

HYDROCARBON

ALKANE

INTRODUCTION

Saturated hydrocarbons are known as alkanes or paraffins (Less reactive). Alkanes with carbon chains that are unbranched are called normal alkanes. Each member of the series differ from the next higher and next lower member by $-\text{CH}_2$ group.

General formula : $\text{C}_n\text{H}_{2n+2}$

Type formula : $\text{R}-\text{H}, \text{RCH}_3, \text{R}(\text{CH}_2)_n\text{R}, \text{R}_1(\text{CH}_2)_n\text{R}_2$

All the carbon atoms in alkanes are in sp^3 state of hybridization. The four bonding orbitals are directed towards the four corners of a regular tetrahedron. All the bond angles are tetrahedral angles i.e. $\text{H}-\text{C}-\text{H}$ or $\text{H}-\text{C}-\text{C}$ bond angle is $109^\circ 28'$ or 109.5° .

Number of angles of $109^\circ 28'$:

$\text{CH}_4 = \text{Six}$, $\text{CH}_3-\text{CH}_3 = \text{Twelve}$

Alkanes are insoluble in water. The reason is that water molecules are polar whereas alkanes are non-polar ($\text{C}-\text{C}$ and $\text{C}-\text{H}$ bonds are nearly purely covalent) Like does not dissolve unlike. Alkane molecules are non planar because all the carbon atoms possess sp^3 hybridisation state.

Properties

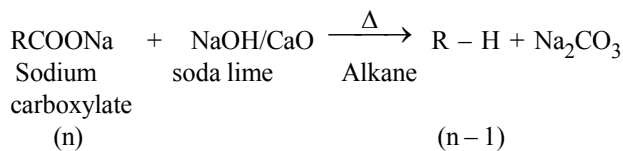
	$\text{C}-\text{C}$	$\text{C}-\text{H}$
(i) Overlapping	sp^3-sp^3	sp^3-s
(ii) Bond length	1.54 \AA	1.112 \AA
(iii) Bond energy	$80-85 \text{ kcal}$	98.6 kcal

The long carbon chains in alkanes are arranged in zig-zag manner.

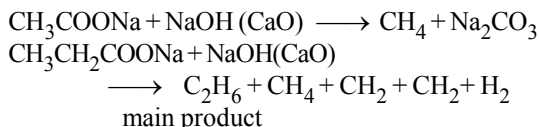
METHODS OF PREPARATION

(i) From Carboxylic acids :

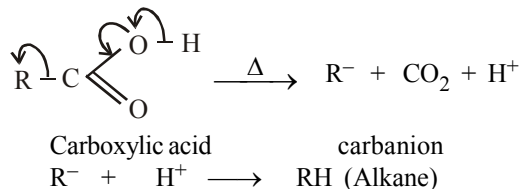
(a) Decarboxylation



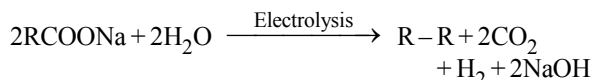
Ex.



Since the $-\text{COOH}$ present in the original acid is removed in the process (in the form of carbonate), the reaction is commonly known as decarboxylation. The reaction is employed for stepping down a homologous series. De-carboxylation proceeds via the formation of carbanion as follows.

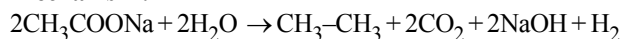


(b) Kolbe's electrolytic synthesis :

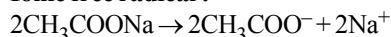


Methane cannot be prepared by this method. The side products are olefins, alcohols (particularly in alkaline solution) and esters. Presence of alkyl groups in α -position decreases the yield of alkane.

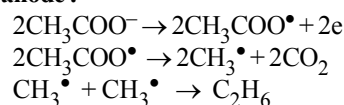
Mechanism :



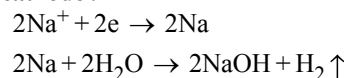
Ionic free radical :



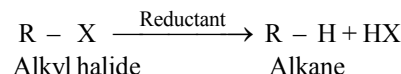
At anode :



At cathode :



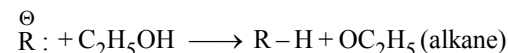
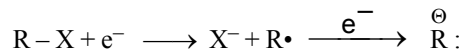
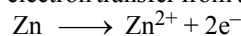
(ii) Reduction of Alkyl Halides :



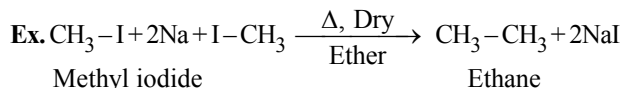
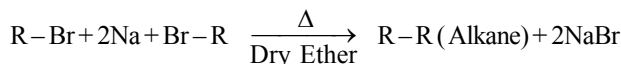
Reductants : $\text{Zn}-\text{Cu}$ couple/ EtOH , $\text{Na}-\text{EtOH}$, $\text{Zn}-\text{HCl}$, Pt or Pd or Ni/H_2 , $\text{Al}-\text{Hg}/\text{EtOH}$, LiAlH_4 etc.

Ex. : $\text{CH}_3\text{I} + \text{Zn}-\text{Cu} / \text{alcohol} \rightarrow \text{CH}_4 + \text{H}-\text{I}$

In the reduction of $\text{R}-\text{X}$ with dissolving metals, nascent hydrogen is not the reducing agent. Reduction is due to the electron transfer from the metal to the substrate ($\text{R}-\text{X}$).

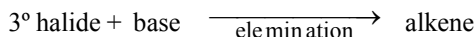


(iii) Wurtz Reaction :

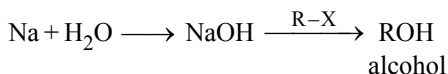


Methane cannot be prepared by this method. The alkane produced is higher and symmetrical i.e., it contains double in the number of carbon atoms present in the alkyl halide taken. When the two reacting alkyl halides are different, a mixture of three different alkanes is obtained. The wurtz reaction is no useful for preparing unsymmetrical alkanes.

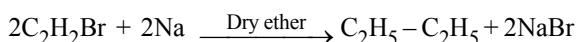
$C_2H_5I + CH_3I \longrightarrow C_2H_6 + C_3H_8 + C_4H_{10}$
Wurtz reaction generally fails with tertiary alkyl halides.



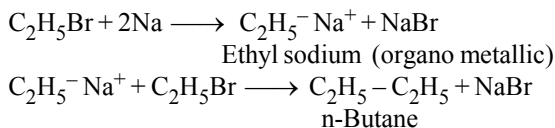
In presence of moist ether then product is alcohol



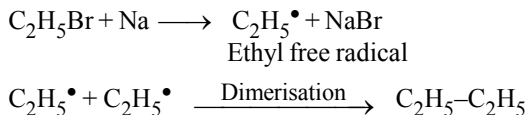
Mechanism : Wurtz reaction may proceed via the formation of organometallic compound or alkyl free radicals.



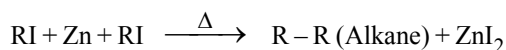
(A) Ionic Reaction :



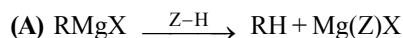
(B) Free radical Reactions :



(iv) Frankland's reaction :

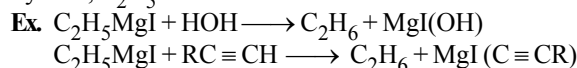


(v) From Grignard reagent :

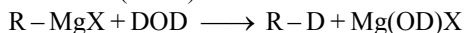


ZH [compound containing active hydrogen]

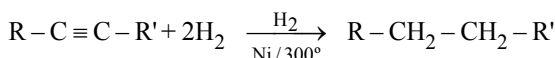
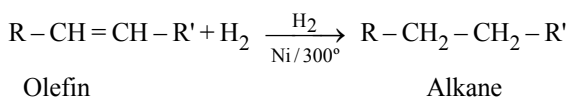
HOH, NH₃, RC≡CH, C₆H₅OH, CH₃COOH, RNH₂, R₂NH, Pyrrole, C₂H₅OH etc.



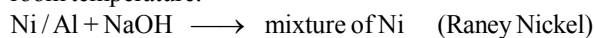
If heavy water, D₂O, is used, then the product is deuterioalkane (R-D).



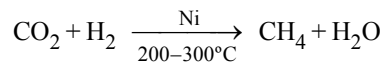
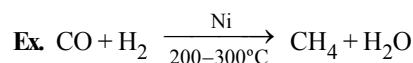
(vi) From Alkenes and Alkynes(Sabatier Senderen's reaction)



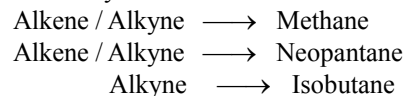
When the catalyst are Pt or Pd, the hydrogenation proceeds smoothly at ordinary temperature and pressure. With Nickel catalyst, higher temperature (250° – 300°C) and pressure are needed. With Raney Nickel, the reaction takes place at room temperature.



Following reaction is too called sabatier senderen's reaction.

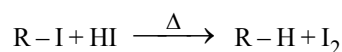
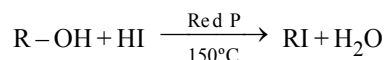


In this reaction following alkanes are not get from unsaturate hydrocarbon



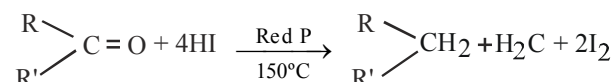
(vii) Reduction of Alcohols, Aldehydes, Ketones and Acids [Red P and HI (150°C)] :

(a) By the reduction of alcohols :

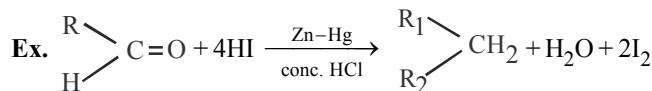


Since iodine is produced during the reaction, it may react with the resulting alkane, so it is removed by adding red phosphorus. $2P + 3I_2 \longrightarrow 2PI_3$

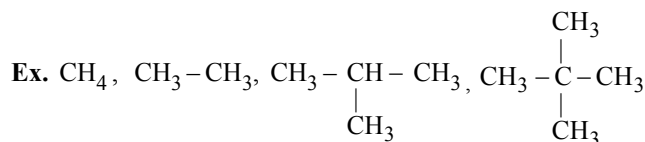
(b) By the reduction of aldehyde and ketones :



Clemmensen's reduction : Only ketones are reduced to parent alkanes by treatment with zinc amalgam and conc. HCl because aldehydes show polymerisation

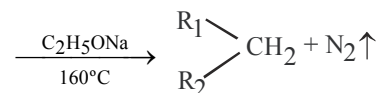
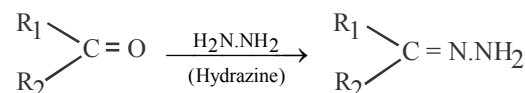
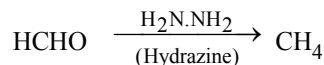


Only alkanes with group CH₂ can be obtained hence in this reaction following alkanes are not formed.

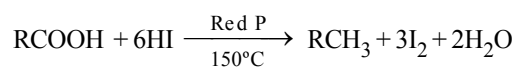


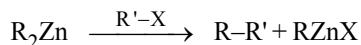
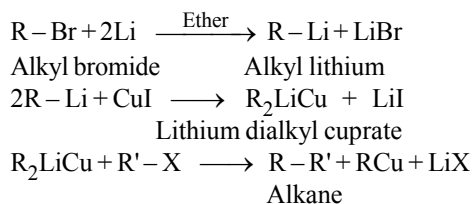
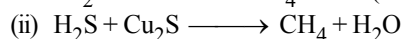
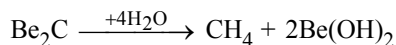
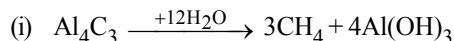
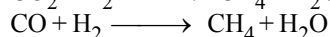
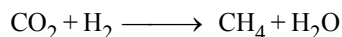
Methane Eathane Iso-butane Neopentane

Wolff-Kishner reduction : Both aldehydes and ketones are reduced to parent alkanes by treatment NH₂ – NH₂ / C₂H₅ONa



(c) By reduction of acid :



(viii) From dialkyl zinc :**(ix) Corey-House Synthesis :****Method of preparation of CH₄ :****(iii) Sabatier senderens :-****PHYSICAL PROPERTIES**

(i) Alkanes from C₁ – C₄ are colourless, odourless gases. C₅ – C₁₇ are colourless liquids, C₁₈ – onwards are waxy, white solids.

(ii) **Boiling points :** Boiling points of alkanes are the lowest of all the groups of organic compounds. The forces of attraction among the alkane molecules are the weakest vander Waal's forces of attraction.

Among isomeric alkanes, the boiling point decreases with increasing branching.

Ex. n-Pentane > iso-Pentane > neo-Pentane

With the increase in branching, the shape of the molecule tends to become spheroidal. Since, vander Waal's forces of attraction.

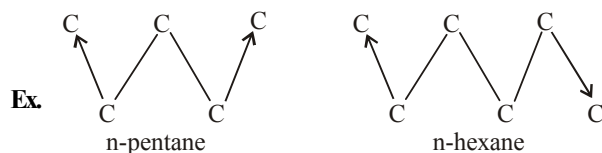
B.P ∝ mol. wt. (for homologous)

B.P ∝ $\frac{1}{\text{lateral chain}}$ (for Isomers)

B.P ∝ vander Waal's ∝ mol. wt
∝ surface area forces of attraction

∝ $\frac{1}{\text{spherical shape}}$

(iii) **Melting point :** Unbranched alkanes containing 2, 4, 6, 8 etc. carbon atoms have higher melting points than the unbranched alkanes containing 3, 5, 7, 9 etc. carbon atoms.



(both methyl group are directed on same side)

(both methyl group are adversely directed)

M.P. even no. of carbon atoms > odd no. of carbon atoms

M.P. ∝ mol.wt. ∝ packing efficiency.

(iv) **Fuel capacity :** Decreasing order of fuel capacity is more branched > less branched > unbranched and lower mol.wt. > higher mol. wt.

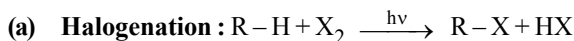
Alkanes are colourless, odourless and tasteless.

Alkanes are lighter than water.

These are insoluble in water and soluble in organic solvents.

CHEMICAL REACTIONS

- Stability
 - Substitution reaction :
 - Halogenation
 - Nitration
 - Sulphonation
 - Chlorosulphonation (Reed reaction)
 - Oxidation
 - Cracking / Pyrolysis
 - Isomerisation
 - Aromatization
 - Addition of CH₂
1. **Stability :** Although alkanes are chemically unreactive under ordinary conditions due to the presence of strong and non-polar C – C and C – H bonds electrophilic (E⁺) and nucleophilic (Nu⁻) does not attack it. They do not react with acid, base and oxidiser.

2. Substitution Reaction

Reactivity order of hydrogen atoms in alkanes is

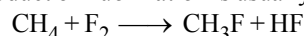
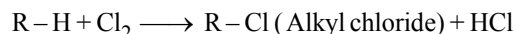


Reactivity order of halogens is F₂ > Cl₂ > Br₂ > I₂

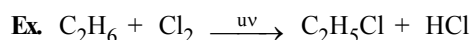
Fluorine can react in dark. Cl₂ and Br₂ require light energy. I₂ does not shown any reaction at room temperature, on heating it shows iodination.

Fluorination : Direct-fluorination of alkanes is usually explosive. CH₄ + F₂ → C + HF

It is carried out successfully by diluting fluorine with nitrogen and carrying out the reaction in a metal tube packed with copper gauze at a temperature of 150°C–350°C. Product of fluorination is usually a complex mixture.

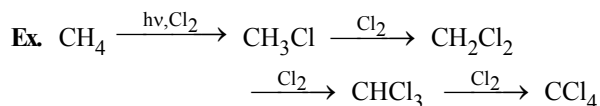
**Chlorination :**

The monochloro derivative of alkane is obtained by taking alkane in large excess.



Ethane (Excess) Ethyl chloride

When chlorine is in excess, a mixture of mono, di tri, tetra and perchloro derivatives is obtained.



Chlorination of alkanes takes place in the following conditions.

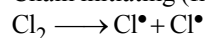
At 300°C in darkness.

At 100°C in the presence of organic peroxides.

At 150°C in the presence of Tetra ethyl lead.

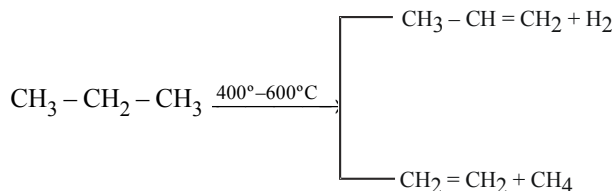
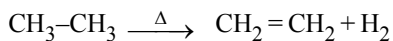
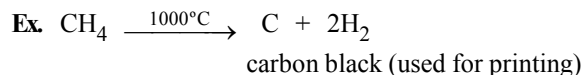
⇒ Chlorination of methane is based on free radical mechanism and it complete in the following three steps :

(a) Chain initiating (first) step

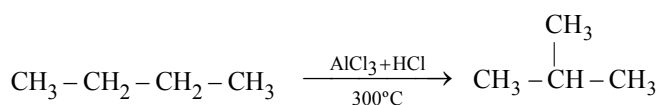


(4) Pyrolysis/Cracking or Thermal Decomposition :

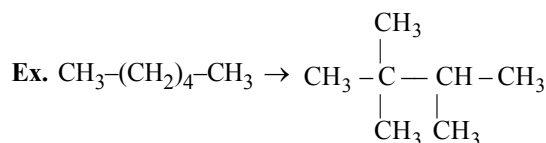
The decomposition of a compound by heat is called pyrolysis. In case of alkanes, thermal decomposition is known as cracking. It leads to the formation of lower alkanes, alkenes and hydrogen.



Cracking is used for manufacture of petrol, petrol gas, oil gas, etc. Mechanism of cracking is free radical.

(5) Isomerisation : Straight chain alkanes are converted into their branched chain isomers when heated in the presence of AlCl_3 at 300°C . Ex.

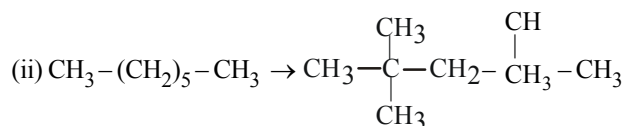
If we taken n-heptane then it converts into most stable form triptane.



n-heptane

Triptane

If we taken n-octane then it converts into most stable form iso-octane.



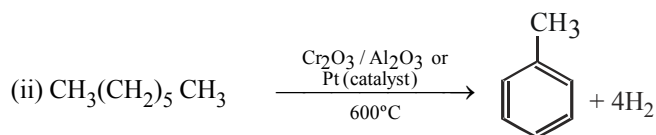
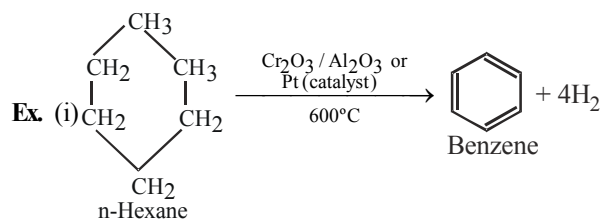
n-octane

iso-octane

Isomerisation of alkanes is of great importance in petroleum industry to increase the octane number of petrol (gasoline).

(6) Aromatization, hydroforming or catalytic reforming :

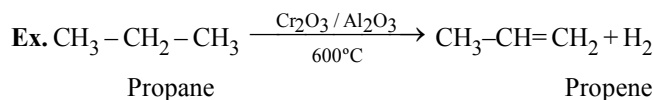
The conversion of aliphatic compounds into aromatic compound is referred to as aromatization. Alkanes having six or more carbon atoms are heated at 600°C in the presence of a catalyst such as Cr_2O_3 supported over alumina or Pt, an aromatic hydrocarbon results.



n-Heptane

Toluene

Aromatization involves cyclization and dehydrogenation.

Dehydrogenation :**Important point about of CH_4 (methane) :**

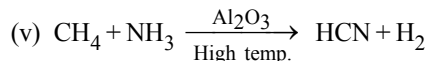
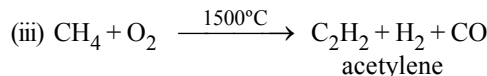
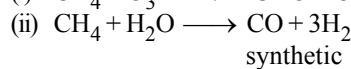
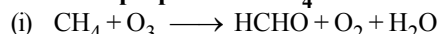
Methane is also called marsh gas or damp fire.

Natural gas = 80% CH_4 + 20% C_2 to C_6

Coal gas = 40% CH_4

CNG (Compressed naturel gas)

= 84% CH_4 + propane + butane + Higher alkane.

Chemical properties of CH_4 

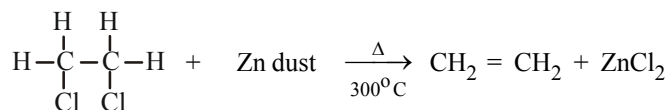
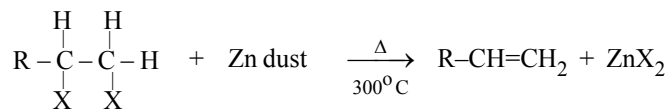
LPG is called as liquified petroleum gas or kitchen gas or domestic gas.

TRY IT YOURSELF-1

- Q.1** The compound with highest boiling point is
(A) n-hexane (B) n-pentane
(C) 2, 2-dimethyl propane (D) 2-methyl butane
- Q.2** Isopropyl bromide undergoes Wurtz reaction to form -
(A) Hexane (B) 2, 3 - Dimethyl butane
(C) Propane (D) Neohexane
- Q.3** The highest boiling point is expected for -
(A) isooctane (B) n-octane
(C) 2, 2, 3, 3-tetramethylbutane (D) n-butane
- Q.4** Which of the following will have least hindered rotation about carbon-carbon bond?
(A) Ethane (B) Ethylene
(C) Acetylene (D) Hexachloroethane
- Q.5** Alkanes are readily attacked by -
(A) Electrophiles (B) Nucleophiles
(C) Free radicals (D) bases
- Q.6** The hydrocarbon which is a liquid at room temperature is
(A) butane (B) propane
(C) decane (D) neopentane
- Q.7** The most volatile alkane is :
(A) n-pentane (B) isopentane
(C) neopentane (D) n-hexane

(b) From vicinal dihalides :

When vicinal dihalides are heated with Zn dust, alkene of same no. of carbon is obtained

**(vi) From Alcohols :**

When alcohol is heated with conc. H_2SO_4 at about 160°C , alkenes are formed after dehydration.

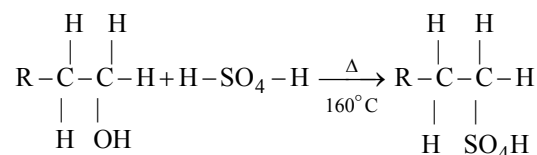
Dehydrating agent = conc. $\text{H}_2\text{SO}_4 \Rightarrow 170^\circ\text{C}$ temp.



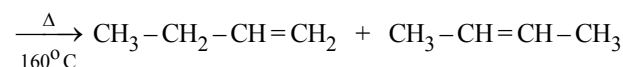
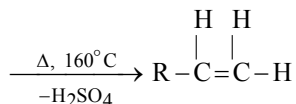
(vapour state)

Order of reactivity of alcohol = $3^\circ > 2^\circ > 1^\circ$ alcohol

According to saytzeff's rule (β -elimination)

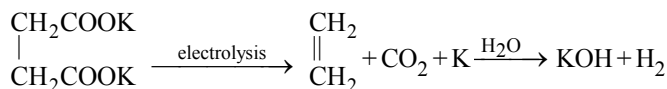


(Alkyl hydrogen sulphate)



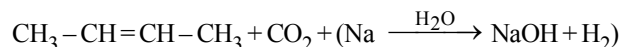
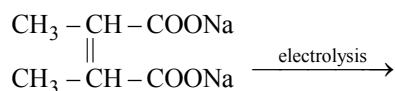
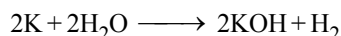
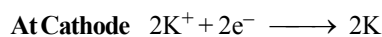
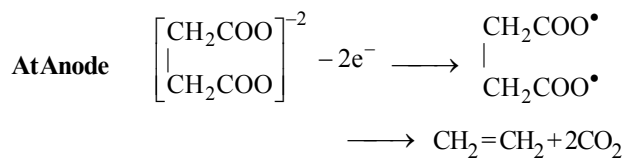
1-butene
(minor product)

2-butene
(major/chief product)

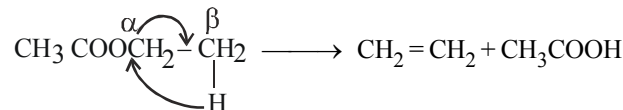
(vii) Kolbe's Synthesis :

At anode

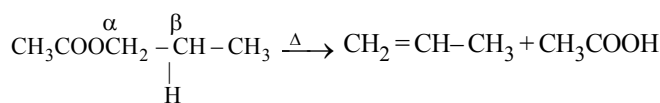
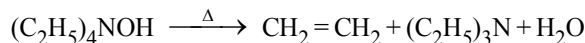
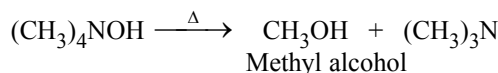
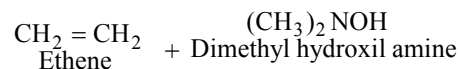
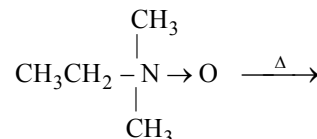
At cathode

**(viii) From ester (Pyrolysis of ester) :**

When esters are heated in presence of liq. N_2 and glass wool, then alkyl part of ester converts into respective alkene while alkanolate part of ester is converted into respective acid.



Elimination of β -H

**(ix) From pyrolysis of tetra alkyl ammonium hydroxide (R_4NOH):****(x) Cope reaction :****PHYSICAL PROPERTIES**

(i) From $\text{C}_2 - \text{C}_4$ they are colourless, odourless gases, from $\text{C}_5 - \text{C}_{17}$ they are colourless liquids, C_{18} onwards alkenes are solids. Ethylene C_2H_4 is a sweet smelling gas.

(ii) Alkenes are practically insoluble in water because they can not form hydrogen bonds with H_2O molecules. They dissolve freely in organic solvents like benzene, chloroform, CCl_4 petroleum ether., etc.

(iii) The boiling and melting points of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable π bond. alkenes are therefore, lesser volatile than the corresponding alkanes.

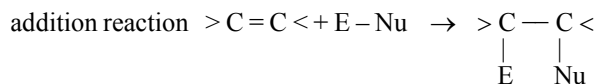
Their boiling points, melting points and specific gravities rise with the increase of molecular weight. The increase in branching in carbon chain decreases the boiling point among isomeric alkenes.

$$\text{MP. and BP.} \propto \text{mol. wt.} \propto \frac{1}{\text{branching in alkenes}}$$

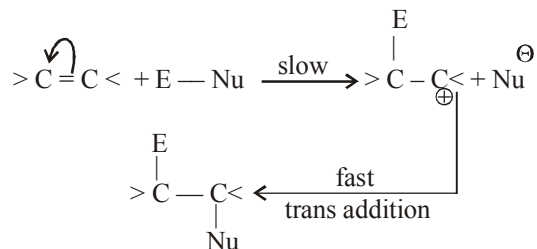
CHEMICAL REACTIONS

- (A) Additions reaction (B) Substitution reaction
(C) Oxidation reaction (D) Isomerisation reaction
(E) Polymersation reaction

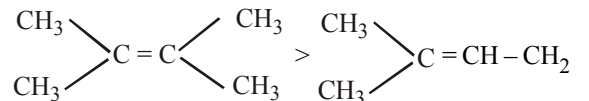
(A) **Additions reaction** : Alkenes are shows electrophilic



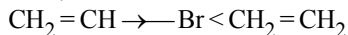
Mechanism :



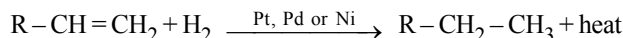
Effect of substituents :- In $CH_2 = CH_2$:
If H is replaced by methyl group the rate of addition increases [due to +I effect of methyl group]
The rate of addition :



$>CH_3CH=CH-CH_3 > CH_3-CH=CH_2 > CH_2=CH_2$
If H is replaced by electron withdrawing group - Br or -COOH, the rate of addition decrease [due to -I effect].



(a) **Hydrogenation (Addition of hydrogen) :**

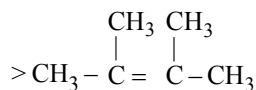
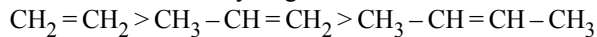


Heat of hydrogenation :

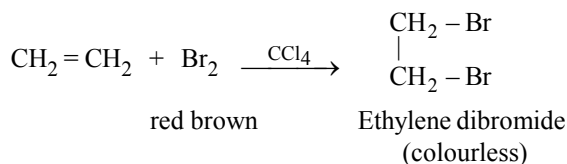
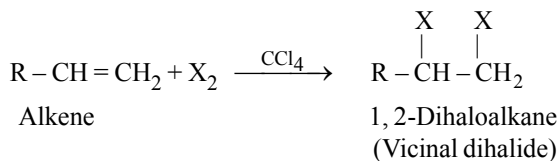
The amount of heat liberated in the hydrogenation of one mole of alkene is known as heat of hydrogenation. Hydrogenation of alkenes is an exothermic process. Heat of hydrogenation decreases as the stability of alkene increases.

$$\text{Stability of alkene} \propto \frac{1}{\text{Heat of hydrogenation}}$$

The relative rates of hydrogenation :

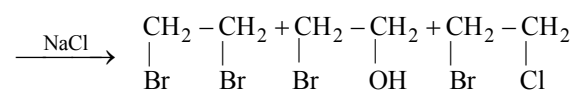
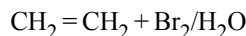


(b) **Addition of halogens** : Alkene readily react with halogens in an inert solvent such as CS_2, CCl_4 , etc. giving vicinal dihalides at ordinary temperatures.

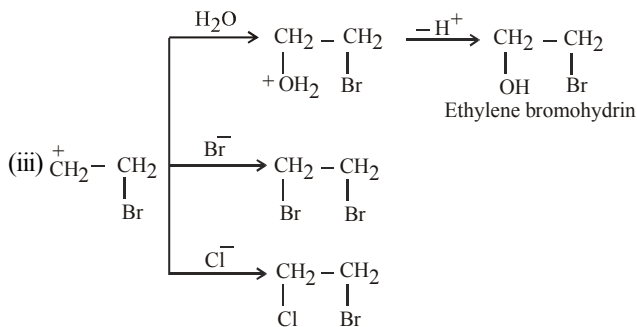
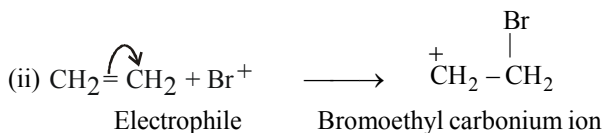
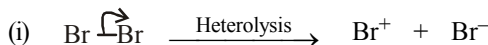


Reactivity order of halogens is $\Rightarrow Cl_2 > Br_2 > I_2$
A 5% solution of Br_2 in CCl_4 solvent is used for the detection of $>C=C<$ bond since red brown colour of Br_2 is discharged due to the formation of a colourless compound. Addition of halogens on alkenes is an example of electrophilic addition. It takes place via the formation of a carbonium ion.

Evidence of fraunsis :

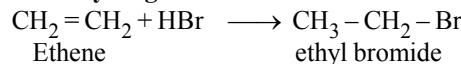


Mechanism of addition of halogens :



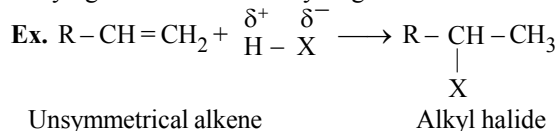
Addition of halogens on alkene is trans addition

(c) **Addition of hydrogen halides :**

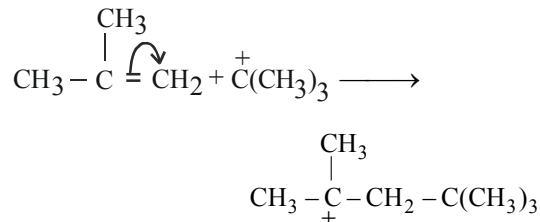


Order of reactivity of $HX \Rightarrow HI > HBr > HCl > HF$.
Addition of HX on unsymmetrical alkenes ($R-CH=CH_2$) takes place according to Markownikoff's rule.

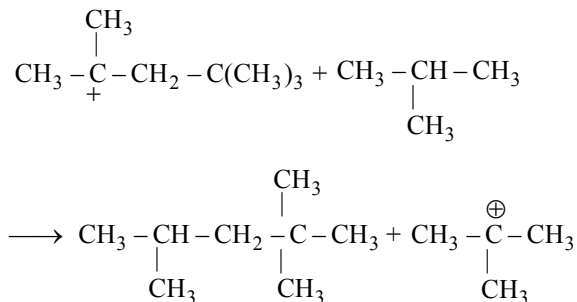
Markownikoff's rule :- Markownikoff's rule states, "the negative part of addendum is added on the carbon atom carrying lesser number of hydrogen atoms".



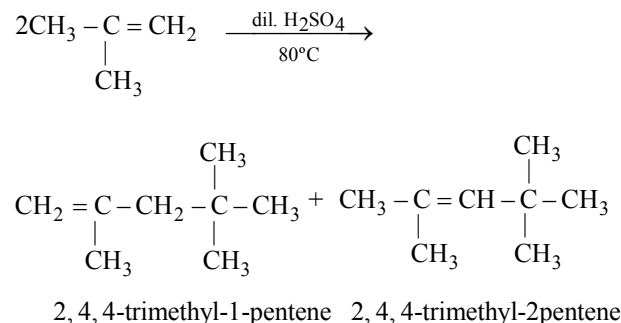
(ii) Addition of t-butyl carbonium ion on isobutylene.



(iii) Intermolecular transfer of hydride ion from isobutane to the carbonium ion formed in step II.



(j) Alkenylation :



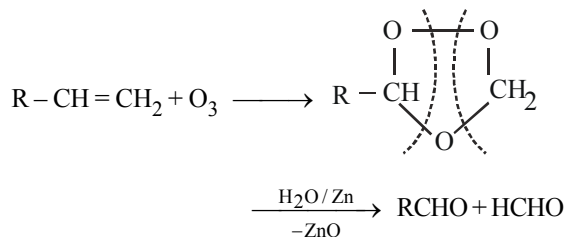
(B) Oxidation :

(i) Combustion : $\text{C}_n\text{H}_{2n} + \frac{3n}{2} \text{O}_2 \rightarrow n \text{CO}_2 + n\text{H}_2\text{O} + \text{Heat}$

$$\frac{\text{Volume of alkene}}{\text{Volume of oxygen}} = \frac{2}{3n}$$

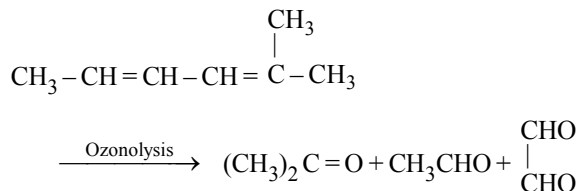
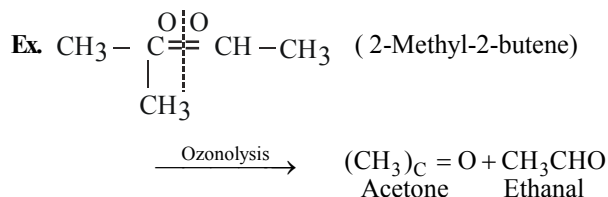
where n is number of carbon atom

(ii) Ozonolysis (Addition of ozone) :- The addition of ozone on the double bonds and subsequent hydrolysis of the ozonide formed is termed ozonolysis.



