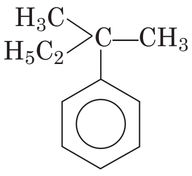
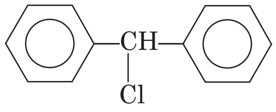


13. When excess of C_6H_6 reacts with CH_2Cl_2 in the presence of anhydrous $AlCl_3$, the following compound is obtained

(a)


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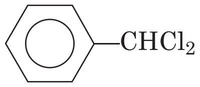

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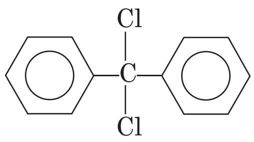

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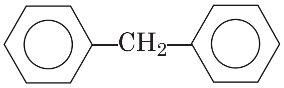
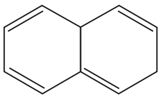
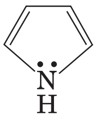
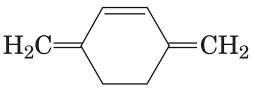
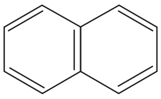


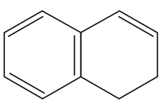
14. Which of the following compounds are aromatic according to Huckel's rule? *(NCERT Exemplar)*

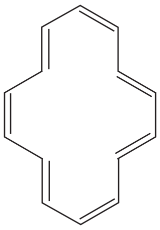
I.


II.


III.


IV.


V.


VI.


(a) I, II, IV, V (b) II, IV, V, VI

(c) II, III, V only (d) IV, V and VI

15. 896 mL vapour of a hydrocarbon '*A*' having carbon 87.80% and hydrogen 12.19% weighs 3.28 g at STP. Hydrogenation of '*A*' gives 2-methylpentane. Also '*A*' on hydration in the presence of H_2SO_4 and $HgSO_4$ gives a ketone '*B*' having molecular formula $C_6H_{12}O$. The ketone '*B*' gives a positive iodoform test. Find the structure of '*A*'. *(NCERT Exemplar)*

(a) $(CH_3)_3CC\equiv C-CH_2CH_3$

(b) $(CH_3)_2CHCH_2C\equiv CH$

(c) $CH_3CH_2C\equiv CCH_2CH_2CH_2CH_3$

(d) $(CH_3)_2CHCH_2CH_2C\equiv CH$

16. Match the reagent from Column I which on reaction with $CH_3-CH=CH_2$ gives some product given in Column II as per the codes given below *(NCERT Exemplar)*

	Column I	Column II
A.	O_3 / Zn + H_2O	1. Acetic acid and CO_2
B.	$KMnO_4$ / H^+	2. Propan-1-ol
C.	$KMnO_4$ / OH^-	3. Propan-2-ol
D.	H_2O / H^+	4. Acetaldehyde and formaldehyde
E.	B_2H_6 / NaOH and H_2O_2	5. Propane-1,2- diol

Codes

	A	B	C	D	E
(a)	4	1	5	2	3
(b)	4	5	1	2	3
(c)	3	2	1	5	4
(d)	4	1	5	3	2

17. Match the following reactants in Column I with the corresponding reaction products in Column II. *(NCERT Exemplar)*

	Column I	Column II
A.	Benzene + $Cl_2 \xrightarrow{AlCl_3}$	1. Benzoic acid
B.	Benzene + $CH_3Cl \xrightarrow{AlCl_3}$	2. Methyl phenyl ketone
C.	Benzene + $CH_3COCl \xrightarrow{AlCl_3}$	3. Toluene
D.	Toluene $\xrightarrow{KMnO_4/NaOH}$	4. Chlorobenzene
		5. Benzene hexachloride

Codes

	A	B	C	D		A	B	C	D
(a)	4	3	2	1	(b)	1	2	3	4
(c)	4	3	1	5	(d)	1	5	2	3

18. In the acid catalysed dehydration of alcohols to alkenes, the reactive intermediate involved is a

(a) carbene (b) free radical

(c) carbocation (d) carbanion

19. When ethyl alcohol is heated with conc. H_2SO_4 at 443 K, ethylene is formed by

(a) intermolecular dehydration

(b) intramolecular dehydration

(c) intermolecular hydration

(d) intramolecular hydration

20. Which one of the following heptanols can be dehydrated to hept-3-ene only?

(a) Heptan-3-ol (b) Heptan-4-ol

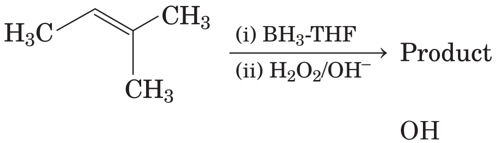
(c) Heptan-2-ol (d) Heptan-1-ol

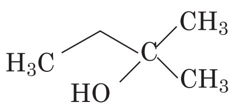
21. 2-phenyl propene on acidic hydration gives

(a) 2-phenyl-2-propanol (b) 2-phenyl-1-propanol

(c) 3-phenyl-1-propanol (d) 1-phenyl-2-propanol

22. The product formed in the following reaction is



(a)


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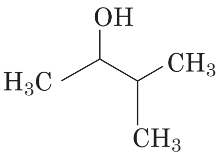
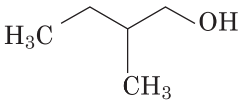
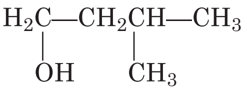


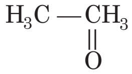
(c)


(d)


$H_2\underset{|}{\overset{}{C}}-CH_2\underset{|}{CH}-CH_3$ with OH under the first carbon and CH_3 under CH: $\underset{OH}{H_2C}-CH_2\underset{CH_3}{CH}-CH_3$

23. $CH_3—C\equiv C—H \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} A$, A is

(a) $CH_3—CH_2—CHO$

(b) 
$H_3C—\underset{\underset{O}{\|}}{C}—CH_3$

(c) $CH_3—CHO$

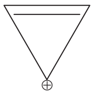
(d) $CH_3—CH_2—CH_2—OH$

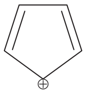
Numeric Value Questions

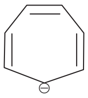
24. No. of chiral compounds are possible on monochlorination of 2-methyl butane?

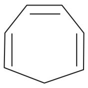
25. No. of chiral compounds possible on monochlorination of 2-methyl butane?

26. Which compound(s) out of the following is/are not aromatic? *(JEE Main 2019)*

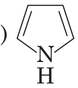

(A)

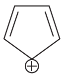

(B)

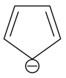

(C)

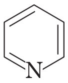

(D)

27. How many of the following compounds is not aromatic ?

(a) 

(b) 

(c) 

(d) 

28. The number of sp^2-hybrid orbitals in a molecule of benzene is …… *(JEE Main 2020)*

29. In the following sequence of reactions the maximum number of atoms present in molecule 'C' in one plane is ....

$$A \xrightarrow[\text{Cu tube}]{\text{Red hot}} B \xrightarrow[\text{Anhydrous } AlCl_3]{CH_3Cl \text{ (1. eq.)}} C$$

(A is a lowest molecular weight alkyne)

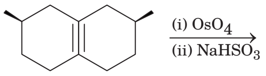
(JEE Main 2020)

30. The total number of monohalogenated organic products in the following (including stereoisomers) reaction is ....

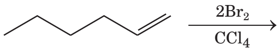
$$\underset{\substack{\text{(Simplest optically}\\\text{active alkene)}}}{A} \xrightarrow[\text{(ii) } X_2/\Delta]{\text{(i) } H_2/Ni/\Delta}$$

(JEE Main 2020)

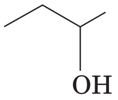
31. How many products will be formed in this reaction?



32. How many stereoisomeric tetrabromides will be formed in the following reaction?



33. The total number of C—C sigma bond/s in mesityl oxide ($C_6H_{10}O$) is ……… . *(JEE Main 2021)*

34. 

$\xrightarrow[\Delta]{H^{\oplus}}$ Possible products (A) $\xrightarrow{Br_2/CCl_4}$ (B)

The (A + B) is …… .

Answers

Round I

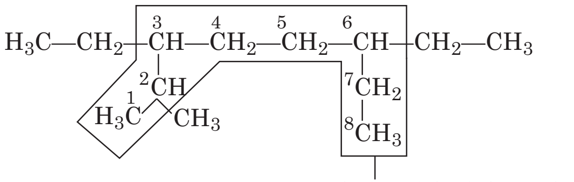
1. (a)	*2.* (d)	*3.* (c)	*4.* (c)	*5.* (c)	*6.* (b)	*7.* (b)	*8.* (a)	*9.* (c)	*10.* (a)
11. (a)	*12.* (a)	*13.* (b)	*14.* (a)	*15.* (c)	*16.* (b)	*17.* (a)	*18.* (b)	*19.* (d)	*20.* (d)
21. (b)	*22.* (a)	*23.* (d)	*24.* (a)	*25.* (b)	*26.* (a)	*27.* (a)	*28.* (b)	*29.* (c)	*30.* (b)
31. (d)	*32.* (a)	*33.* (c)	*34.* (c)	*35.* (a)	*36.* (a)	*37.* (c)	*38.* (a)	*39.* (c)	*40.* (d)
41. (b)	*42.* (b)	*43.* (d)	*44.* (c)	*45.* (c)	*46.* (b)	*47.* (b)	*48.* (c)	*49.* (c)	*50.* (d)
51. (d)	*52.* (c)	*53.* (d)	*54.* (b)	*55.* (c)	*56.* (d)	*57.* (d)	*58.* (d)	*59.* (a)	*60.* (a)
61. (b)	*62.* (c)	*63.* (c)	*64.* (b)	*65.* (b)	*66.* (d)	*67.* (b)	*68.* (b)	*69.* (b)	*70.* (c)
71. (b)	*72.* (a)	*73.* (a)	*74.* (b)	*75.* (c)	*76.* (b)	*77.* (d)	*78.* (a)	*79.* (b)	*80.* (a)
81. (b)	*82.* (d)	*83.* (a)	*84.* (c)	*85.* (b)	*86.* (b)	*87.* (b)	*88.* (b)	*89.* (b)	*90.* (a)
91. (c)	*92.* (a)	*93.* (d)	*94.* (b)	*95.* (b)	*96.* (b)	*97.* (d)	*98.* (c)	*99.* (b)	*100.* (d)

Round II

1. (d)	*2.* (b)	*3.* (b)	*4.* (a)	*5.* (a)	*6.* (c)	*7.* (b)	*8.* (b)	*9.* (b)	*10.* (d)
11. (a)	*12.* (b)	*13.* (d)	*14.* (b)	*15.* (b)	*16.* (d)	*17.* (a)	*18.* (c)	*19.* (b)	*20.* (b)
21. (a)	*22.* (b)	*23.* (a)	*24.* (4)	*25.* (2)	*26.* (1)	*27.* (1)	*28.* (18)	*29.* (13)	*30.* (8)
31. (2)	*32.* (3)	*33.* (5)	*34.* (8)						

Solutions

Round I

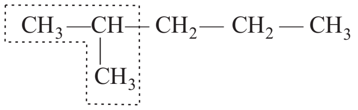
1. 

Longest chain with eight carbons

3,6-diethyl-3-methyloctane

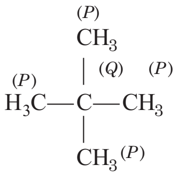
Name of the substituent are given alphabetically when more than one substituent are present.

2. *iso* word is used for those alkanes which have a methyl group attached to the second last carbon atom of the continuous chain. Hence, 2-methylpentane is a compound with an *iso*-propyl group.



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_2-CH_3$$

iso-propyl group

3. 

$$\overset{(P)}{H_3C}-\underset{\underset{CH_3^{(P)}}{|}}{\overset{\overset{(P)}{CH_3}}{\overset{|}{C}}}\,{}^{(Q)}-\overset{(P)}{CH_3}$$

neo-pentane

Here, P = Primary carbon atom

Q = Quaternary carbon atom

Thus, *neo*-pentane has 4-primary carbon atoms, 0-secondary, 0-tertiary and 1 quaternary carbon atom.

4. Beryllium carbide gives CH_4, magnesium carbide (MgC_2) and calcium carbide (CaC_2) give acetylene on hydrolysis while silicon carbide being covalent does not undergo hydrolysis.

5. Incomplete combustion of methane results in the formation of carbon black C(s).

6. Reduction of CH_3COCH_3 with HI and red P will give propane.

$$CH_3COCH_3 \xrightarrow{\text{HI, Red P}} CH_3CH_2CH_3$$

7. If two different alkyl halides (R_1-X and R_2-X) are used, a mixture of three alkanes is obtained which is difficult to separate.

8. $$CH_3I + 2[H] \xrightarrow{\text{Zn-Cu}} \underset{\text{Methane}}{CH_4} + HI$$

$$2CH_3I \xrightarrow{\text{Na}} \underset{\text{Ethane}}{CH_3CH_3}$$

9. Alkyl halides undergo reduction with red phosphorus and hydrogen iodide and result in the formation of alkane.

$$\underset{\text{Propyl iodide}}{CH_3CH_2CH_2I} \xrightarrow[\text{150°C}]{\text{Red P/HI}} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

The products obtained in the other reactions are as follows:

(a) $CH_3-CH=CH_2 \xrightarrow[\text{2.AgNO}_3\text{/NaOH}]{\text{1.B}_2\text{H}_6} CH_3-CH_2-CH_2OH$

(b) $CH_3CH_2CH_2-Cl \xrightarrow[\text{2.H}_2\text{O}_2]{\text{1.Mg/ether}} CH_3CH_2CH_2OH$

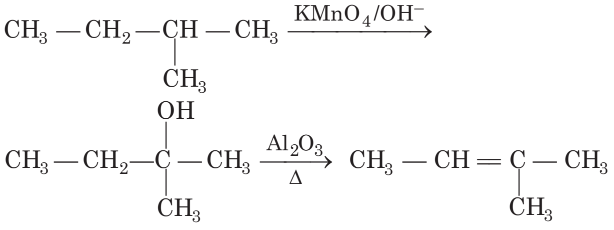
(c) $CH_3CH_2CO\overset{-}{O}\overset{+}{Na} \xrightarrow[\Delta]{\text{NaOH(CaO)}} CH_3-CH_3$

10. Boiling point $\propto$ molecular mass

$$\propto \frac{1}{\text{branching}} \quad (\because \text{Surface area decreases})$$

$\therefore$ n-hexane (straight chain) has the highest boiling point among the given alkanes.

11. The reaction is oxidation followed by Saytzeff elimination, as the compound contains 3° H atom.

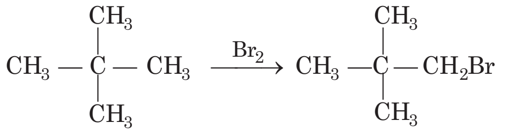


$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow{KMnO_4/OH^-}$$

$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3 \xrightarrow[\Delta]{Al_2O_3} CH_3-CH=\underset{\underset{CH_3}{|}}{C}-CH_3$$

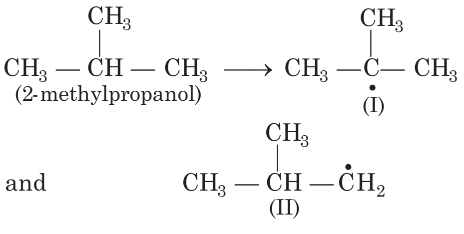
(A)

12. Among the halogens, fluorine being most electronegative is highly reactive and reactivity decreases on moving down the group. Thus, the correct order is $I_2 < Br_2 < Cl_2 < F_2$.

13. 

$$\underset{\text{2,2-dimethyl propane}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3} \xrightarrow{Br_2} \underset{(C_5H_{11}Br = 151)}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2Br}$$

14. 2-methylpropane gives two types of radicals.

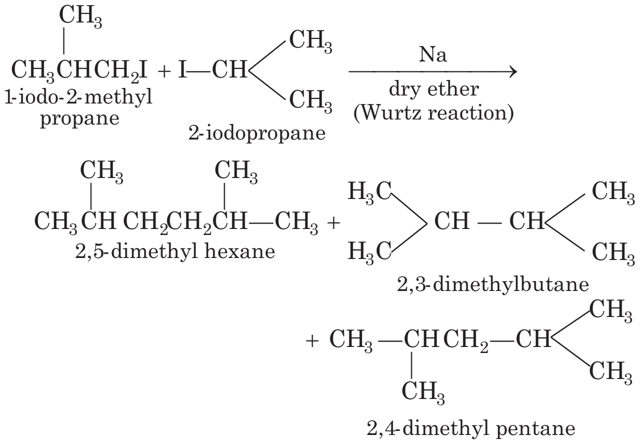


$$\underset{\text{(2-methylpropanol)}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3} \longrightarrow \underset{\text{(I)}}{CH_3-\underset{\bullet}{\overset{\overset{CH_3}{|}}{C}}-CH_3}$$

and $$\underset{\text{(II)}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-\dot{C}H_2}$$

Radical (I) is more stable because it is 3° and stabilized by nine hyperconjugative structures (as it has 9α-hydrogens).

Radical (II) is less stable because it is 1° and stabilized by only one hyperconjugative structure (as it has only 1 α-hydrogen).

15. 

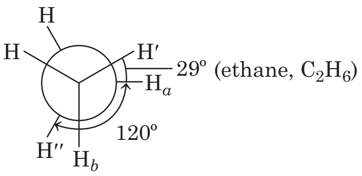
$$\underset{\text{1-iodo-2-methyl propane}}{CH_3\overset{CH_3}{\overset{|}{C}}HCH_2I} + \underset{\text{2-iodopropane}}{I{-}CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}} \xrightarrow[\text{dry ether (Wurtz reaction)}]{Na}$$

$$\underset{\text{2,5-dimethyl hexane}}{CH_3\overset{CH_3}{\overset{|}{C}}H\,CH_2CH_2\overset{CH_3}{\overset{|}{C}}H{-}CH_3} + \underset{\text{2,3-dimethylbutane}}{\begin{smallmatrix}H_3C\\H_3C\end{smallmatrix}CH{-}CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}$$

$$+\ \underset{\text{2,4-dimethyl pentane}}{CH_3{-}\underset{CH_3}{\underset{|}{C}}HCH_2{-}CH\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}}$$

16. A dihedral angle is the angle between two C—H bonds projected on a plane orthogonal to the C—C bond. In the given skew conformation, having Newman's projection the dihedral angle is

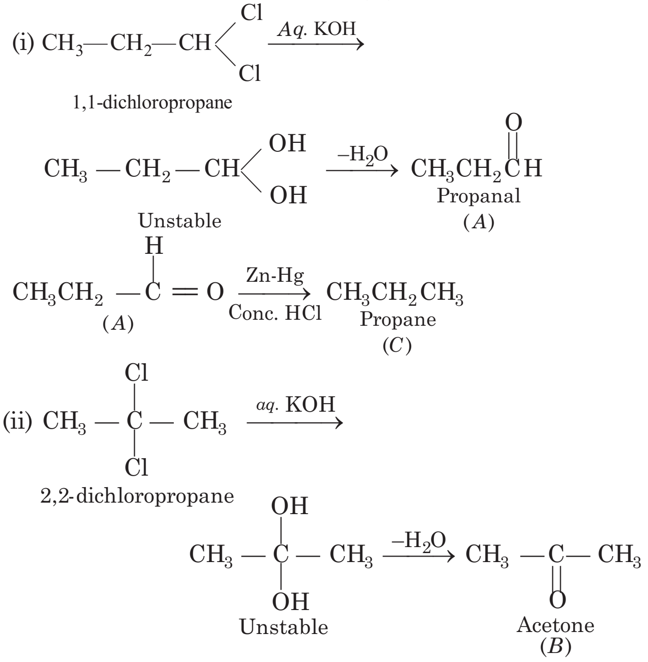
$$H'{-}C{-}C{-}H'' = (H'{-}C{-}C{-}H_a) + (H_a{-}C{-}C{-}H'')$$
$$= 29°+120° = 149°$$



17. All the H-atoms of *neo*-pentane are equivalent and thus it will yield monochloro product.

18. The thermal decomposition of alkanes is known as cracking. It leads to the formation of lower alkanes, alkenes and hydrogen.

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{400\text{-}600°C} \underset{\substack{\text{Ethylene}\\(X)}}{CH_2{=}CH_2} + \underset{\substack{\text{Methane}\\(Y)}}{CH_4}$$

20. 

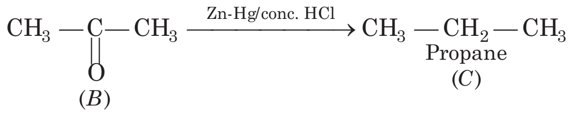
$$\text{(i)}\ \underset{\text{1,1-dichloropropane}}{CH_3{-}CH_2{-}CH\begin{smallmatrix}Cl\\Cl\end{smallmatrix}} \xrightarrow{Aq.\ KOH}$$

$$\underset{\text{Unstable}}{CH_3{-}CH_2{-}CH\begin{smallmatrix}OH\\OH\end{smallmatrix}} \xrightarrow{-H_2O} \underset{\substack{\text{Propanal}\\(A)}}{CH_3CH_2\overset{O}{\overset{\|}{C}}H}$$

$$\underset{(A)}{CH_3CH_2{-}\overset{H}{\overset{|}{C}}{=}O} \xrightarrow[\text{Conc. HCl}]{\text{Zn-Hg}} \underset{\substack{\text{Propane}\\(C)}}{CH_3CH_2CH_3}$$

$$\text{(ii)}\ \underset{\text{2,2-dichloropropane}}{CH_3{-}\overset{Cl}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}{-}CH_3} \xrightarrow{aq.\ KOH}$$

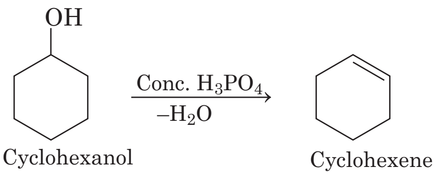
$$\underset{\text{Unstable}}{CH_3{-}\overset{OH}{\overset{|}{\underset{OH}{\underset{|}{C}}}}{-}CH_3} \xrightarrow{-H_2O} \underset{\substack{\text{Acetone}\\(B)}}{CH_3{-}\underset{O}{\underset{\|}{C}}{-}CH_3}$$

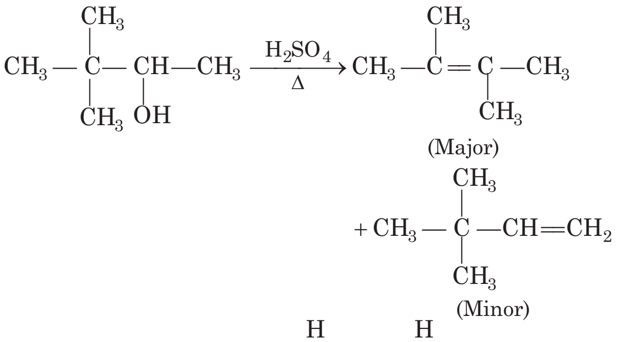


$$\underset{(B)}{CH_3{-}\underset{O}{\underset{\|}{C}}{-}CH_3} \xrightarrow{\text{Zn-Hg/conc. HCl}} \underset{\substack{\text{Propane}\\(C)}}{CH_3{-}CH_2{-}CH_3}$$

Hence, compound (*C*) is propane.

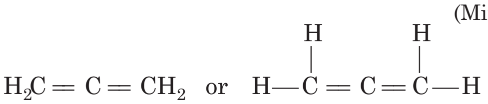
21. The best method to prepare cyclohexene from cyclohexanol is by using conc. H_3PO_4 because among given options dehydrating agent is only conc. H_3PO_4



22. 

$$CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}\underset{OH}{\underset{|}{C}H}{-}CH_3 \xrightarrow[\Delta]{H_2SO_4} \underset{\text{(Major)}}{CH_3{-}\overset{CH_3}{\overset{|}{C}}{=}\underset{CH_3}{\underset{|}{C}}{-}CH_3}$$

$$+\ \underset{\text{(Minor)}}{CH_3{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH{=}CH_2}$$

23. 

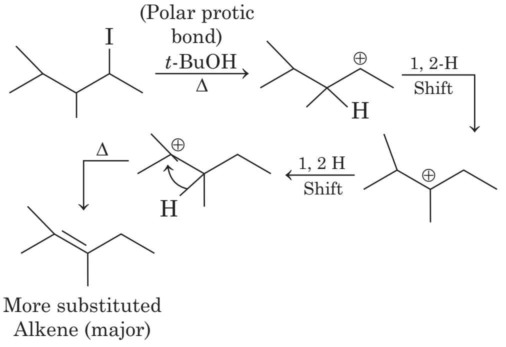
$$H_2C{=}C{=}CH_2 \quad \text{or} \quad H{-}\overset{H}{\overset{|}{C}}{=}C{=}\overset{H}{\overset{|}{C}}{-}H$$

Allene (C_3H_4)

It has two double and four single bonds.

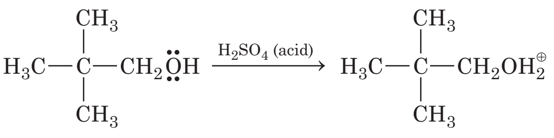
24. Conjugate dienes are more stable than the other dienes.

25. Complete reaction is as follows



The alkene formed is stable according to Saytzeff's rule. It states that alkenes with less number of hydrogen on the double bonded carbon atoms are preffered product.