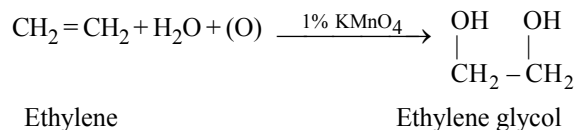
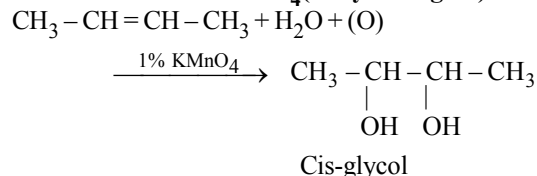
The hydrogen peroxide formed in the reaction is removed by adding zinc dust because it being an oxidising aldehydes into carboxylic acids.

Ozonolysis of alkene offers a valuable method of detection and location of double bonds in complex organic molecules. For knowing the ozonolysis products of an alkene, remove the $> \text{C} = \text{C} <$ bond and add oxygen atom 'O' on both the doubly bonded carbon atoms, Ex.



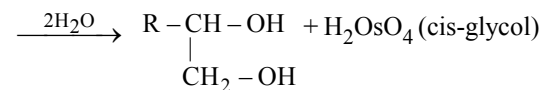
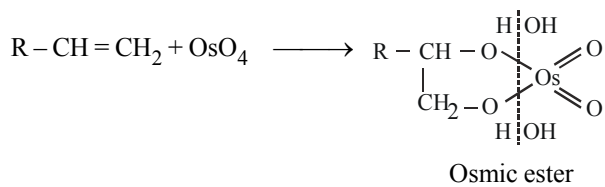
(iii) Hydroxylation : Addition of (O-H)

(a) With 1% alkaline KMnO_4 (Baeyer reagent) :

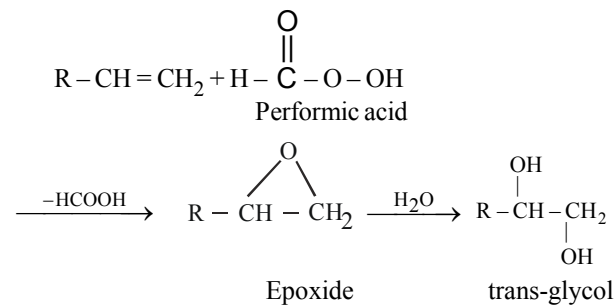


The pink colour of KMnO_4 solution is discharged and a brown ppt of MnO_2 is formed. It is used as a test for the presence of unsaturation in organic compounds (Baeyer's test). Chromic acid also converts alkenes into glycols (or epoxides).

(b) With Osmium tetra oxide (OsO_4) :-

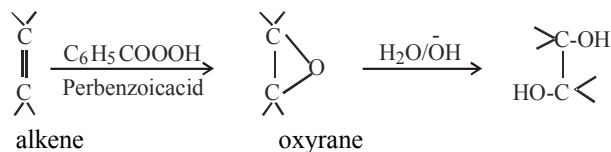


(c) With per acid (RCOOOH) :

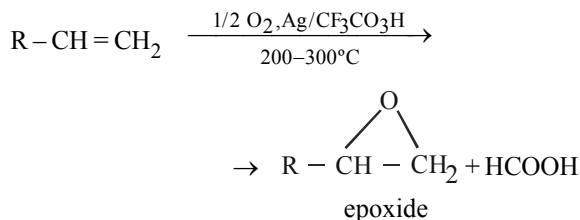
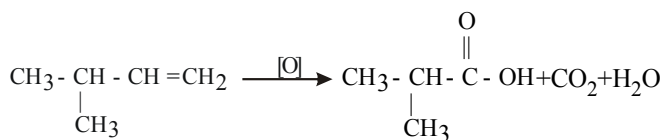
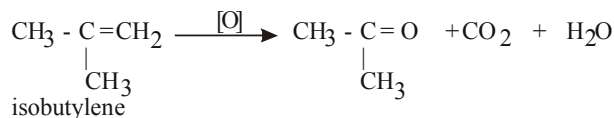
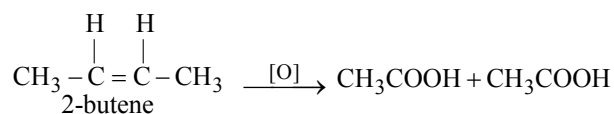
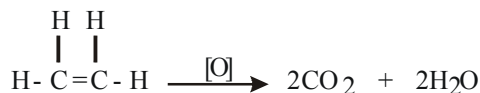
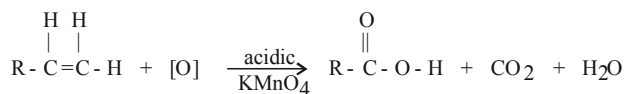


(iv) Epoxidation :

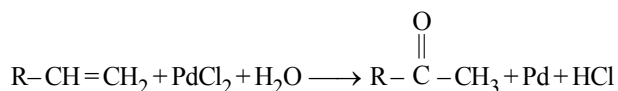
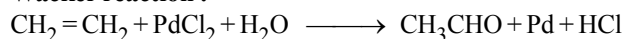
(a) **Prileschaiev Reaction/Reaction with Performic acid:** Alkenes react with peracids (per benzoic acid C_6H_5COOOH , per formic acid $-99\% H_2O_2 + HCHO$) to form oxyranes. (1, 2-epoxide), which on hydrolysis converted into dihydroxy compounds.



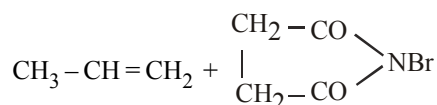
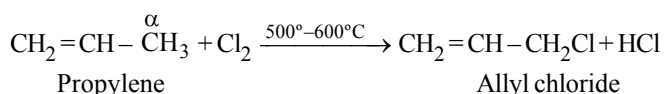
(b) With Ag catalyst :

(v) With Acidic $KMnO_4$ /Hot $KMnO_4$:

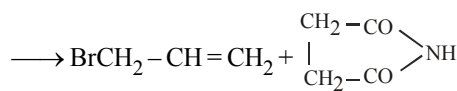
(vi) Wacker reaction :



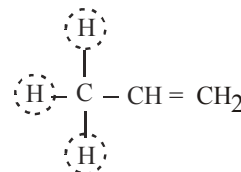
(c) **Substitution reaction :** Alkenes containing alkyl group when treated with chlorine at high temperature (about $500-600^\circ C$), the α -hydrogen atom of alkyl group is substituted by chlorine. Under these conditions Cl_2 is not added across the double bond. Thus, propylene gives allyl chloride.



NBS ; * NBS = N-bromosuccinimide

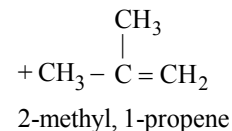
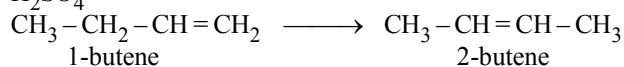


Succinimide



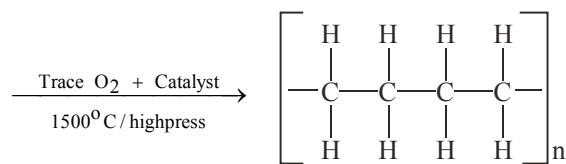
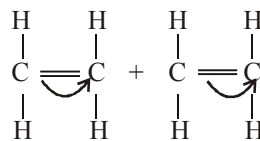
*The circled hydrogens are allylic hydrogen.

(D) **Isomerisation :** Alkenes isomerise when heated at high temperature ($500-700^\circ C$) or at lower temperatures ($200-300^\circ C$) in the presence of anhyd. $AlCl_3$, or $Al_2(SO_4)_3/H_2SO_4$



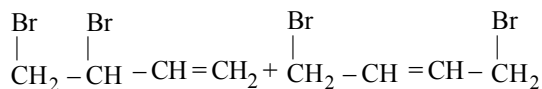
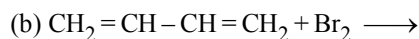
(E) **Polymerisation :** The process in which many simple molecules combine together to form a large single molecule without elimination of anything is known as polymerisation. The simple molecule is called a monomer and the single large molecule is called a polymer. Polymerisation is a reversible process. Mechanism is based on ionic or free radicals both.

In alkene polymer name of polymer is given on the basis of name of monomer only 'Poly' prefix is used. If in polymerisation Zeigler-Natta catalyst (trialkyl aluminium + Titanium tetrachloride (C_2H_5)₃Al + $TiCl_4$) is used than polymerisation is names as Ziegler-Natta Polymerisation.

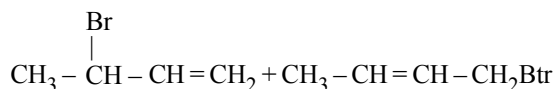
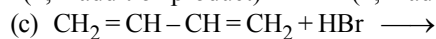


Polymer or $(-CH_2-)_n$ polythene

Note : If propylene is reacted then polypropylene is formed its commercial name is 'Koylene'. By the use of vinyl chloride polyvinyl chloride is formed. Zeigler-Natta catalyst is used in addition polymerisation.

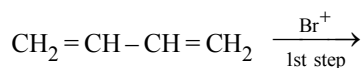


3, 4-Dibromo-1-butene (1, 2-addition product) 1, 4-Dibromo-2-butene (1, 4-addition product)

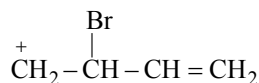


3-Bromo-1-butene (1, 2-addition) 1-Bromo-2-butene (1, 4-addition)

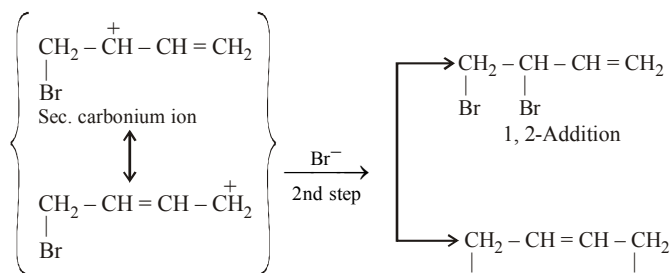
The formation of two products can be explained on the basis of higher stability of the intermediate secondary carbonium ion (due to resonance) than the primary carbonium ion. The two resonating structures of the secondary carbonium ion will be forming two products when attacked by Br^- ion.



Butadiene



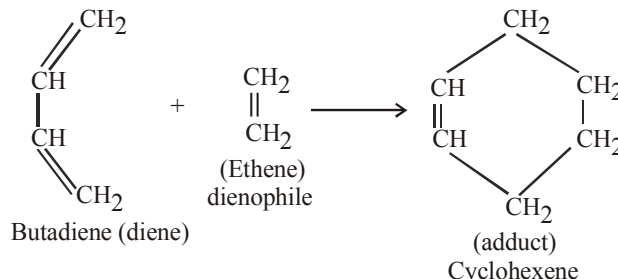
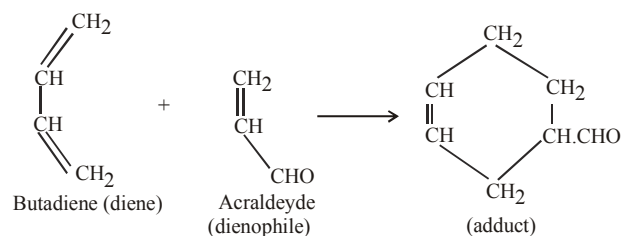
Primary carbonium ion (unstable)



The major product obtained depends upon the nature of the solvent and temperature during reaction.

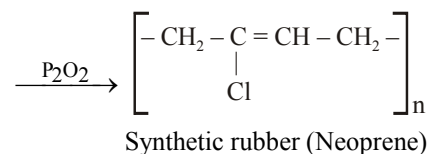
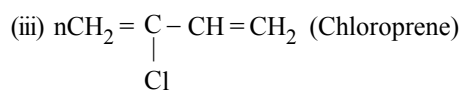
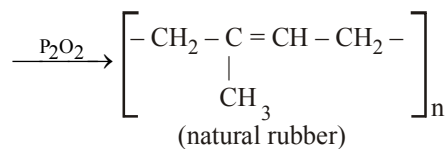
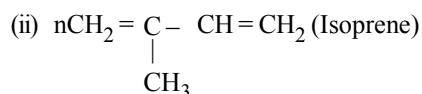
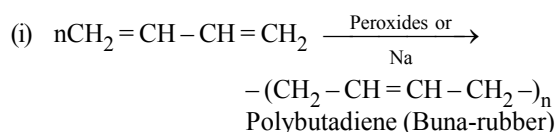
(3) Diene synthesis or Diel's Alder reaction :

In addition to abnormal addition reactions, conjugated dienes undergo other reactions not characteristic to the normal olefins, viz. they undergo Diel's -Alder reaction¹ and readily polymerise.



Note : This reaction consists of the addition of a conjugated diene to a second unsaturated molecule (usually having an electron-attracting group) called as a dienophile, resulting in the formation of a cyclic product usually called as adduct. Ethylene is the simplest dienophile, however reaction with ethylene requires high temperature (200°C).

(4) **Polymerisation :** Polymerisation of butadiene leading to a soft product, called buna rubber, is initiated by free radicals. Buna rubber is found to be a mixture of 1, 2- and 1, 4- addition products.



TRY IT YOURSELF-2

Q.1 Alkene can be formed from carbonium ion by

- (A) Combination of proton
(B) Elimination of hydride ion
(C) Elimination of proton
(D) First combination of H then removal of H

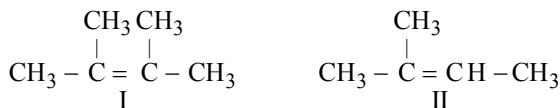
Q.2 The presence of unsaturation in an organic compound can be tested with-

- (A) Schiff's reagent (B) Tollen's reagent
(C) Fehling solution (D) Baeyer's reagent

Q.3 Propylene is more stable than ethylene. The reason for this is the -

- (A) Electromeric effect (B) Hyper conjugation
(C) Inductive effect (D) Resonance effect

Q.4 The relative stability of the compounds



is in the order -

- (A) I > II > III > IV (B) IV > III > II > I
(C) I > III > II > IV (D) II > I > IV > III

Q.5 The formation of 2-butene from 2-butanol in the presence of conc. H_2SO_4 is in accordance with -

- (A) Hoffmann's rule (B) Saytzeff's rule
(C) Markownikoff's rule (D) Kharasch rule

Q.6 The structural formula of the compound which yields ethylene upon reaction with zinc -

- (A) $\text{CH}_2\text{Br}-\text{CH}_2\text{Br}$ (B) $\text{CHBr}_2-\text{CHBr}_2$
(C) $\text{CHBr}=\text{CHBr}$ (D) None

Q.7 The most common reactions of alkenes are-

- (A) Nucleophilic substitution
(B) Electrophilic substitution
(C) Electrophilic addition
(D) Nucleophilic addition

Q.8 Anti-Markownikoff addition of HBr is not observed in

- (A) propene (B) butene
(C) 2-butene (D) 2-pentene

Q.9 The addition of HCl in the presence of peroxide does not follow anti-Markownikoffs rule because

- (A) HCl bond is too strong to be broken homolytically
(B) Cl atom is not reactive enough to add on to a double bond
(C) Cl combines with H to give back HCl
(D) HCl is a reducing agent

Q.10 The ozonolysis of an olefin gives only propanone. The olefin is :

- (A) propene (B) but-1-ene
(C) but-2-ene (D) 2,3-dimethyl but-2-ene

ANSWERS

- (1) (C) (2) (D) (3) (B)
(4) (A) (5) (B) (6) (A)
(7) (C) (8) (C) (9) (A)
(10) (D)

ALKYNE

INTRODUCTION

Their general formula is $\text{C}_n\text{H}_{2n-2}$

Type formula $\text{R}-\text{C}\equiv\text{C}-\text{H}$ IUPAC name is alkynes.

Functional group is $-\text{C}\equiv\text{C}-$ (acetylenic group).

Hybridization of both carbon is sp

Triple bond is made up of 2π and one sigma bonds.

Properties

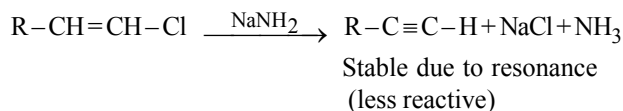


- (i) overlapping σ bond = sp-sp sp-s
(coaxial) π bond = $2P_y - 2P_y$ \times
(colleteral) π bond = $2P_z - 2P_z$ \times

- (ii) bond length 1.20Å 1.08Å
(iii) bond energy 195 kcal mole⁻¹ 121 kcal mole⁻¹
The first member of the alkyne series is acetylene, (3σ and 2π bond) $\text{H}-\text{C}\equiv\text{C}-\text{H}$
Shape of the molecule is linear and C-C-H bond angle is 180°. Total angle of $180^\circ = 2$

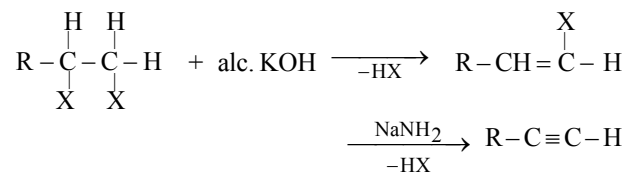
METHODS OF PREPARATION

(i) From Vinyl Halide :



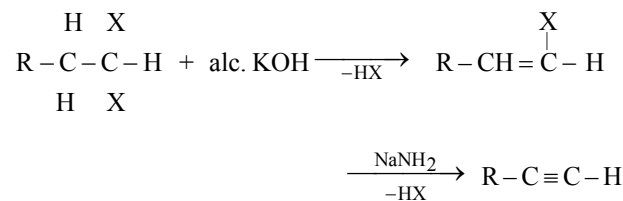
(ii) From Dihalide (Dehydrohalogenation) :

(a) Vicinal Dihalides :

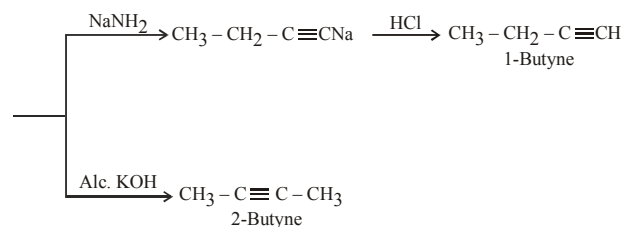
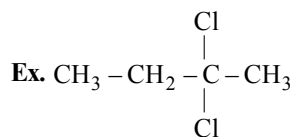


NaNH_2 is more reductant than alc. KOH.

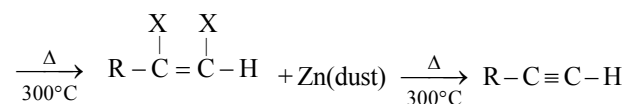
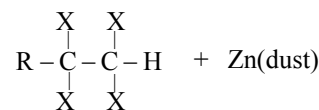
(b) Gem Dihalides :



Stereo selective reaction



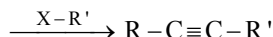
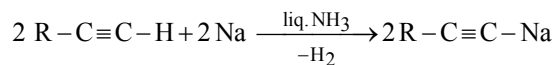
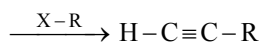
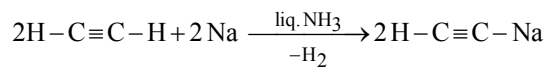
(iii) From Tetrahaloalkanes (Dehalogenation) :



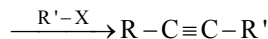
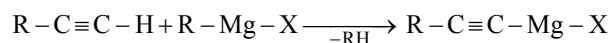
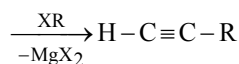
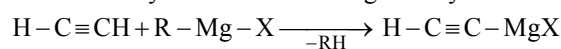
Note : In the above reaction it is necessary that the four halogen atoms must be attached at vicinal carbons. If they are attached at the two ends then the product cyclo alkene is obtained.

(iv) Synthesis of Higher Alkynes :

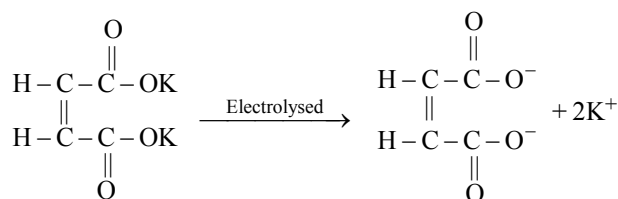
(a) With Na : When acetylene or 1-alkyne react with Na in presence of liq. NH₃ then an intermediate compound sodium acetylide or sodium alkynide is formed which gives higher alkyne with alkyl halide.



(b) With GR : When acetylene or 1-alkyne react with GR then alkane and unsaturated GR is formed which further react with alkyl halide and form higher alkyne.



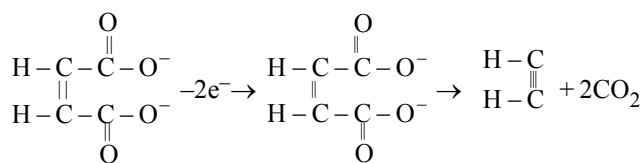
(v) From Kolbe's Synthesis :



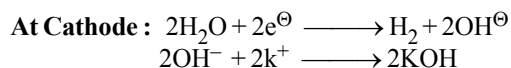
Potassium Maleate

Maleate ion

At Anode :

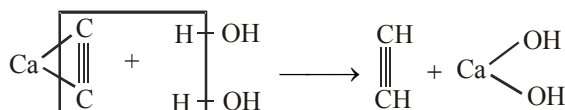


Unstable

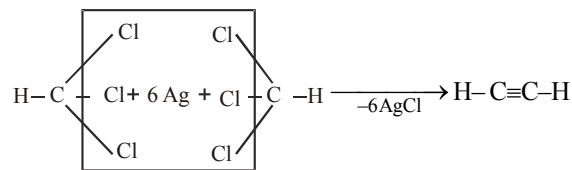


(vi) Preparation of Acetylene :

(a) In laboratory acetylene is prepared by hydrolysis of calcium carbide.



(b) It can also be prepared from CHCl₃ with Ag dust.



PHYSICAL PROPERTIES

- (i) Alkynes are colourless, odourless and tasteless.
- (ii) Lower alkynes are partially soluble in H₂O. (It is due to its polarizability)
- (iii) Higher alkynes are insoluble in water due to more % of covalent character.
- (iv) Completely soluble in organic solvents.
- (v) Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.
- (vi) Upto C₄ alkynes are gaseous. C₅ - C₁₁ liquid, C₁₂ & above are solids.
- (vii) Acetylene & 1-alkyne are acidic in nature. It is due to presence of active H.
- (viii) Order of Solubility, density, B.P., M.P. and Acidic nature :
 Alkyne > Alkene > Alkane
 All terminal alkynes are acidic in nature.
 Acidity order :
 H₂O > R-OH > H-C≡C-H > NH₃ > CH₂=CH₂ > CH₃-CH₃

CHEMICAL REACTIONS

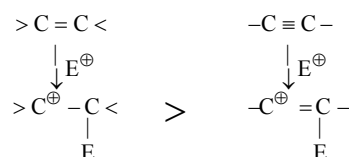
- (A) Addition (B) Oxidation (C) Substitution
 (D) Isomerisation (E) Polymerization

(A) Addition :

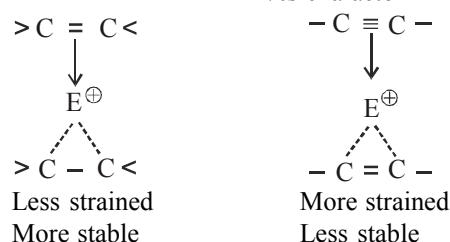
(a) Electrophilic addition : Alkene > Alkyne

Reason : (i) Stability of intermediate :

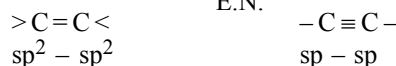
Order of Stability :



Stability of carbocation $\propto \frac{1}{\%s \text{ character}}$

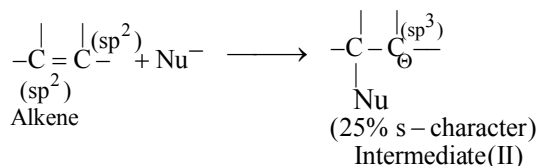
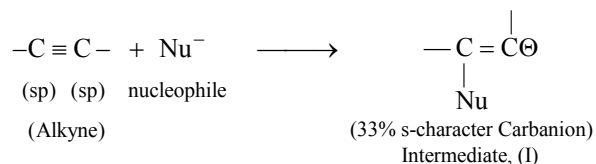


(ii) Reactivity of E[⊕] $\propto \frac{1}{\text{E.N.}}$



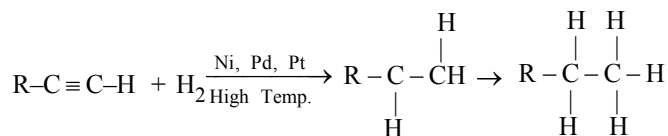
electro negativity = C_{sp} > C_{sp²}

(b) Nucleophilic addition : Alkyne > Alkene
Nucleophilic addition reaction is complete in presence of heavy metal ion (Hg^{+2} , Pb^{+2} , Ba^{+2})

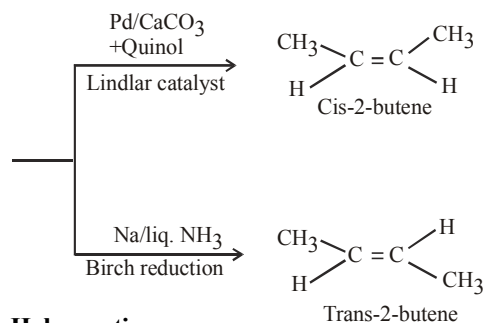


Intermediate (I) is more stable than (II) because negative charge is present on sp^2 hybridized carbon atom which can better sustain the charge due to greater s-character.

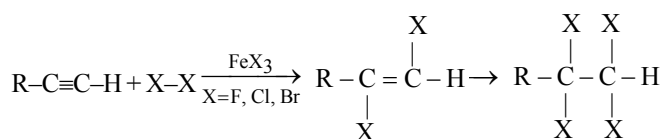
(i) With Hydrogen (Sabatier-Senderson's reaction) :



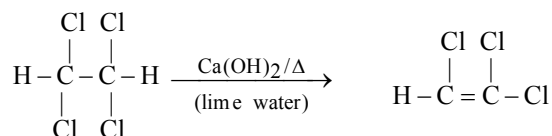
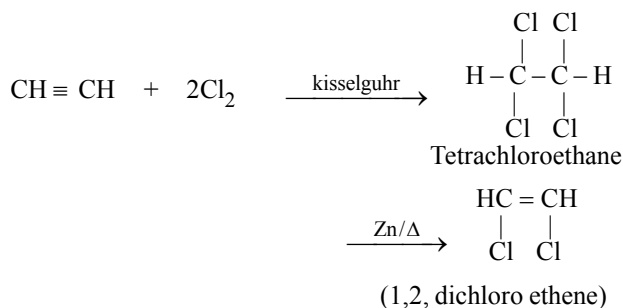
Stereo selective reaction : Ex. $CH_3-C \equiv C-CH_3 + H_2$



(ii) Halogenation :



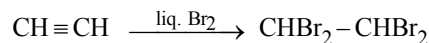
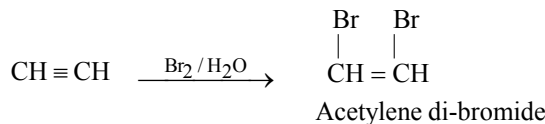
Chlorination : Explotion reaction takes place between ethyne and chlorine and carbene and HCl is formed. But in presence of catalyst tetra chloro ethane is formed. Which is to be converted into 1, 2 dichloro ethyne and trichloroethene.



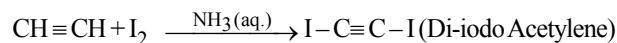
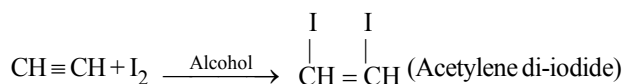
Tetrachloethane (westron)

Trichloro ethene (westrosol)

Bromination :

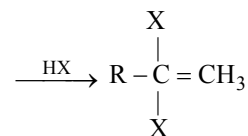
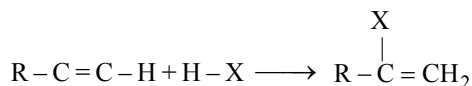


Iodination :



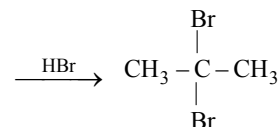
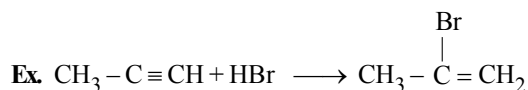
(iii) Reaction with HX/Hydrohalogenation : Alkyne form gem dehalide with HX because reaction follows markownikoff's 1st and 2nd rule both.

Reactivity order : $HI > HBr > HCl > HF$



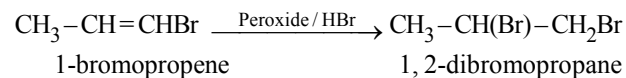
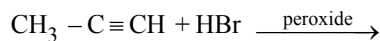
gem dihalidedihalide

Markownikorr's addition :

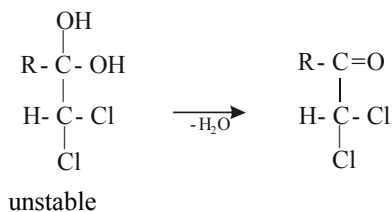
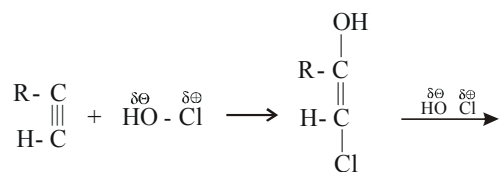


2, 2-dibromo propane

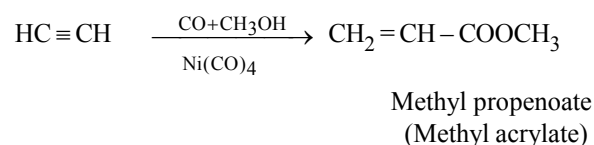
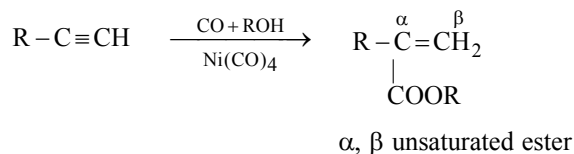
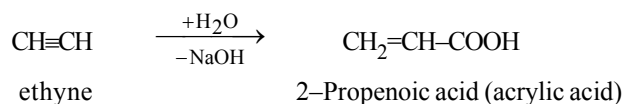
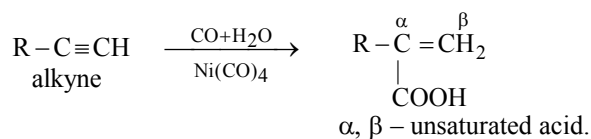
Peroxide effect (Addition of HBr) :



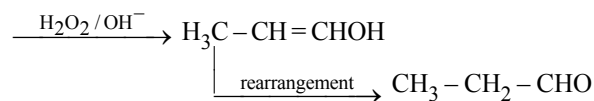
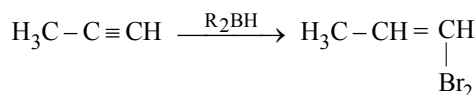
(iv) Reaction with Hypochlorous acid or Chlorine water :

(v) Carbonylation [Addition of (CO + H₂O) or (CO + ROH)]

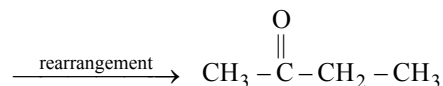
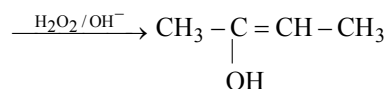
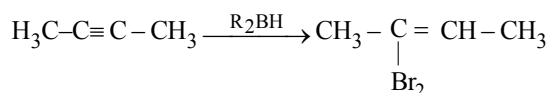
Alkyne on reaction with CO + H₂O and CO + ROH in presence of Ni(CO)₄, respectively alkyneic acid and alkenoic ester is formed.



(vi) Hydroboration :

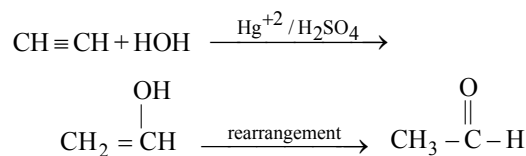


1-alkyne gives aldehyde while other alkynes give ketones.



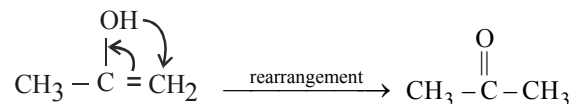
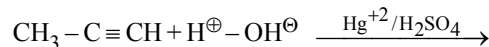
2-butanone

(vii) Hydration :

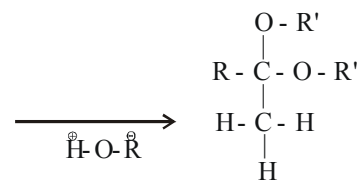
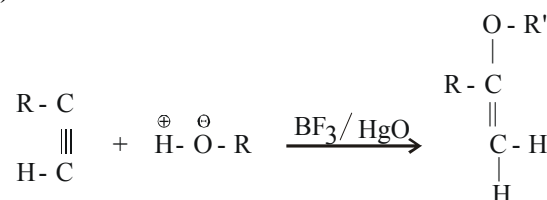


Vinyl Alcohol

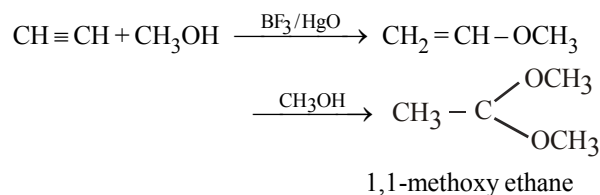
Also known as Kuchrov's reaction.



(viii) Reaction with Alcohol :

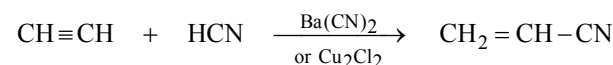
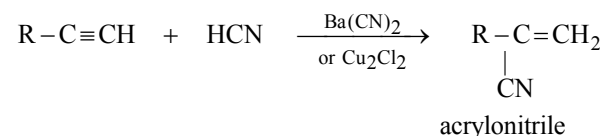


acetal/ketal



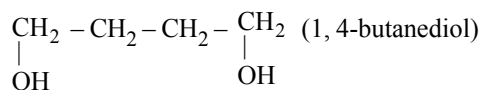
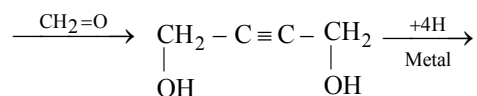
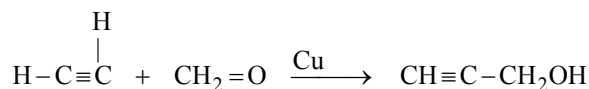
(ix) Reaction with HCN :

In presence of Barium Cyanide or Cu₂Cl (copper salt) HCN after reacting with alkyne, vinyl cyanide derivative is formed. With ethyne vinyl cyanide (acrylonitrile) is form.



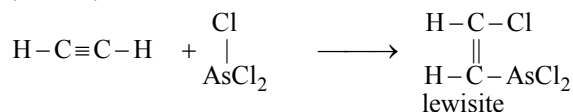
(x) Reaction with Formaldehyde :

1-Alkyne in the presence of copper react with methanal to form alkynol.



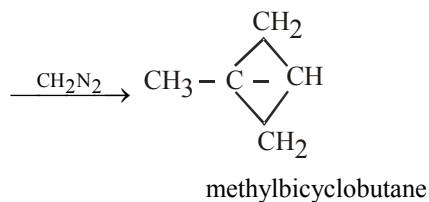
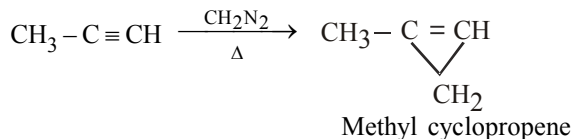
(xi) Reaction with Arsenic Trichloride :

Ethyne by addition reaction with arsenic tri chloride (AsCl_3) form a poisonous gas β -chlorovinyl-dichloro arsine (lewisite)



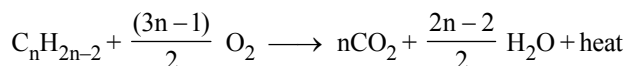
Lewisite is a powerful poisonous gas. It is four times more active than mustard gas. It causes immediate death because it readily penetrates clothes and skin. Antidote of Lewisite is BAL (British Anti Lewisite). 2,3-Dimercapto-1-propanol is BAL.