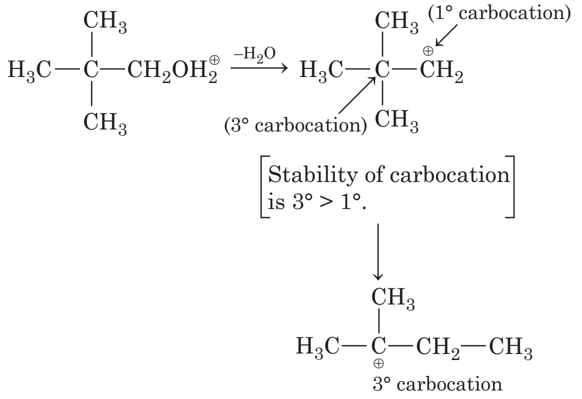
26. Reaction is as follows



$$H_3C{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_2\ddot{\underset{\cdot\cdot}{O}}H \xrightarrow{H_2SO_4\ \text{(acid)}} H_3C{-}\overset{CH_3}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}{-}CH_2OH_2^{\oplus}$$

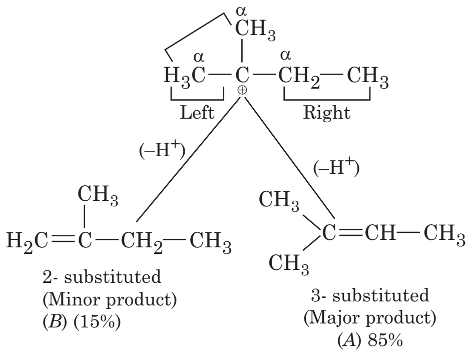
H_2SO_4 is sulphuric acid, that contain $H^{\oplus}$ and alcohol of contain lone pair.

Lone pair of oxygen accept $H^{\oplus}$ ion and form $H_2\overset{\oplus}{O}$ but oxygen is electronegative element and here O contain positive charge means it is unstable. Then H_2O will remove from here.



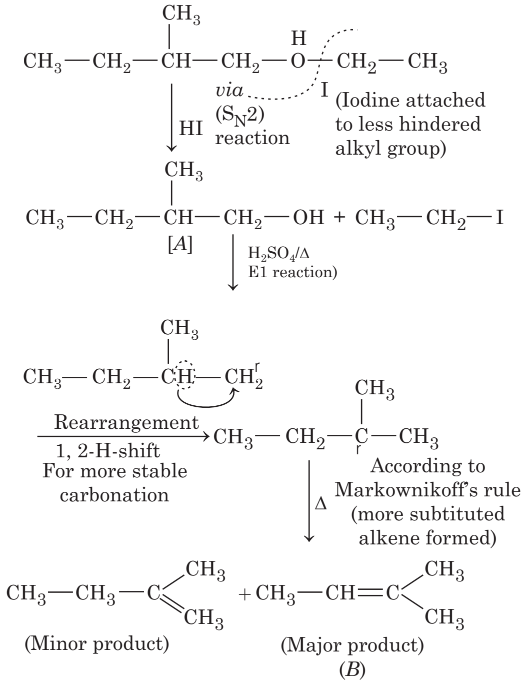
Stability of carbocation is 3° > 1°.

On heating 3° carbocation, 2 possible products are possible. These are as follows



So, correct option is (a).

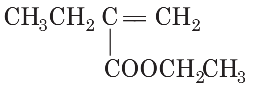
27.



28. Presence of strong base (EtO^-) and heat indicates elimination.

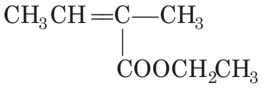
Thus, the compound undergo dehydrohalogenation and alkene is produced. As per the position of Cl in substrate, following 2 alkenes are formed as product:

(i)



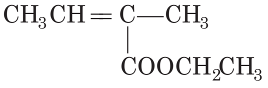
$CH_3CH_2\underset{COOCH_2CH_3}{C}=CH_2$

(ii)



$CH_3CH=\underset{COOCH_2CH_3}{C}-CH_3$

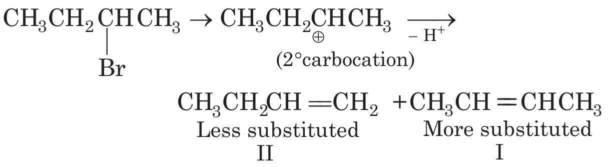
In accordance with Saytzeff rule



$CH_3CH=\underset{COOCH_2CH_3}{C}-CH_3$

will be the major product.

29.



$CH_3CH_2\underset{Br}{C}HCH_3 \rightarrow CH_3CH_2\overset{\oplus}{C}HCH_3 \xrightarrow[-H^+]{} CH_3CH_2CH=CH_2 + CH_3CH=CHCH_3$

Stability of I > II, hence I is predominant.

30. All given three alkadienes are isomers. Upon combustion, all of them gives same product. The most stable isomer will have least heat of combustion. Between two geometrical isomers of an acyclic alkene, *trans* is more stable than *cis*. In the given options, (a) have both double bonds that are *trans,* (b) have one *cis* and other one *trans* and (c) have both *cis*. So, the correct stability order of heat of combustion is $A < B < C$.

31. Heat of hydrogenation $\propto \frac{1}{\text{stability}}$

Among the given buta-1,3-diene is resonance stabilised, i.e. more stable, thus it has the lowest heat of hydrogenation.

32. $Cl_3\ C-CH=CH_2 \xrightarrow[\text{anti-Markownikoff's rule}]{HCl} Cl_3C-CH_2-CH_2Cl$

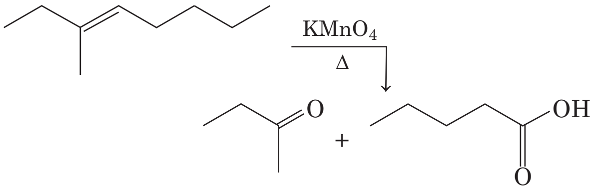
($\because$ CCl_3 is highly electron attracting group.)

33. Reactivity of halogen acids towards addition reactions increases with increase in the size of halogen atoms as this reaction involves dissociation of H—X bond.

34. Addition of HBr to an alkene in the presence of peroxide is the example of free radical addition reaction.

$$R-O-O-R \longrightarrow 2R-O^{\bullet}$$
$$R-O^{\bullet} + HBr \longrightarrow R-OH + Br^{\bullet}$$
$$R-CH=CH_2 + Br^{\bullet} \longrightarrow R-\dot{C}H-CH_2Br$$
$$R-\dot{C}H-CH_2Br \xrightarrow{HBr} RCH_2CH_2Br + Br^{\bullet}$$
$$Br^{\bullet} + Br^{\bullet} \longrightarrow Br_2$$

35.



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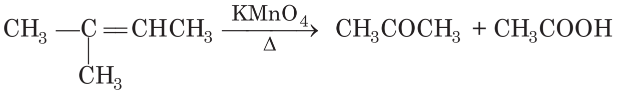
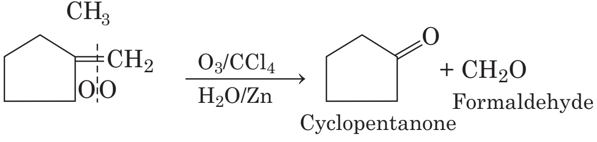


$$CH_3-\underset{\underset{CH_3}{|}}{C}=CHCH_3 \xrightarrow[\Delta]{KMnO_4} CH_3COCH_3 + CH_3COOH$$

37.



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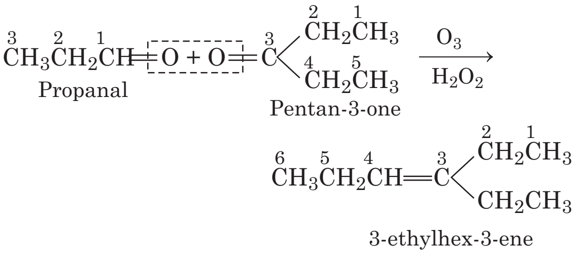
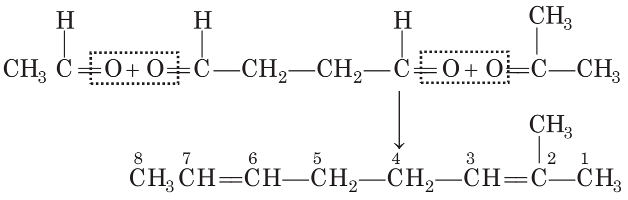


39. $OHC-CH_2-CH_2-CHO$, CH_3CHO and
(Butane-1,4-dial) (Ethanal)

CH_3COCH_3
(Propanone)

Hence, the structure of compound *A* is

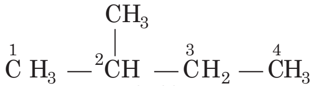


$$CH_3\overset{\overset{H}{|}}{C}=O + O=\overset{\overset{H}{|}}{C}-CH_2-CH_2-\overset{\overset{H}{|}}{C}=O + O=\overset{\overset{CH_3}{|}}{C}-CH_3$$

$$\overset{8}{C}H_3\overset{7}{C}H=\overset{6}{C}H-\overset{5}{C}H_2-\overset{4}{C}H_2-\overset{3}{C}H=\overset{\overset{CH_3}{|}}{\overset{2}{C}}-\overset{1}{C}H_3$$

(*A*) 2-methylocta-2,6-diene

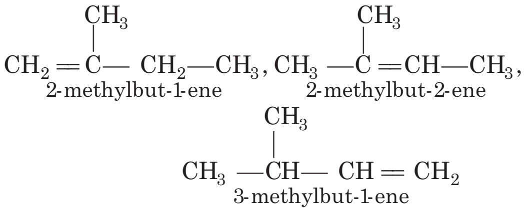
40. Structure of 2-methyl butane is



$$\overset{1}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{3}{C}H_2-\overset{4}{C}H_3$$

2-methyl butane

The structures of the given alkenes are as,



$$CH_2=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3,\ CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_3,$$

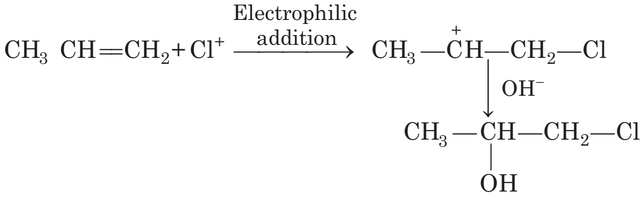
2-methylbut-1-ene, 2-methylbut-2-ene

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-CH=CH_2$$

3-methylbut-1-ene

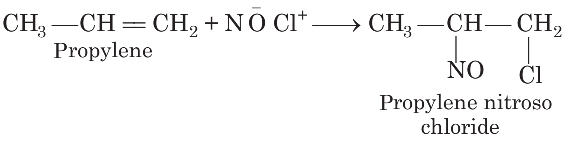
Thus, all give 2-methyl butane on hydrogenation.

41. HOCl has Cl^+ and OH^- ions



$$CH_3\ CH=CH_2+Cl^+ \xrightarrow{\text{Electrophilic addition}} CH_3-\overset{+}{C}H-CH_2-Cl \xrightarrow{OH^-} CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-Cl$$

42.



$$\underset{\text{Propylene}}{CH_3-CH=CH_2} + N\bar{O}\ Cl^+ \longrightarrow \underset{\text{Propylene nitroso chloride}}{CH_3-\underset{\underset{NO}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}}$$

43. $$\underset{\substack{\text{1,3-butadiene}\\(A)}}{CH_2=CH-CH=CH_2} \xrightarrow[\text{1 mole}]{H_2,\ Ni} \underset{\substack{\text{1,4-addition product}\\(B)}}{CH_3CH=CH-CH_3}$$

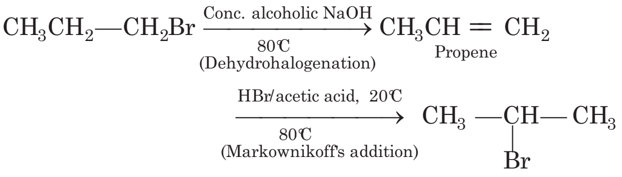
45. Peroxide effect is not observed in case of HCl and HI as for reaction to occur, both the propagation steps must be exothermic.

But one of the steps (i.e reaction of HCl with carbon radical and addition of iodine radical in case of HI) is endothermic in both the cases.

46. Peroxide effect is not observed in case of HCl. Instead it occurs by carbocation mechanism.

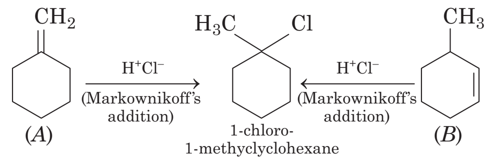
$$CH_3-CH=CH_2+H^+\longrightarrow \underset{\text{(I)}}{CH_3-\overset{+}{C}H-CH_3}$$

47.

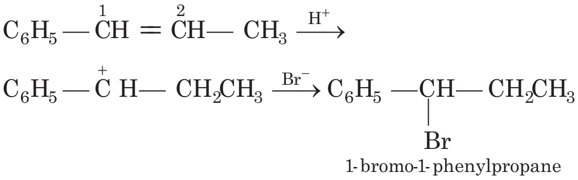


$$CH_3CH_2-CH_2Br \xrightarrow[\substack{80℃\\\text{(Dehydrohalogenation)}}]{\text{Conc. alcoholic NaOH}} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[\substack{80℃\\\text{(Markownikoff's addition)}}]{\text{HBr/acetic acid, }20℃} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

48.