(xii) Addition of carbene :



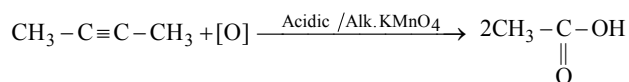
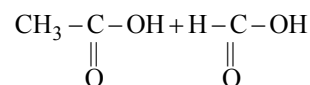
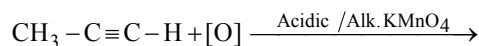
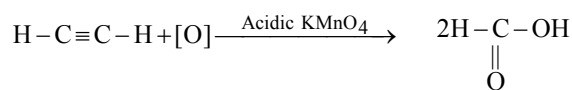
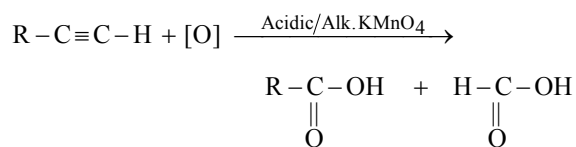
(B) Oxidation :

(i) Combustion :

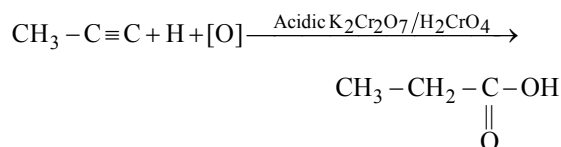
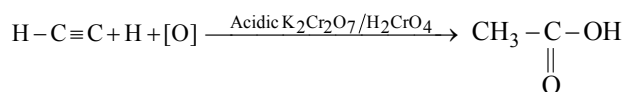
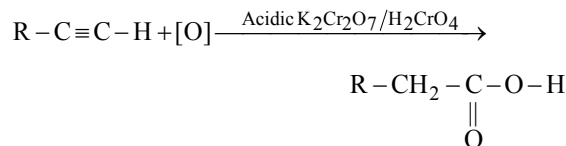


(n = number of carbon atom)

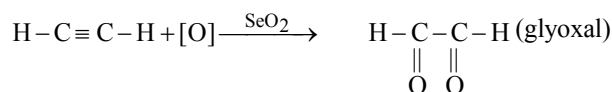
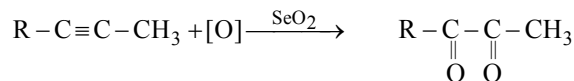
(ii) With acidic or alkaline KMnO_4 alkyne break into two parts from triply bonded carbon and every part forms respective acid.



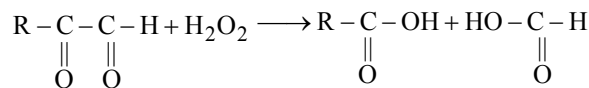
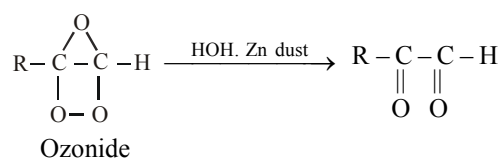
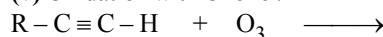
(iii) If terminal alkyne is oxidised with acidic $\text{K}_2\text{Cr}_2\text{O}_7$ or H_2CrO_4 (Cromic acid) then they converts into respective acid.



(iv) If oxidation occurs with selenium oxide (SeO_2) then triply bonded carbon oxidises into carbonyl group and product will be dicarbonyl compound.



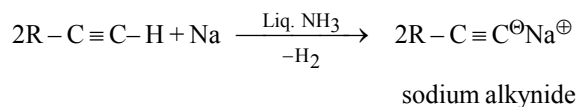
(v) Oxidation with Ozone :

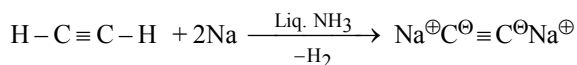


(C) Substitution :

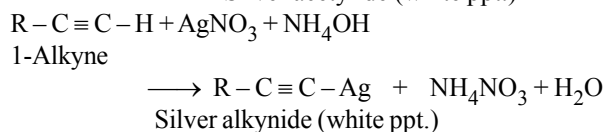
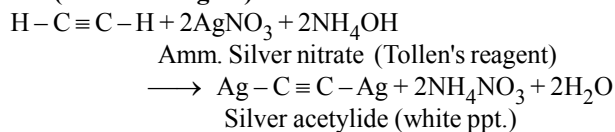
In 1-alkyne or acetylene, the H which is linked with sp hybridised carbon is called as acidic or active H. It can easily be substituted by metal or alkaline species. Hence 1-alkyne or acetylene are acidic in nature.

(i) Reaction with Na :

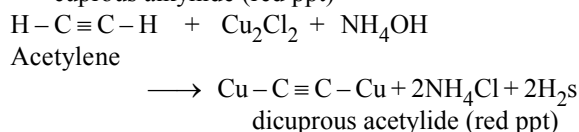
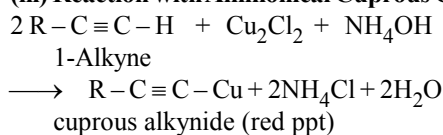




(ii) Reaction with Ammonical Silver Nitrate solution : (Tollen's Reagent)

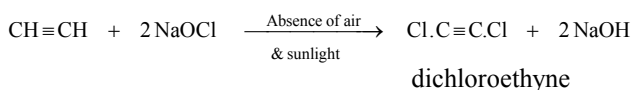


(iii) Reaction with Ammonical Cuprous Chloride solution



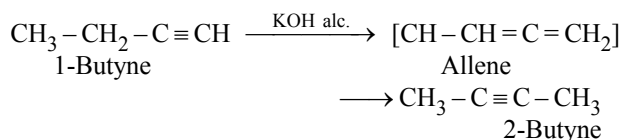
(iv) Reaction with sodium hypochlorite (NaOCl) :

In the absence of air and sunlight ethyne after reacting with NaOCl dichloro ethyne is formed. This is substitution reaction.

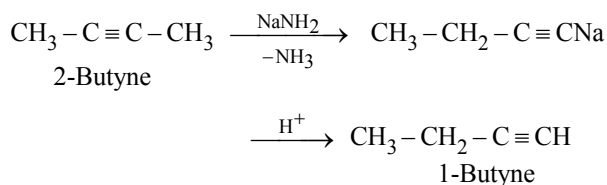


(D) Isomerisation :

1-Alkynes are converted to 2-alkynes (isomer) when warmed with alcoholic KOH.



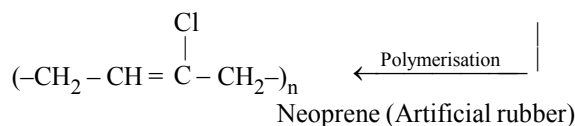
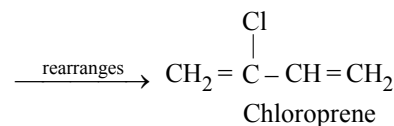
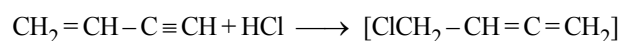
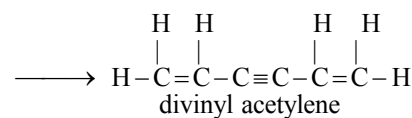
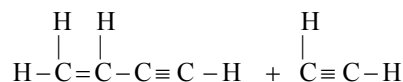
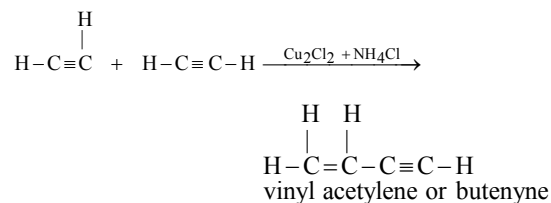
2-Alkyne are converted in to 1-alkyne when warmed with sodamide.



(E) Polymerisation :

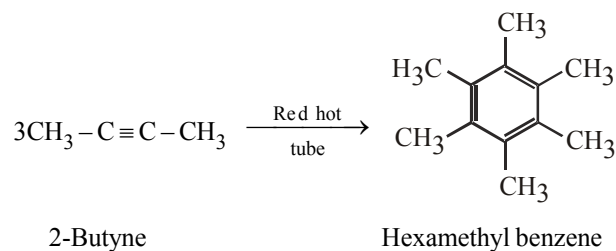
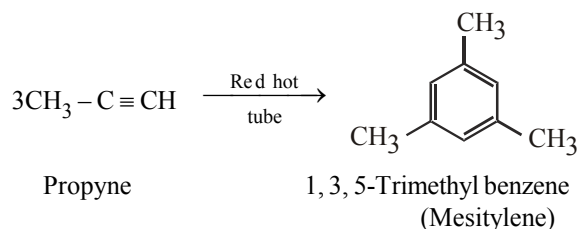
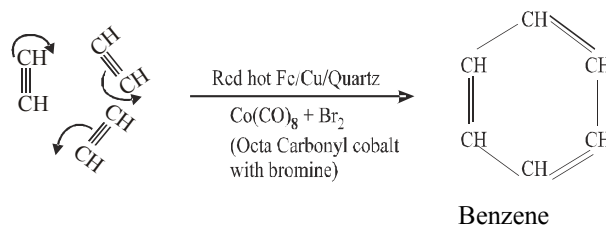
(i) Linear polymerisation : Two mole acetylene reacts with Cu_2Cl_2 & NH_4Cl and forms vinyl acetylene.

Note : If acetylene would be in excess then product would be divinyl acetylene and the reaction is called trimerisation.

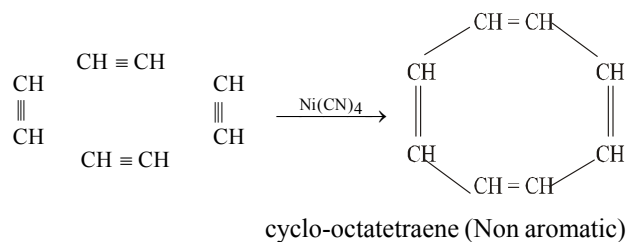


(ii) Cyclic polymerisation :

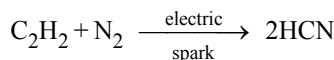
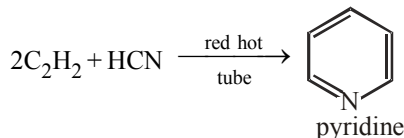
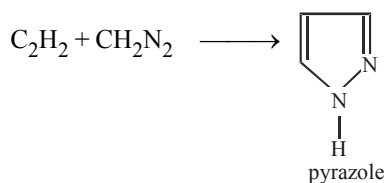
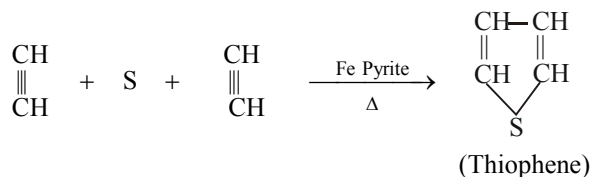
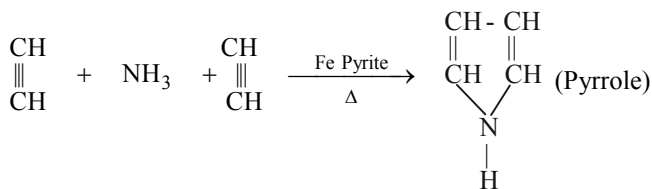
(a) Trimerisation : If three mole of acetylene is passed into red hot iron or Cu or quartz tube at 900K then a cyclic trimer is formed which is called benzene.



(b) Tetramerisation : According to the name four moles of acetylene are heated with nickel tetra cyanide, then acetylene forms a cyclic tetramer cyclooctatetraene.



(c) Formation of heterocyclic compounds :



The smell of acetylene is like that of garlic (it is due to impurities of PH_3 and H_2S). Acetylene is known as norsiline.

TRY IT YOURSELF-3

- Q.1** Which order is correct for bond length -
 (A) $\equiv\text{C}-\text{H} > -\text{C}-\text{H} > =\text{C}-\text{H}$
 (B) $-\text{C}-\text{H} < \equiv\text{C}-\text{H} < =\text{C}-\text{H}$
 (C) $\equiv\text{C}-\text{H} < =\text{C}-\text{H} < -\text{C}-\text{H}$
 (D) None of these
- Q.2** Which one of these will react with sodium metal-
 (A) Ethyne (B) Ethene
 (C) Ethane (D) Ether
- Q.3** Given the following reactions propyne + $\text{HCl}(\text{g}) \rightarrow \text{A}$
 $\text{A} + \text{HI}(\text{g}) \rightarrow \text{B}$
 The compounds A and B are respectively:
 (A) 1-chloropropene and 1-chloro-1-iodopropane
 (B) 1-chloropropene and 1-chloro-2-iodopropane
 (C) 2-chloropropene and 2-chloro-2-iodopropane
 (D) 2-chloropropene and 1-iodo-2-chloropropene
- Q.4** Ethene can be separated from ethyne by passing the mixture through
 (A) concentrated H_2SO_4 (B) ammonical Cu_2Cl_2
 (C) pyrogallol (D) charcoal powder
- Q.5** Acetylene when passed through 20% H_2SO_4 at 80°C gives acetaldehyde. The catalyst required for this conversion is
 (A) Anhydrous AlCl_3 (B) HgSO_4
 (C) Pd (D) Pt

- Q.6** A gas on passing through ammonical solution of AgNO_3 does not give any precipitate but decolourises alkaline KMnO_4 solution. The gas may be :
 (A) C_2H_2 (B) C_2H_4
 (C) C_3H_4 (D) C_3H_3

- Q.7** $\text{CH}_3-\text{C}\equiv\text{CH} + \text{H}_2\text{O} \xrightarrow[\text{Hg}^{+2}]{\text{H}^+}$ 'A' Here A is :

- (A) Aldehyde (B) Ketone
 (C) Alkane (D) Alcohol

- Q.8** Which of the following is most acidic?

- (A) Methane (B) Ethane
 (C) Ethylene (D) Acetylene

- Q.9** Acetylene reacts with ammonical silver nitrate to form-

- (A) Silver mirror (B) Metallic silver
 (C) Silver acetate (D) Silver acetylide

ANSWERS

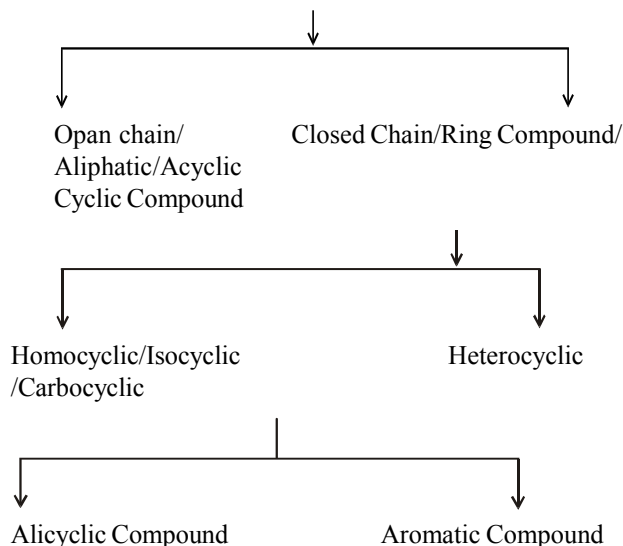
- (1) (C) (2) (A) (3) (C)
 (4) (B) (5) (B) (6) (B)
 (7) (B) (8) (D) (9) (D)

AROMATIC HYDROCARBON

INTRODUCTION

Aromatic \longrightarrow Aroma (Greek word) \longrightarrow "Sweet Smell"

Organic Compounds



Aromatic compounds are those compounds which have in their structure at least one unsaturated ring in which π electrons are continuously delocalised in cyclic fashion.

Characteristics of Aromatic compounds :

- The ratio of weights of carbon and hydrogen are very high as compared to the respective aliphatic compounds. Therefore, aromatic compounds burn with smoky flame.
- In aromatic compounds the ring may be composed of 3, 5, 6, 7 atoms and these are in flat or planar geometry.
- The aromatic compounds being unsaturated they show unexpected stability and resistance towards addition reactions. This character is called "Aromaticity".

4. The aromatic compounds undergo substitution more readily than the addition reaction.

High stability of aromatic compounds is explained on the basis of hydrogenation energy.

Heat of hydrogenation of a C = C bond \Rightarrow 28.6 kcal/mol

So heat of hydrogenation of benzene should be (Having there C = C) = 85.8 Kcal/mol

But in Actual it is = 49.8 kcal/mol

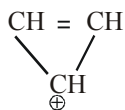
Difference in energies = 36.0 kcal/mol

This difference of energy is the resonance energy of benzene which is used in stabilisation of benzene.

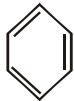
5. Aromatic compounds have the cyclic system and contain $(4n + 2) \pi$ electrons [Eric huckel's rule]
when $n = 0, 1, 2, 3, 4, \dots$

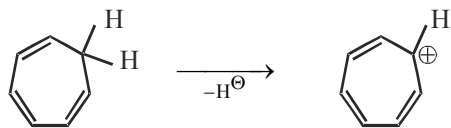
Hence delocalisation alone is not sufficient criterion for aromaticity,

Ex. When $n = 0 \quad \pi e^- = 2$



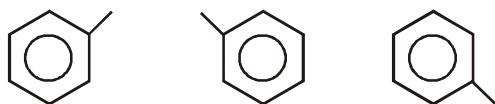
Cyclopropenyl cation (Planar)

Ex. When $n = 1$; $\pi e^- = 4(1) + 2 = 6$  (Benzene)

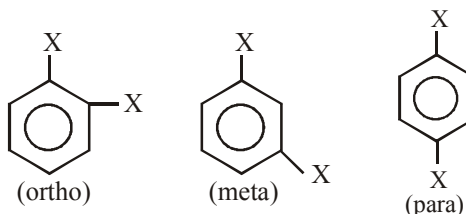


Cycloheptatriene Cycloheptatrienyl cation
(Tropylium cation)

6. These compounds basically give electrophilic substitution reaction.
7. Nitration of compounds takes place by nitronium ion (NO_2^+).
8. Halogenation of comp. takes place by halonium ion (X^+)
9. Sulphonation of compounds takes place by natural electrophilic sulphur trioxide (SO_3)
10. A monosubstituted derivative of benzene is found in only one form i.e. it can not show positional isomerism on the ring.



11. A disubstituted derivative of benzene is found in three positional isomeric forms, which are called ortho (-o), meta (-m), para (-p) disubstituted derivatives of benzene.



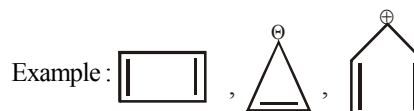
12. All the six carbon of benzene ring are in sp^2 hybridisation state and all C - C bond lengths have a value of 1.397 Å. The value of all the six C - H bond lengths is 1.09 Å and the molecule has planar hexagonal geometry. The value of all bond angles is 120° .
13. There are total twelve σ bonds and three π -bonds in benzene molecule. These three π -bonds are distributed over all the six carbon atoms.

Antiaromatic compounds :

According to Huckel rule, compound will be antiaromatic if it fulfils the following four conditions:

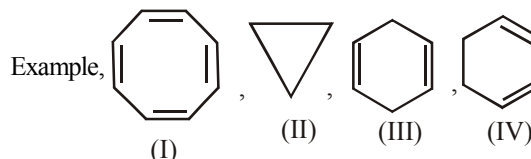
- Compound should be cyclic.
- Compound should be planar.
- Compound should be conjugated through out ring
- Compound should have $(4n)\pi$ conjugated or delocalised electrons where n is a whole number.
 $n = 1, 2, 3, 4, 5, 6$

$n = 1, 2, 3, 4, 5, \dots$
$(4n)\pi$ electron = 4 8 12 16 20



Non-aromatic compounds :

These compounds are neither aromatic nor antiaromatic.



Although cyclooctatetraene has $(4n)\pi$ electrons but even then it is not an antiaromatic. Geometry of this compound is non-planar. Thus it is non-aromatic. IInd, IIIrd & IVth compounds are not completely conjugated.

Note : Due to Aromatically extra stability is achieved by aromatic molecule, than non-aromatic or antiaromatic molecule.

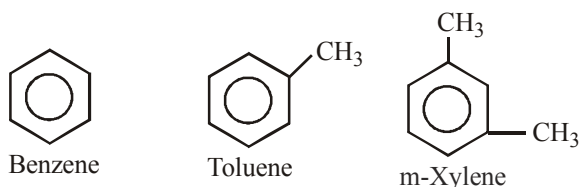
CLASSIFICATION OF AROMATIC COMPOUNDS

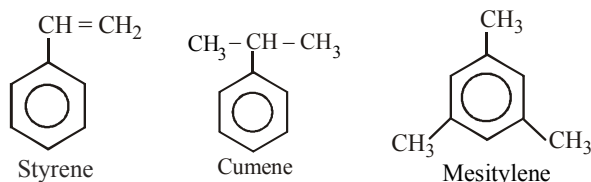
(A) Aromatic homocyclic (B) Aromatic heterocyclic

(A) Aromatic homocyclic are two type :

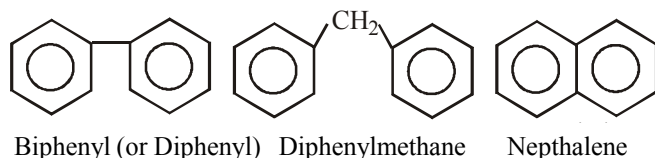
(i) Aromatic hydrocarbon [Arens] :

(a) Monocyclic arens : The Compounds having only one ring in the structural formula.



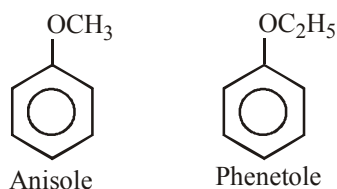
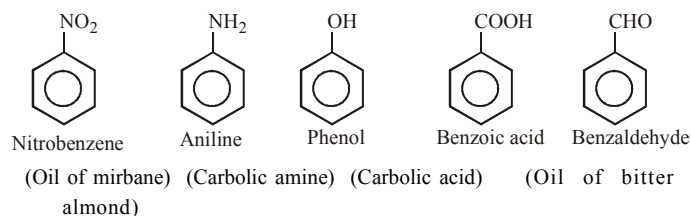


(b) Polycyclic arens : Aromatic hydrocarbon having more than one ring in their structural formula are called polycyclic arens.

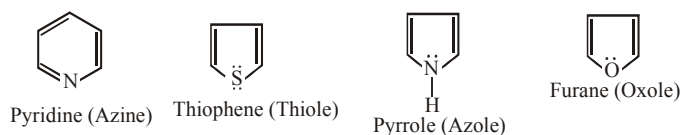


(ii) Aromatic hydrocarbon derivatives / Functional aromatic compound :

An aromatic compound with at least one functional group in the structural formula is known as F.A.C.



(B) Heterocyclic aromatic Compounds :



SOURCE OF AROMATIC COMPOUNDS

The main source of aromatic compounds is coal tar. Bituminous coal when subjected to destructive distillation in absence of air (1100 – 1200°C) the chief constituent obtained is coal-tar.

The following fractions are obtained on destructive distillation of bituminous coal [Carbonisation of coal]

- (i) Coal gas \longrightarrow 17% (Mixture of uncondensed gases)
- (ii) Ammonical liquor \longrightarrow 8 – 10%
- (iii) Coke \longrightarrow 70% (Solid Residue)
- (iv) Coal tar \longrightarrow 4 – 5%

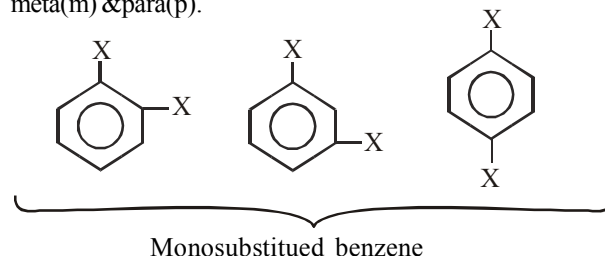
The coal tar is a black coloured pungent smelling vicious liquid having relative density 1.1 – 1.2;

Aromatic compounds are obtained by fractional distillation of coal-tar.

Fraction	Temperature range	Chief-constituents
1. Light oil or Crude naphtha	80 – 170°	Benzene, Toluene, Xylene etc.
2. Middle oil or carbolic oil	170 – 230°C	Phenol, Naphthalene, etc.
3. Heavy oil or cresole oil	230 – 270°C	Naphthalene, Cresol, etc.
4. Green oil or Anthracene oil	270 – 360°C	Anthracene, Phenanthrene, etc.
5. Pitch	Residue	90 – 95% Carbon.

DIRECTIVE INFLUENCE OF SUBSTITUENTS

In monosubstitution reactions of benzene, only one monosubstituted product is formed because all the positions in the ring are identical. Any of them can be occupied by the substituent. But in case of disubstitution, three isomeric products are possible. These are ortho(o), meta(m) & para(p).

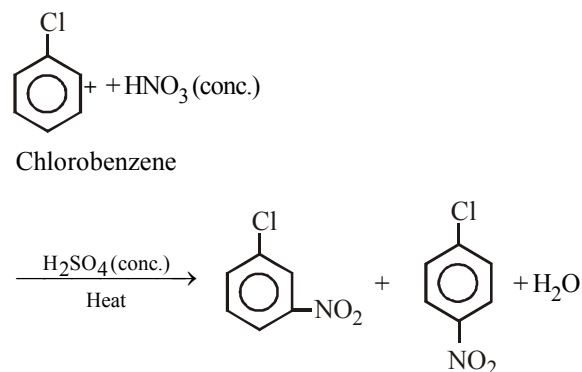


ortho, meta and para disubstituted benzene

Note : It may be noted that the position to be occupied by the second entering group depends upon the nature of the group already present. In other words, the group already present in the ring directs the new group to a particular position (ortho, meta or para). This is known as the directive influence. In general, the groups have been classified into two types : (I) Ortho and para directing groups (II) Meta directing groups

(I) Ortho and Para directing groups :

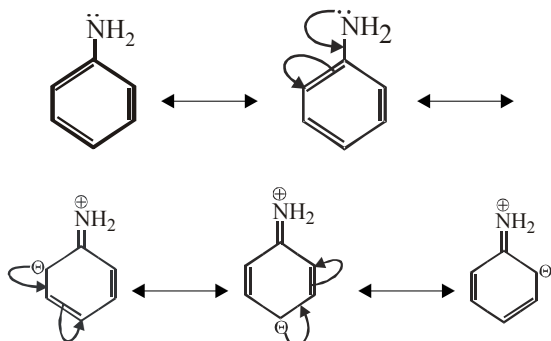
It has been observed that a group which directs the new coming group to ortho position in the ring also directs that same to the para position. In other words, a mixture of isomeric products is formed. For example,



o-Chloronitro benzene p-Chloronitro benzene

The common examples of the ortho and para directing groups are : $-\ddot{N}H_2$, $\ddot{N}HR$, $-\ddot{N}R_2$, $-\ddot{O}H$, \ddot{X} , $-\ddot{R}$ (alkyl)

Explanation for the directive influence % With the exception of alkyl group, all other groups have atleast one lone pair electron on the atom directly attached to the ring. It is involved in resonance or conjugation with the π -electrons present in the ring. As a result, the ortho and para positions in the ring become the points of high electron density or negatively charged. The new entering group which is an electrophile will prefer to come to ortho and para positions rather than the meta position in the ring. Let us illustrate the directive influence of the amino ($-\text{NH}_2$) group.

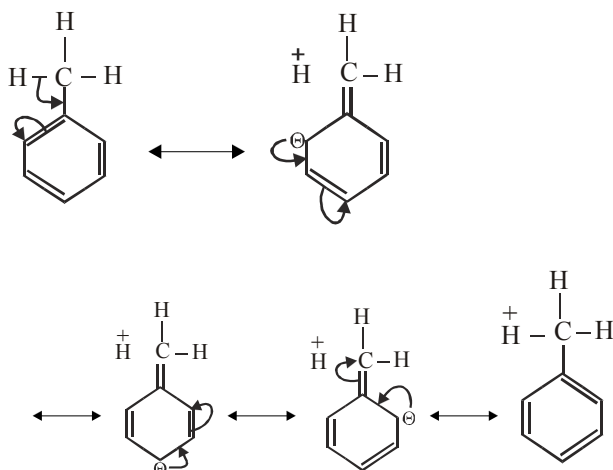


Since the ring gets highly activated due to the increase in electron density, therefore, the disubstitution in this case readily takes place even at room temperature.

Exception % The activating influence is not so marked when a halogen such as chlorine is present in the ring. Although it has a very strong resonance effect (+R effect), it has also a strong $-I$ effect. The latter tends to deactivate the ring and the ortho and para disubstitution does not take place at room temperature but at elevated, temperature.

Directive Influence of alkyl group :

The alkyl group (R) does not have a lone pair of electron. Its directive influence is explained with the help of hyperconjugation. This is shown with the help of methyl ($-\text{CH}_3$) group in toluene.



Ratio of the ortho and para isomers in disubstitution :

We have seen that for disubstitution in benzene, two ortho and one para positions are available. Therefore, ortho and para isomers must be formed in the ratio of 2 : 1. But this is

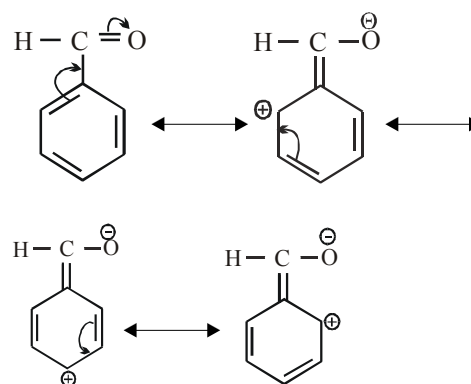
contrary to what we actually observe. In most of the cases, the para isomer is formed in greater proportion as compared to the ortho isomer. This is probably due to the reason that the new entering group experiences greater steric hindrance at the ortho position by the group already present in the ring as compared to the para position. Therefore, it prefers to occupy the para position which is less sterically hindered.

(II) Meta Directing Groups :

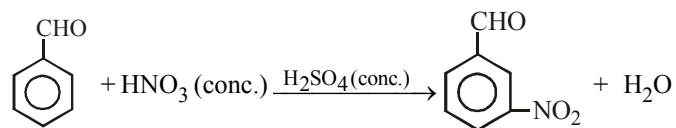
A group has a meta directing influence in case the atom of the group which is directly attached to the ring has more electronegative atom linked to it by multiple bond. The list of some common meta directing groups is.

$-\text{CHO}$, $-\text{COOH}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{SO}_3\text{H}$ etc.

Explanation for the directive influence : In this case, under the influence of the attacking electrophile, the ortho and para positions in the ring get positively charged because of conjugation with the electron withdrawing group. This is illustrated with the help of benzaldehyde in which $-\text{CHO}$ group is an electron withdrawing group. The resonating structure for the molecule are



The meta positions become comparatively the centre of high electron density. Therefore, the attacking electrophile will prefer to attack the meta position and the disubstitution is meta in nature. For example,



Benzaldehyde

m-Nitrobenzaldehyde

Since the ring has been deactivated because of electron withdrawing group, the disubstitution in the ring is not so easy and usually takes place under drastic conditions.

Remember : An ortho and para directing group activates the ring towards electrophilic substitution. A meta directing group deactivates the ring towards electrophilic substitution.

BENZENE

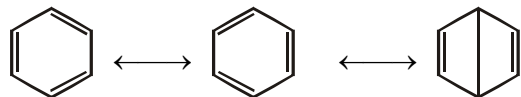
Benzene was discovered by Michael Faraday in 1825. Benzene was obtained by Hoffmann in 1845 from Coal tar. Structure of benzene was given by Kekule. The hybridisation of carbon atom in benzene is sp^2 .

The structure of benzene molecule is planar. All the six carbon atoms of benzene lie at the corners of regular hexagon. Bond angle in benzene is 120° . C–C bond length in benzene is 1.39 \AA and C–H bond length is 1.09 \AA .

Benzene molecule contains 12 σ and 3 π bond. Benzene is a cyclic trimer of acetylene.

Light oil or crude naphtha fraction contains benzene.

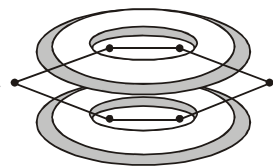
Its alternate double bond structure was given by Kekulé



Resonance hybrid structure :



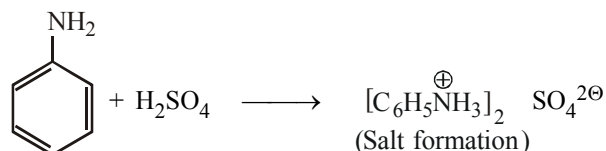
π -cloud in benzene.



METHODS OF PREPARATION

(1) Isolation from light oil fraction [Industrial method]

In light oil at least 60 – 65% benzene is present. Alkaline impurities (Aniline, Pyridine, quinoline, etc.) are removed by washing light oil with cold and conc. H_2SO_4 .



The acidic impurities are removed by washing with dilute NaOH solution. After that NaOH is removed by washing with water. Three fractions are obtained at different temperature range by fractional distillation of neutral oil.

- | | | |
|----|-----------------|--------------|
| 1. | 90% Benzol | (80–110°C) |
| 2. | 50% Benzol | (110–140°C) |
| 3. | Solvent naphtha | (140°–170°C) |

Among these 90% Benzol contains about 70% benzene, 4–14% toluene and remaining xylene and other hydrocarbon. Fractional distillation gives.

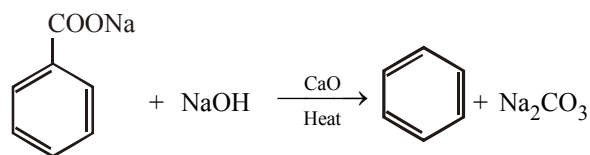
Benzene – 80°C ; Toluene – 110°C

Mixture of Benzene / Toluene / Xylene – $137 - 145^\circ\text{C}$

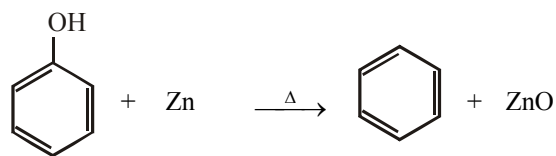
Crystals are formed on cooling benzene from which pure benzene can be obtained by melting the crystals.

(2) Decarboxylation of sodium benzoate (Laboratory method):

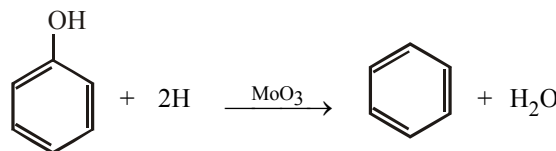
Benzene is prepared in the lab by heating the mixture of sodium benzoate and sodalime.



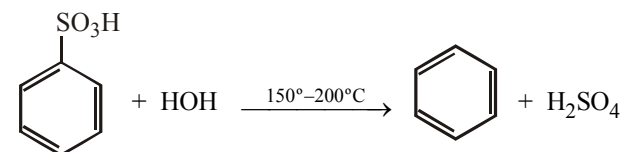
(3) Dehydroxylation of Phenol : Benzene is obtained by distillation of phenol with zinc dust.



(iv) Reduction of Phenol :– Benzene is obtained by reduction of phenol in presence of MoO_3 .

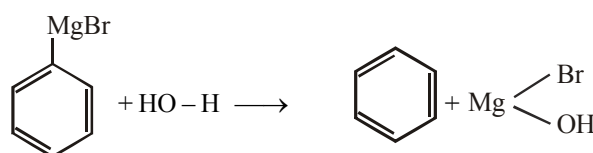
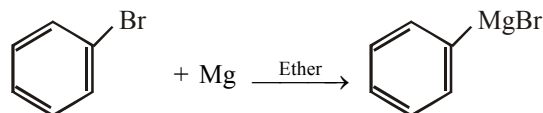


(v) Hydrolysis of Benzene sulphonic acid : Benzene is obtained by hydrolysis of benzene sulphonic acid.

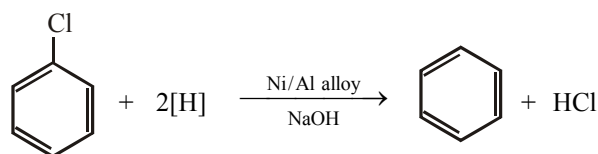


(Benzene sulphonic acid)

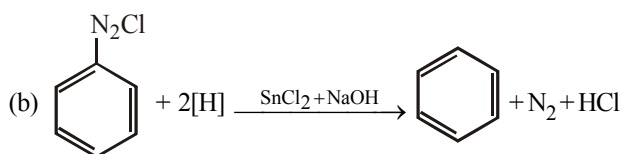
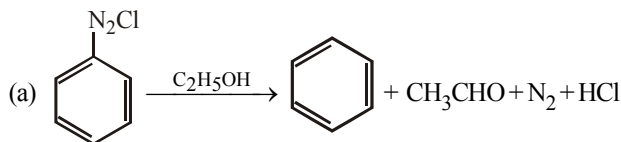
(vi) From Grignards reagent : First prepare grignard reagent and hydrolysis it.

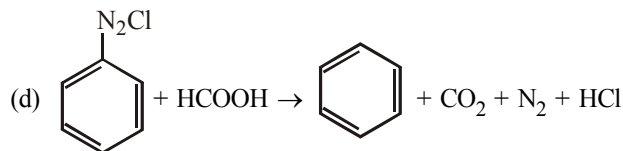
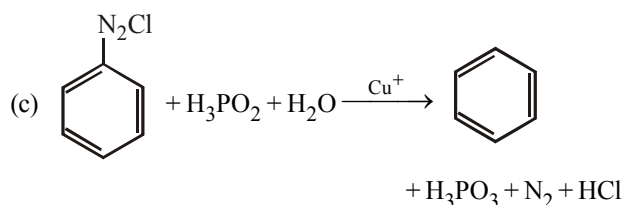


(vii) Reduction of Chlorobenzene : By reduction of chlorobenzene with Ni–Al and NaOH.

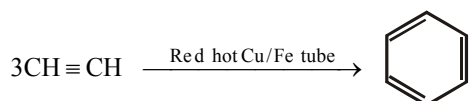


(viii) Reduction of Benzenediazonium chloride : Benzene diazonium chloride is reduced to benzene by SnCl_2 and NaOH or $\text{C}_2\text{H}_5\text{OH}$ or H_3PO_2 .

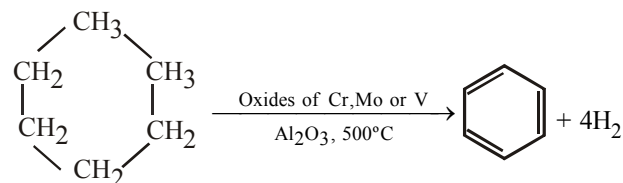




(ix) **From Acetylene :** When acetylene is passed through red hot metallic tube cyclic polymerisation takes place and benzene is formed.



(x) **By Catalytic reforming / Hydroforming / Aromatisation :**



PHYSICAL PROPERTIES

Colourless liquid (B.P. = 80°C) having specific smell. Lighter than water (relative density = 0.879) and is immiscible with water. Nonpolar in nature and its dipole moment is zero. Insoluble in water, soluble in organic solvents like alcohol, ether, acetone, acetic acid, CCl₄, CS₂ etc. It is itself a good solvent. It is highly inflammable and burns with smoky flame.

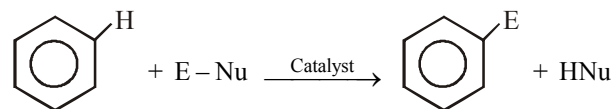
CHEMICAL PROPERTIES

Benzene is a stable compound. It is not so reactive as alkenes or alkynes. It does not form any addition product with halogen acids and hypohalous acid. It resists oxidation by alkaline KMnO₄.

Benzene shows following chemical properties :

- (1) Electrophilic substitution reaction
- (2) Addition reaction
- (3) Oxidation reaction
- (4) π-Complex formation
- (5) Catalytic pyrolysis

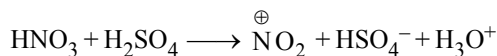
(1) **Electrophilic substitution reaction :** The reactions in which hydrogen atom of the benzene ring is replaced by an electrophile are called electrophilic aromatic substitution reaction. The reaction can be represented by.



Some important electrophiles used in the aromatic substitution are.

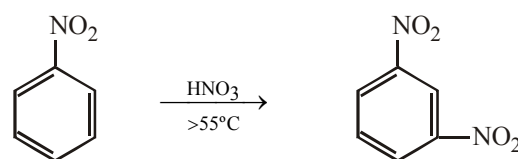
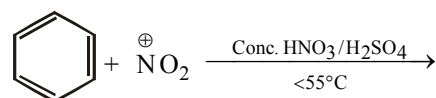
Electrophile	Source	Name of reaction
Cl [⊕] (Chloronium)	Cl ₂ + AlCl ₃ or FeCl ₃	Chlorination
Br [⊕] (Bromonium)	Br ₂ + AlBr ₃ or FeBr ₃	Bromination
N [⊕] O ₂ (Nitronium)	HNO ₃ + H ₂ SO ₄	Nitration
SO ₃ (Sulphur trioxide)	Conc. H ₂ SO ₄ , Fuming Sulphuric acid	Sulphonation
R [⊕] (Alkyl Carbonium)	RX + AlX ₃ (X = Cl or Br)	Friedel – Craft's (Alkylation)
R – C [⊕] = O (Acetyl carbonium)	R – COCl + AlCl ₃	Friedel – craft's (Acetylation)

(a) **Nitration :** Benzene undergoes nitration when treated with conc. HNO₃ and conc. H₂SO₄ to give nitrobenzene.

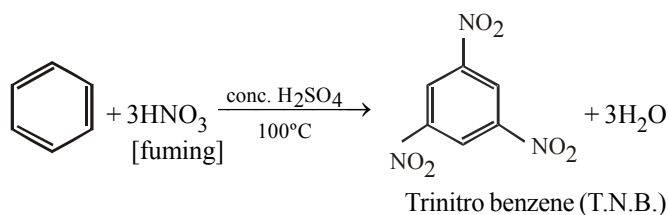


Attacking species is NO₂[⊕].

H₂SO₄ acts as Bronsted acid and HNO₃ acts as bronsted base.

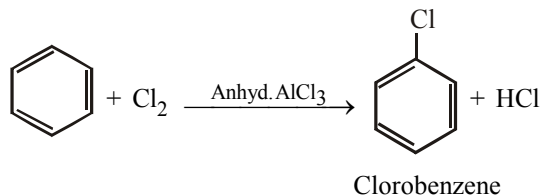


Nitrobenzene m-dinitro benzene
On heating benzene with fuming HNO₃ and conc. H₂SO₄ at 100°C trinitrobenzene is formed.



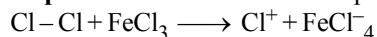
T.N.B. is a powerful explosive.

- (b) **Halogenation** : Benzene undergoes chlorination when it is treated with chlorine in presence of AlCl_3 or FeCl_3 .

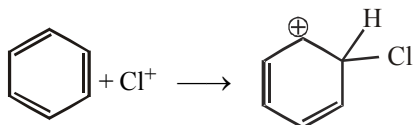


Mechanism :

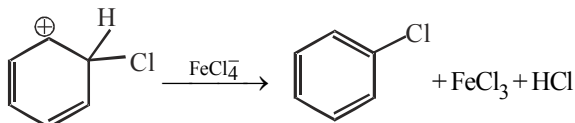
Step-1 : Formation of the electrophile (Cl^+)



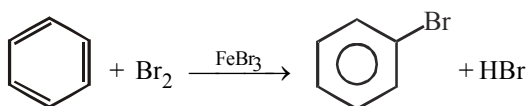
Step-2 : The electrophile attacks the benzene to give a carbonium ion.



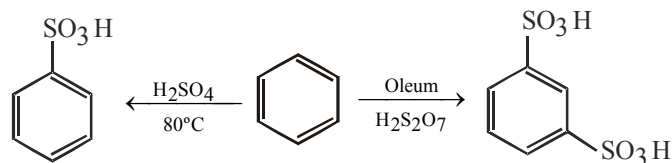
Step-3 : Removal of proton gives chlorobenzene.



Similarly benzene undergoes bromination when it is treated with bromine in presence of FeBr_3 .



- (c) **Sulphonation** : Benzene forms benzene sulphonic acid with hot conc. H_2SO_4 while with oleum m-benzene di sulphonic acid is formed.

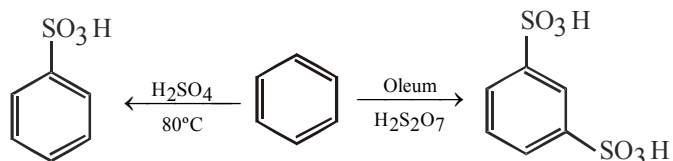


Attacking species is neutral $\rightarrow \text{SO}_3$

- (d) **Friedel Crafts reaction :**

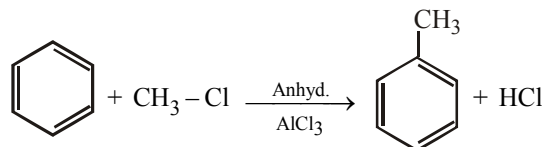
This reaction is used for introducing an alkyl or acyl group in benzene nucleus by an alkylating or acylating agent in presence of a suitable catalyst. The alkylating agent is an alkylhalide, an alcohol or an alkene while acylating agent may be acid chloride or acid anhydride.

The catalyst may be AlCl_3 , FeCl_3 , SnCl_4 , BF_3 or ZnCl_2 but anhydrous AlCl_3 is commonly used.

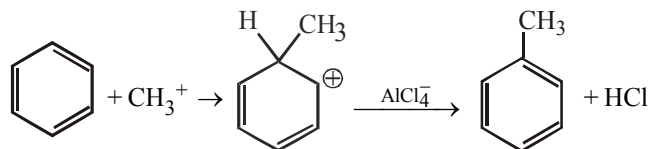


- (1) **Alkylation (Formation of benzene homologues) :**

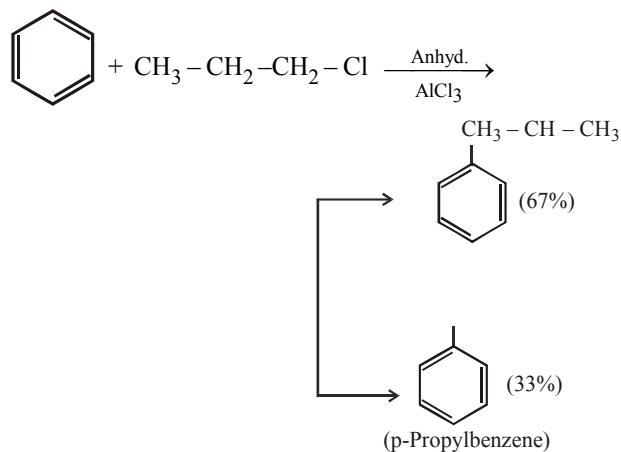
- (i) **Formation of Toluene :**



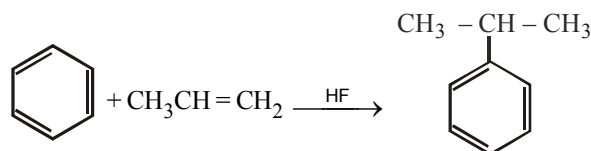
Mechanism : $\text{AlCl}_3 + \text{CH}_3\text{Cl} \longrightarrow \text{AlCl}_4^- + \text{CH}_3^+$



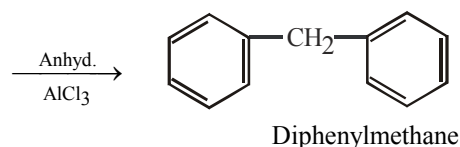
- (ii) **Formation of cumene :**



Cumene is also formed by following reaction.

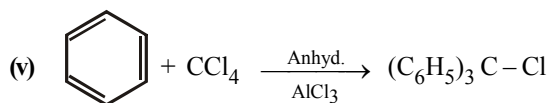


- (iii) $\text{C}_6\text{H}_6 + \text{CH}_2\text{Cl}_2$ (Methylene dichloride)



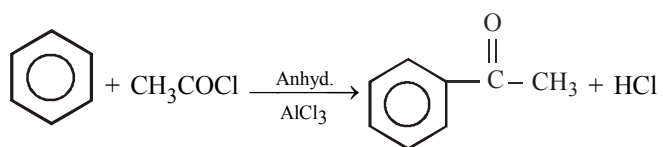
- (iv) $\text{C}_6\text{H}_6 + \text{CHCl}_3 \xrightarrow[\text{AlCl}_3]{\text{Anhyd.}} (\text{C}_6\text{H}_5)_3\text{CH}$

Triphenyl methane

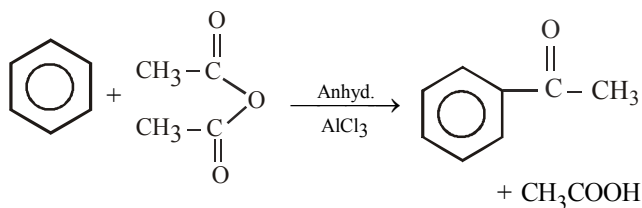
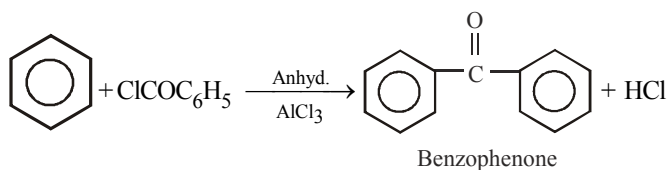


(Triphenyl chloride)

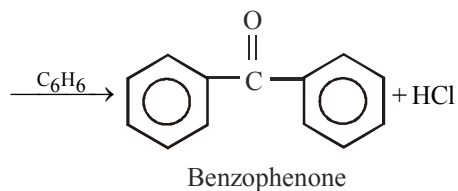
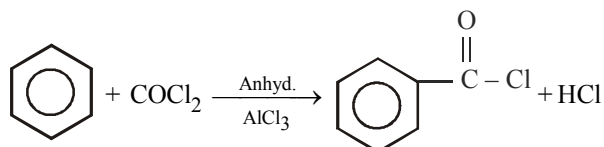
Note : In the reaction tetra phenyl methane is not formed because of steric hinderance of three phenyl groups already attached on the carbon atom is so high that no room remains available for the fourth phenyl group to come closer to the central carbon atom.

(b) Acetylation :

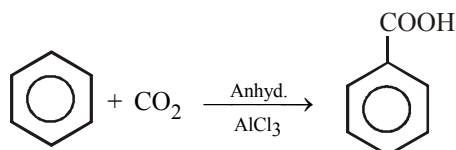
Acetophenone

**(c) Benzoylation :**

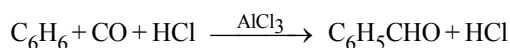
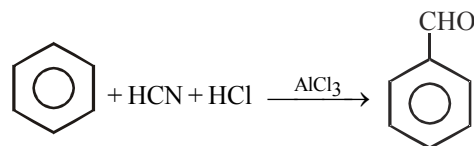
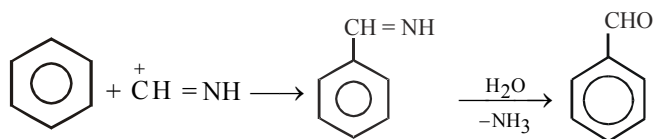
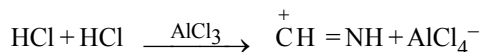
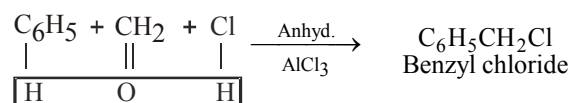
Benzophenone



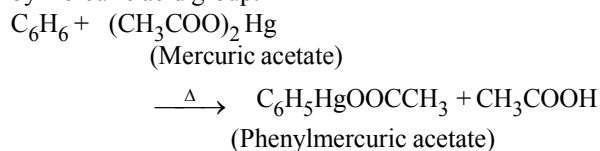
Benzophenone

(d) Carboxylation :**(e) Formylation (Gattermann - koch reaction) :**

It is a direct method for introducing an aldehydic group in benzene. When a mixture of dry HCl gas and CO is used in presence of anhydrous AlCl_3

**(f) Formylation (Gattermann aldehyde synthesis) :****Mechanism :****(g) Chloromethylation [Blace reaction] :**

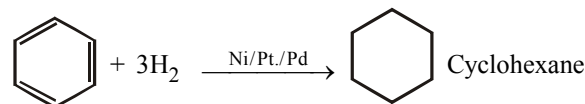
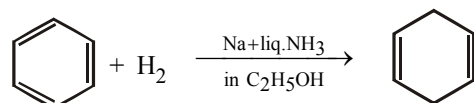
(h) Mercuration : When benzene is treated with alc. solution of mercuric acetate, a hydrogen atom is replaced by mercuric acid group.



This reaction is used in the preparation of certain medicines.

(II) Addition reaction (Benzene behaves like unsaturated hydrocarbon) :**(A) Hydrogenation (Addition of hydrogen) :**

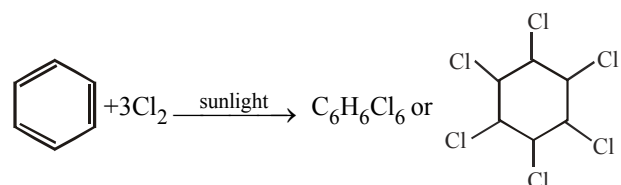
(a) Complete : Benzene reacts with hydrogen in the presence of Ni (or Pt) catalyst at 150°C . Under pressure to form cyclohexane.

**(b) Partial (Birch reaction) :— Reduction by Na/liquid NH_3** 

1, 4-cyclohexadiene

This reaction is called Birch reaction.

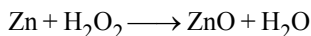
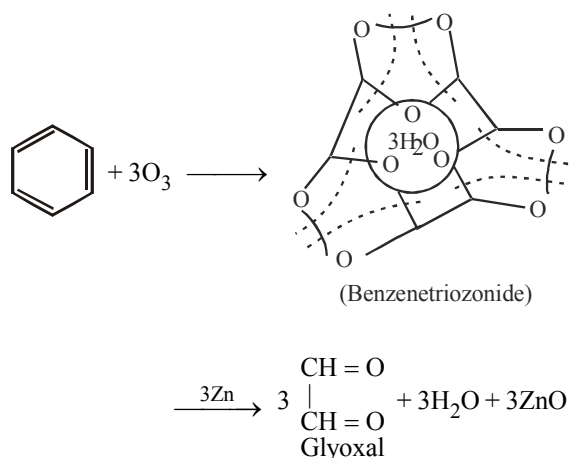
(B) Addition of halogen $[\text{Cl}_2/\text{Br}_2]$: Benzene reacts with Cl_2 or Br_2 (but not with I_2) in presence of sun light to produce crystalline hexachlorides or hexabromides.



Benzene hexachloride (BHC)

The mechanism reaction of free radical addition reaction. BHC : is well known insecticide. It exists in nine isomeric forms normally α , β , ν , δ , ... etc. out of which ν -isomer is more active and used as insecticide and is known as Gammexane / 666 / lindane. This reaction shows that benzene has three double bonds and each double bond requires one mole chlorine.

(c) Ozonolysis / Addition of ozone : When treated with ozone, benzene triozone is produced which on hydrolysis yields glyoxal.

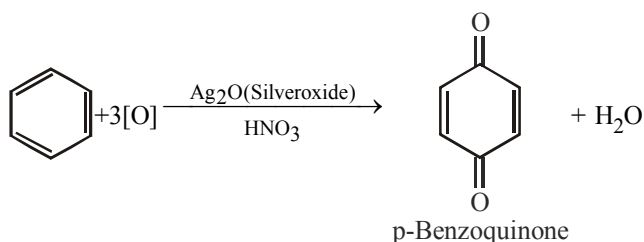
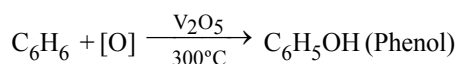
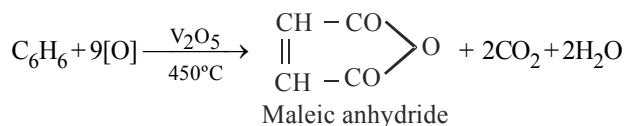


Reaction with H_2 , Cl_2 and O_3 shows structure of benzene has three double bonds.

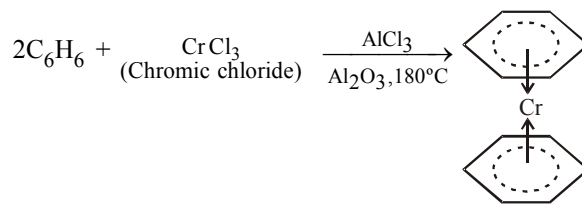
(iii) Oxidation reaction :

(a) Combustion : Benzene is stable compound. Strong oxidising agents converts benzene slowly into CO_2 and water on heating. $2\text{C}_6\text{H}_6 + 15\text{O}_2 \longrightarrow 12\text{CO}_2 + 6\text{H}_2\text{O}$

(b) Catalytic oxidation : When vapours of benzene and air are passed over vanadium pentoxide at $450^\circ\text{C} - 500^\circ\text{C}$ maleic anhydride is obtained.



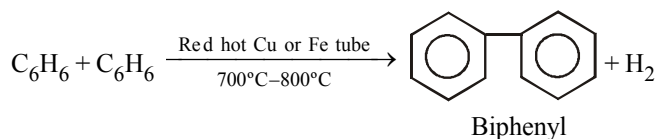
(iv) Sandwich compound formation or charge transfer reaction or π -Complex formation : When benzene is heated with CrCl_3 , AlCl_3 and Al_2O_3 at 180°C a product is obtained which on reduction gives dibenzene chromium.



π -complex dibenzene chromium

The reaction is known as charge transfer reaction. In the reaction e^- charge of π -cloud of benzene is attracted towards the d-orbital of chromium atom. Here benzene behaves as a π -base.

(V) Catalytic Pyrolysis :



USES OF BENZENE

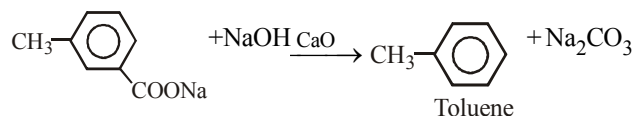
- (i) As an industrial solvent
- (ii) In dry cleaning
- (iii) As a constituent of power alcohol $\text{C}_2\text{H}_5\text{OH} + \text{C}_6\text{H}_6 + \text{Petrol}$
- (iv) In manufacturing of dyes, perfumes, medicines, etc.
- (v) As a fuel.

TOLUENE

When a methyl group is directly attached with benzene ring, the compound is called Toluene. Toluene is a higher homologue of benzene. It can be obtained by the light oil which is obtained from distillation of Coal-tar. Toluene is the compound, which is more reactive than benzene in chemical reactions.

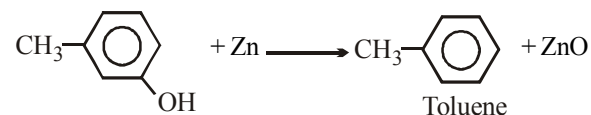
METHODS OF PREPARATION

(i) From Toluic acid : When sodium salt of o-, m- or p- toluic acid is heated with sodalime forms toluene.



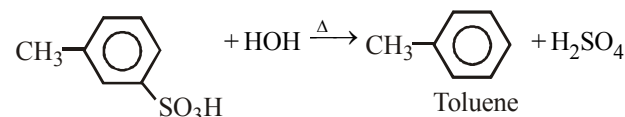
(ii) From Cresol :

o-, m-, or p- cresol is heated with zinc dust to form toluene.



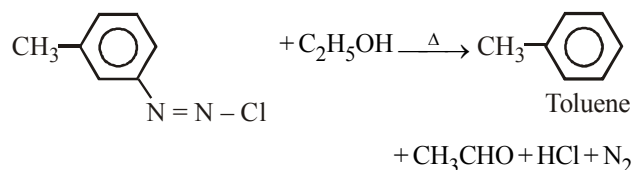
(iii) From Toluene sulphonic acid :

When o-, m or p- toluene sulphonic acid is heated strongly with water, toluene is formed.

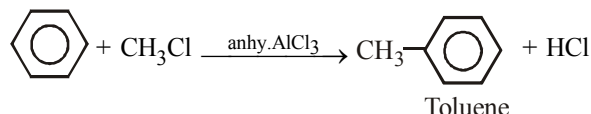


(iv) From diazonium salt of Toluene :

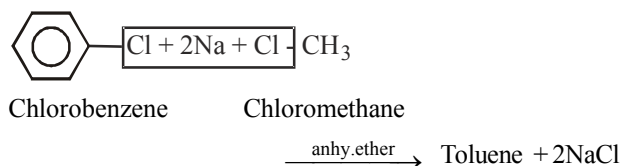
o-, m or p- toluene diazonium chlorides are reduced by ethanol toluene is obtained.

**(v) From Friedel-Craft's reaction :**

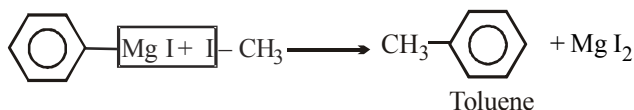
Methyl chloride reacts with benzene in the presence of anhy. AlCl_3 and forms toluene.

**(vi) From Wurtz-Fitting reaction :**

A mixture of aryl & alkyl halide reacts in ether solution with sodium and forms toluene.

**(vii) From Grignard's reagent :**

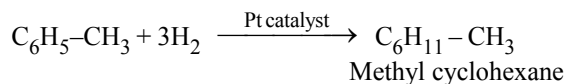
Phenyl magnesium iodide reacts with pure methyl iodide and forms toluene.

**PHYSICAL PROPERTIES**

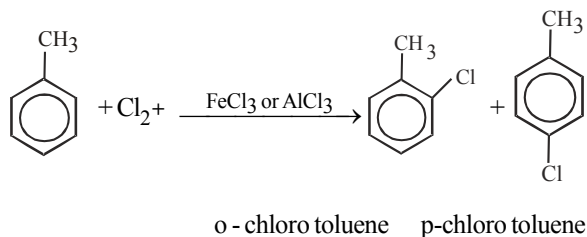
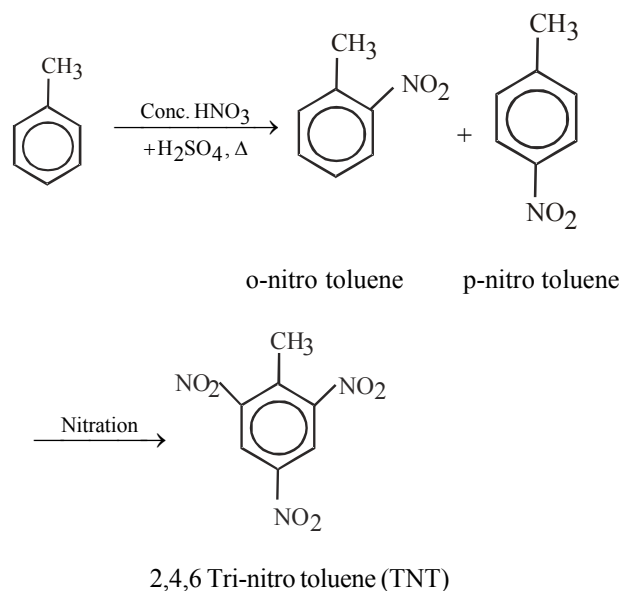
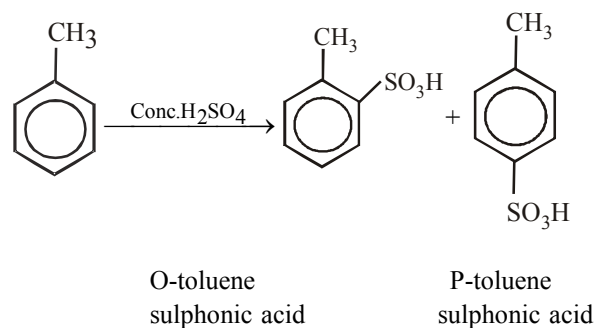
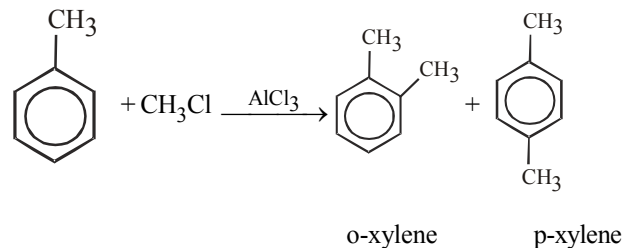
- (i) Colourless liquid with benzene like smell.
- (ii) b.p. 111°C .
- (iii) Lighter than water and insoluble in it but soluble in organic solvents.

CHEMICAL PROPERTIES**(i) Addition reactions :**

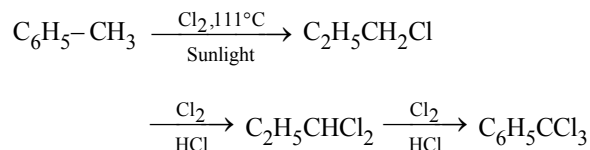
Toluene on catalytic hydrogenation forms methyl cyclohexane:



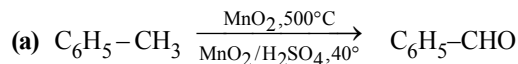
- (ii) **Ring substitution reactions :** Like benzene, toluene also gives electrophilic substitution reactions. Methyl group is o- & p-director so, substituent is placed at o- & p-positions. Halogenation, nitration and sulphonation are as shown below

(a) Halogenation :**(b) Nitration :****(c) Sulphonation :****(d) Alkylation :**

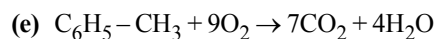
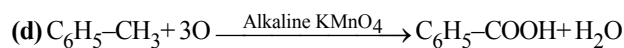
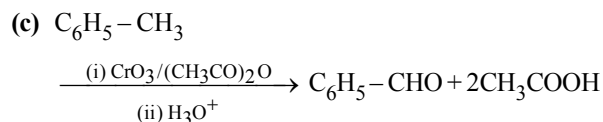
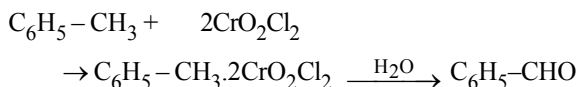
(iii) Side chain substitution reaction :



(iv) Oxidation reaction :



(b) Etard reaction :



USES

- (i) In the formation of TNT explosive.
- (ii) As a solvent
- (iii) In the formation of chloramine T and saccharine
- (iv) In the formation of benzaldehyde and Benzoic acid etc.

TRY IT YOURSELF-4

Q.1 Which of the following group is divalent-

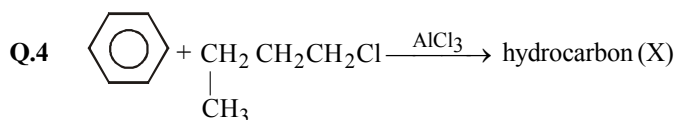
- (A) Benzoyl (B) Benzyl
(C) Benzal (D) p-Tolyl

Q.2 The number of benzylic hydrogen atoms in ethylbenzene is -

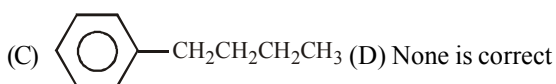
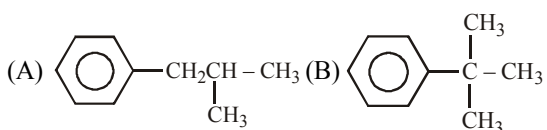
- (A) 3 (B) 5
(C) 2 (D) 7

Q.3 Which of the following is not the property of benzene

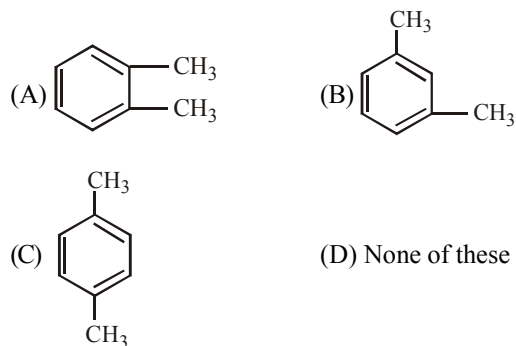
- (A) Characteristic smell (B) Inflammable
(C) Addition reactions (D) Colourless



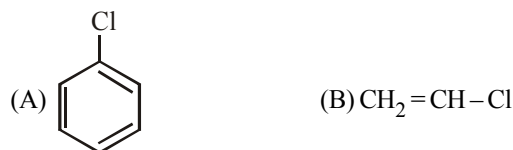
major product X is -



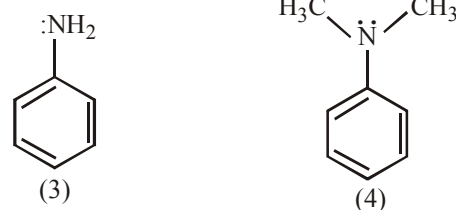
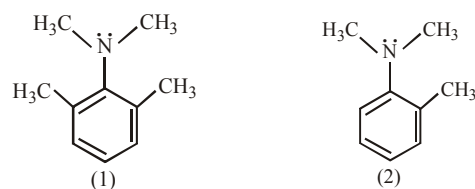
Q.5 Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is -



Q.6 Which of the following can be used in Friedel Crafts reaction to generate electrophile?



Q.7 The benzene rings with the most and the least π -electron density respectively -

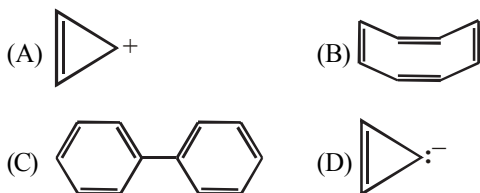


- (A) 3, 1 (B) 3, 2
(C) 1, 2 (D) 1, 4

Q.8 For an electrophilic substitution reaction, the presence of a halogen atom in the benzene ring _____.

- (A) deactivates the ring by inductive effect
- (B) deactivates the ring by resonance
- (C) increases the charge density at ortho and para position relative to meta position by resonance
- (iv) directs the incoming electrophile to meta position by increasing the charge density relative to ortho and para position.

Q.9 Four structures are given in options (A) to (D). Examine them and select the aromatic structures.



ANSWERS

- (1) (C) (2) (C) (3) (C)
 (4) (D) (5) (C) (6) (CD)
 (7) (A) (8) (AC) (9) (AC)

ADDITIONAL EXAMPLES

Example 1 :

Alkanes which cannot be produced by Kolbe electrolysis of sodium or potassium salts of carboxylic acids?

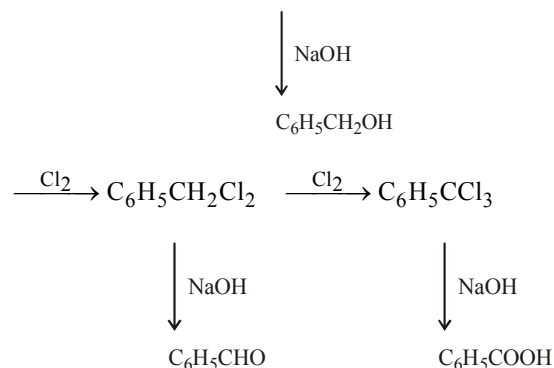
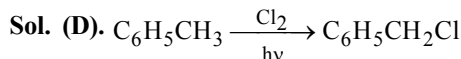
- (A) Methane (B) Ethane
 (C) Butane (D) Hexane

Sol. (A). In Kolbe electrolysis, the alkane is formed by union of two alkyl groups. The alkane formed has, thus, two or more carbon atoms.