49. Addition of H^+ occurs on C_2 rather than C_1 as it generates a carbocation which is stabilised by resonance over the benzene ring

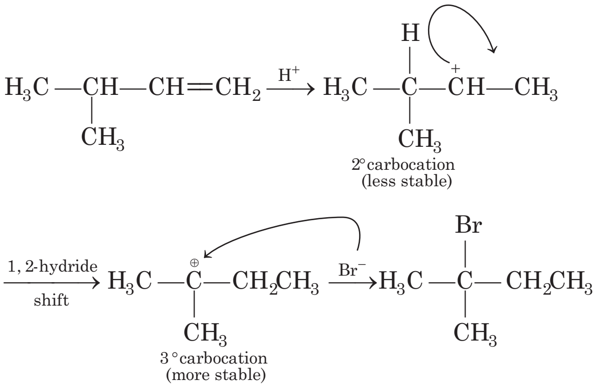


$$C_6H_5-\overset{1}{C}H=\overset{2}{C}H-CH_3 \xrightarrow{H^+}$$

$$C_6H_5-\overset{+}{C}H-CH_2CH_3 \xrightarrow{Br^-} C_6H_5-\underset{\underset{Br}{|}}{CH}-CH_2CH_3$$

1-bromo-1-phenylpropane

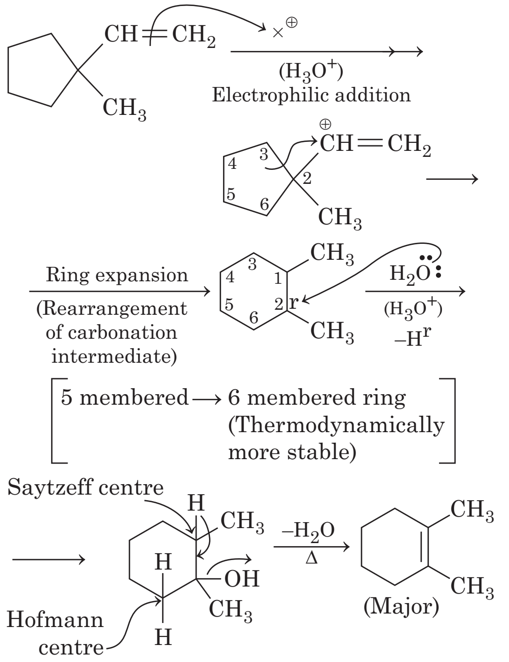
50.



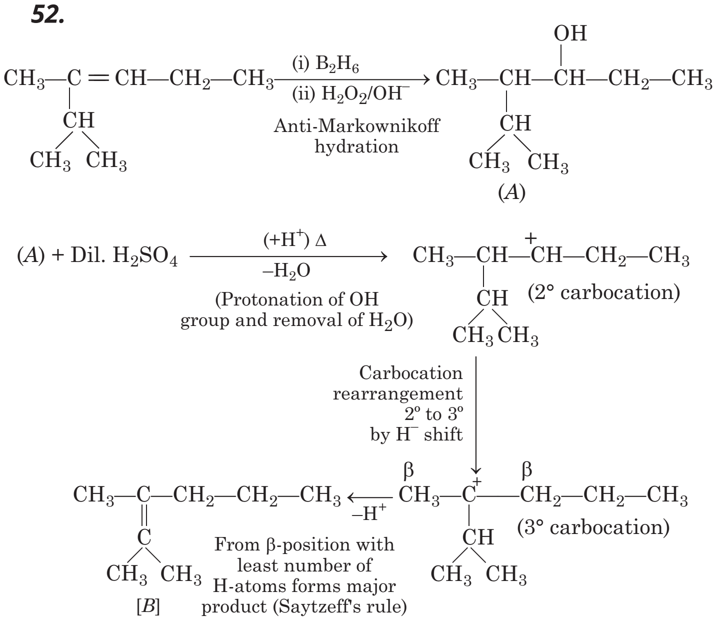
$$H_3C-\underset{\underset{CH_3}{|}}{CH}-CH=CH_2 \xrightarrow{H^+} \underset{\substack{2°\text{carbocation}\\\text{(less stable)}}}{H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-\overset{+}{C}H-CH_3}$$

$$\xrightarrow[\text{shift}]{\text{1, 2-hydride}} \underset{\substack{3°\text{carbocation}\\\text{(more stable)}}}{H_3C-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_2CH_3} \xrightarrow{Br^-} H_3C-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_2CH_3$$

51. Complete mechanism is as follows



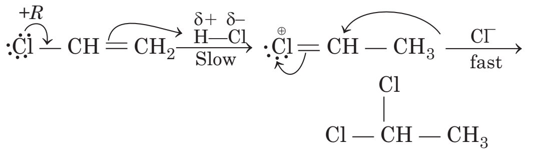
52.



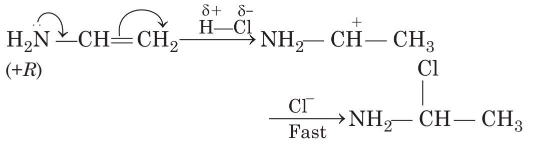
53. Attachment of electron donating group (+ *R* or + *I*) with sp^2-carbon of an unsymmetrical alkene supports Markownikov's addition rule through electrophilic-addition-pathway.

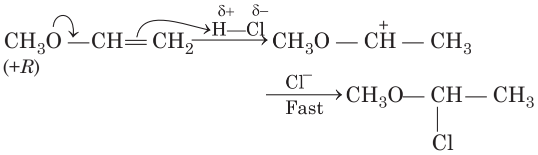
But, attachment of electron-withdrawing group (– *R* or – *I*) for the same will follow anti-Markownikov's pathway (even in absence of organic peroxide which favours free radical addition) through electrophilic addition pathway.

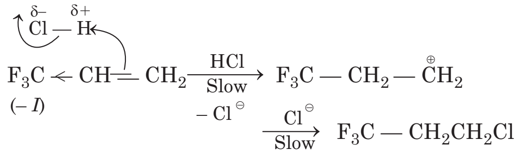
The product formed by given alkenes when treated with HCl.

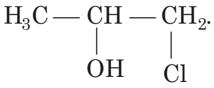


Similarly,

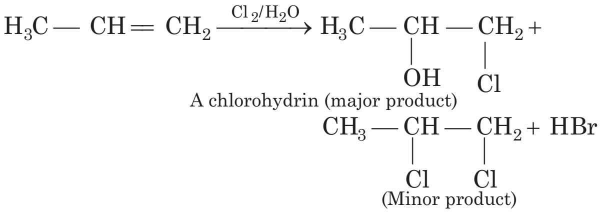




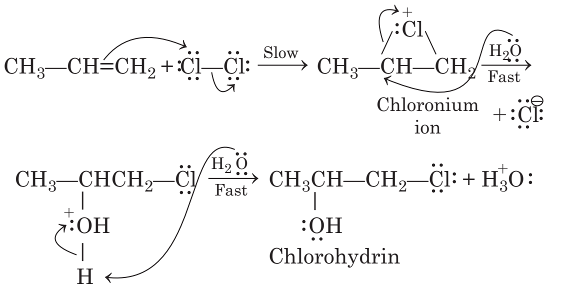




54. The major product of the given addition reaction is $H_3C-CH(OH)-CH_2Cl$. In this reaction, H_2O is used as a solvent and the major product of the reaction will be a *vicinal* halohydrin. A halohydrin is an organic molecule that contains both OH group and a halogen. In a *vicinal* halohydrin, the OH and halogen are bonded to adjacent carbons.



The reaction proceeds through following mechanism :



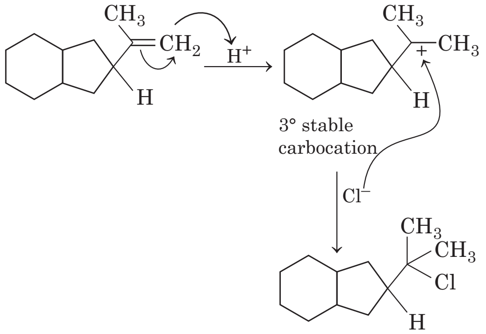
55. But-2-ene on reaction with alkaline $KMnO_4$ at elevated temperature followed by acidification will give acetic acid (CH_3COOH). Hot alkaline solution of potassium permanganate followed by acidification oxidatively cleaved alkenes.

The reaction proceed as follows

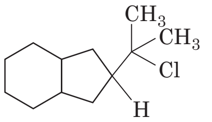
$$CH_3—CH=CH—CH_3 \xrightarrow[H_3O^+]{\text{Alk. KMnO}_4\text{, heat}} \underset{\text{Acetic acid}}{2CH_3COOH}$$

56. It is a simple case of Markownikoff addition.

The reaction proceeds as



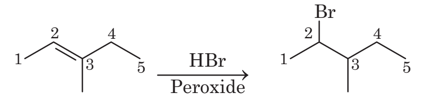
The structure of options given may confuse with ring expansion but that is seen as the minor product only [Due to the formation of a 3° stable carbocation in the process] the major product is



57. The number of stereoisomers in molecules which are not divisible into two equal halves and have n number of asymmetric C-atoms $= 2^n$.

3-methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product i.e. 2-bromo-3-methyl pentane.

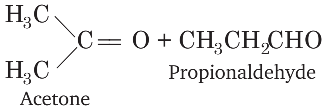
It has two chiral centres. Therefore, 4 stereoisomers are possible



3-methylpent-2-ene

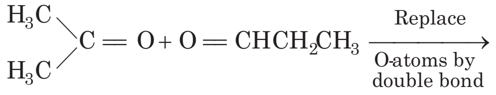
Anti-Markownikoff's addition
Four stereoisomers are possible
(As molecule has two chiral
centres and asymmetric).

58. Alkene $\xrightarrow{O_3/H_2O/Zn}$



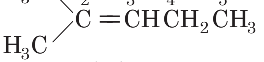
$$\underset{\text{Acetone}}{(H_3C)_2C=O} + \underset{\text{Propionaldehyde}}{CH_3CH_2CHO}$$

To identify alkene (from ozonolysis products) place these products with O-atoms face to face.
Replace O-atoms by $=$ (double) bond.



$$(H_3C)_2C=O + O=CHCH_2CH_3 \xrightarrow[\text{O-atoms by double bond}]{\text{Replace}}$$

O-atom face to face



$$(H_3C)_2\overset{2}{C}=\overset{3}{C}H\overset{4}{C}H_2\overset{5}{C}H_3$$

2-methyl-2-pentene

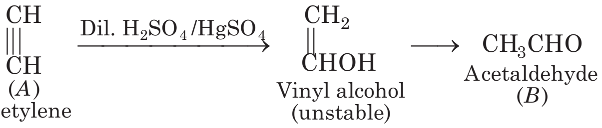
59. C_5H_8 has three possible alkynes. These are

$\underset{\text{Pent-1-yne}}{CH_3CH_2CH_2C\equiv CH}$, $\underset{\text{Pent-2-yne}}{CH_3CH_2C\equiv C—CH_3}$

$$CH_3—\overset{CH_3}{\overset{|}{C}H}—C\equiv CH$$

3-methylbut-1-yne

60. $CaC_2 + 2H_2O \longrightarrow \underset{(A)}{C_2H_2} + Ca(OH)_2$



$$\underset{\substack{(A)\\ \text{Acetylene}}}{CH\equiv CH} \xrightarrow{\text{Dil. }H_2SO_4/HgSO_4} \underset{\substack{\text{Vinyl alcohol}\\ \text{(unstable)}}}{CH_2=CHOH} \longrightarrow \underset{\substack{\text{Acetaldehyde}\\ (B)}}{CH_3CHO}$$

61. Since, the final product is alkyne which is obtained by dehydrohalogenation of respective halide which in turn obtained by the addition of halogen over double bond, thus, Y must be an alkene having three carbon atoms and alkene is obtained by dehydration of alcohols having the same number of carbon atoms. Thus, alcohol is propanol. The reactions are as follows

$$\underset{\substack{n\text{-propanol}\\ (X)}}{CH_3CH_2CH_2OH} \xrightarrow[H_2SO_4]{\text{Conc.}} \underset{\substack{\text{Propene}\\ (Y)}}{CH_3CH=CH_2} \xrightarrow[\text{(ii) Alc. KOH}]{\text{(i) Br}_2} \underset{\text{Propyne}}{CH_3—C\equiv CH}$$

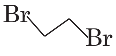
62. $CH_3CH_2Br \xrightarrow[-\text{HBr}]{\text{KOH (alc.)}} \underset{(X)}{CH_2=CH_2} \xrightarrow{Br_2} \underset{(Y)}{BrCH_2—CH_2Br}$

$\xrightarrow[-\text{2HBr}]{\text{KOH (alc.)}} \underset{(Z)}{HC\equiv CH}$

63. 1, 1-dihaloalkanes on treatment with KOH in C_2H_5OH give alkynes.

64. $CH_3CH_2CHCl_2 + 2NaNH_2 \xrightarrow[196\text{ K}]{\text{Liq. NH}_3}$

$CH_3C\equiv CH + 2NaCl + 2NH_3$

65.  $\xrightarrow[-\text{HBr}]{\text{KOH (alc.)}} Br—CH=CH_2 \xrightarrow[-\text{HBr}]{NaNH_2}$

$H—C\equiv C—H$

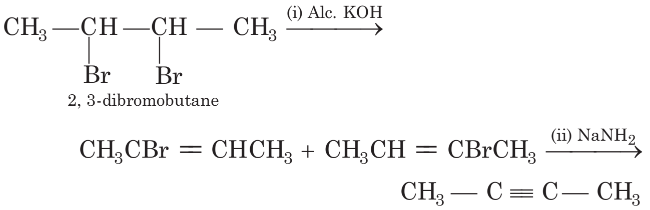
Dehydrohalogenation of vinyl halides is best carried out with $NaNH_2$

66. $CH_3CH_2CH_2OH \xrightarrow[180°–180°C]{H_2SO_4} CH_3CH=CH_2$

$\xrightarrow{Br_2} \underset{(Y)}{CH_3CHBr—CH_2Br} \xrightarrow[-\text{HBr}]{\text{Alc. KOH}}$

$[\underset{(A)}{CH_3CBr=CH_2} + \underset{(B)}{CH_3CH=CHBr}] \xrightarrow[-\text{HBr}]{NaNH_2} \underset{(Z)}{CH_3C\equiv CH}$

Alc. KOH smoothly brings about dehydrobromination of Y give a mixture of vinyl bromide (A and B) while $NaNH_2$ being a stronger base than KOH readily brings above dehydrobromination of less reactive vinyl bromides to give propyne (Z).

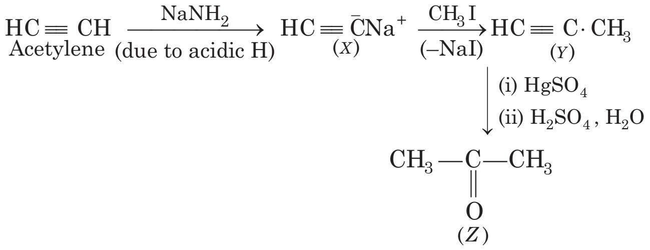
67. 

$$\underset{\text{2, 3-dibromobutane}}{CH_3-\underset{Br}{\underset{|}{C}H}-\underset{Br}{\underset{|}{C}H}-CH_3} \xrightarrow{\text{(i) Alc. KOH}}$$

$$CH_3CBr=CHCH_3 + CH_3CH=CBrCH_3 \xrightarrow{\text{(ii) NaNH}_2} \underset{\text{2-butyne}}{CH_3-C\equiv C-CH_3}$$

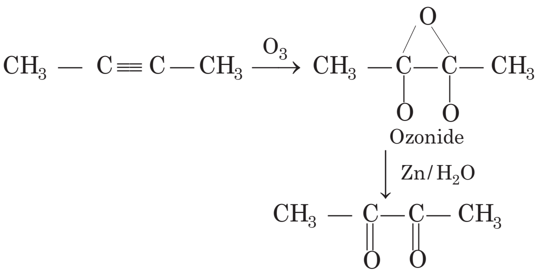
68. $\underset{\text{2-butanone}}{CH_3-CO-CH_2CH_3} \xrightarrow[-\,POCl_3]{PCl_5} CH_3-CCl_2-CH_2CH_3$

$\xrightarrow[\Delta\,(-2HCl)]{\text{KOH (alc.)}} \underset{\text{2-butyne}}{CH_3C\equiv CCH_3}$

69. 

$$\underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow[\text{(due to acidic H)}]{NaNH_2} \underset{(X)}{HC\equiv \bar{C}Na^+} \xrightarrow[(-NaI)]{CH_3I} \underset{(Y)}{HC\equiv C\cdot CH_3} \xrightarrow[\text{(ii) }H_2SO_4,\,H_2O]{\text{(i) }HgSO_4} \underset{(Z)}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$

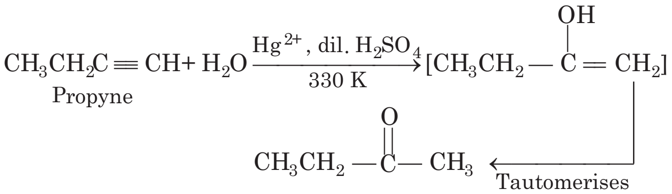
70. The reagent is O_3 as it is the reagent that introduces two O atoms at the successive triple bonded carbon atoms.



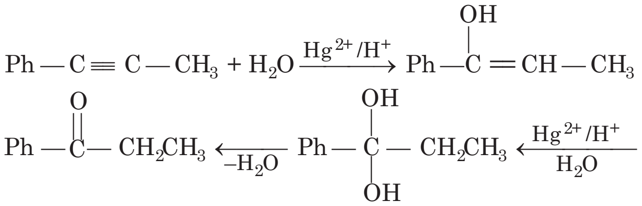
$$CH_3-C\equiv C-CH_3 \xrightarrow{O_3} \underset{\text{Ozonide}}{CH_3-C-C-CH_3} \xrightarrow{Zn/H_2O} CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

71. Reaction of 4-octyne and H_2 can be arrested at the alkene stage only by using palladium partially inactivated with trace of quinoline. The product is *cis*-alkene.

72. In the presence of dil. H_2SO_4 and mercury salts, alkynes add a molecule of H_2O to form aldehydes or ketones.



$$\underset{\text{Propyne}}{CH_3CH_2C\equiv CH} + H_2O \xrightarrow[330\text{ K}]{Hg^{2+},\text{ dil. }H_2SO_4} [CH_3CH_2-\overset{OH}{\overset{|}{C}}=CH_2] \xrightarrow{\text{Tautomerises}} CH_3CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

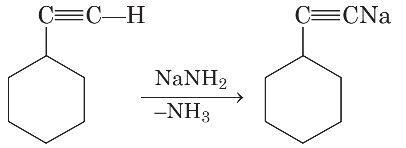
73. 

$$Ph-C\equiv C-CH_3 + H_2O \xrightarrow{Hg^{2+}/H^+} Ph-\overset{OH}{\overset{|}{C}}=CH-CH_3 \xrightarrow[H_2O]{Hg^{2+}/H^+} Ph-\underset{OH}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2CH_3 \xrightarrow{-H_2O} Ph-\overset{O}{\overset{\|}{C}}-CH_2CH_3$$

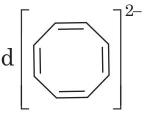
74. $CH\equiv CH \xrightarrow{NaNH_2} \underset{\text{'}A\text{'}}{CH\equiv C^-Na^+} \xrightarrow[-NaBr]{CH_3Br} \underset{\text{'}B\text{'}}{CH\equiv C-CH_3}$

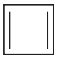
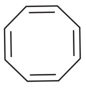
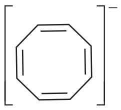
75. $\underset{\text{Acetylene}}{CH\equiv CH} + 2HCHO \longrightarrow \underset{\text{2-butyne-1, 4-diol}}{HOH_2C-C\equiv C-CH_2OH}$

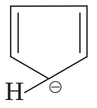
76. Only terminal alkynes when heated with sodamide ($NaNH_2$ in liq. NH_3), result in the formation of alkynide



Sodium alkynide

77. Compound  has 8 + 2 = 10π-electrons, hence is aromatic.

 has 4 πe^-,  has $8\pi e^-$, while  has $8 + 1 = 9\pi e^-$, hence, all these species are not aromatic.

78. 

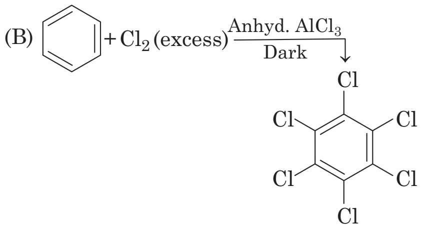
Cyclopentadienyl anion

π electrons = 4 + 2 = 6

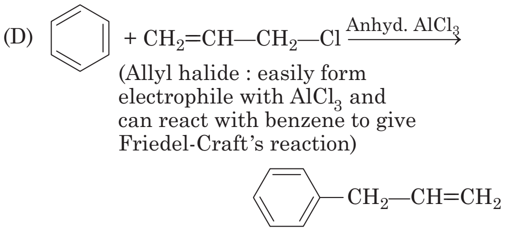
As it obeys Huckel rule, it is aromatic.

79. Cyclodecapentene and cyclooctatetraene both are non-aromatic. Cyclobutadiene is anti-aromatic while benzene having 6π-electrons is aromatic.

80. (*A*) and (*C*) are not possibe : Aryl halides and vinyl halides in the presence of anhyd. $AlCl_3$ do not act as electrophiles to give Friedel-Crafts' reaction with benzene. Therefore, these reactions are not possible.



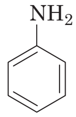
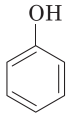
(This reaction is possible)



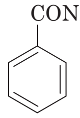
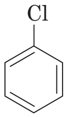
(Allyl halide : easily form electrophile with $AlCl_3$ and can react with benzene to give Friedel-Craft's reaction)

(This is also possible)

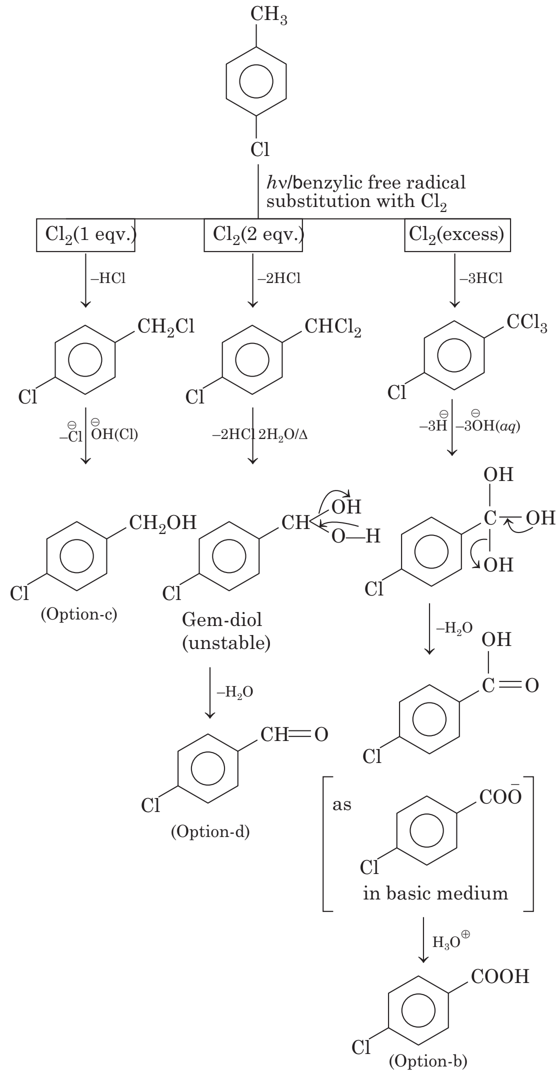
81. Friedel-Crafts' reaction is an electrophilic substitution reaction. In general, the rate of these reactions is highest when benzene have some electron releasing groups, (i.e. $—NH_2$, $—OH$) attached to the nucleus.

But in  and , $—\ddot{N}H_2$ and $—\ddot{\underset{\bullet\bullet}{O}}H$ groups are deactivated because the Lewis acid (anhydrous $AlCl_3$) used in these reactions form an adduct with the '$—NH_2$' or '$—OH$' groups and becomes ineffective.

'$—\overset{\overset{\displaystyle O}{\|}}{C}—NH_2$' is a electron withdrawing (deactivating) group.

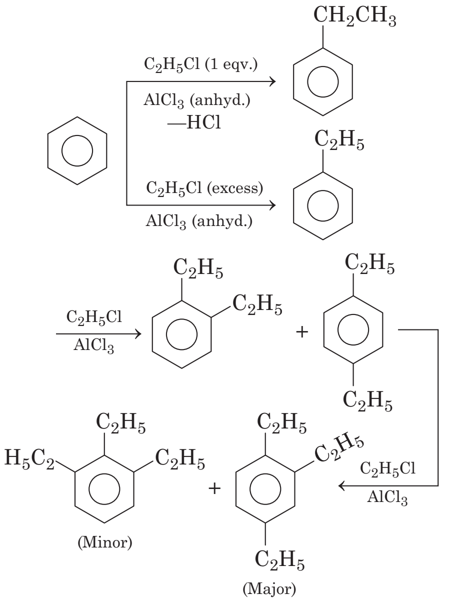
∴  is not highly reactive. '—Cl' in  is weakly electron withdrawing (deactivating) group, but among the given options, it is most reactive towards Friedel-Crafts' reaction.

82.