Example 2:

Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives –

- (A) o-Cresol (B) p-Cresol
 (C) 2,4-Dihydroxy toluene (D) Benzoic acid

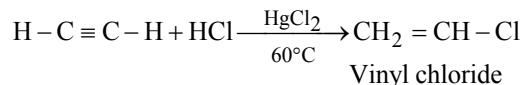


Example 3 :

Acetylene when treated with dilute HCl at 60°C (333K) in presence of $HgCl_2$ produces –

- (A) Methyl chloride (B) Vinyl chloride
 (C) Acetaldehyde (D) Formaldehyde

Sol. (B).

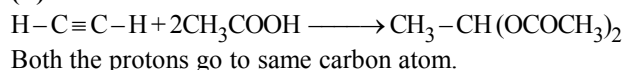


Example 4 :

Excess of CH_3COOH is reacted with $CH \equiv CH$ in presence of Hg^{2+} , the product is –

- (A) $CH_3CH(OOCCH_3)_2$
 (B) $CH_2 = CH(OOCCH_3)$
 (C) $(CH_3COO)CH_2 - CH_2(OOCCH_3)$
 (D) None of these

Sol. (A).



Example 5 :

Which of the following is not correctly matched :

- (A) Hydrolysis of phenyl magnesium iodide - benzene
 (B) γ -Isomer of BHC - lindane
 (C) $(2n + 4)\pi$ Rule - aromaticity
 (D) Trimerisation of propyne - mesitylene

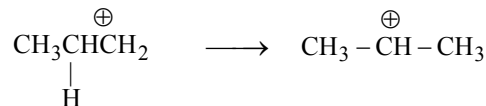
Sol. (C). The Huckel rule to account for aromaticity is closed ring of $(4n + 2)\pi$ electrons.

Example 6 :

Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give predominantly :

- (A) n-Propylbenzene (B) Isopropylbenzene
 (C) 3-Propyl-1-chlorobenzene (D) No reaction

Sol. (B). Propyl carbonium ion, $CH_3CH_2CH_2^+$ is primary carbonium ion, it rearranges to the more stable secondary carbonium ion $CH_3CH^+CH_3$, which then reacts to form isopropylbenzene.

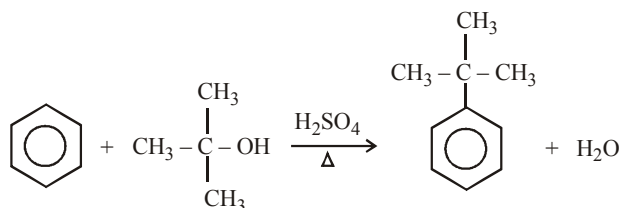
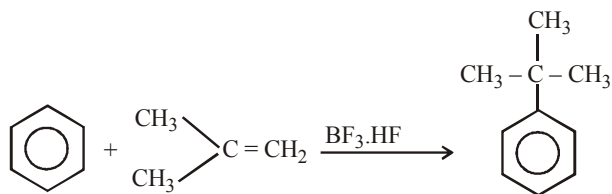
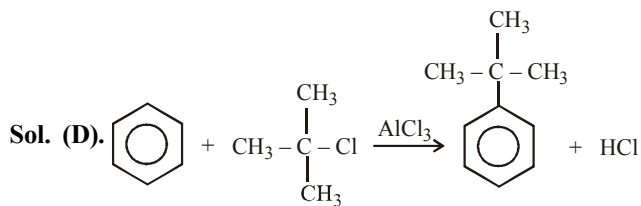


Propyl carbonium ion (1°) Iso Propyl carbonium ion (2°)

Example 7 :

In which of the following reaction t-butylbenzene is formed (A) Benzene + t-butyl chloride, $AlCl_3$

- (B) Benzene + $(CH_3)_2C = CH_2 \xrightarrow{BF_3 \cdot HF}$
 (C) Benzene + t-butyl alcohol $\xrightarrow{H_2SO_4}$
 (D) All of these



Example 8 :

The order of reactivity of –
 $\phi-\text{CH}_3$ (I), $\phi-\text{CH}_2-\text{CH}_3$ (II), $\phi-\text{CH}(\text{CH}_3)_2$ (III) and
 $\phi-\text{C}(\text{CH}_3)_3$ (IV)

Where $\phi = \text{C}_6\text{H}_5$

(A) $\text{I} > \text{II} > \text{III} > \text{IV}$ (B) $\text{IV} > \text{III} > \text{II} > \text{I}$

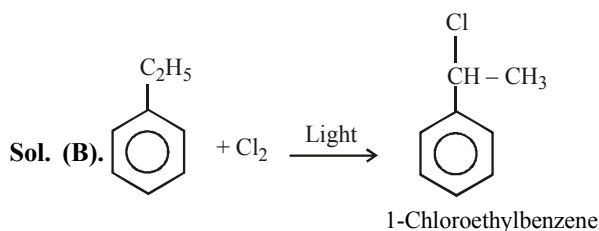
(A) $\text{II} > \text{I} > \text{III} > \text{IV}$ (D) $\text{III} > \text{II} > \text{I} > \text{IV}$

Sol. (A). More are the number of α -hydrogen present in the alkyl group attached to the benzene ring more pronounced will be the hyperconjugation and the benzene ring will be more electron rich and easily be attacked by an electrophile α -hydrogen in $-\text{CH}_3$, $-\text{CH}_2-\text{CH}_3$, $-\text{CH}(\text{CH}_3)_2$ and $-\text{C}(\text{CH}_3)_3$ respectively are three, two one and zero.

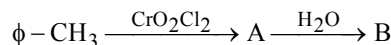
Example 9 :

Ethylbenzene + $\text{Cl}_2 \xrightarrow{\text{Light}}$ (main) compound is –

- (A) o- & p- Chloroethylbenzene (B) 1-Chloroethylbenzene
 (C) 2-Chloroethylbenzene (D) m-Chloroethylbenzene



Example 10:



The functional group present in B and name of the reaction would be –

- (A) $-\text{CHO}$, Gattermann aldehyde synthesis
 (B) $-\text{CHO}$, Etard reaction
 (C) $-\text{COCH}_3$, Friedel Crafts reaction
 (D) $-\text{CHO}$, Oxo reaction

Sol. (B). The compound B is benzaldehyde and the reaction is called Etard reaction.

Example 11 :

Formation of which of the following compound confirms the unsaturation character of benzene:

- (A) Cyclohexane
 (B) Gammexane
 (C) Triozonide
 (D) All the above

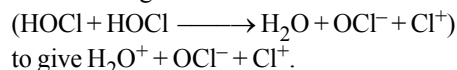
Sol. (D). Formation of all the three compounds are the result of addition reaction. Hence confirm the unsaturation nature of benzene.

Example 12 :

The reaction of propene with HOCl proceeds via the addition of –

- (A) H^+ in the first step
 (B) Cl^+ in the first step
 (C) OH^- in the first step
 (D) Cl^+ & OH^- in a single step

Sol. (B). Alkenes undergo electrophilic addition reactions. HOCl undergoes self-ionization.



So, it is the Cl^+ that attacks in the first step.

Example 13 :

Which of the following used for the conversion of 2-hexyne into trans-2-hexane –

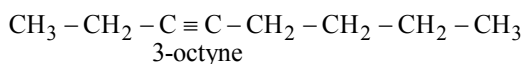
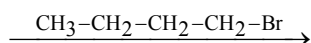
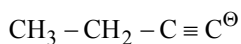
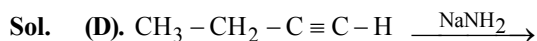
- (A) $\text{H}_2/\text{Pd}/\text{BaSO}_4$
 (B) H_2 , PtO_2
 (C) NaBH_4
 (D) $\text{Li}-\text{NH}_3/\text{C}_2\text{H}_5\text{OH}$

Sol. (D). Li/NH_3 brings about trans addition of H_2 .

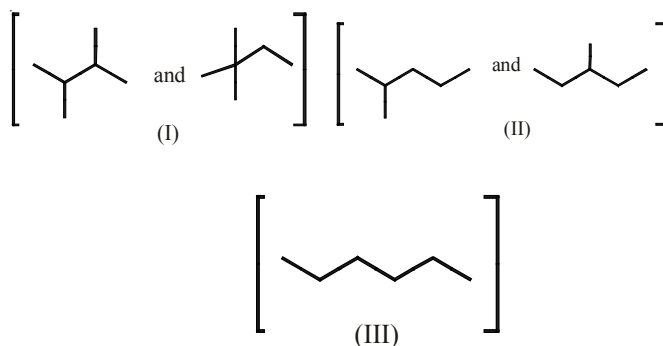
Example 14 :

The synthesis of 3-octyne is achieved by adding a bromoalkane into a mixture of sodium amide and an alkyne. The bromoalkane and alkyne respectively are –

- (A) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
 (B) $\text{BrCH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CH}$
 (C) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{C}\equiv\text{CH}$
 (D) $\text{BrCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$

**Example 15 :**

Isomers of hexane, based on their branching, can be divided into three distinct classes as shown in the figure.

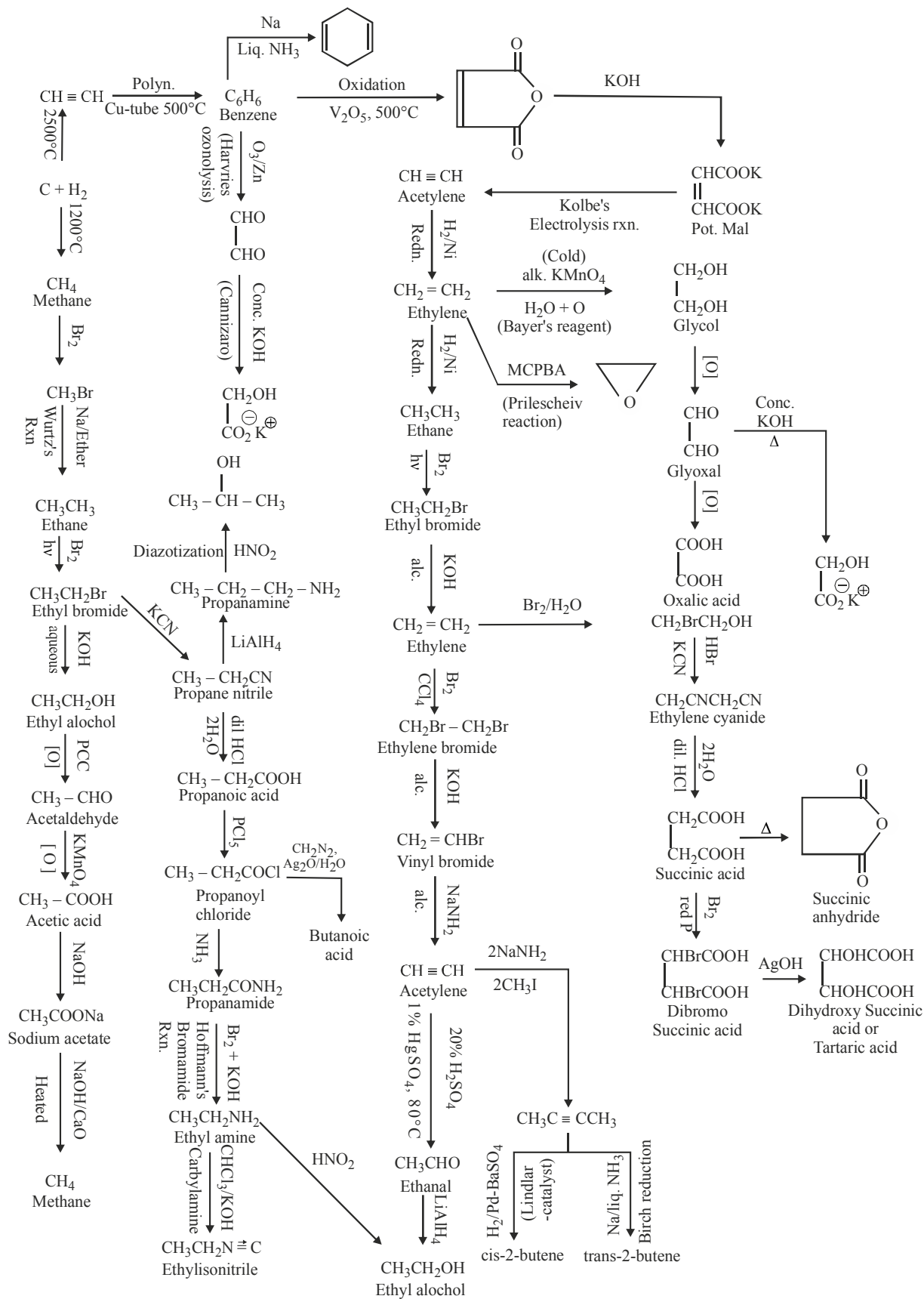


The correct order of their boiling point is –

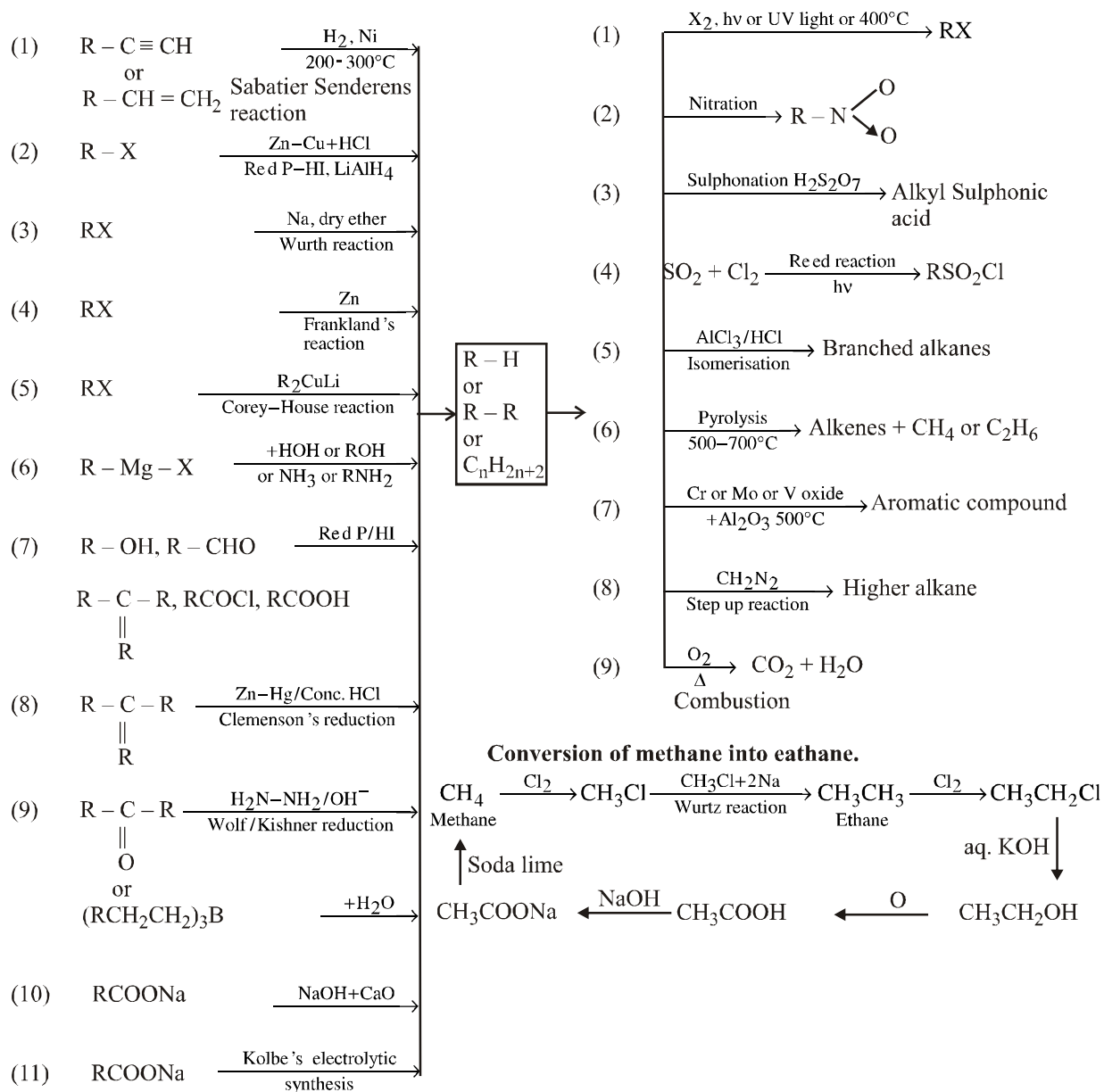
- (A) $\text{I} > \text{II} > \text{III}$ (B) $\text{III} > \text{II} > \text{I}$
 (C) $\text{II} > \text{III} > \text{I}$ (D) $\text{III} > \text{I} > \text{II}$

Sol. (B). As branching increases boiling point decreases, so order of boiling point is $\text{III} > \text{II} > \text{I}$.

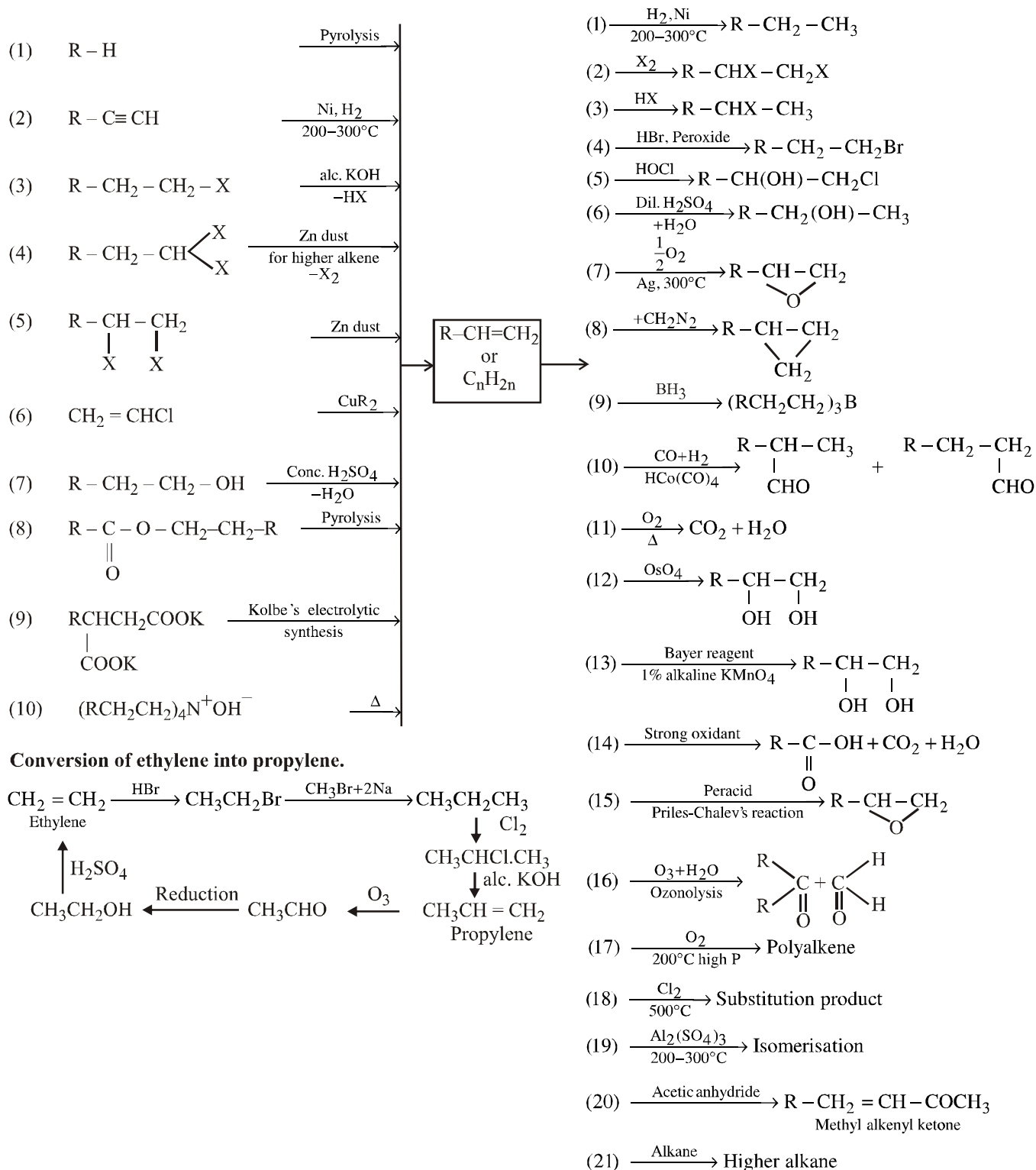
MIND MAP (ORGANIC CHEMISTRY)



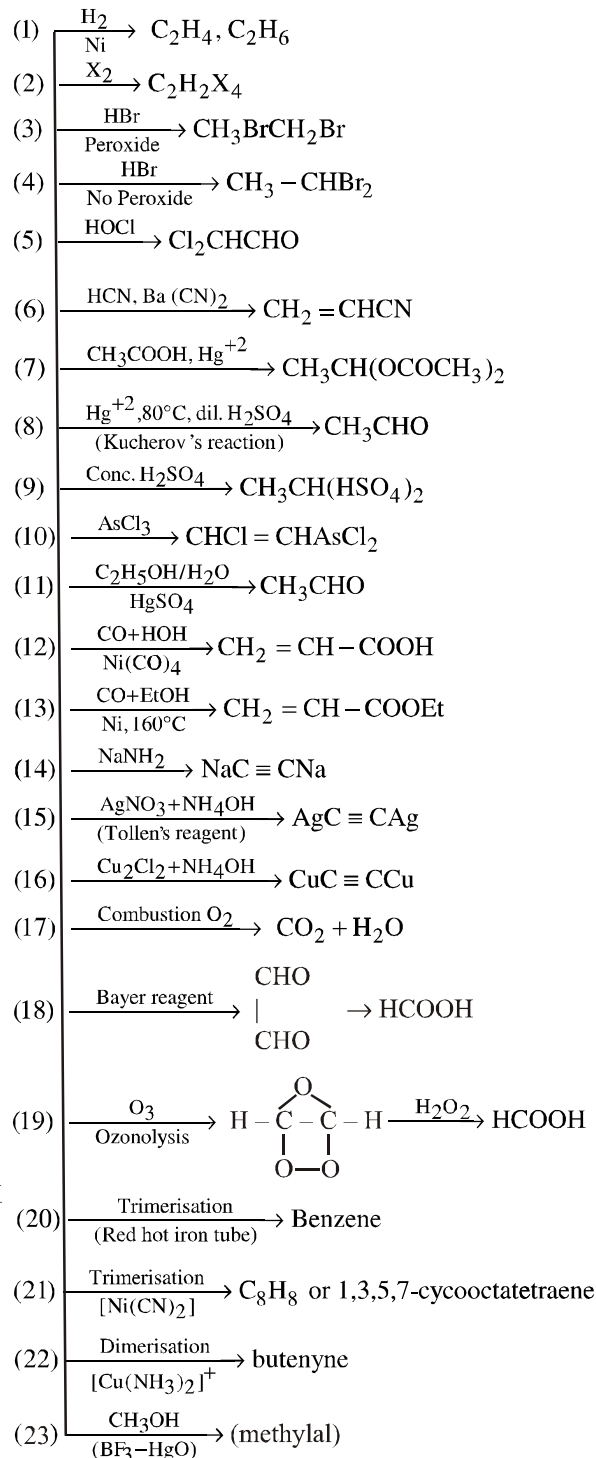
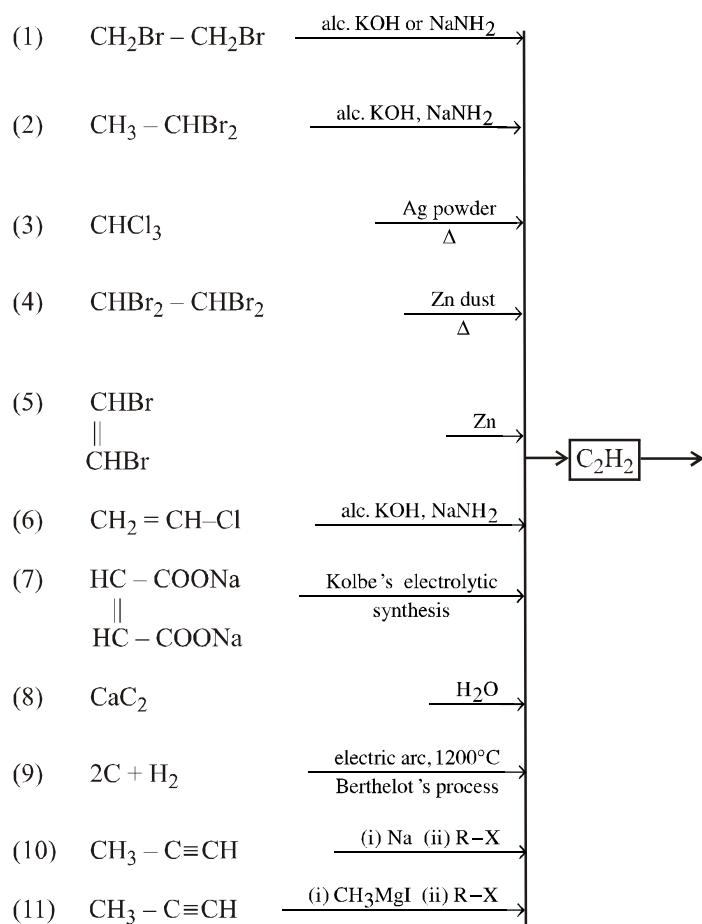
REACTION CHART FOR ALKANES



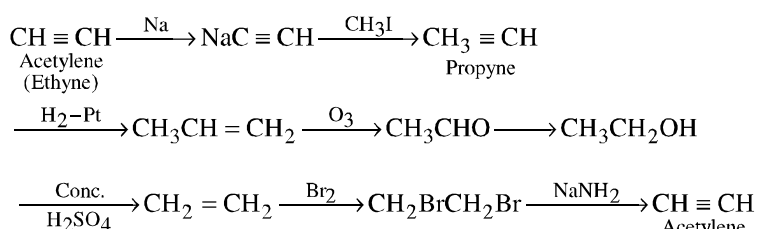
REACTION CHART FOR ALKENES



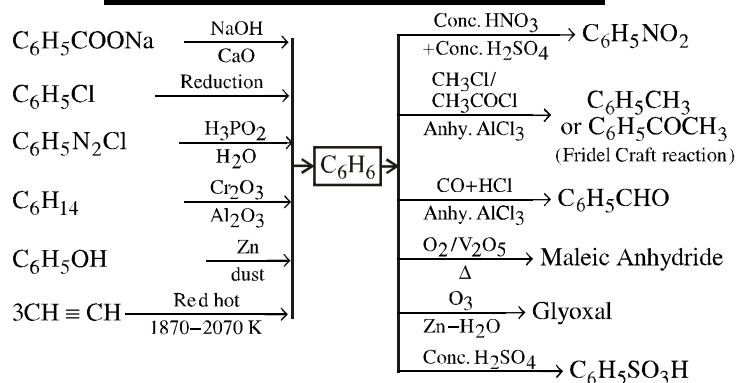
REACTION CHART FOR ALKYNES



Conversion of ethyne into propyne.



Reaction Chart for Benzene



QUESTION BANK
CHAPTER 12 : HYDROCARBONS
EXERCISE - 1 [LEVEL-1]

Choose one correct response for each question.

PART - 1 : ALKANES

- Q.1** Chlorination of alkanes is a photochemical process. It is initiated by the process of –
 (A) heterolysis (B) homolysis
 (C) pyrolysis (D) hydrolysis
- Q.2** When n-butane is heated in the presence of AlCl_3/HCl it will be converted into –
 (A) Ethane (B) Propane
 (C) Butene (D) Isobutane
- Q.3** Product of the Wolff-Kishner reduction is –
 (A) Alkene (B) Alkyne
 (C) Alkane (D) Amine
- Q.4** Which of the following should be subjected to Wurtz reaction to obtain the best yield of n-hexane?
 (A) Ethyl chloride and n-butyl chloride
 (B) Methyl bromide and n-propyl bromide
 (C) n-Propyl bromide
 (D) Ethyl bromide and n-butyl bromide
- Q.5** 2-Methylbutane on reacting with bromide in the presence of sunlight gives mainly –
 (A) 1-Bromo-3-methylbutane
 (B) 2-Bromo-3-methylbutane
 (C) 2-Bromo-2-methylbutane
 (D) 1-Bromo-2-methylbutane
- Q.6** Alkyl halides react with dialkyl copper reagents to give
 (A) Alkenyl halides (B) Alkanes
 (C) Alkyl copper halides (D) Alkene
- Q.7** The number of conformation (s) for ethane are
 (A) 1 (B) 2
 (C) 3 (D) Infinite
- Q.8** The Kolbe synthesis of alkane using a sodium salt of butanoic acid gives –
 (A) n-hexane (B) isobutane
 (C) n-butane (D) propane
- Q.9** A mixture of ethyl iodide and n-propyl iodide is subjected to Wurtz reaction. The hydrocarbon that will not be formed is :
 (A) n-Butane (B) n-Heptane
 (C) n-Pentane (D) n-Hexane
- Q.10** Suitable for preparation of higher alkanes from a lower alkyl halide is subjected to –
 (A) Reduction
 (B) Hoffmann bromamide reaction
 (C) Hunsdiecker reaction
 (D) Wurtz reaction
- Q.11** Aqueous solution of which compound gave ethane on electrolysis
 (A) Acetic acid (B) Acetamide
 (C) Potassium acetate (D) Ethyl acetate
- Q.12** What is not true for alkanes –
 (A) Are characterised by their general unreactivity.
 (B) Do not show isomerism as they are saturated molecules.
 (C) Undergo substitution reactions.
 (D) Can be prepared by heating the sodium salt of the corresponding acid with soda lime called decarboxylation.
- Q.13** In the complete combustion of $\text{C}_n\text{H}_{2n+2}$, the number of oxygen moles required is –
 (A) $\frac{n}{2\text{O}_2}$ (B) $\left(\frac{n+1}{2}\right)\text{O}_2$
 (C) $\left(\frac{3n+1}{2}\right)\text{O}_2$ (D) $\left(\frac{n+2}{2}\right)\text{O}_2$
- Q.14** The inhibitor used to control halogenation of alkanes is –
 (A) Tetra Ethyl Lead (B) Ozone
 (C) Inert gas (D) Oxygen
- Q.15** Anhydrous sodium acetate on heating with sodalime gives
 (A) Acetic acid (B) Methane
 (C) Calcium acetate (D) Ethane
- Q.16** A fuel contains 25% n-heptane and 75% iso-octane. Its octane number is
 (A) 50 (B) 75
 (C) 100 (D) 25
- Q.17** What is the molecular formula of the alkane, the 5.6 litre of which weight 11 g at STP
 (A) C_6H_{14} (B) C_4H_{10}
 (C) C_3H_8 (D) C_2H_6
- Q.18** CH_4 is formed when –
 (A) Sodium acetate is heated with sodalime.
 (B) Iodomethane is reduced.
 (C) Aluminium carbide reacts with water.
 (D) All of these
- Q.19** Boiling point of branched chain alkanes as compared to straight chain alkanes are
 (A) Lower
 (B) Equal
 (C) Higher
 (D) Independent of the chain
- Q.20** In paraffins, with the increasing molecular weight, it is found that –
 (A) Freezing point decreases
 (B) Boiling point decreases
 (C) Boiling point increases
 (D) Vapour pressure decreases
- Q.21** Arrange the halogens F_2 , Cl_2 , Br_2 , I_2 , in order of their increasing reactivity with alkanes.
 (A) $\text{I}_2 < \text{Br}_2 < \text{Cl}_2 < \text{F}_2$
 (B) $\text{Br}_2 < \text{Cl}_2 < \text{F}_2 < \text{I}_2$
 (C) $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$
 (D) $\text{Br}_2 < \text{I}_2 < \text{Cl}_2 < \text{F}_2$

- Q.38** The compound formed when alcoholic solution of ethylene dibromide is heated with granulated zinc is –
 (A) ethene (B) ethyne
 (C) ethane (D) bromo ethane
- Q.39** Geometrical isomerism is caused
 (A) by restricted rotation around C = C bond.
 (B) by the presence of one asymmetric carbon atom.
 (C) due to the different groups attached to the same functional group.
 (D) by swing of hydrogen atom between two divalent atoms.
- Q.40** Which of the following reactions does not show the correct products of the reaction?
 (A) $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[\text{peroxide}]{\text{HBr}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Br}$
 (B) $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[\text{peroxide}]{\text{HCl}} \text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Cl}$
 (C) $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{HBr}} \text{CH}_3 - \overset{\text{Br}}{\text{CH}} - \text{CH}_3$
 (D) $\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow{\text{HCl}} \text{CH}_3 - \underset{\text{Cl}}{\text{CH}} - \text{CH}_3$
- Q.41** Pentene-1 with HCl gives –
 (A) 3-chloropentane (B) 2-chloropentane
 (C) 1,2-dichloropentane (D) 1-chloropentane
- Q.42** A mixture of 1-chloropropane and 2-chloropropane when treated with alcoholic KOH, it gives
 (A) 1-Propene
 (B) 2-Propene
 (C) Isopropylene
 (D) A mixture of 1-propene and 2-propene
- Q.43** What is the order of reactivity of hydrogen atoms attached to carbon atom in an alkene?
 (A) $3^\circ > 1^\circ > 2^\circ$ (B) $2^\circ > 1^\circ > 3^\circ$
 (C) $3^\circ > 2^\circ > 1^\circ$ (D) $1^\circ > 2^\circ > 3^\circ$

PART - 3 : ALKYNES

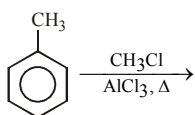
- Q.44** Ethylene may be obtained by dehydration of which of the following with concentrated H_2SO_4 at $160-170^\circ\text{C}$
 (A) $\text{C}_2\text{H}_5\text{OH}$ (B) CH_3OH
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ (D) $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
- Q.45** Propylene on hydrolysis with sulphuric acid forms
 (A) n-propyl alcohol (B) Isopropyl alcohol
 (C) Ethyl alcohol (D) Butyl alcohol
- Q.46** $\text{R} - \text{CH}_2 - \text{CCl}_2 - \text{R} \xrightarrow{\text{Reagent}} \text{R} - \text{C} \equiv \text{C} - \text{R}$
 The reagent is
 (A) Na (B) HCl and H_2O
 (C) KOH in $\text{C}_2\text{H}_5\text{OH}$ (D) Zn
- Q.47** Which of the following is used to distinguish ethylene and acetylene
 (A) Alkaline KMnO_4
 (B) Bromine water
 (C) Ammoniacal cuprous chloride
 (D) Conc. H_2SO_4
- Q.48** When acetylene is passed into dilute sulphuric acid containing Hg^{2+} ions, the product formed is –
 (A) Acetone (B) Acetic acid
 (C) Acetaldehyde (D) Formaldehyde
- Q.49** What is the product when 2-butyne is treated with liquid NH_3 in presence of lithium
 (A) n-butane (B) cis-2-butene
 (C) trans-2-butene (D) 1-butene
- Q.50** Shortest C–C bond length is present in
 (A) $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$ (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 (C) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ (D) $\text{CH} \equiv \text{C} - \text{C} \equiv \text{CH}$
- Q.51** What happens when a mixture of acetylene and hydrogen is passed over heated Lindlar's catalyst
 (A) Ethane and water are formed
 (B) Ethylene is formed
 (C) Acetylene and ethane are formed
 (D) None of these
- Q.52** Alkene and alkyne gives following types of polymerisation–
 (A) Addition (B) Condensation
 (C) Substitution (D) Replacement
- Q.53** When sodium fumarate is electrolysed, which alkyne is formed at anode –
 (A) propyne (B) butyne
 (C) Ethyne (D) None
- Q.54** Alkynes can be reduced to alkenes by hydrogenation in presence of –
 (A) Raney Ni (B) Anhy. AlCl_3
 (C) Pd (D) Lindlar's catalyst
- Q.55** What happens when calcium carbide is treated with water?
 (A) Ethane is formed.
 (B) Methane and ethane are formed.
 (C) Ethyne is formed.
 (D) Ethene and ethyne are formed.
- Q.56** When 1-butyne undergoes oxymercuration with the help of $\text{HgSO}_4 + \text{H}_2\text{SO}_4$, the product(s) formed is/are –
 (A) $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$ (B) $\text{CH}_3\text{CH}_2\text{COCH}_3$
 (C) $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$
- Q.57** Which of the following alkynes is most acidic?
 (A) $\text{CH}_3\text{C} \equiv \text{CH}$ (B) $\text{CH}_3\text{C} \equiv \text{CCH}_3$
 (C) $\text{CH}_3\text{CH}_2\text{C} \equiv \text{CH}$ (D) $\text{CH} \equiv \text{CH}$
- Q.58** The most acidic hydrogen atoms are present in
 (A) ethane (B) ethene
 (C) ethyne (D) benzene
- Q.59** Identify the product for the following reaction:
 $\text{CH} \equiv \text{CH} + \text{HOCl} \rightarrow$
 (A) Cl_2CHCHO (B) $\text{CH}(\text{OH}) = \text{CHCl}$
 (C) $\text{ClCH}_2\text{CH}_2\text{OH}$ (D) CH_3COCl
- Q.60** The correct trend of acidic nature of the following alkynes is –
 (A) $\text{CH} \equiv \text{CH} > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH}_3\text{C} \equiv \text{CCH}_3$
 (B) $\text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH} \equiv \text{CH} > \text{CH}_3\text{C} \equiv \text{CCH}_3$
 (C) $\text{CH}_3\text{C} \equiv \text{CCH}_3 > \text{CH}_3 - \text{C} \equiv \text{CH} > \text{CH} \equiv \text{CH}$
 (D) $\text{CH} \equiv \text{CH} > \text{CH}_3\text{C} \equiv \text{CCH}_3 > \text{CH}_3\text{C} \equiv \text{CH}$

PART - 4 : AROMATIC HYDROCARBONS

- Q.61** Coal tar is the main source of –
 (A) aromatic compounds (B) alicyclic compounds
 (C) aliphatic compounds (D) nitro compounds.
- Q.62** The following reaction is known as

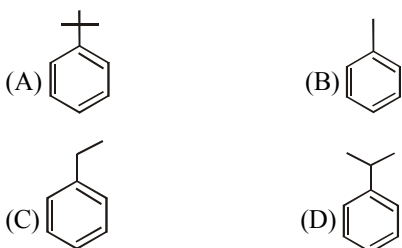
$$\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow[\text{(Anhy.)}]{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$$

 (A) Wurtz-Fittig reaction (B) Friedel-Crafts reaction
 (C) Rosenmund reaction (D) Sandmeyer reaction.
- Q.63** The correct order of reactivity towards electrophilic substitution is
 (A) benzene > phenol > benzoic acid > chlorobenzene
 (B) phenol > benzene > chlorobenzene > benzoic acid
 (C) chlorobenzene > benzoic acid > phenol > benzene
 (D) benzoic acid > chlorobenzene > benzene > phenol.
- Q.64** Major product of the reaction will be –

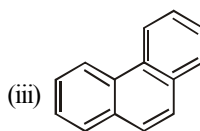
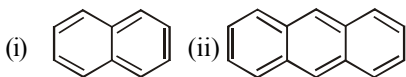


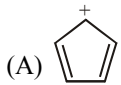
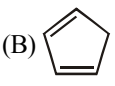
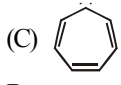
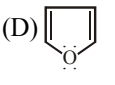
- (A) o-xylene (B) p-xylene
 (C) Cumene (D) m-xylene
- Q.65**
$$\text{C}_6\text{H}_6 \xrightarrow[\text{AlCl}_3]{\text{CH}_3\text{COCl}} \text{A} \xrightarrow[\text{HCl}]{\text{Zn-Hg}} \text{B}$$

 The end product in the above sequence is –
 (A) Toluene (B) Ethyl benzene
 (C) Both the above (D) None of these
- Q.66** Which of the following will undergo sulphonation at fastest rate?