So, considering the second reaction condition, Cl^-, H_2O, Δ in the statement of the question, the correct answer is option (d).

83. Through aromatic electrophilic substitution mechanism (ArS_E2) when mono-alkylation (Friedel-Crafts' reaction) is performed, we get mono-alkylated benzene. As, the alkyl group is ring activating (towards ArS_E2) in nature, again *o*- and *p*-substituted alkyl benzene will be obtained and so on. e.g.



84. Aromatic electrophilic substitution reactions are fast in those compounds in which the attacking site possess high electron density. Electron withdrawing groups (EWGs) reduces the electron density in the benzene ring due to its strong –*I* effect and makes further substitution difficult. Hence, called as deactivating groups. While electron releasing groups (ERGs) increases the electron density in the benzene due to resonance. Therefore, activates the benzene ring for the attack by an electrophile.

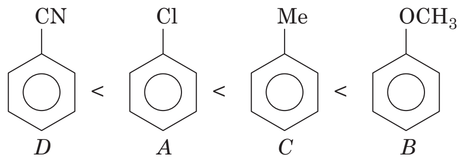
Hence, called as activating groups.

In given options,

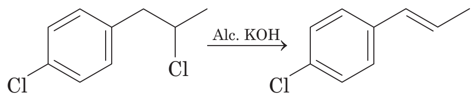
Activating groups are $\underset{(+I,\,+R)}{—CH_3} < \underset{\text{Strong } +R\text{-effect}}{—\ddot{\underset{\bullet\bullet}{O}}CH_3}$

Deactivating groups are $\underset{\text{Strong } -I\text{-effect}}{—CN} > \underset{(-I\,>\,-R)}{—Cl}$

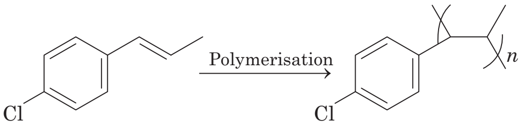
So, the correct order is



85. In presence of alc. KOH, the given halide undergoes elimination reaction.

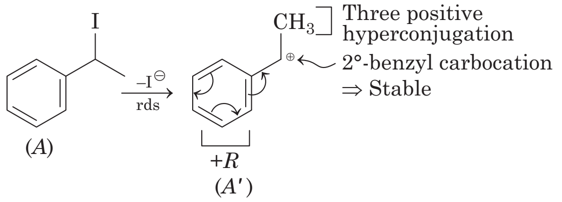


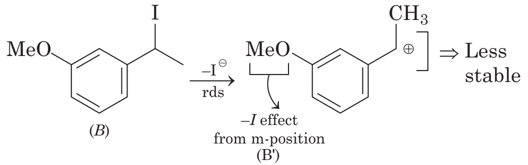
The alkene produced undergoes polymerisation *via* free radical mechanism.

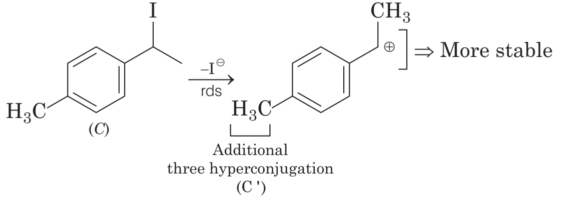


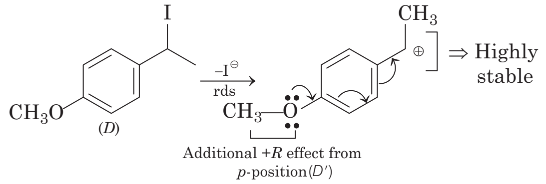
Polymer

86. More stable the carbocation intermediate, higher will be the rate of S_N1 reaction. The reaction involving carbocation intermediate formation for the given compounds are as follows:





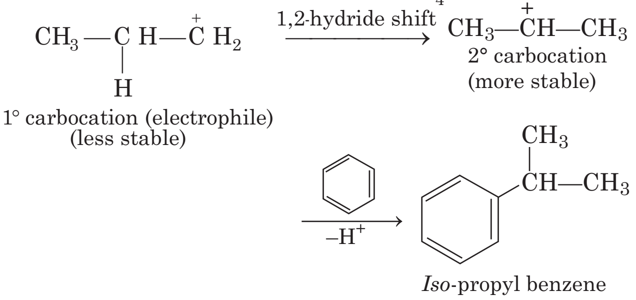




Stability of intermediates will follow the order

So, the rate of S_N1 reaction with the given compounds will be, $B < A < C < D$

87. $CH_3—CH_2—CH_2—Cl + AlCl_3 \xrightarrow[-AlCl_4^-]{}$



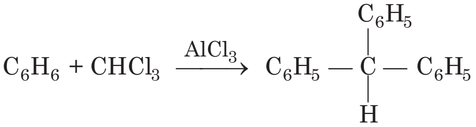
$$\underset{\substack{\text{1° carbocation (electrophile)}\\ \text{(less stable)}}}{CH_3—\underset{\displaystyle H}{\underset{|}{C}}H—\overset{+}{C}H_2} \xrightarrow{\text{1,2-hydride shift}} \underset{\substack{\text{2° carbocation}\\ \text{(more stable)}}}{CH_3—\overset{+}{C}H—CH_3} \xrightarrow[-H^+]{C_6H_6} C_6H_5—\overset{\displaystyle CH_3}{\overset{|}{C}}H—CH_3$$

Iso-propyl benzene

88. Benzophenone (diphenyl ketone) can be prepared by the Friedel-Crafts condensation between benzoyl chloride and benzene.

$$C_6H_6 + C_6H_5COCl \xrightarrow{AlCl_3} C_6H_5COC_6H_5 + HCl(80\%)$$

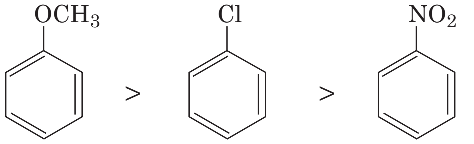
89.



$$C_6H_6 + CHCl_3 \xrightarrow{AlCl_3} C_6H_5 — \underset{\displaystyle H}{\underset{|}{\overset{\displaystyle C_6H_5}{\overset{|}{C}}}} — C_6H_5$$

90. —OCH_3 (methoxy group) is an electron releasing group. It increases electron density in benzene nucleus due to resonance effect (+ *R* effect). Hence, makes anisole more reactive than benzene towards electrophiles. In case of aryl halides, halogens are moderately deactivating because of their strong – *I* effect and +*R* effect thus, overall electron density on benzene ring decreases.

It makes further substitution difficult. —NO_2 group is electron withdrawing group. It decreases the electron density in benzene nucleus due to strong – *I* effect.



Anisol Chlorobenzene Nitrobenzene

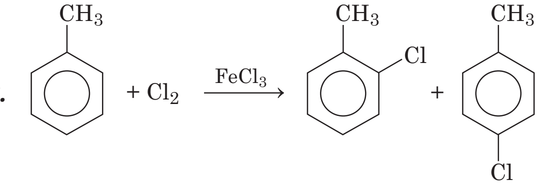
91. Reactivity towards electrophilic substitution increases as the electron density in the benzene ring increases.

Since CH_3 is a strong electron donating group thus toluene ($C_6H_5CH_3$) can be most readily sulphonated.

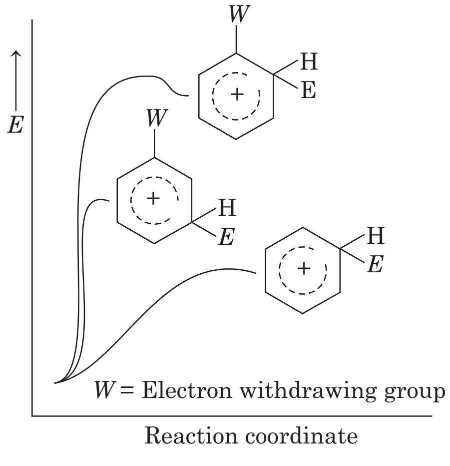
92. In the laboratory, nitrobenzene is prepared by nitration of benzene with the mixture of nitric acid and sulphuric acid at temperature below 60°C. In which HNO_3 acts as a base.

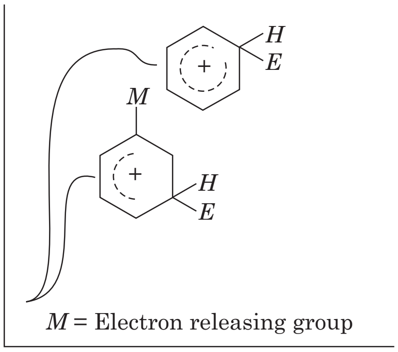
$$\underset{\substack{\text{Base}\\ \text{(as proton acceptor)}}}{HNO_3} + \underset{\text{Acid}}{H_2SO_4} \longrightarrow \underset{\substack{\downarrow\\ H_2O + NO_2^+}}{H_2NO_3^+} + HSO_4^-$$

93.



94.





M = Electron releasing group

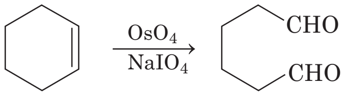
95. Presence of electron releasing group (or activating group) increases the electron density in benzene nucleus. Therefore, electrophile will attack benzene nucleus easily. But the presence of electron withdrawing group like $—NO_2$ decreases the electron density in benzene ring.

Therefore, electrophile will attack benzene nucleus with difficulty. The order of reactivity towards electrophile, E^+ in the order of their decreasing relative reactivity is

Toluene > p-$CH_3—C_6H_4—NO_2$

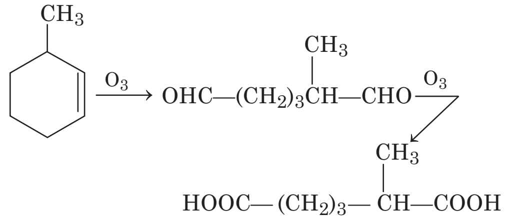
Chlorobenzene > p-nitrochlorobenzene
> 2,4-dinitrochlorobenzene

96.



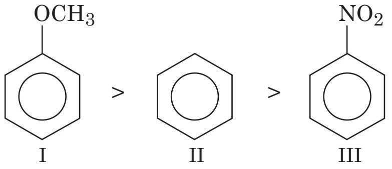
Hexane-1,6-dial

97.

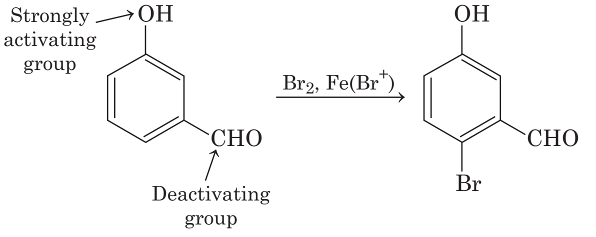


Substituted adipic acid

98. Activating groups like $—OCH_3$, —OH etc., activates the benzene ring towards electrophilic substitution while deactivating groups like NO_2, COOH etc., deactivates the benzene ring towards electrophilic substitution. Thus, order of reaction with electrophile (of the given compounds) is as,

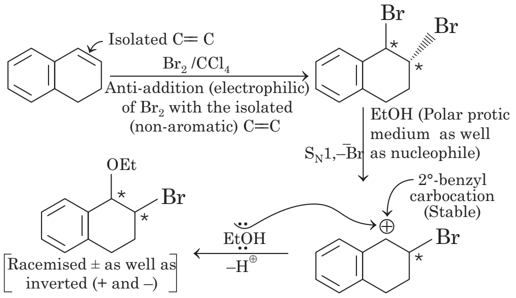


99.



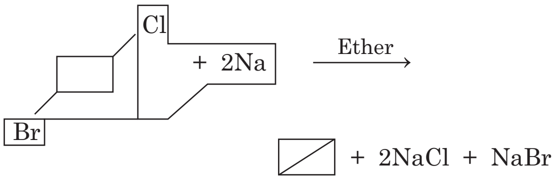
(∵ Strongly activating group generally win over the deactivating group and —OH is a *ortho/para* directing group. p-product predominates.)

100. The road map of the given reaction is

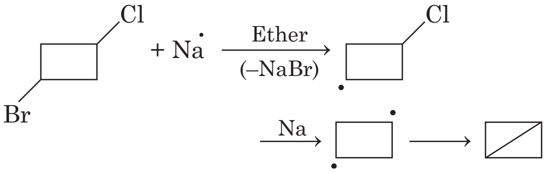


Round II

1. This reaction is of Wurtz's type reaction .

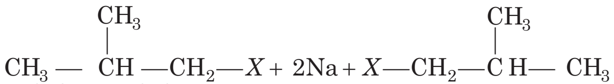


In this reaction, following mechanism is possible.



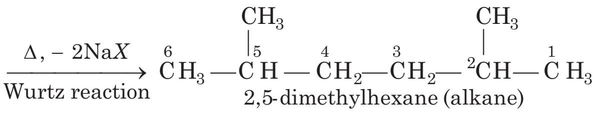
(Order of removal of halogen I > Br > Cl).