- Q.67** Which is most reactive towards sulphonation?
 (A) m-Xylene (B) o-Xylene
 (C) Toluene (D) p-Xylene
- Q.68** Identify the aromatic compound –



- (A) (i) and (ii) (B) (ii) and (iii)
 (C) (i), (ii) and (iii) (D) (i) and (iii)
- Q.69** Nitration and chlorination of benzene are –
 (A) nucleophilic and electrophilic substitution respectively.
 (B) electrophilic and nucleophilic substitution respectively.
 (C) electrophilic substitution in both the reactions
 (D) nucleophilic substitution in both the reactions.
- Q.70** In halogenation of aromatic hydrocarbon, a halogen carrier is used which is generally a Lewis acid. The main function of this reagent is to generate the species
 (A) X (B) X⁻
 (C) X⁺ (D) X*
- Q.71** Although benzene is highly unsaturated it does not undergo addition reactions. The explanation of this can be suggested as
 (A) π-electrons of benzene ring are delocalised.
 (B) Since π-electrons are present inside the ring, addition cannot take place.
 (C) Cyclic structures do not show addition reactions.
 (D) Benzene is not a reactive compound.
- Q.72** What is the carbon-carbon bond length in benzene?
 (A) 1.20 Å and 1.31 Å (B) 1.39 Å
 (C) 1.39 Å and 1.20 Å (D) 1.20 Å
- Q.73** Which of the following species is aromatic?
 (A)  (B) 
 (C)  (D) 
- Q.74** Benzene easily shows
 (A) ring fission reactions since it is unstable.
 (B) addition reactions since it is unsaturated.
 (C) electrophilic substitution reactions due to stable ring and high π electron density.
 (D) nucleophilic substitution reactions due to stable ring and minimum electron density.

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.


- Q.1**
$$(\text{CH}_3\text{-CH}_2\text{-})_3\text{B} \begin{cases} \xrightarrow{\text{H}^+} \text{A} \\ \xrightarrow[\text{+NaOH}]{\text{AgNO}_3} \text{B} \end{cases}$$

 The ratio of molecular weight of A and B is –
 (A) ≈ 1 (B) ≈ 2
 (C) ≈ 3 (D) ≈ 4

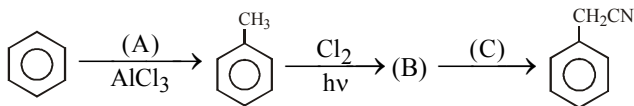
- Q.2** Which of the following has maximum melting point –
 (A) C₄H₁₀ (B) C₅H₁₂
 (C) C₆H₁₄ (D) C₇H₁₆
- Q.3**
$$\text{C}_2\text{H}_6 + \text{SO}_2 + \text{Cl}_2 \xrightarrow{\text{U.V. Light}} \text{product.}$$

 In this reaction product will be –
 (A) C₂H₄ (B) CH₃CH₂Cl
 (C) CH₃CH₂SO₂Cl (D) C₂H₂

- Q.4** Consider the following reactions.
- $$\text{CH}_3\text{CHOHCH}_3 \xrightarrow{\text{HBr}} \text{A} \xrightarrow[\text{C}_2\text{H}_5\text{OH}]{\text{Zn-Cu}} \text{B}$$
- The end product (B) is -
- (A) $\text{CH}_3\text{CH}_2\text{CH}_3$ (B) $\text{CH}_3\text{CH}(\text{OC}_2\text{H}_5)\text{CH}_3$
- (C) $\text{CH}_3\text{CHBrCH}_3$ (D) $\text{CH}_3\text{CH}=\text{CH}_2$
- Q.5** Which of the following reactions is expected to readily give a hydrocarbon product in good yield -
- (A) $(\text{CH}_3)_3\text{C}-\text{Cl} \xrightarrow{\text{C}_2\text{H}_5\text{OH}}$ (B) $\text{RCO}_2\text{K} \xrightarrow{\text{electrolysis}}$
- (C) $\text{CH}_3-\text{CH}_3 \xrightarrow[\text{h}\nu]{\text{Cl}_2}$ (D) $\text{RCO}_2\text{Ag} \xrightarrow{\text{Br}_2}$
- Q.6** Which of the following alkyl bromides may be used for the synthesis of 2, 3-dimethylbutane by Wurtz reaction
- (A) n-Propyl bromide (B) Isopropyl bromide
- (C) Isobutyl bromide (D) s-Butyl bromide
- Q.7** The number of isomeric sodium salt that will be required to obtain neopentane.
- (A) 3 (B) 1
- (C) 4 (D) 6
- Q.8** Iodoethane reacts with sodium in presence of ether. The product is :
- (A) Pentane (B) Propane
- (C) Butene (D) Butane
- Q.9** The organic reaction product from the reaction of methyl magnesium bromide and ethyl alcohol is -
- (A) Methane (B) Ethane
- (C) Propane (D) Butane
- Q.10** Halogenation of paraffins is a process of following nature
- (a) Oxidative (b) Reductive
- (c) Substitutive (d) Additive
- (A) a & c (B) b & d
- (C) a & d (D) b & c
- Q.11** What would be the product when ethene reacts with Br_2 water in presence of brine ?
- (A) $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \quad | \\ \text{Br} \quad \text{Br} \end{array}$
- (B) $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \text{ and } \text{CH}_2 - \text{CH}_2 \\ | \quad | \quad | \quad | \\ \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{Cl} \end{array}$
- (C) $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \text{ and } \text{CH}_2 - \text{CH}_2 \\ | \quad | \quad | \quad | \\ \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{NO}_2 \end{array}$
- (D) $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \text{ and } \text{CH}_2 - \text{CH}_2 \\ | \quad | \quad | \quad | \\ \text{Br} \quad \text{Br} \quad \text{Br} \quad \text{NO}_3 \end{array}$
- Q.12** Which compound has the lowest boiling point -
- (A) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ (B) $\text{CH}_3\text{CH}=\text{CHCH}_2\text{CH}_3$
- (C) $\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$ (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- Q.13** $\text{RCH}=\text{CH}_2 + \text{BH}_3 \rightarrow \text{intermediate} \xrightarrow{\text{OH}^-/\text{NH}_2\text{Cl}} \text{product}$, product will be -
- (A) $\text{RCH}_2-\text{CH}_2-\text{NH}_2$
- (B) $\begin{array}{c} \text{RCH} - \text{CH}_2 \\ | \quad | \\ \text{NH}_2 \quad \text{NH}_2 \end{array}$
- (C) $\text{R}-\text{CH}_2-\text{NH}_2$
- (D) $\text{RNH}_2 + \text{CH}_2=\text{CH}-\text{NH}_2$
- Q.14** In ethane and cyclohexane which one of the following pairs of conformations are more stable
- (A) Eclipsed and chair conformations
- (B) Staggered and chair conformations
- (C) Staggered and boat conformations
- (D) Eclipsed and boat conformations
- Q.15** Propionic acid is subjected to reduction with hydroiodic acid in the presence of a little P, the product formed is
- (A) Ethane (B) Propane
- (C) Butane (D) None
- Q.16** The addition of tetraethyl lead to petrol -
- (A) Lowers its octane number
- (B) Raises its octane number
- (C) May raise or lower the octane number
- (D) Has no effect on octane number
- Q.17** A mixture of propene and methane is obtained by the cracking of
- (A) 1-butene (B) 2-butene
- (C) n-butane (D) Isobutane
- Q.18** Isomerism in saturated hydrocarbons is due to
- (A) Change in the valence of carbon
- (B) Change in the ratio of elements in compounds
- (C) Formation of branches in the chain of C atoms
- (D) Formation of double bond
- Q.19** In which of the following, addition of HBr does not take place against Markonikov's rule
- (A) Propene (B) But-1-ene
- (C) But-2-ene (D) Pent-2-ene
- Q.20** When ethene is heated at 400°C under high pressure, the product is/are
- (A) Carbon and H_2 (B) Polyethylene
- (C) Acetylene and H_2 (D) None of these
- Q.21** Addition of HCl to propene in presence of peroxides gives
- (A) 1-Chloropropane (B) 2-Chloropropane
- (C) 3-Chloropropane (D) Propene dichloride
- Q.22** A compound is treated with NaNH_2 to give sodium salt. Identify the compound
- (A) C_2H_2 (B) C_6H_6
- (C) C_2H_6 (D) C_2H_4
- Q.23** Which will undergo reaction with ammoniacal AgNO_3
- (A) $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array} \text{CH} - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_3$
- (B) $\text{CH}_3 - \text{CH} = \text{CH} - \text{C} \equiv \text{CH}$
- (C) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 - \text{CH}_3$
- (D) $\text{CH}_2 = \text{CH} - \text{CH}_2 - \text{CH}_3$

- Q.24** Anhydrous AlCl_3 is used in the Friedel-Craft's reaction because it is
 (A) Electron rich
 (B) Soluble in ether
 (C) Insoluble to chloride and aluminium ions
 (D) Electron deficient
- Q.25** In the reaction of p-chlorotoluene with KNH_2 in liquid NH_3 , the major product is -
 (A) o-Toluidine (B) m-Toluidine
 (C) p-Toluidine (D) p-Chloroaniline
- Q.26** $\text{R}-\text{CH}=\text{CH}_2 + \text{CO} + \text{H}_2\text{O} \xrightarrow[200^\circ-300^\circ\text{C}]{\text{Co/ThO}_2} \text{R}-\underset{\text{COOH}}{\text{CH}_2}$
 Above reaction is known as -
 (A) Oxo reaction (B) Carbonylation
 (C) Both of the above (D) None of these
- Q.27** NBS react with 1-butene to give -
 (A) 3-bromobutene-1 (B) 1,2-dibromobutane
 (C) 1-bromobutene (D) 1,2-dibromobutene-1
- Q.28** Alkene $\text{R}-\text{CH}=\text{CH}_2$ reacts readily with B_2H_6 & the product of oxidation with alkaline hydrogen peroxide produces -
 (A) $\text{R}-\text{CH}_2-\text{CHO}$ (B) $\text{R}-\text{CH}_2-\text{CH}_2-\text{OH}$
 (C) $\text{R}-\underset{\text{O}}{\underset{\parallel}{\text{C}}}-\text{CH}_3$ (D) $\text{R}-\underset{\text{OH}}{\text{CH}}-\underset{\text{OH}}{\text{CH}_2}$
- Q.29** Reaction of HBr with propene in the presence of peroxide gives -
 (A) 3-bromo propane (B) allyl bromide
 (C) n-propyl bromide (D) isopropyl bromide
- Q.30** An unsaturated hydrocarbon was treated with ozone and resulting ozonide on hydrolysis gives 2-pentanone and acetaldehyde. What is the structure of alkene?
 (A) $\text{C}_3\text{H}_7-\text{CH}=\text{CH}-\text{CH}_3$ (B) $\text{C}_3\text{H}_7-\text{C}(\text{CH}_3)=\text{C}(\text{H})-\text{CH}_3$
 (C) $\text{CH}_3-\text{C}(\text{CH}_3)=\text{C}(\text{C}_2\text{H}_5)-\text{CH}_3$ (D) $\text{C}_3\text{H}_7-\text{C}(\text{CH}_3)=\text{C}(\text{CH}_3)-\text{CH}_3$
- Q.31** Propene on reaction with methylene iodide in presence of Zn-Cu couple gives :
 (A) Cyclopropane (B) Cyclopropen
 (C) Methyl Cyclopropane (D) Cyclobutene
- Q.32** Choose the correct statement -
 (A) In eclipsed conformation hydrogen atoms attached to two carbons are as closed together.
 (B) In staggered conformation hydrogens are as far apart as possible.
 (C) In Sawhorse projections the molecule is viewed along the molecular axis.
 (D) All of these
- Q.33** Terminal alkynyl hydrogen is tested by reacting it with
 (A) Ammoniacal cuprous chloride
 (B) Ammoniacal silver nitrate
 (C) Both of the above
 (D) None of these
- Q.34** When acetylene and sulphur react in the presence of hot iron pyrite, product formed -
 (A) Pyrrole (B) Benzene
 (C) Toluene (D) Thiophene
- Q.35** The product of reaction between one mole of acetylene and two mole of HCHO in the presence of Cu is -
 (A) $\text{HOCH}_2-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$
 (B) $\text{H}_2\text{C}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_2\text{OH}$
 (C) $\text{HC}\equiv\text{C}-\text{CH}_2\text{OH}$
 (D) None of these
- Q.36** What is the chief product of reaction between β -butylene chloride and alc. KOH/NaNH_2
 (A) 1,2-butadiene (B) 1,3-butadiene
 (C) 2-butyne (D) 1-butyne
- Q.37** Acetylene magnesium chloride reacts with ethyl bromide, the product is -
 (A) 1-butyne (B) 2-butyne
 (C) 1,2-butadiene (D) 1,3-butadiene
- Q.38** Which of the following acid is dibasic -
 (A) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 (B) $(\text{CH}_3)_2\text{C}=\text{CH}_2$
 (C) $\text{CH}_3-\text{C}\equiv\text{CH}$
 (D) $\text{CH}\equiv\text{CH}$
- Q.39** What happens when methane reacts with conc. HNO_3 at high temperature?
 (A) Nitromethane is formed
 (B) Methanol is formed.
 (C) CO_2 and H_2O are formed.
 (D) CO and H_2O are formed.
- Q.40** Which of the following products is formed when n-heptane is passed over $(\text{Al}_2\text{O}_3 + \text{Cr}_2\text{O}_3)$ catalyst at 773 K?
 (A) Benzene (B) Toluene
 (C) Polyheptane (D) Cycloheptane
- Q.41** Choose the correct reagents used in the conversion.
 $\text{CH}_2=\text{CH}_2 \xrightarrow{\text{p}} \underset{\text{Br}}{\text{CH}_2}-\underset{\text{Br}}{\text{CH}_2} \xrightarrow{\text{q}}$
- $\text{CH}_2=\text{CHBr} \xrightarrow{\text{r}} \text{CH}\equiv\text{CH} \xrightarrow{\text{s}}$ 
- (A) p : Br_2 , q : alc. KOH , r : NaOH , s : Al_2O_3
 (B) p : HBr , q : alc. KOH , r : CaC_2 , s : KMnO_4
 (C) p : HBr , q : alc. KOH , r : NaNH_2 , s : red hot iron tube
 (D) p : Br_2 , q : alc. KOH , r : NaNH_2 , s : red hot iron tube
- Q.42** Which of the following compounds gives methane on reaction with water?
 (A) CaC_2 (B) B_4C
 (C) SiC (D) Al_4C_3
- Q.43** 2-Bromopentane is treated with alcoholic KOH solution. What will be the major product formed in this reaction and what is the type of elimination called?
 (A) Pent-1-ene, β -Elimination
 (B) Pent-2-ene, β -Elimination
 (C) Pent-1-ene, Nucleophilic substitution
 (D) Pent-2-ene, Nucleophilic substitution.

Q.44 Identify the unknown compounds.

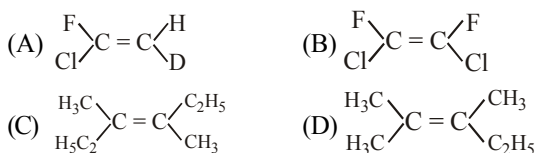


- (A) A : CH_3COCl , B : $\text{C}_6\text{H}_5\text{Cl}$, C : NaCN
 (B) A : CH_3Cl , B : $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, C : KCN
 (C) A : CH_4 , B : $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$, C : AgCN
 (D) A : CH_3Cl , B : $\text{C}_6\text{H}_5\text{COCl}$, C : KCN

Q.45 Which of the following isomeric heptanes can yield seven different monochlorinated products upon free radical chlorination?

- (A) 2,2-Dimethylpentane (B) 2-Methylhexane
 (C) 3-Methylhexane (D) 2,4-Dimethylpentane

Q.46 Which of the following will not show geometrical isomerism?



Q.47 Which compounds will show cis-trans isomerism?

- (A) $(\text{CH}_3)_2\text{C}=\text{CH}-\text{C}_2\text{H}_5$ (B) $\text{H}_2\text{C}=\text{CCl}_2$
 (C) $\text{CH}_3\text{HC}=\text{CClCH}_3$ (D) $\text{HCIC}=\text{CH}_2$

Q.48 $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \xrightarrow[170^\circ\text{C}]{\text{Conc. H}_2\text{SO}_4} \text{A} \xrightarrow[500^\circ\text{C}]{\text{Cl}_2} \text{B}$.

A and B are –

- (A) A = $\text{CH}_3\text{CH}_2\text{CH}_3$, B = $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
 (B) A = $\text{CH}_3\text{CH}=\text{CH}_2$, B = $\text{CH}_2\text{ClCH}=\text{CH}_2$
 (C) A = $\text{CH}_2=\text{CH}_2$, B = $\text{CH}_3\text{CH}_2\text{Cl}$
 (D) A = $\text{CH}_3\text{CH}_2\text{CH}_3$, B = $\text{CH}_3\text{CH}=\text{CH}_2$

Q.49 Which alkane is produced when sodium salt of butanoic acid is heated with sodalime?

- (A) CH_3CH_3 (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 (C) CH_4 (D) $\text{CH}_3\text{CH}_2\text{CH}_3$

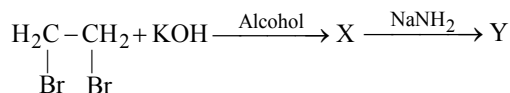
Q.50 Which of the following alkynes can be identified and distinguished from the rest of the alkynes on reaction with ammoniacal silver nitrate to give a white precipitate

- (A) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$ (B) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
 (C) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_3$ (D) $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$

Q.51 Which one of the following gives only one monochloro derivative?

- (A) neo-Pentane (B) n-Hexane
 (C) 2-Methylpentane (D) 3-Methylpentane

Q.52 Identify X and Y in the following reaction.

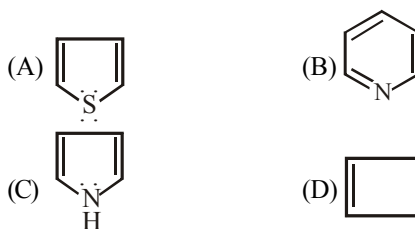


- (A) X : CH_3CHBr , Y : $\text{CH}_2=\text{CH}_2$
 (B) X : $\text{CH}_2\text{OH}-\text{CH}_2\text{OH}$, Y : $\text{CH}_2=\text{CH}_2$
 (C) X : $\text{CH}_2=\text{CHBr}$, Y : $\text{CH}\equiv\text{CH}$
 (D) X : $\text{CH}\equiv\text{CBr}$, Y : $\text{CH}\equiv\text{CH}$

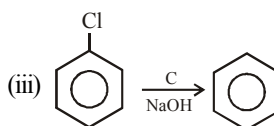
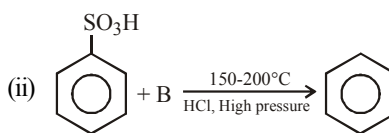
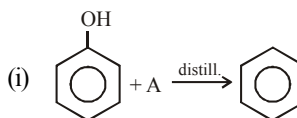
Q.53 Presence of unsaturation in organic compounds can be tested with –

- (A) Fehling's reagent (B) Tollens' reagent
 (C) Baeyers reagent (D) Fittig's reaction

Q.54 Which of the following species does not show aromaticity?

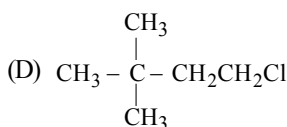
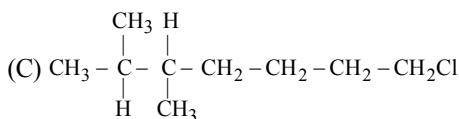
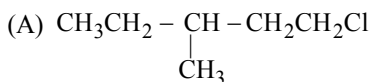


Q.55 Complete the following reactions:

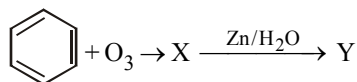


- (A) A = Ni, B = H_2O (liquid), C = H_2O
 (B) A = Zn, B = H_2O (steam), C = H (Ni-Al alloy)
 (C) A = Mg, B = H_2O (liquid), C = HCl
 (D) A = Zn, B = H_2O (boiling), C = SnCl_2

Q.56 An alkyl halide X reacts with sodium to form 3,8-dimethyldecane. What is X?

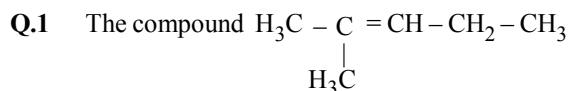


Q.57 Similar to alkenes and alkynes benzene also undergoes ozonolysis. In the sequence of the given reaction identify X and Y



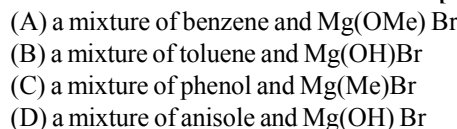
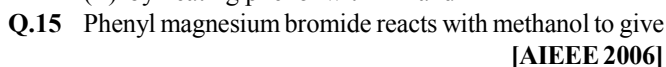
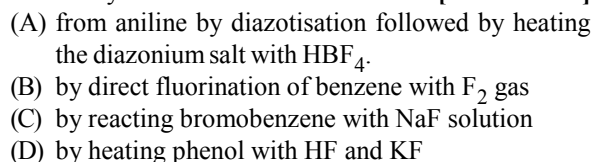
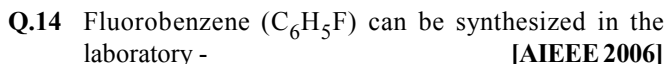
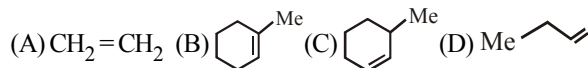
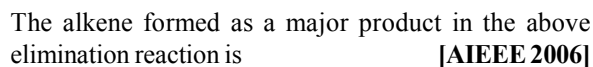
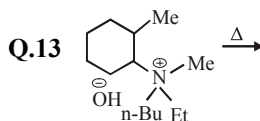
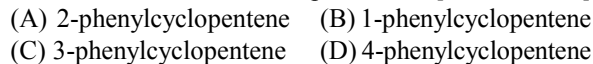
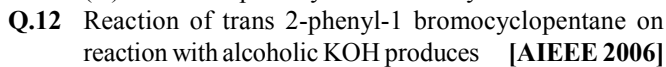
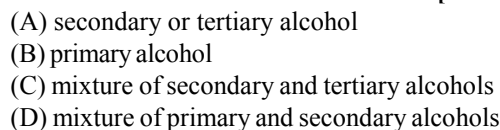
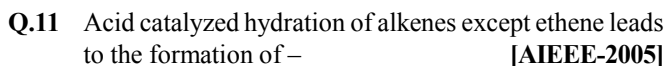
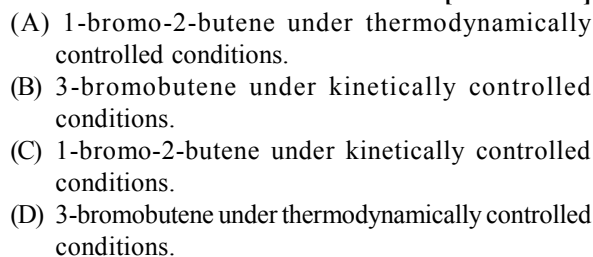
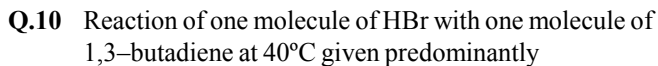
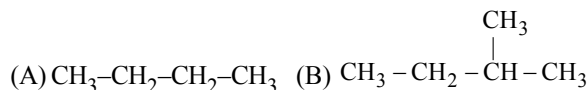
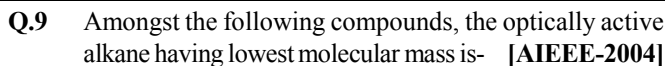
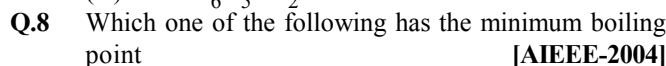
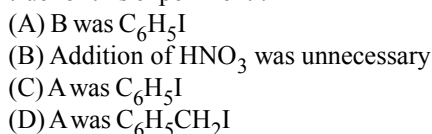
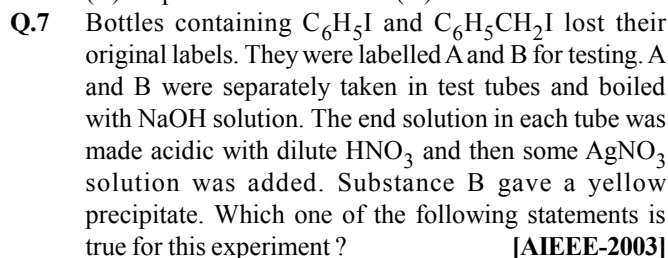
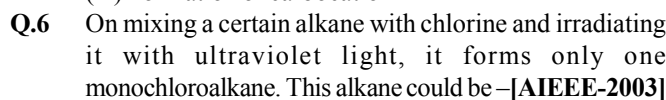
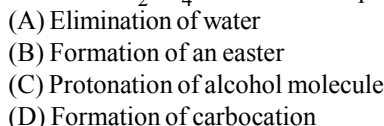
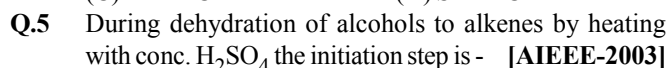
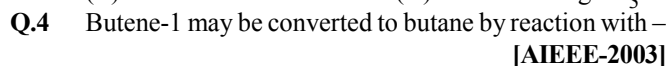
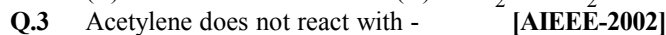
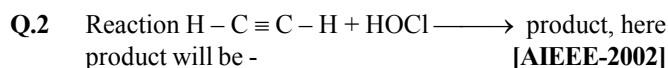
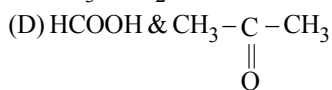
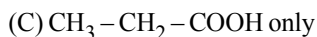
- (A) X = Triozonide, Y = Glyoxal
 (B) X = Diozonide, Y = Succinic acid
 (C) X = Monoozonide, Y = Benzoic acid
 (D) X = Triozonide, Y = Benzaldehyde.

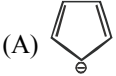
EXERCISE - 4 [PREVIOUS YEARS AIEEE / JEE MAIN QUESTIONS]



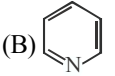
$\xrightarrow{\text{Vigorous oxidation}}$ product, here product is

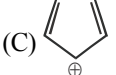
[AIEEE-2002]



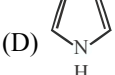
- Q.16** The reaction of toluene with Cl_2 in presence of FeCl_3 gives predominantly- [AIEEE 2007]
 (A) benzoyl chloride (B) benzyl chloride
 (C) o- and p-chlorotoluene (D) m-chlorotoluene
- Q.17** Which of the following reactions will yield 2, 2-dibromopropane? [AIEEE 2007]
 (A) $\text{CH}_3-\text{C}\equiv\text{CH} + 2\text{HBr} \rightarrow$ (B) $\text{CH}_3\text{CH}=\text{CHBr} + \text{HBr} \rightarrow$
 (C) $\text{CH}\equiv\text{CH} + 2\text{HBr} \rightarrow$ (D) $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow$
- Q.18** In the following sequence of reactions, the alkene affords the compound 'B'
 $\text{CH}_3\text{CH}=\text{CHCH}_3 \xrightarrow{\text{O}_3} \text{A} \xrightarrow[\text{Zn}]{\text{H}_2\text{O}} \text{B}$, The compound B is [AIEEE 2008]
 (A) CH_3COCH_3 (B) $\text{CH}_3\text{CH}_2\text{COCH}_3$
 (C) CH_3CHO (D) $\text{CH}_3\text{CH}_2\text{CHO}$
- Q.19** The treatment of CH_3MgX with $\text{CH}_3\text{C}\equiv\text{C}-\text{H}$ produces [AIEEE 2008]
 (A) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3$ (B) $\text{CH}_3-\overset{\text{H}}{\underset{\text{H}}{\text{C}}}=\text{C}-\text{CH}_3$
 (C) CH_4 (D) $\text{CH}_3-\text{CH}=\text{CH}_2$
- Q.20** The hydrocarbon which can react with sodium in liquid ammonia is [AIEEE 2008]
 (A) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$
 (B) $\text{CH}_3\text{CH}=\text{CHCH}_3$
 (C) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_3$
 (D) $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$
- Q.21** Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains - [AIEEE 2008]
 (A) mixture of o- and p-dibromobenzenes
 (B) mixture of o- and p-bromoanilines
 (C) mixture of o- and m-bromotoluenes
 (D) mixture of o- and p-bromotoluenes
- Q.22** The alkene that exhibits geometrical isomerism is - [AIEEE 2009]
 (A) 2-methyl-2-butene (B) propene
 (C) 2-methyl propene (D) 2-buten
- Q.23** One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44u. The alkene is - [AIEEE 2010]
 (A) propene (B) 1-butene
 (C) 2-butene (D) ethene
- Q.24** Out of the following, the alkene that exhibits optical isomerism is - [AIEEE 2010]
 (A) 3-methyl-2-pentene (B) 4-methyl-1-pentene
 (C) 3-methyl-1-pentene (D) 2-methyl-2-pentene
- Q.25** How many chiral compounds are possible on monochlorination of 2-methyl butane? [AIEEE 2012]
 (A) 8 (B) 2
 (C) 4 (D) 6
- Q.26** Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide? [AIEEE 2012]
 (A) Tertiary butyl chloride (B) Neopentane
 (C) Isohexane (D) Neohexane
- Q.27** 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
- Q.28** The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is: [JEE MAIN 2014]
 (A) 2-Butyne (B) 2-Butene
 (C) Acetylene (D) Ethene
- Q.29** The reaction of propene with HOCl ($\text{Cl}_2 + \text{H}_2\text{O}$) proceeds through the intermediate: [JEE MAIN 2016]
 (A) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{Cl}$ (B) $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2^+$
 (C) $\text{CH}_3-\text{CHCl}-\text{CH}_2^+$ (D) $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{OH}$
- Q.30** 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) Four (B) Six
 (C) Zero (D) Two
- Q.31** The trans-alkenes are formed by the reduction of alkynes with: [JEE MAIN 2018]
 (A) $\text{Na}/\text{liq. NH}_3$ (B) $\text{Sn}-\text{HCl}$
 (C) $\text{H}_2-\text{Pd}/\text{C}, \text{BaSO}_4$ (D) NaBH_4
- Q.32** Which of the following compounds is not aromatic? [JEE MAIN 2019 (JAN)]
- 

(A)



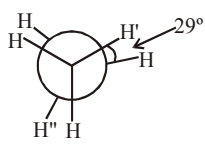
(B)
- 

(C)



(D)
- Q.33** Which one of the following alkenes when treated with HCl yields majorly an antiMarkovnikov product? [JEE MAIN 2019 (APRIL)]
 (A) $\text{F}_3\text{C}-\text{CH}=\text{CH}_2$ (B) $\text{Cl}-\text{CH}=\text{CH}_2$
 (C) $\text{CH}_3\text{O}-\text{CH}=\text{CH}_2$ (D) $\text{H}_2\text{N}-\text{CH}=\text{CH}_2$
- Q.34** The major product of the following reaction is : [JEE MAIN 2019 (APRIL)]
 $\text{CH}_3\text{C}\equiv\text{CH} \xrightarrow[\text{(ii) DI}]{\text{(i) DCl (1 equiv.)}}$
- (A) $\text{CH}_3\text{CD}(\text{Cl})\text{CHD}(\text{I})$

(B) $\text{CH}_3\text{CD}_2\text{CH}(\text{Cl})(\text{I})$
- (C) $\text{CH}_3\text{CD}(\text{I})\text{CHD}(\text{Cl})$

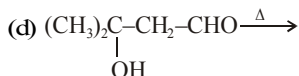
(D) $\text{CH}_3\text{C}(\text{I})(\text{Cl})\text{CHD}_2$
- Q.35** In the following skew conformation of ethane, $\text{H}'-\text{C}-\text{C}-\text{H}''$ dihedral angle is : [JEE MAIN 2019 (APRIL)]
- 
- (A) 120°

(B) 58°
- (C) 149°

(D) 151°

Q.36 Consider the following reactions :

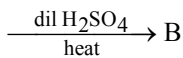
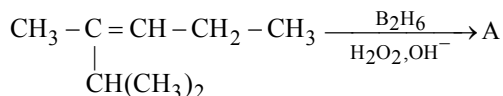
[JEE MAIN 2020 (JAN)]



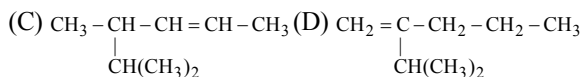
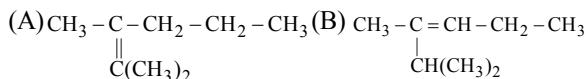
Which of these reaction(s) will not produce Saytzeff product ?

- (A) (c) only (B) (a), (c) and (d)
 (C) (d) only (D) (b) and (d)

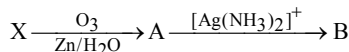
Q.37 Find the final major product of the following reactions



[JEE MAIN 2020 (JAN)]

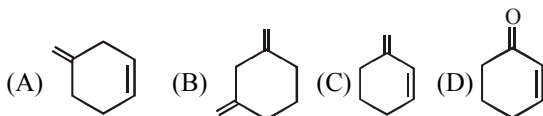


Q.38 An unsaturated hydrocarbon X absorbs two hydrogen molecules on catalytic hydrogenation, and also gives following reaction : [JEE MAIN 2020 (JAN)]

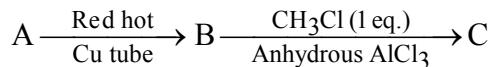


(3-oxo-hexanedicarboxylic acid)

X will be :



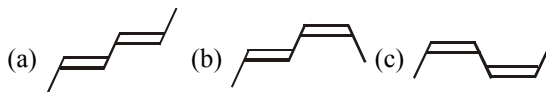
Q.39 In the following sequence of reactions the maximum number of atoms present in molecule 'C' in one plane is _____.



(Where A is the alkyne of lowest molecular mass)

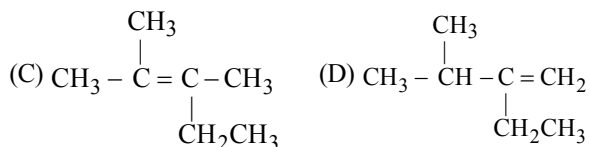
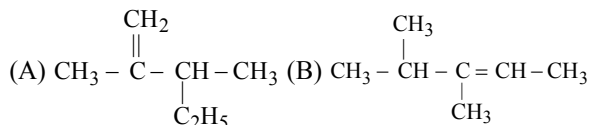
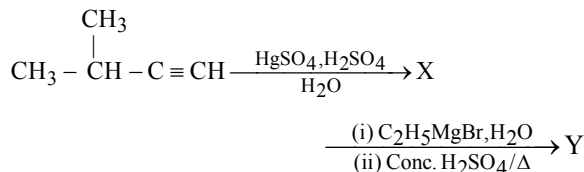
[JEE MAIN 2020 (JAN)]

Q.40 The correct order of heat of combustion for following alkadienes is : [JEE MAIN 2020 (JAN)]

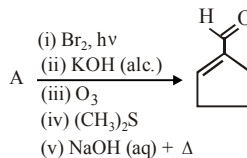


- (A) (a) < (b) < (c) (B) (b) < (c) < (a)
 (C) (c) < (b) < (a) (D) (a) < (c) < (b)

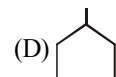
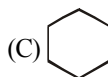
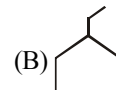
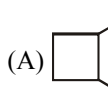
Q.41 The major product (Y) in the following reactions is



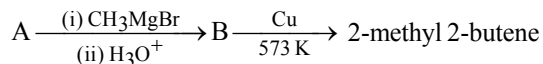
Q.42 In the following reaction A is :



[JEE MAIN 2020 (JAN)]



Q.43 Consider the following reactions



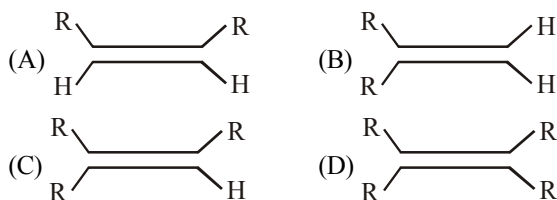
The mass percentage of carbon in A is _____.

[JEE MAIN 2020 (JAN)]

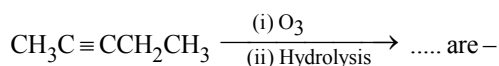
EXERCISE - 5 (PREVIOUS YEARS AIPMT/NEET EXAM QUESTIONS)

Choose one correct response for each question.

- Q.1** Which one of the following alkenes will react faster with H_2 under catalytic hydrogenation conditions – (R = Alkyl substituent) [AIPMT 2005]



- Q.2** Products of the following reaction

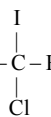
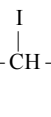
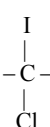
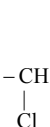


[AIPMT 2005]

- (A) $CH_3COOH + CO_2$
 (B) $CH_3COOH + HOOCCH_2CH_3$
 (C) $CH_3CHO + CH_3CH_2CHO$
 (D) $CH_3COOH + CH_3COCH_3$

- Q.3** Predict the product C obtained in the following reaction of butyne-1. [AIPMT 2007]



- (A)  (B) 
- (C)  (D) 

- Q.4** Which of the compounds with molecular formula C_5H_{10} yields acetone on ozonolysis – [AIPMT 2007]

- (A) 3-methyl-1-butene (B) cyclopentane
 (C) 2-methyl-1-butene (D) 2-methyl-2-butene

- Q.5** Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form: [AIPMT 2009]

- (A) Chlorobenzene (B) Benzylchloride
 (C) Xylene (D) Toluene

- Q.6** Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4 in the mixture, nitric acid acts as a/an: [AIPMT 2009]

- (A) acid (B) base
 (C) catalyst (D) reducing agent

- Q.7** Which of the following compounds will exhibit cis-trans [geometrical] isomerism? [AIPMT 2009]

- (A) 2-butene (B) Butanol
 (C) 2-butyne (D) 2-butanol

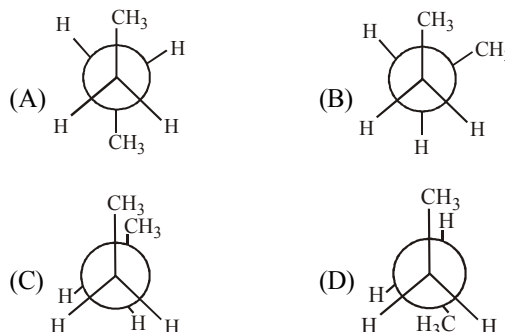
- Q.8** Liquid hydrocarbons can be converted to a mixture of gaseous hydrocarbons by – [AIPMT (PRE) 2010]

- (A) Oxidation
 (B) Cracking
 (C) Distillation under reduced pressure
 (D) Hydrolysis

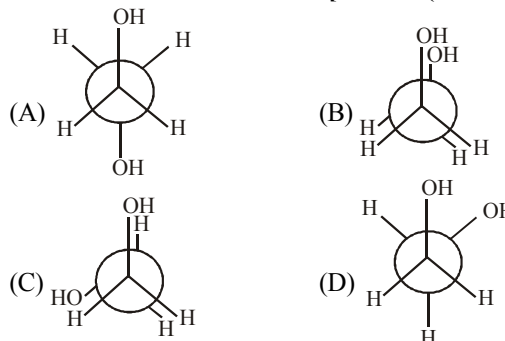
- Q.9** The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are: [AIPMT (PRE) 2010]

- (A) X = Benzal chloride, Y = o-chlorotoluene
 (B) X = m-chlorotoluene, Y = p-chlorotoluene
 (C) X = o- and p-chlorotoluene, Y = Trichloromethyl benzene
 (D) X = Benzyl chloride, Y = m-chlorotoluene

- Q.10** In the following the most stable conformation of n-butane is [AIPMT (PRE) 2010]



- Q.11** Which of the following conformers for ethylene glycol is most stable? [AIPMT (MAINS) 2010]

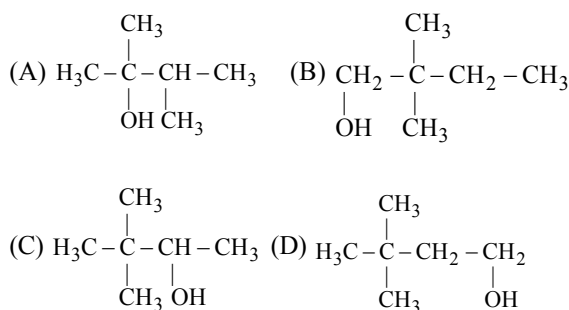


- Q.12** Among the following compounds the one that is most reactive towards electrophilic nitration is: [AIPMT (PRE) 2012]

- (A) Benzoic Acid (B) Nitrobenzene
 (C) Toluene (D) Benzene

- Q.13**
$$H_3C - \overset{\overset{CH_3}{|}}{C} - CH = CH_2 \xrightarrow{H_2O/H^+} \text{Major Product A} + \text{Minor Product B}$$

The major product is: [AIPMT (PRE) 2012]




Q.14 Which of the following reagents will be able to distinguish between 1-butyne and 2-butyne?

- [AIPMT (MAINS) 2012]
(A) NaNH_2 (B) HCl
(C) O_2 (D) Br_2

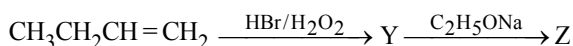
Q.15 Which of the following compounds will not undergo Friedal-Craft's reaction easily – [NEET 2013]

- (A) Toluene (B) Cumene
(C) Xylene (D) Nitrobenzene

Q.16 The radical,  is aromatic because it has

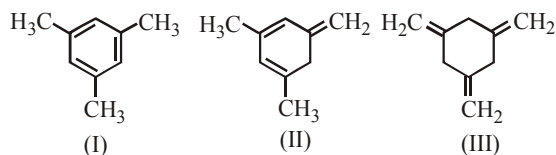
- (A) 6p-orbitals and 7 unpaired electrons [NEET 2013]
(B) 6p-orbitals and 6 unpaired electrons
(C) 7p-orbitals and 6 unpaired electrons
(D) 7p-orbitals and 7 unpaired electrons

Q.17 Identity Z in the sequence of reactions,



- (A) $\text{CH}_3-(\text{CH}_2)_3-\text{O}-\text{CH}_2\text{CH}_3$ [AIPMT 2014]
(B) $(\text{CH}_3)_2\text{CH}_2-\text{O}-\text{CH}_2\text{CH}_3$
(C) $\text{CH}_3(\text{CH}_2)_4-\text{O}-\text{CH}_3$
(D) $\text{CH}_3\text{CH}_2-\text{CH}(\text{CH}_3)-\text{O}-\text{CH}_2\text{CH}_3$

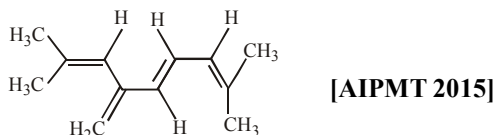
Q.18 Given :



The enthalpy of hydrogenation of these compounds will be in the order as : [AIPMT 2015]

- (A) $\text{III} > \text{II} > \text{I}$ (B) $\text{II} > \text{III} > \text{I}$
(C) $\text{II} > \text{I} > \text{III}$ (D) $\text{I} > \text{II} > \text{III}$

Q.19 The total number of π -bond electrons in the structure is



- (A) 8 (B) 12
(C) 16 (D) 4

Q.20 2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid ?

- (A) $(\text{CH}_3)_2\text{C}=\text{CH}-\text{CH}_2-\text{CH}_3$ [RE-AIPMT 2015]
(B) $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$
(C) $(\text{CH}_3)_2\text{CH}-\underset{\text{CH}_3}{\text{CH}}-\text{CH}=\text{CH}_2$

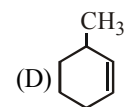
(D) $(\text{CH}_3)_3\text{C}-\text{CH}=\text{CH}_2$

Q.21 In the reaction with HCl , an alkene reacts in accordance with the Markovnikov's rule, to give a product 1-chloro-1-methylcyclohexane. The possible alkene is

[RE-AIPMT 2015]



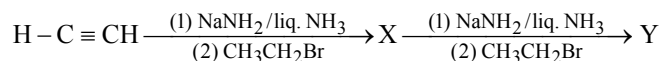
(C) Both (A) and (B)



Q.22 The oxidation of benzene by V_2O_5 in the presence of air produces : [RE-AIPMT 2015]

- (A) benzoic acid (B) benzaldehyde
(C) benzoic anhydride (D) maleic anhydride

Q.23 In the reaction



X and Y are

[NEET 2016 PHASE 1]

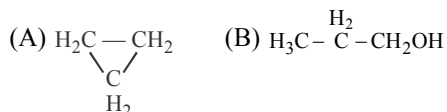
- (A) X = 1-Butyne; Y = 3-Hexyne
(B) X = 2-Butyne; Y = 3-Hexyne
(C) X = 2-Butyne; Y = 2-Hexyne
(D) X = 1-Butyne; Y = 2-Hexyne

Q.24 The correct statement regarding the comparison of staggered and eclipsed conformations of ethane is

[NEET 2016 PHASE 1]

- (A) The staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain.
(B) The eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain.
(C) The eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain.
(D) The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain.

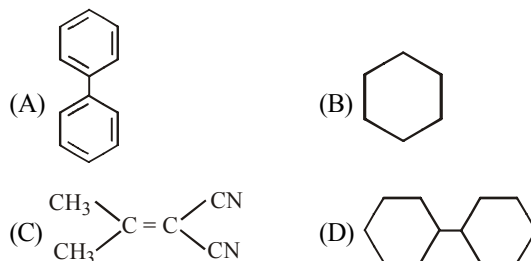
Q.25 Which of the following compounds shall not produce propene by reaction with HBr followed by elimination or direct only elimination reaction? [NEET 2016 PHASE 2]

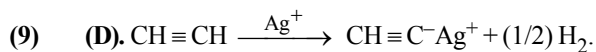
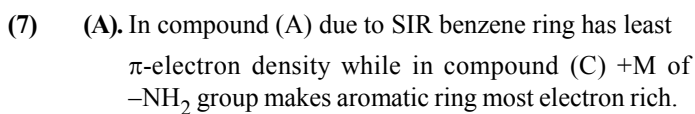
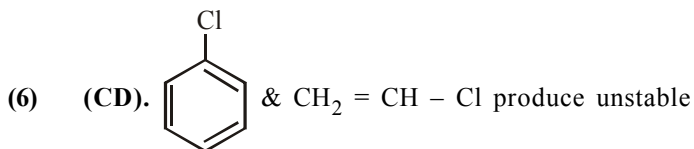
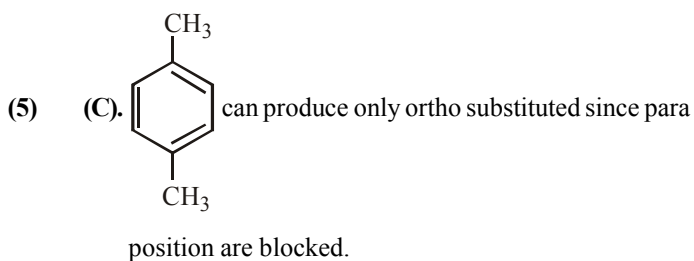
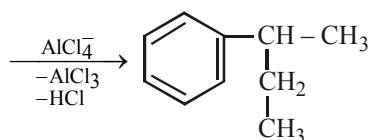
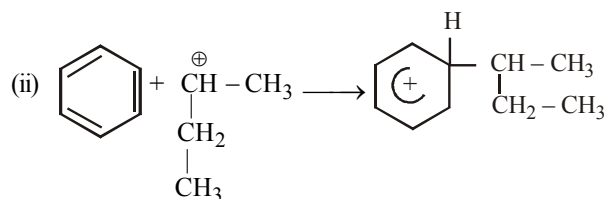
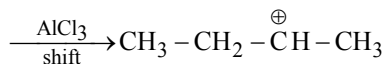
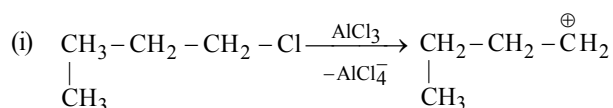
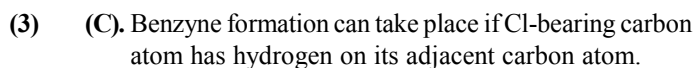
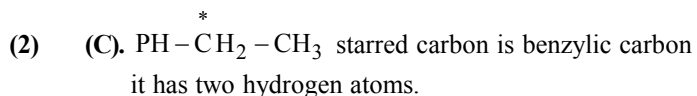
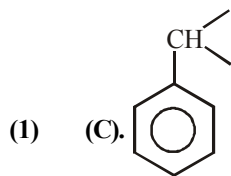


Q.26 The compound that will react most readily with gaseous bromine has the formula [NEET 2016 PHASE 2]

- (A) C_3H_6 (B) C_2H_2
(C) C_4H_{10} (D) C_2H_4

Q.27 In which of the following molecules, all atoms are coplanar? [NEET 2016 PHASE 2]

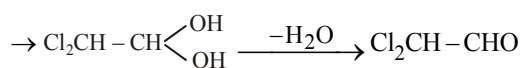



TRY IT YOURSELF-4


- (29) (A). $\text{CH}_3\text{-CH=CH}_2 + \text{Cl}_2 \xrightarrow{\text{CCl}_4} \text{CH}_3\text{-}\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}\text{-}\overset{\text{H}}{\underset{\text{Cl}}{\text{C}}}\text{-H}$
- (30) (A). 1% KMnO_4 sol. of light violet colour is Bayer's reagent. When alkenes are oxidised with cold, alkaline KMnO_4 dihydroxy compounds (diols or glycols) are formed.
- $$\begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array} + \text{H}_2\text{O} + \text{O} \xrightarrow{\text{KMnO}_4} \begin{array}{c} \text{H}_2\text{C-OH} \\ | \\ \text{H}_2\text{C-OH} \end{array}$$
- (31) (D). Oxidation of ethene using hot, conc. KMnO_4 produces CO_2 and H_2O .
- (32) (A). $\text{CH}_3\text{-CH=CH}_2 + \text{Cl}_2 \xrightarrow{500^\circ\text{C}} \begin{array}{c} \text{CH}_2\text{-CH=CH}_2 + \text{HCl} \\ | \\ \text{Cl} \end{array}$
- This reaction is called allylic halogenation reaction because halogenation occurs at the allylic position of an alkene
- (33) (B). $\text{CH}_3\text{-CH}_2\text{-Cl} \xrightarrow{\text{alc. KOH}} \text{CH}_2=\text{CH}_2 + \text{KCl} + \text{H}_2\text{O}$
Ethyl Chloride Alkene
- (34) (B). $\text{CH}_2=\text{CH-Cl} \xrightarrow{\text{HCl}} \text{CH}_3\text{-CH}\begin{array}{l} \text{Cl} \\ / \\ \text{Cl} \end{array}$
- According to Markovnikov's rule H atom of the reagent goes to that carbon atom which is more hydrogenated.
- (35) (C). $\text{CH}_3\text{-}\overset{\text{Br}}{\text{CH}}\text{-CH}_2\text{-CH}_3 \rightarrow \text{CH}_3\text{-CH=CH-CH}_3 + \text{HBr}$
2-Bromo butane
- (36) (D). $\begin{array}{c} \text{H}_3\text{C} \quad \quad \text{H} \\ \quad \quad \quad \diagdown \quad \diagup \\ \quad \quad \quad \text{C} = \text{C} \\ \quad \quad \quad \diagup \quad \diagdown \\ \text{CH}_3 \quad \quad \quad \text{H} \end{array}$
- (37) (C). Birch reduction
- (38) (A). $\begin{array}{c} \text{CH}_2\text{Br} \\ | \\ \text{CH}_2\text{Br} \end{array} + \text{Zn} \xrightarrow[\text{heat}]{\text{alcohol}} \begin{array}{c} \text{CH}_2 \\ || \\ \text{CH}_2 \end{array} + \text{ZnBr}_2$
- (39) (A). Geometrical isomerism arises due to restricted rotation around $\text{C}=\text{C}$ bond.
- (40) (B). Only addition of HBr gives anti-Markovnikov's product in presence of peroxide. Presence of peroxide does not make any difference while reaction with HCl .
- (41) (B). $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH=CH}_2 + \text{HCl} \rightarrow \text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}\overset{\text{Cl}}{\text{CH}}\text{-CH}_3$
2-Chloropentane
- (42) (A). $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{KOH(alc.)}} \text{CH}_3\text{CH=CH}_2$
- (43) (C). The order of reactivity of hydrogen atoms attached to C atom is
Tertiary > Secondary > Primary.
- (44) (A). $\text{CH}_3\text{-CH}_2\text{-OH} \xrightarrow[160-170^\circ\text{C}]{\text{Conc. H}_2\text{SO}_4} \text{CH}_2=\text{CH}_2 + \text{H}_2\text{O}$
- (45) (B). $\text{CH}_2=\text{CH-CH}_3 + \text{H}_2\text{O} \xrightarrow{\text{H}_2\text{SO}_4} \text{CH}_3\text{-}\overset{\text{OH}}{\text{CH}}\text{-CH}_3$
Propylene Isopropyl alcohol
Thus in this reaction isopropyl alcohol is formed.
- (46) (C). $\text{R-CH}_2\text{-CCl}_2\text{-R} \xrightarrow{\text{KOH} + \text{C}_2\text{H}_5\text{OH}} \text{R-C}\equiv\text{C-R} + 2\text{HCl}$
- This reaction is an example of dehydrohalogenation Hence, alcoholic KOH is used as a reagent.
- (47) (C). Acetylene reacts with ammonical cuprous chloride to give brown ppt where as ethylene does not give this reaction.
- (48) (C). $\text{CH}\equiv\text{CH} \xrightarrow[1\% \text{ HgSO}_4]{40\% \text{ H}_2\text{SO}_4} \text{CH}_2=\text{CH-OH}$
Vinyl alcohol
- $\xrightarrow{\text{Rearrangement}} \text{CH}_3\text{-CHO}$
Acetaldehyde
- (49) (C). Reduction of alkynes with liquid NH_3/Li gives trans alkenes.
- (50) (D). Bond length decrease with increase in Bond order. Triple bonded carbon has minimum bond length.
 C-C bond length = 1.54 Å
 C=C bond length = 1.33 Å
 $\text{C}\equiv\text{C}$ bond length = 1.22 Å
- (51) (B). $\text{CH}\equiv\text{CH} + \text{H}_2 \xrightarrow[\text{Catalyst}]{\text{Lindlar}} \text{CH}_2=\text{CH}_2$
Acetylene Ethylene
pd. BaSO_4
- (52) (A). Due to unsaturation alkene and alkyne gives addition polymerisation.
- (53) (C). In Kolbe's synthesis, sodium or potassium salt of maleic acid or fumaric acid on electrolysis gives acetylene or ethyne at anode.
- (54) (D). $\text{CH}\equiv\text{CH} \xrightarrow[\text{Catalyst}]{\text{Lindlar}} \text{CH}_2=\text{CH}_2$
Lindlar catalyst prevents further reduction of ethene to ethane.
- (55) (C). When CaC_2 reacts with water, it gives ethyne.
 $\text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}\equiv\text{CH} + \text{Ca(OH)}_2$
- (56) (B). $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH} \xrightarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} \begin{array}{c} \text{OH} \\ | \\ \text{CH}_3\text{CH}_2\text{C}=\text{CH}_2 \end{array} \rightleftharpoons \begin{array}{c} \text{O} \\ || \\ \text{CH}_3\text{CH}_2\text{C} \end{array} \text{CH}_3$
- (57) (D). $\text{CH}\equiv\text{CH}$ is most acidic due to 50% s-character.
- (58) (C). As the s-character increases, acidity of hydrogen atom increases.

Ethane : $\text{CH}_3 - \text{CH}_3$; sp^3 , 25% s-character
 Ethene : $\text{CH}_2 = \text{CH}_2$; sp^2 , 33% s-character
 Ethyne : $\text{CH} \equiv \text{CH}$; sp , 50% s-character
 Benzene: C_6H_6 ; sp^2 , 33% s-character

(59) (A). $\text{CH} \equiv \text{CH} + 2\text{HOCl}$

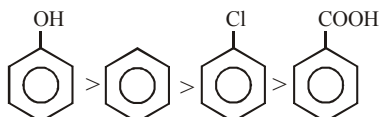


(60) (A). The hydrogen atoms attached to triply bonded carbons are acidic and not all the hydrogen atoms of alkynes.

(61) (A). Aromatic compounds are present in coal tar, one of the fractions obtained during destructive distillation of coal.

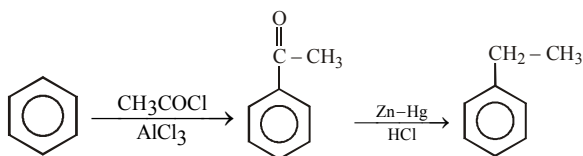
(62) (B). Alkylation and acylation of benzene in the presence of anhydrous aluminium chloride are known as Friedel-Crafts reaction.

(63) (B). In general, electron releasing groups activate and electron withdrawing groups deactivate the benzene ring towards electrophilic substitution. Hence, the correct order is



(64) (D). m-xylene is thermodynamically more stable therefore at high temperature m-xylene is obtained.

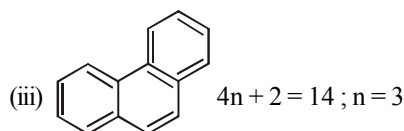
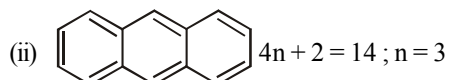
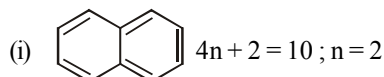
(65) (B).



(66) (B). can be sulphonated at fastest rate since benzene is activated by hyperconjugation of $3\alpha\text{H}$.

(67) (A). starred position can be activated by two methyl group while in others example one position is not being activated by both the methyl group.

(68) (C). All are aromatic compounds.



(69) (C). Nitration is carried out by electrophile NO_2^+ .
 $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2^+ + 2\text{HSO}_4^- + \text{H}_3\text{O}^+$
 Halogenation is carried out by electrophile Cl^+ (X^+).

(70) (C). Halogen carrier generates an electrophile with the help of halogen. e.g. during chlorination Cl^+ is generated.

$\text{AlCl}_3 + \text{Cl}_2 \rightarrow \text{AlCl}_4^- + \text{Cl}^+$
 or $\text{AlX}_3 + \text{X}_2 \rightarrow \text{AlX}_4^- + \text{X}^+$

(71) (A). π -electrons of benzene ring are delocalised throughout the molecule. This makes the molecule very stable. The stability resists breaking of double bonds for addition.

(72) (B). All C-C and C=C bond lengths are same in benzene. It is the intermediate between single and double bond. Hence, C-C bond length in benzene is 1.39 Å.

(73) (D). Furan is aromatic because according to Huckel's rule, $4n + 2 = 6$ (including 1 lone pair)
 $4n = 4$ or $n = 1$

(74) (C). The most common reactions shown by benzene are electrophilic substitution reactions.

EXERCISE-2

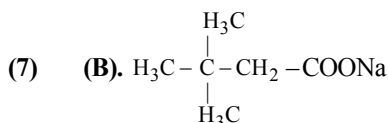
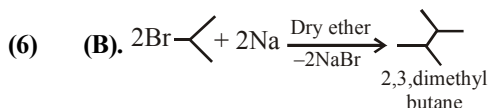
(1) (B). $(\text{CH}_3 - \text{CH}_2)_3\text{B} \xrightarrow{\text{H}^+} \text{CH}_3 - \text{CH}_3$
 $(\text{CH}_3 - \text{CH}_2)_3\text{B} \xrightarrow[\text{NaOH}]{\text{AgNO}_3} \text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$

(2) (C). Due to symmetrical crystal structure C_6H_{14} has maximum melting point.

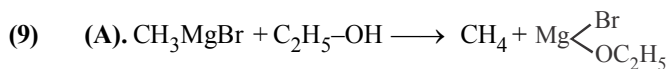
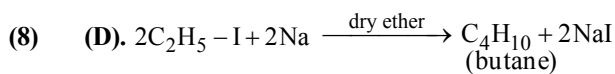
(3) (C). Reaction is Reed reaction and product is sulphonyl chloride.

(4) (A). Reducing metal/HCl as Zn/HCl or Zn/NaOH or Zn/ CH_3COOH or Zn-Cu couple and alcohol reduces alkyl halide to alkane.

(5) (B). When aqueous solution of Na or K salt of monocarboxylic acid, saturated dicarboxylic, unsaturated dicarboxylic acid are electrolysed it gives symmetrical alkane, alkene, alkyne respectively.

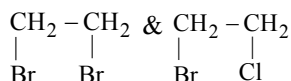


will give neopentane on decarboxylation.



(10) (A). Halogenation of alkanes involves substitution as well as oxidation of alkanes.

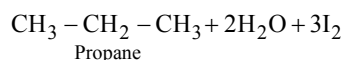
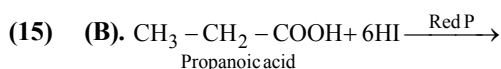
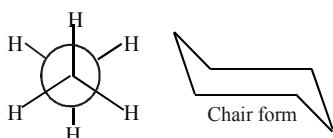
(11) (B). In the presence of NaCl solution the products are



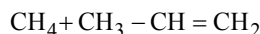
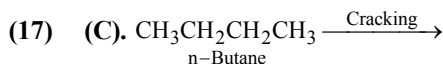
(12) (D). $CH_3CH_2CH_2CH_3$ has the lowest boiling point.

(13) (A). Intermediate trialkyl borane react with NH_2Cl in NaOH and gives same carbon number alkyl amine.

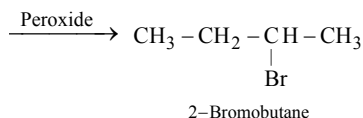
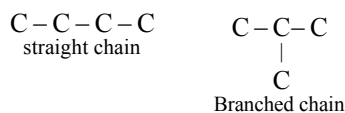
(14) (B). In ethane staggered form and in cyclohexane chair form is more stable.



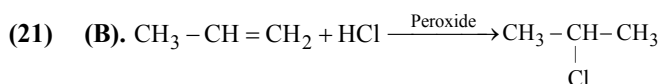
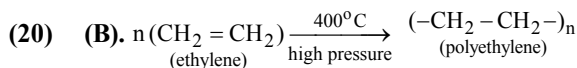
(16) (B). Tetraethyl lead is anti-knocking agent it increases the octane number of the fuel.



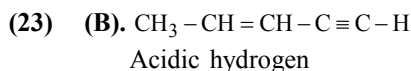
(18) (C). Formation of branches in the chain of C atoms



Anti-markonikov's rule is not applicable to symmetrical alkenes.

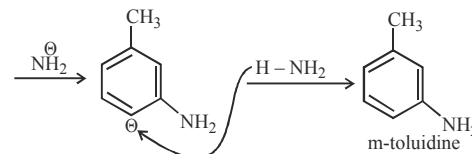
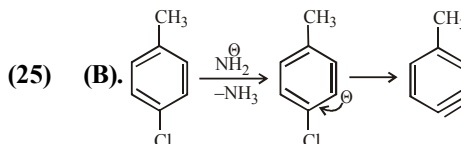
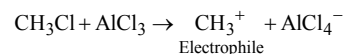


Peroxide rule is applicable only to HBr.



(H atom attached to triple bond) is present therefore it gives reaction with ammoniacal $AgNO_3$.

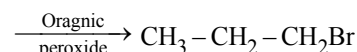
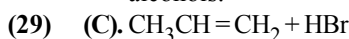
(24) (D). $AlCl_3$ is an electron deficient compound. It generates electrophile in the reaction



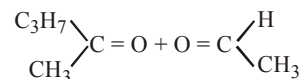
(26) (C). Reaction is named as Oxo and Carbonylation. If $CO + H_2$ is taken than the reaction is named as a hydroformylation.

(27) (A). NBS is used for the bromo substitution of allylic hydrogen.

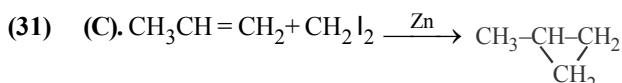
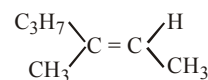
(28) (B). Hydroboration-oxidation transforms alkenes into alcohols.



(30) (B). Products of ozonolysis are



Hence, the structure of an alkene is



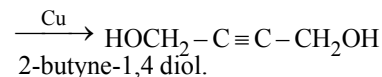
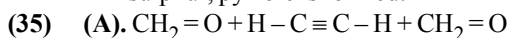
(32) (D). In eclipsed conformation hydrogen atoms attached to two carbons are as closed together.

In staggered conformation hydrogens are as far apart as possible.

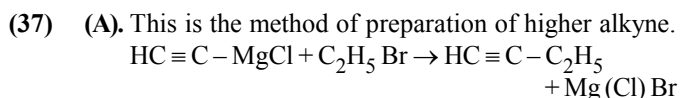
In Sawhorse projections the molecule is viewed along the molecular axis.

(33) (C). Terminal hydrogen is acidic therefore with ammonical cuprous chloride and ammoniacal silver nitrate respectively precipitate is formed (Red and white)

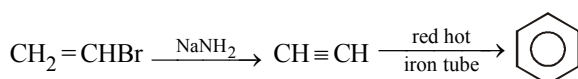
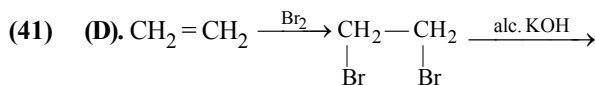
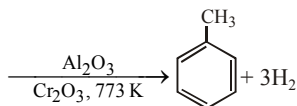
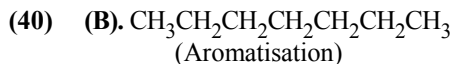
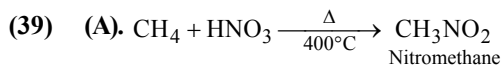
(34) (D). In the presence of hot iron pyrite thiophene is formed as a product, when NH_3 is taken at the place of sulphur, pyrrole is formed.



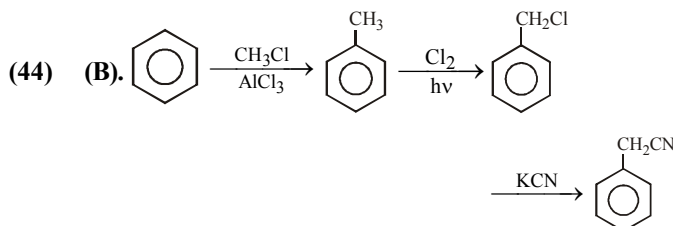
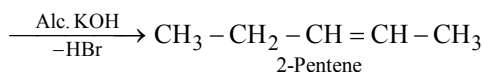
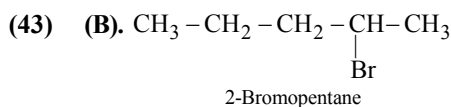
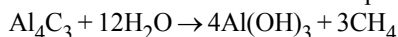
(36) (C). 2-butyne is the chief product according to Saytzeff's rule.



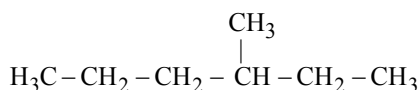
(38) (D). Acetylene contains two active hydrogen atoms.



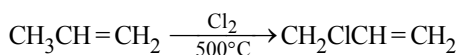
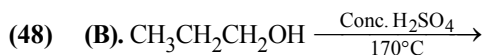
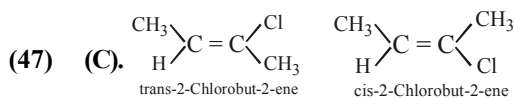
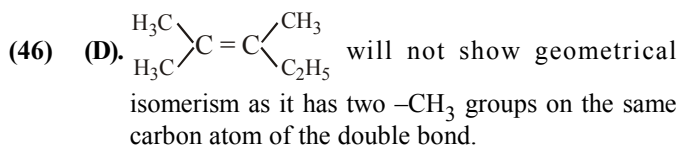
(42) (D). Methane is prepared by action of water or dilute HCl on aluminium carbide at room temperature.