2. Since, alkane C_8H_{18} on monobromination yields a single isomer of a tertiary bromide, therefore alkane must contain tertiary hydrogen. This is possible if primary alkyl halide (which undergoes Wurtz reaction) has a tertiary hydrogen.



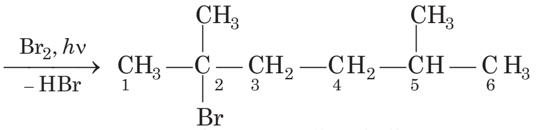
$$CH_3-\overset{CH_3}{CH}-CH_2-X + 2Na + X-CH_2-\overset{CH_3}{C}H-CH_3$$

1-halo-2-methylpropane



$$\xrightarrow[\text{Wurtz reaction}]{\Delta,\,-2NaX} \overset{6}{C}H_3-\overset{CH_3}{\overset{5}{C}}H-\overset{4}{C}H_2-\overset{3}{C}H_2-\overset{CH_3}{{}^{2}CH}-\overset{1}{C}H_3$$

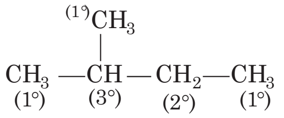
2,5-dimethylhexane (alkane)



$$\xrightarrow[-HBr]{Br_2,\,h\nu} \underset{1}{CH_3}-\underset{\underset{Br}{2}}{\overset{CH_3}{C}}-\underset{3}{CH_2}-\underset{4}{CH_2}-\underset{5}{\overset{CH_3}{CH}}-\underset{6}{CH_3}$$

2-bromo-2,5-dimethylhexane
(3° bromide)

3.



$$\underset{(1°)}{CH_3}-\underset{(3°)}{\overset{{}^{(1°)}CH_3}{CH}}-\underset{(2°)}{CH_2}-\underset{(1°)}{CH_3}$$

Relative amount of monochlorinated product

= Number of hydrogen × Relative reactivity

For (1°) monochlorinated product = $9 \times 1 = 9$

(2°) monochlorinated product = $2 \times 3.8 = 7.6$

(3°) monochlorinated product = $1 \times 5 = 5$

Total amount of monochlorinated compounds

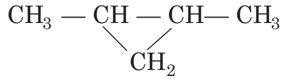
$$= 9 + 7.6 + 5 = 21.6$$

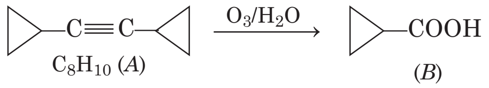
% of 1° monochlorinated product $= \frac{9 \times 100}{21.6} = 41.67$

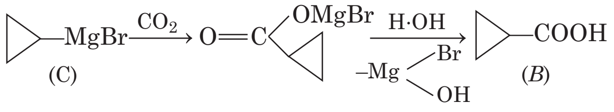
% of 2° monochlorinated product $= \frac{7.6 \times 100}{21.6} = 35.18$

% of 3° monochlorinated product $= \frac{5 \times 100}{21.6} = 23.15$

$CH_3CH = CH - CH_3 + :CH_2 \longrightarrow$



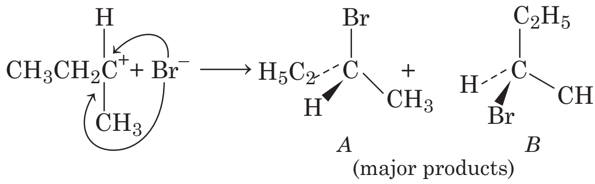
4. 



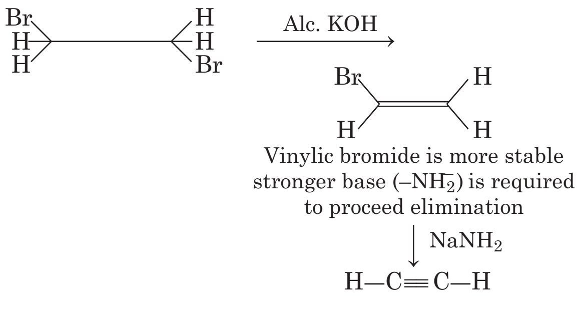
5. $CH_3CH_2CH = CH_2 + H^+ \longrightarrow CH_3CH_2\overset{+}{C}H - CH_3$ 2° (planar) (more stable major)

$+ CH_3CH_2CH_2 - \overset{+}{C}H_2$ 1° (less stable)

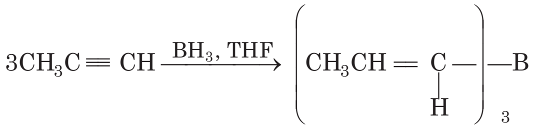
$CH_3CH_2CH_2\overset{+}{C}H_2 + Br^- \longrightarrow \underset{(C)}{CH_3CH_2CH_2CH_2Br}$



6. $\underset{\text{2-methyl-3-hexyne}}{(CH_3)_2CH - C \equiv C - CH_2CH_3} \xrightarrow{[O]} (CH_3)_2CHCOOH + CH_3CH_2COOH$

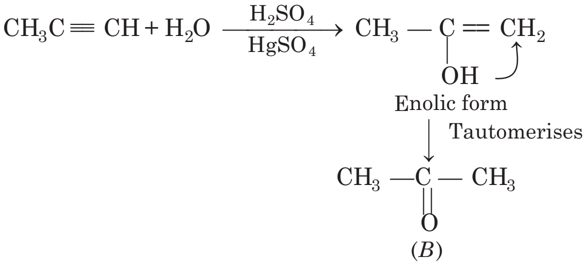
7. 

Vinylic bromide is more stable stronger base ($-NH_2$) is required to proceed elimination

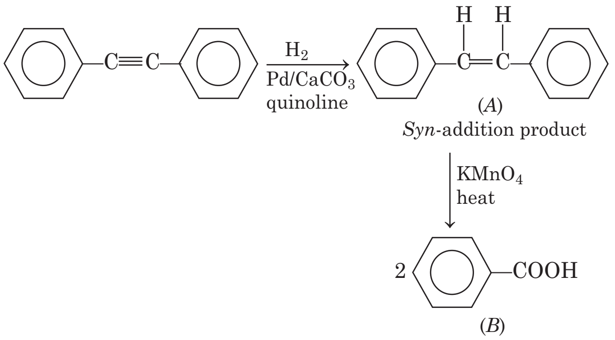
8. 

$$3CH_3C \equiv CH \xrightarrow{BH_3,\ THF} \left(CH_3CH = \underset{H}{C} - \right)_3 B$$

$$\xrightarrow{H_2O_2,\ OH^-} CH_3CH = CHOH \xrightarrow{\text{Tautomerises}} \underset{(A)}{CH_3CH_2CHO}$$



$$CH_3C \equiv CH + H_2O \xrightarrow[HgSO_4]{H_2SO_4} \underset{\text{Enolic form}}{CH_3 - \underset{OH}{C} = CH_2} \xrightarrow{\text{Tautomerises}} \underset{(B)}{CH_3 - \underset{O}{\overset{\|}{C}} - CH_3}$$

9. 

10. The two compounds should react differently with the reagent used to distinguish them.

∵ Propyne ($CH_3-C \equiv CH$) and propene ($CH_3CH = CH_2$) both are unsaturated compounds.

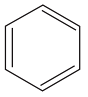
∴ Both of them decolourise alk. $KMnO_4$ and Br_2 in CCl_4 and both of them give addition reaction with conc. H_2SO_4.

∵ Propyne reacts with $AgNO_3$ in NH_3 to give white ppt. of silver acetylide and propene does not react with it. (only terminal alkynes react with $AgNO_3$ in NH_3.

$$\underset{\text{(Propyne)}}{CH_3-C \equiv CH} + AgNO_3 + NH_3 \longrightarrow \underset{\substack{\text{Silver acetylide} \\ \text{(white ppt.)}}}{CH_3-C \equiv CAg}$$

$$CH_3-CH = CH_2 + AgNO_3 + NH_3 \longrightarrow \text{No reaction}$$

11. The hybridisation state of carbon in the given compounds is

 ; $CH_3-(CH_2)_4-CH_3$ $HC \equiv CH$

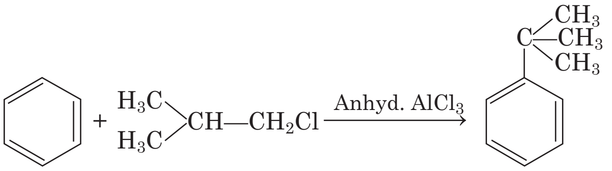
	Benzene	Hexane	Ethyne
Type of hybridisation	sp^2	sp^3	sp
s-character	33.33%	25%	50%

Acidic character increases with increase in *s*-character of the orbital.

Hence, decreasing order of acidic behaviour of benzene, *n*-hexane and ethyne is as follows

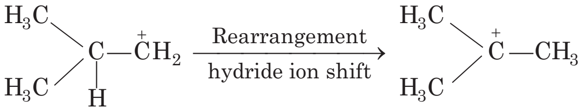
Ethyne > Benzene > Hexane

12.

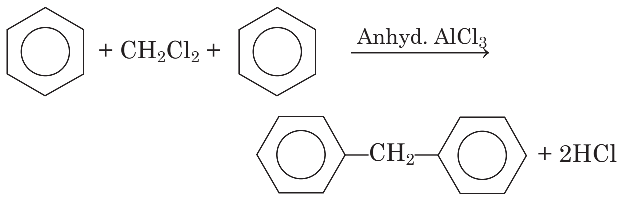


This reaction is an example of Friedel-Crafts reaction.

Mechanism



13. When excess of benzene reacts with CH_2Cl_2 in the presence of anhyd. $AlCl_3$, diphenylmethane is obtained.



Diphenylmethane

This reaction is an example of Friedel-Crafts reaction.

14. I. has 8π electrons, does not follow Huckel rule. Orbitals of one carbon atom are not in conjugation. It is not aromatic.

II. has 6π delocalised electrons. Hence, is aromatic.

III. has 6π electrons in conjugation but not in the ring. Non aromatic.

IV. 10π electrons in planar rings, aromatic.

V. Out of 8π electrons it has delocalised 6π electrons in one six membered planar ring, which follows Huckel's rule due to which it will be aromatic.

VI. 14π electrons are in conjugation and are present in a ring. Huckel's rule is being followed. Compound will be aromatic if ring is planar.

15. (i) Determination of empirical formula of hydrocarbon *A*

Element	Percent age	Atomic mass	Relative ratio	Relative number of atoms	Simplest ratio
C	87.8	12	$\frac{87.8}{12} = 7.31$	$\frac{7.31}{7.31} = 1$	$1 \times 3 = 3$
H	12.19	1	$\frac{12.19}{1} = 12.19$	$\frac{12.19}{7.31} = 1.66$	$1.66 \times 3 = 5$

∴ Empirical formula of hydrocarbon $(A) = C_3H_5$

Empirical formula mass $= 12 \times 3 + 5 \times 1 = 41$ u

(ii) Determination of molecular mass of hydrocarbon (*A*)

896 mL vapours of hydrocarbon (*A*) weigh at STP = 3.28 g

∴ 22400 mL vapours of *A* will weigh at STP

$$= \frac{3.28 \times 22400}{896} \text{ g mol}^{-1} = 82 \text{ g}$$

∴ Molecular mass of hydrocarbon $(A) = 82 \text{ g mol}^{-1}$

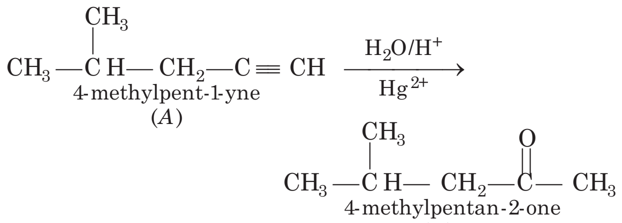
(iii) Determination of molecular formula of hydrocarbon *A*.

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{82}{41} = 2$$

Therefore, molecular formula of hydrocarbon

$$(A) = n \times \text{Empirical formula} = 2 \times C_3H_5 = C_6H_{10}$$

Since, hydrogenation of *A* gives 2-methyl pentane therefore compound '*A*' have 5 carbon atoms in straight chain. It should be an alkyne because compound '*A*' adds a molecule of H_2O in the presence of Hg^{2+} and H^+ to give a ketone '*B*'. Ketone '*B*' gives iodoform test so it should be a methyl ketone. Therefore, the structures of compound *A* and compound *B* are as follows

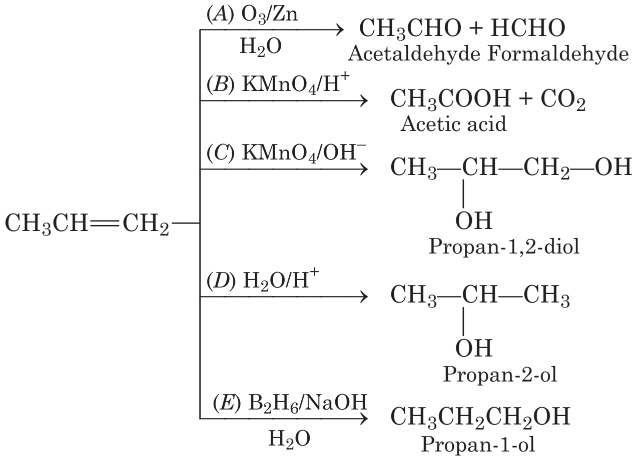


$$CH_3—\overset{CH_3}{C}H—CH_2—C\equiv CH \xrightarrow[Hg^{2+}]{H_2O/H^+} CH_3—\overset{CH_3}{C}H—CH_2—\overset{O}{\overset{\|}{C}}—CH_3$$

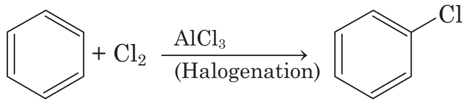
4-methylpent-1-yne (*A*)

4-methylpentan-2-one (*B*)

16.