(45) (C). 3-Methylhexane can yield seven different monochlorinated products on chlorination.

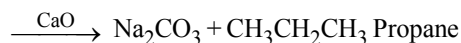
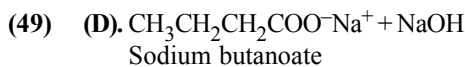


Each carbon atom on chlorination gives a different product.



(A)

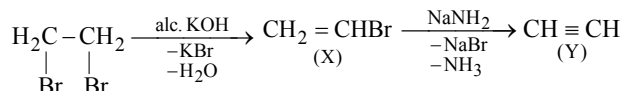
(B)



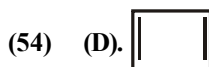
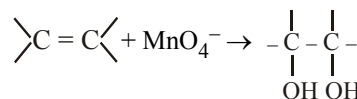
(50) (B). Only terminal alkynes react with ammoniacal silver nitrate to give white precipitate of silver acetylides.

(51) (A). neo-Pentane or 2,2-dimethylpropane has only primary hydrogen hence it can give only monochloro derivative. All other compounds have 1° , 2° and 3° hydrogens hence they give mono, di or trisubstituted products.

(52) (C).

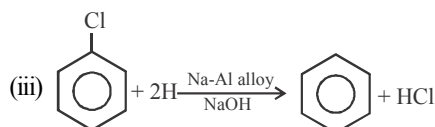
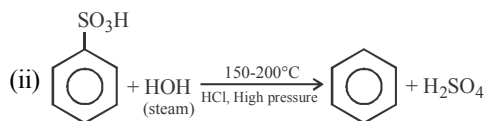
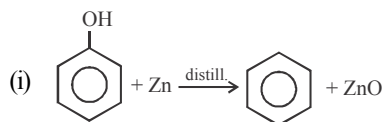


(53) (C). Baeyer's reagent (alk. KMnO_4) which is pink in colour is decolourised due to presence of unsaturation.



$$4n + 2 = 4 \text{ or } 4n = 4 - 2 = 2; n = 0.5$$

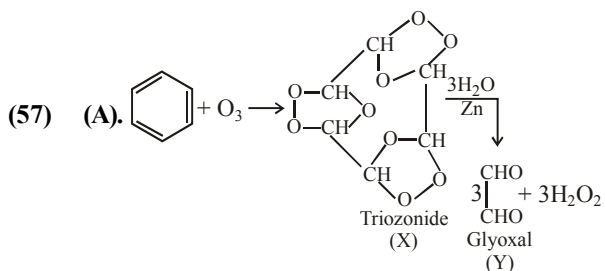
(55) (B).

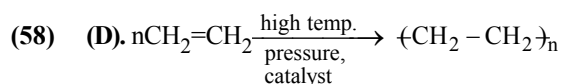


(56) (A). In Wurtz reaction, two molecules of RCl combine to give R-R , 3,8-Dimethyldecane can be formed by combining two molecules of

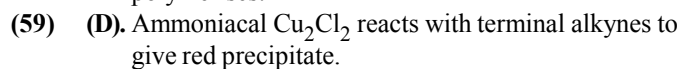


1-Chloro-3-methylpentane

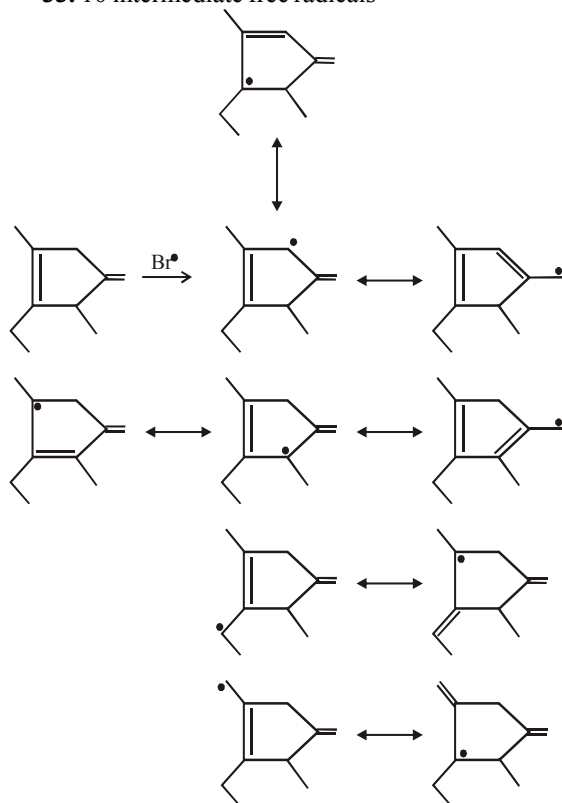
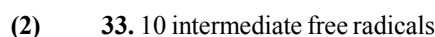
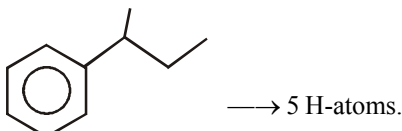
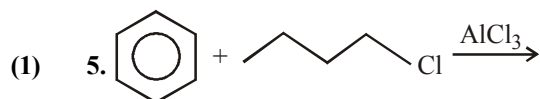




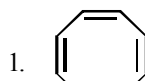
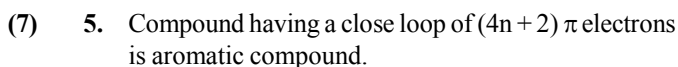
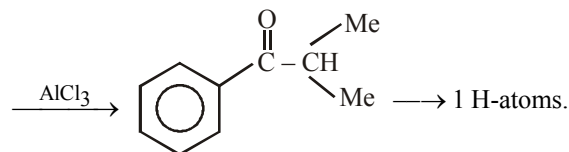
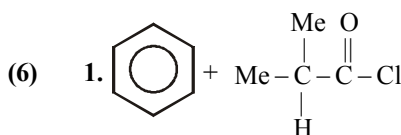
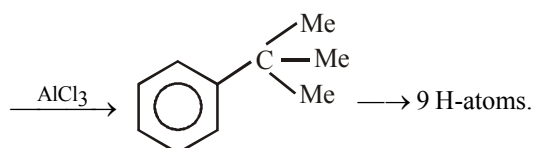
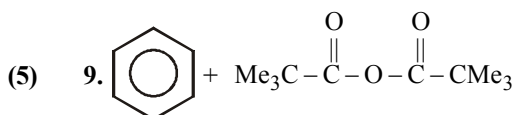
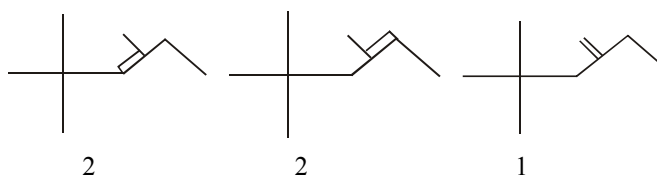
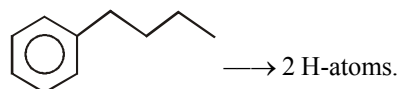
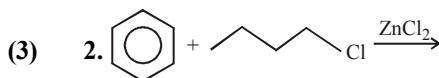
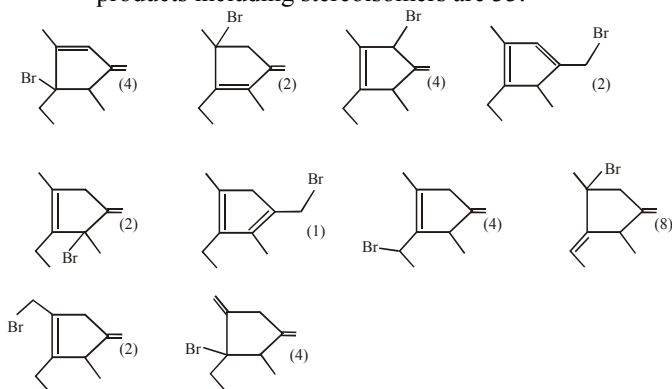
A linear polyethene polymer is formed when ethene polymerises.



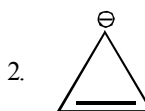
EXERCISE-3



So 10 structural isomeric products are formed and total products including stereoisomers are 33.



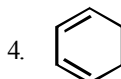
Not aromatic due to non planar tub shape structure.



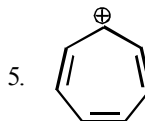
Antiaromatic due to close loop of $4\pi e^-$



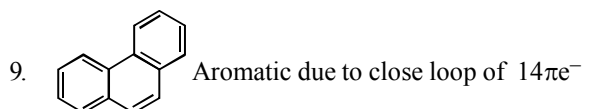
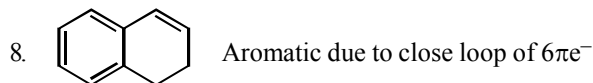
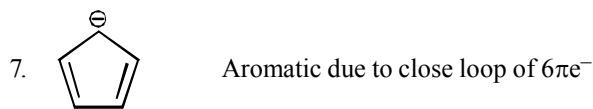
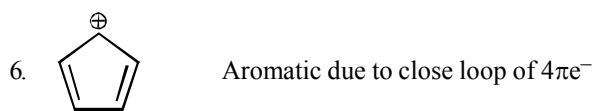
Aromatic due to close loop of $2\pi e^-$



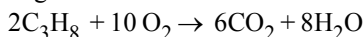
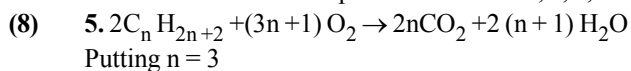
Not aromatic due to absence of close loop of electrons.



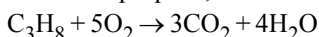
Aromatic due to close loop of $6\pi e^-$



Number of aromatic compounds is five i. e. 3, 5, 7, 8 and 9.

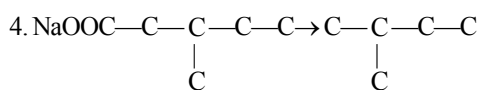
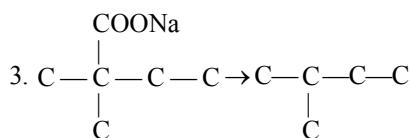
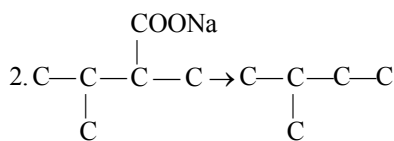
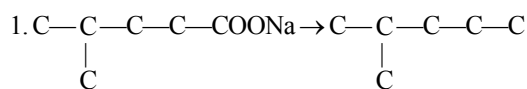


For 1 mole of propane, we have

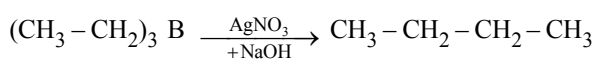
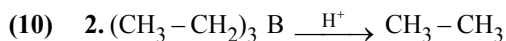


Hence required mole of $O_2 = 5$.

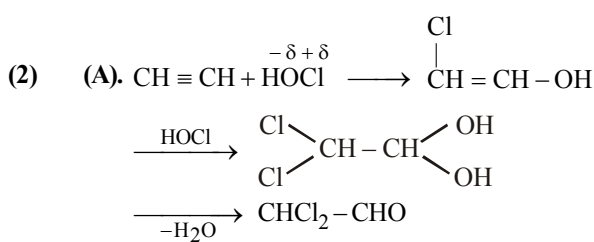
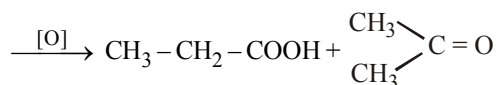
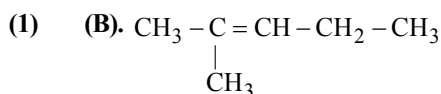
(9) 4.



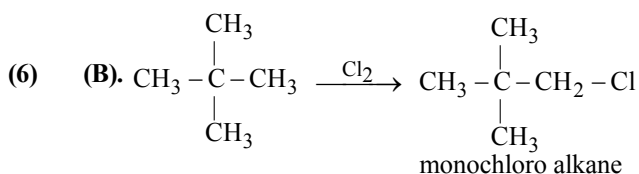
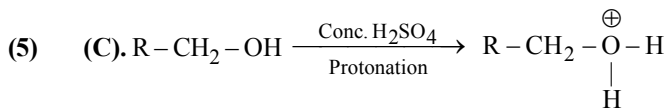
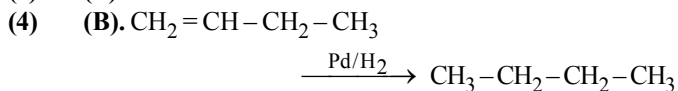
Total 4 isomeric structures.



EXERCISE-4



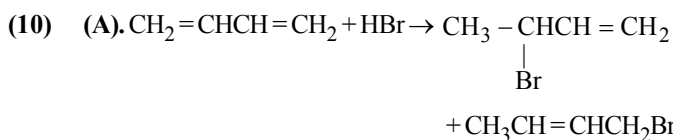
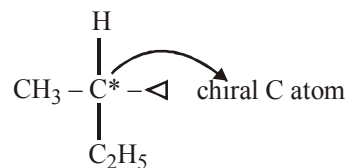
(3) (B).



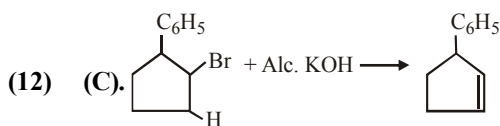
(7) (C).

(8) (D). Branched alkane have lower surface area so they possess low Boiling point.

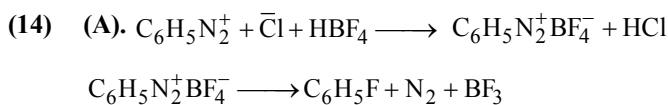
(9) (C). Optical active molecule



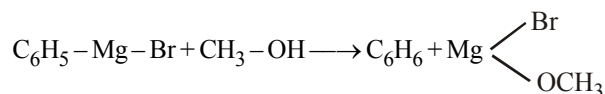
(11) (C).

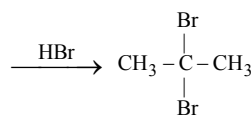
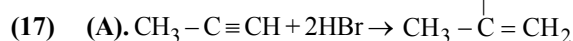
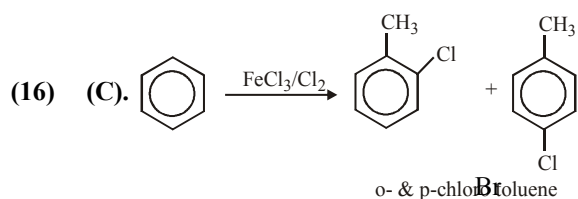


(13) (A).

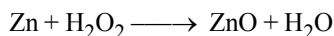
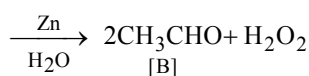
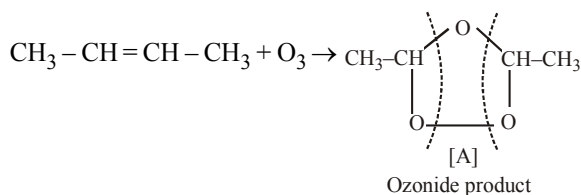


(15) (A).

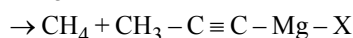
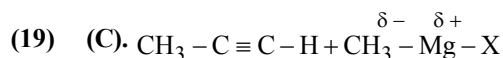




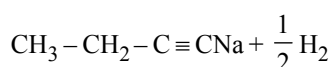
(18) (C).



So, B is $\text{CH}_3 - \text{CHO}$



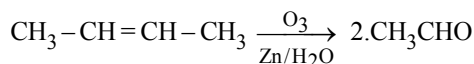
(20) (A). 1-alkynes react with sodium because they have acidic hydrogen.



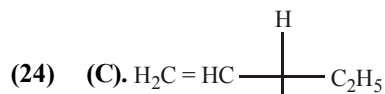
(21) (D).

(22) (D). Terminal alkenes never show geometrical isomerism and non-terminal alkene with 2 different groups attached to each atom having restricted rotation is capable of showing geometrical isomerism.

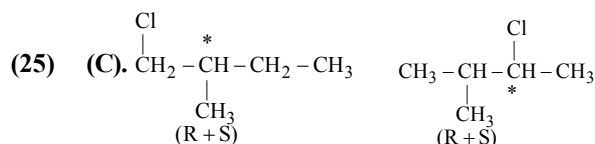
(23) (C). 2-butene is symmetrical alkene



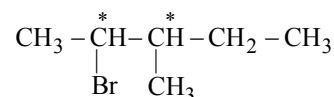
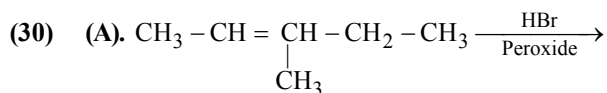
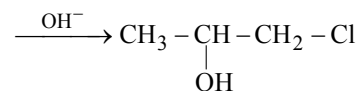
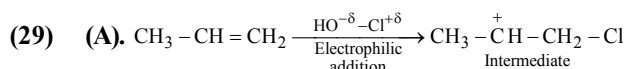
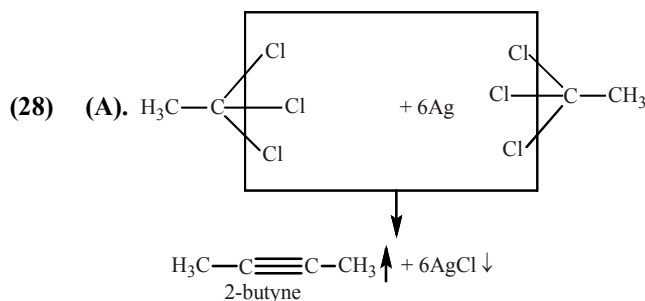
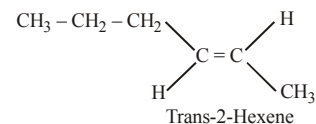
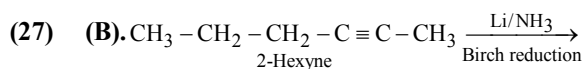
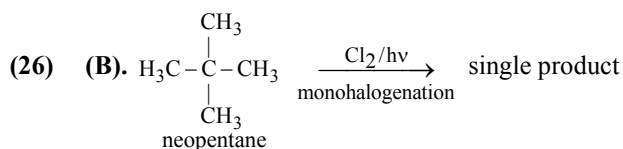
Molar mass of CH_3CHO is 44 u.



Only 3-methylpentene has a chiral carbon

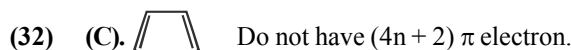
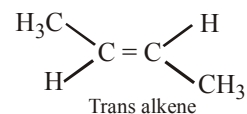
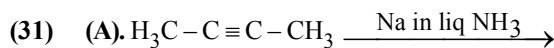


Four monochloro derivatives are chiral.

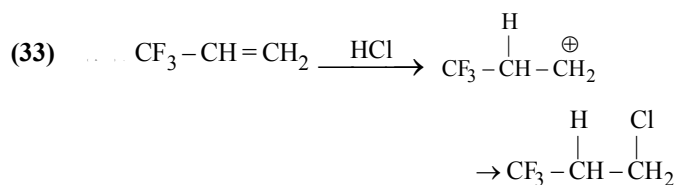


Number of stereoisomers = $2^n = 2^2 = 4$

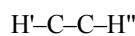
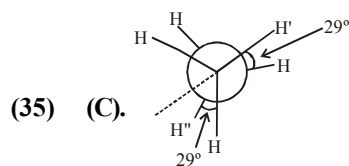
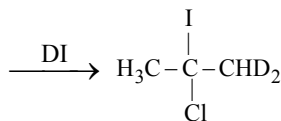
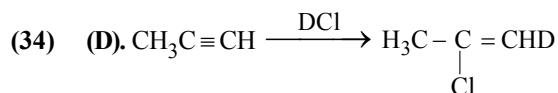
[n = Number of chiral carbon atoms]



It has $4n\pi$ electrons. So it is Anti aromatic.

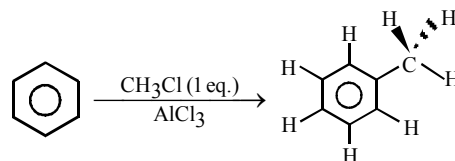
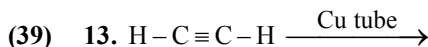
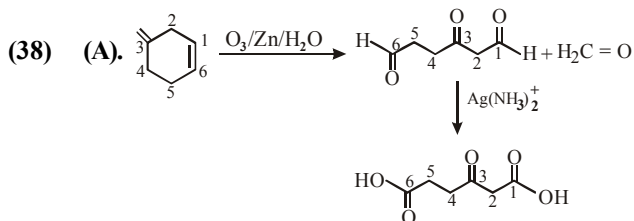
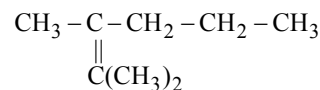
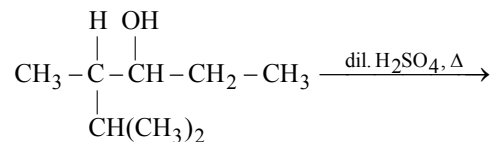
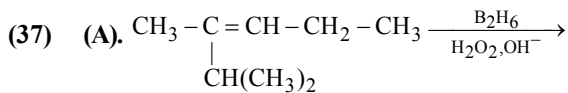
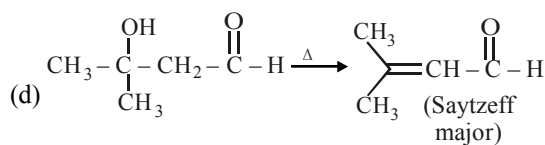
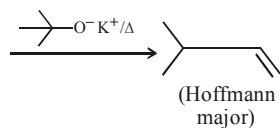
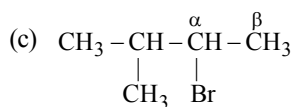
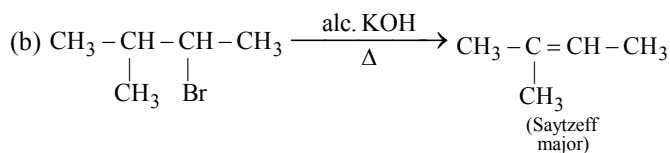
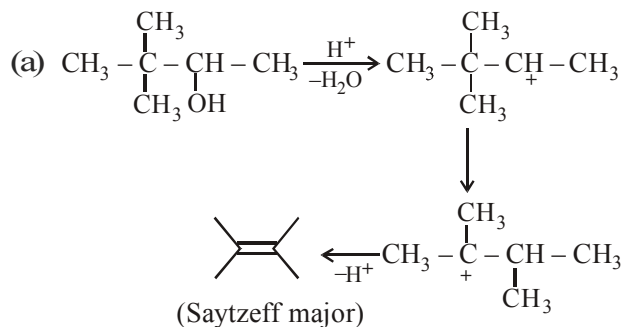


Due to higher e^- withdrawing nature of CF_3 group. It follow anti markovnikoff product.

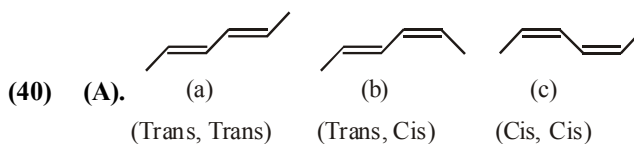


Hence angle between $\text{H}'-\text{C}-\text{C}-\text{H}''$ is $(120^\circ + 29^\circ) = 149^\circ$.

(36) (A).



Number of atoms in one plane = 13.

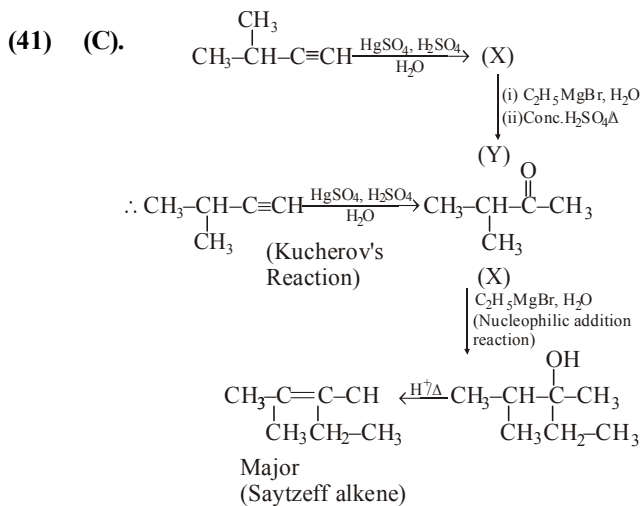


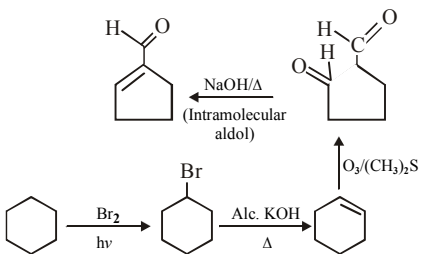
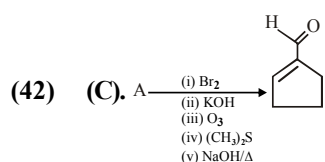
\therefore Generally trans is more stable then cis form.

Heat of combustion (HOC) $\propto \frac{1}{\text{Stability}}$

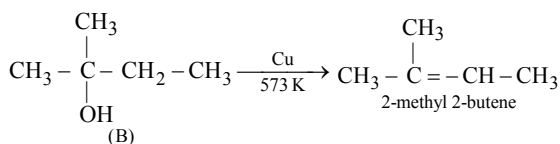
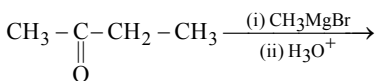
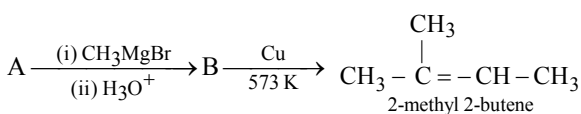
Stability : $a > b > c$

HOC : $c > b > a$





(43) (66.67)



C $\Rightarrow 12 \times 4 = 48$

H $\Rightarrow 8 \times 1 = 8$

O $\Rightarrow 16 \times 1 = 16$

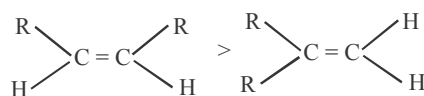
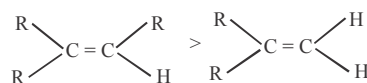
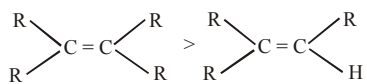
Total 72

% of C = $\frac{48}{72} \times 100 = 66.66\%$

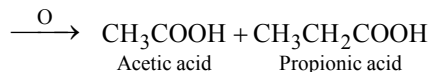
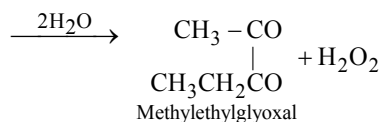
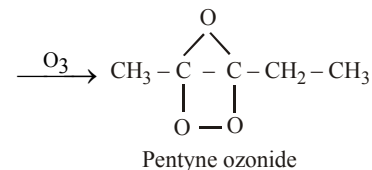
EXERCISE-5

(1) (B). Heat of hydrogenation of alkene $\propto \frac{1}{\text{Stability of alkene}}$

Hence the alkene which will react fastest with H₂ will be the least stable. Among the given options the compound having least number of alkyl groups (R) will be the least stable. Further the relative rates of hydrogenation decrease with increase of steric hindrance. Order of stability :

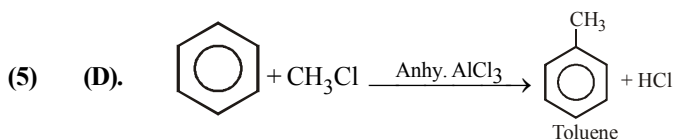
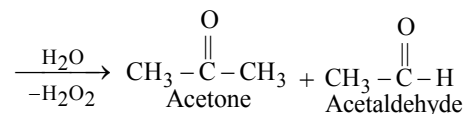
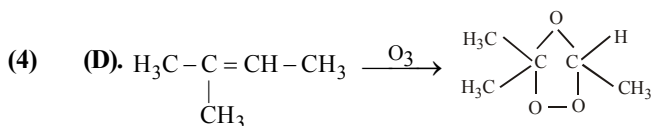
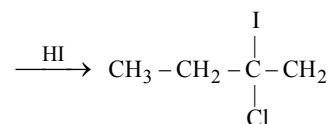
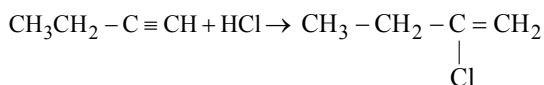


(2) (B). CH₃-C≡C-CH₂-CH₃



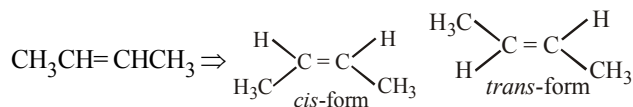
The glyoxal formed as an intermediate is oxidised by H₂O₂ to give the acids.

(3) (C). This reaction occurs according to Markonikov's rule which states that when an unsymmetrical alkene undergo hydrohalogenation, the negative part goes to that C-atom which contain lesser number of H-atom.



(6) (B). HONO₂ + H₂SO₄ \rightarrow NO₂⁺ + H₂O + HSO₄⁻
Nitric acid acts as a base by accepting a proton.

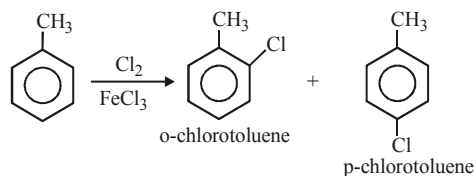
(7) (A). Compounds which have at least one double bond (C=C) and the groups attached with double bonded carbon atoms are different, exhibit geometrical isomerism.



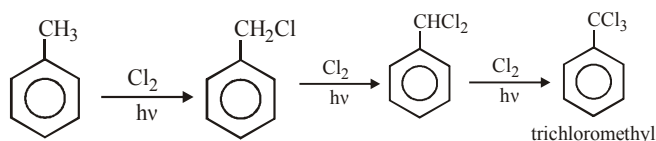
- (8) (B). Lower hydrocarbons exist in gaseous state while higher ones are in liquid state or solid state.

On cracking or pyrolysis, the hydrocarbon with higher molecular mass gives a mixture of hydrocarbons having lower molecular mass. Hence, we can say that by cracking a liquid hydrocarbon can be converted into a mixture of gaseous hydrocarbons.

- (9) (C). In the presence of halogen carrier, electrophilic substitution occurs while in the presence of sunlight, substitution occurs.



(∵ -CH₃ is an o/p directing group.)

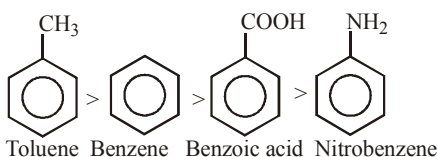


- (10) (A). The conformation in which the heavier groups are present at maximum possible distances, so that the forces of repulsion get weak, is more stable.

Among the given conformation of n-butane, the conformation is most stable as in it the bulkier group (ie, CH₃ group) are present at maximum possible distance.

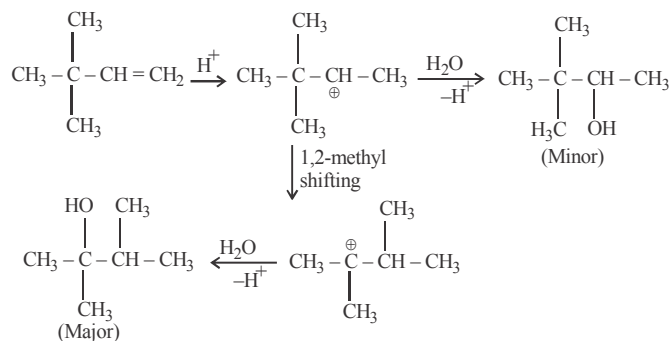
- (11) (D). The conformation (D) is most stable because of intermolecular H-bonding.

- (12) (C). Electrophilic rate order

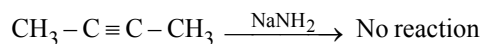
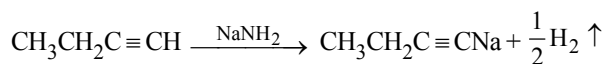


Toluene is most reactive

- (13) (A).



- (14) (A). NaNH₂ is used to distinguish between 1-butyne and 2-butyne.

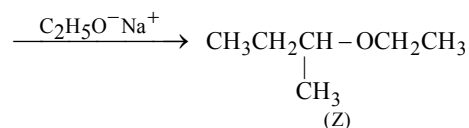


- (15) (D). Friedal Craft reaction fails when strong deactivating group is attached with benzene ring.

- (16) (B). Benzyl free radical is aromatic as per

Huckel's rule it has 6π electrons present in p-orbital of carbon atoms involved in formation of benzene ring (Aromatic nature).

- (17) (D). $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{H}_2\text{O}_2} \text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}}-\text{CH}_3$ (Y)



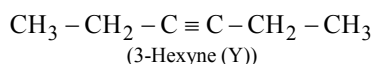
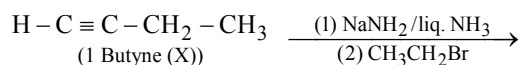
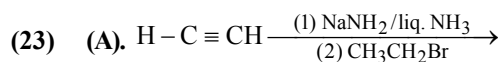
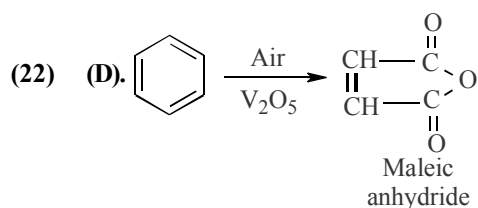
- (18) (A). Ethalpy of hydrogenation is inversally proportional to stability of alkene.

- (19) (A). π-bond electrons

$$= \text{Number of double bond} \times 2 = 4 \times 2 = 8\pi \text{ electrons}$$

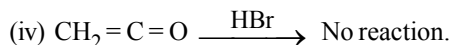
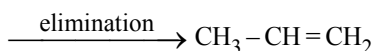
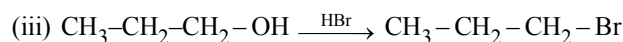
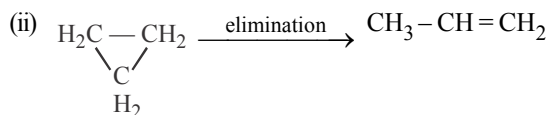
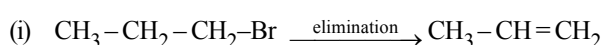
- (20) (D).

- (21) (C).

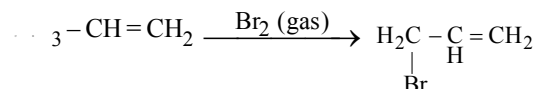


(24) (D). The staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain.

(25) (C). $\text{H}_2\text{C}=\text{C}=\text{O}$, has only two carbon atom, cannot be converted into propene as the conditions are given.

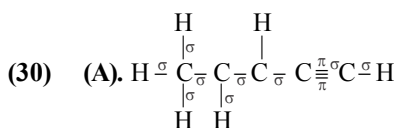
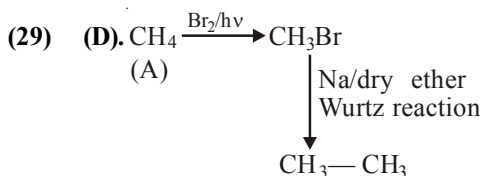


(26) (A). Gaseous Bromine reacts with alkene to give allylic substituted product by free radical mechanism



(27) (A). Biphenyl is a planar system, where all the carbon atoms and H-atoms are in same plane. All carbon atom is sp^2 hybridised and its geometry is trigonal planar.

(28) (C). In conformation bond angle and bond length remain same.



Number of σ bonds = 10
 and number of π bonds = 3

(31) (B).