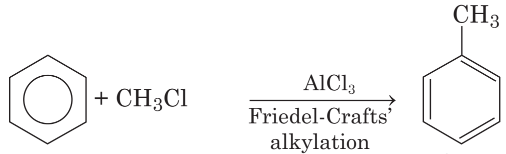


17. (A)

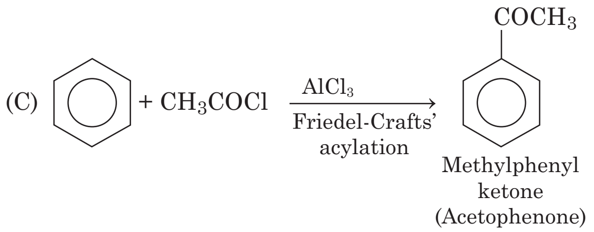


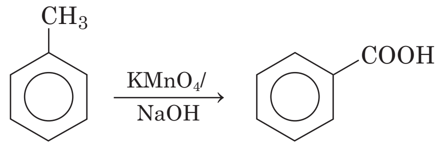
Chlorobenzene

(B)



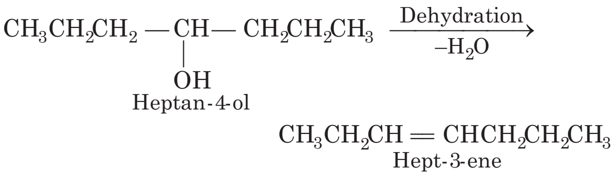
Toluene

(C)


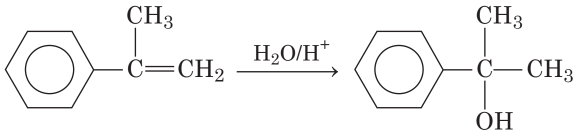
(D)


18. Dehydration of alcohols to alkene is carried out through carbocation formation.

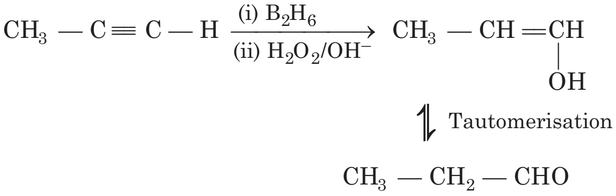
19. Intramolecular dehydration since H_2O is lost from one molecule of ethyl alcohol.

20.


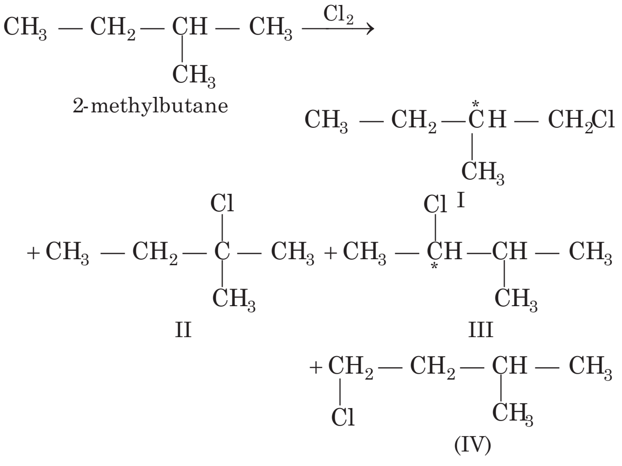
$$\underset{\text{Heptan-4-ol}}{CH_3CH_2CH_2-\underset{OH}{\underset{|}{C}H}-CH_2CH_2CH_3} \xrightarrow[-H_2O]{\text{Dehydration}} \underset{\text{Hept-3-ene}}{CH_3CH_2CH=CHCH_2CH_2CH_3}$$

21.


22. Hydroboration oxidation, anti-Markownikoff's addition of water gives product.

23.


$$CH_3-C\equiv C-H \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6} CH_3-CH=\underset{OH}{\underset{|}{C}H} \xrightleftharpoons{\text{Tautomerisation}} CH_3-CH_2-CHO$$

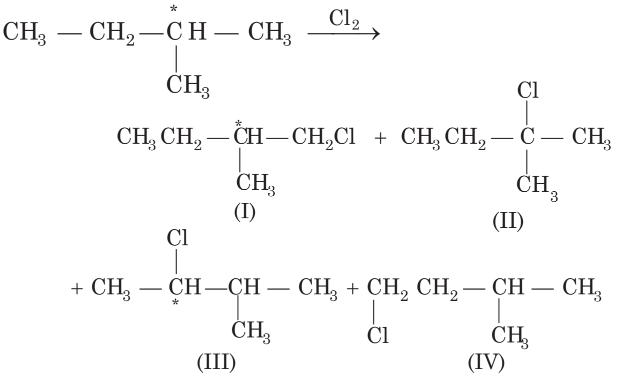
24.


$$\underset{\text{2-methylbutane}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_3} \xrightarrow{Cl_2} \underset{\text{I}}{CH_3-CH_2-\underset{CH_3}{\underset{|}{\overset{*}{C}H}}-CH_2Cl}$$

$$+\underset{\text{II}}{CH_3-CH_2-\overset{Cl}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3} + \underset{\text{III}}{CH_3-\overset{Cl}{\overset{|}{\underset{*}{C}H}}-\underset{CH_3}{\underset{|}{C}H}-CH_3} + \underset{\text{(IV)}}{\underset{Cl}{\underset{|}{C}H_2}-CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_3}$$

I and III have chirality (*). Thus, in all four (including enantiomers) optical isomers are obtained.

25. 2-methylbutane on monochlorination gives 4 isomers, among which I and III are chiral in nature.



$$CH_3-CH_2-\underset{CH_3}{\underset{|}{\overset{*}{C}H}}-CH_3 \xrightarrow{Cl_2}$$

$$\underset{\text{(I)}}{CH_3CH_2-\underset{CH_3}{\underset{|}{\overset{*}{C}H}}-CH_2Cl} + \underset{\text{(II)}}{CH_3CH_2-\overset{Cl}{\overset{|}{\underset{CH_3}{\underset{|}{C}}}}-CH_3}$$

$$+\underset{\text{(III)}}{CH_3-\overset{Cl}{\overset{|}{\underset{*}{C}H}}-\underset{CH_3}{\underset{|}{C}H}-CH_3} + \underset{\text{(IV)}}{\underset{Cl}{\underset{|}{C}H_2}CH_2-\underset{CH_3}{\underset{|}{C}H}-CH_3}$$

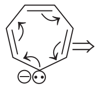
Hence, 2 chiral compounds are formed in the above reaction.

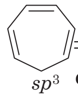
26. A compound is considered to be aromatic, if it follows three rules

(a) Must be cyclic and planar.
(b) Must have conjugated system in it.
(c) It must follow Huckel rule which states that number of π-electrons = $(4n + 2)$

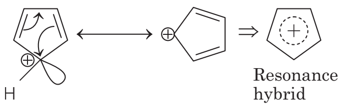
(A)  $\Rightarrow 2\pi\text{-}e^-$ system $[(4n+2)\pi, n = 0]$ $\Rightarrow$ Aromatic

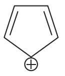
(B)  $\Rightarrow 4\pi\text{-}e^-$ system $[4n\pi, n = 1]$ $\Rightarrow$ Anti-aromatic

(C)  $\Rightarrow 8\pi\text{-}e^-$ system $[4n\pi, n = 2]$ $\Rightarrow$ Anti-aromatic

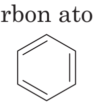
(D)  $\Rightarrow$ The sp^3-carbon does not support conjugation and also devoids planarity. $\Rightarrow$ Non-aromatic

27. Aromaticity of a compound can be decided by Huckel's rule. In cyclopentadienyl cation (b), resonance takes place as follows:



Hence,  is anti-aromatic does not follow Huckel's rule as it has conjugated 4π-electron $(4n\pi, n = 1)$ system. Rest of the species are aromatic as each of them belongs to 6π-electron $[(4n + 2)\pi, n = 1]$ system.

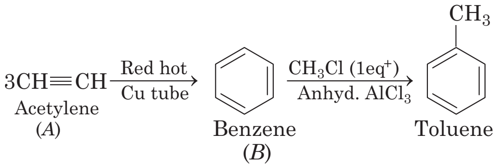
28. In benzene, every carbon atom is sp^2-hybridised.

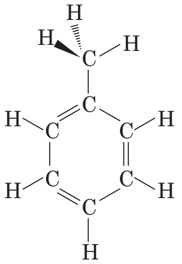


Each sp^2-hybridised atom has three sp^2 hybrid orbitals.

∴ Total number of sp^2 hybrid orbitals in a molecule of benzene is $= 6 \times 3 = 18$

29. $A \Rightarrow CH{\equiv}CH$



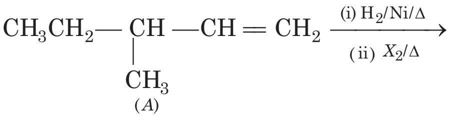


All ring atoms and attached atoms are always coplanar (ring carbons are sp^2).

∴ $6C + 5H + 1C = 12$

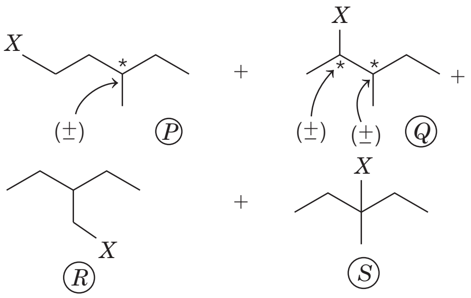
Additionally, one more 'H' from CH_3 group can be on the same plane also.

∴ The maximum number of atoms present in one plane in the molecule (toluene) is = 13

30. 

$$\underset{(A)}{CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH=CH_2} \xrightarrow[\text{(ii) } X_2/\Delta]{\text{(i) } H_2/Ni/\Delta}$$

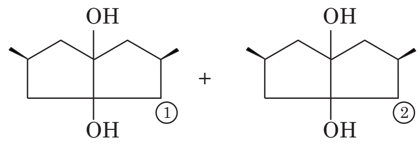
(Simplest optically active alkene)

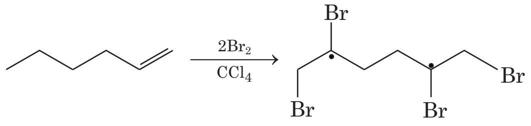


In the reaction, total number of monohalogenated products (including stereoisomers)

$P = 2$, $Q = 4$, $R = 1$, $S = 1$, i.e. Total = 8

31. Two products will be obtained by addition reaction above and below the plane of ring. It is the example of syn hydroxylation

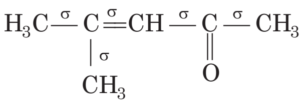


32. 

$n = 2$ terminal group same

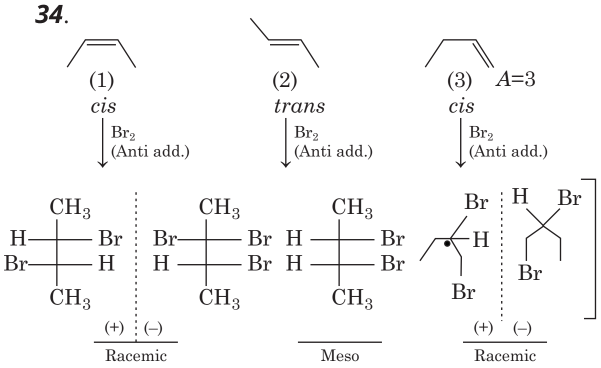
No. of isomers $= 2^{n-1} + 2^{\frac{n+1}{2}} = 2 + 1 = 3$

33. Mesityl oxide



$$H_3C\overset{\sigma}{-}\underset{\underset{\displaystyle CH_3}{|\,\sigma}}{C}\overset{\sigma}{=}CH\overset{\sigma}{-}\underset{\underset{\displaystyle O}{\|}}{C}\overset{\sigma}{-}CH_3$$

∴ $C\underset{\sigma}{-}C = 5$

34. 

$B = 5$
$A + B = 8$