Hydrocarbons (Alkanes, Alkenes, Alkynes & Benzene)

Contents

JEE (Advanced) Syllabus

Alkanes : Halogenation of alkanes
Alkenes : Electrophilic addition reactions of alkenes with X_2, HX, HOX and H_2O; Acid catalysed hydration of alkenes and alkynes (excluding the stereochemistry of addition and elimination)
Alkynes : Electrophilic addition reactions of alkynes.
Benzene: Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of o-, m- and p-directing groups in monosubstituted benzenes.

JEE (Main) Syllabus

Alkanes : Chemical reactions including free radical mechanism of halogenation
Alkenes : Chemical reactions: addition of hydrogen, halogen, water, hydrogen halides (Markovnikov's addition and peroxide effect),
Alkynes : Chemical reactions: acidic character of alkynes, addition reaction of - hydrogen, halogens, hydrogen halides and water.
Benzene: Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of o-, m- and p-directing groups in monosubstituted benzenes.

1. Alkanes

Alkanes are saturated hydrocarbons having general formula C_nH_{2n+2}. Alkanes are colourless, odourless and non-polar compounds and are also known as paraffins.

1.1. Physical properties of alkanes

(a) CH_4 to C_4H_{10} are gases, Neopentane is also a gas but n-pentane and isopentane are low boiling point liquids. Next members from C_5 to C_{17} are colourless liquids and above C_{17} are waxy solids at 298 K.

(b) **Density** : Density of alkanes increases with increase in molecular weight and becomes constant at around 0.8 g/mL. Thus all alkanes are lighter than water.

(c) **Solubility** : Alkanes being non polar and thus insoluble in water but soluble in non-polar solvents (C_6H_6, CCl_4 ,ether etc). The solubility of alkanes decreases with increase in molecular weight. Liquid alkanes are themselves good non-polar solvents.

(d) **Boiling point** : Boiling point increases with molecular weight (for n-alkanes).

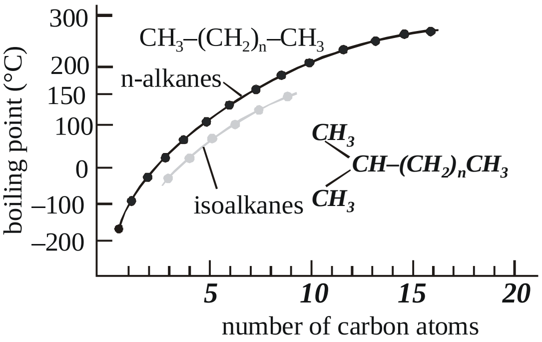
Note: (i) Van der waal's forces of attraction increases with molecular weight as well as surface area of molecule. Order of boiling point → Pentane < Hexane < Heptane

(ii) The shape approaches to spherical when branching increase which results in decrease of Van der waals forces (as surface area decreases).

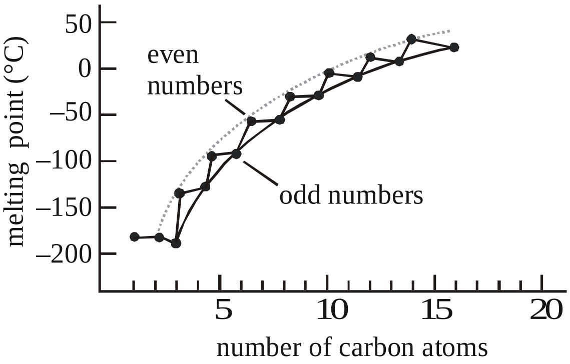
$$\text{Boiling point of isomers of alkanes} \propto \frac{1}{\text{number of side chains}}$$

Thus boiling point order is : n–Pentane > Isopentane > Neopentane

(iii) Variation of boiling point with number of carbon atoms takes place as follows :



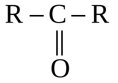
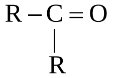
(e) **Melting point :** Melting point of alkanes do not show regular trend. Alkanes with even number of carbon atoms have higher melting point than alkanes with odd number of carbon atoms. The abnormal trend in melting point is due to the fact that alkanes with odd number of carbon atoms have their end carbon atom on the same side and in alkane with even number of carbon atom have their end carbon atom on opposite side.



Thus alkanes with even carbon atoms are packed closely in crystal lattice to permit greater intermolecular attractions.

Melting point order : Neopentane > n-pentane > isopentane
: $C_3H_8 < CH_4 < C_2H_6 < C_4H_{10}$ (n-butane)< C_5H_{12}(n-pentane)
: Isobutane □ Isopentane < n-butane < neopentane

1.2 General methods of preparation of alkanes

S. No	Name	Substrate	Reagent	Product
1	Sabatier Senderens reaction	R–C≡CH or R–CH=CH_2	H_2, Ni	$RCH_2–CH_3$
2	Reduction of alkyl halides	R–X	Zn-Cu, HCl or Red P + HI or $LiAlH_4$	RH
3	Acid base reaction of Grignard reagent	R–Mg–X	H_2O or ROH or NH_4Cl	RH
4	Wurtz reaction	RX	Na, dry ether	R–R
5	Frankland reaction	RX	Zn, dry ether	R-R
6	Clemensen reduction	 $R-\underset{\underset{O}{\parallel}}{C}-R$	Zn-Hg, Conc. HCl	RCH_2R
7	Wolff Kishner reduction	 $R-\underset{\underset{R}{\vert}}{C}=O$	NH_2-NH_2, KOH	RCH_2R
8	Soda lime decarboxylation	RCOONa	NaOH + CaO heat	RH
9	Kolbe electrolysis	RCOONa	Electrolysis	R–R
10	Hydrolysis of carbide	Al_4C_3	H_2O	CH_4

1.3. Chemical reactions of alkanes

Characteristic reaction of alkanes is **free radical substitution** reaction. These reactions are generally chain reactions, which are completed in three steps.

(i) Chain initiation (ii) Chain propagation (iii) Chain termination

1.3.1 Halogenation of alkanes

$$R-H + X_2 \xrightarrow[250^\circ - 400^\circ C]{\text{UV Light or temp}} R-X + HX$$

(a) Mechanism

(i) Chain initiation → It is an endothermic step.

$$X_2 \xrightarrow[250^\circ - 400^\circ C]{\text{UV or temp.}} 2\dot{X}$$

(ii) Chain propagation → Repeated steps, quantum yield is very high (with one photon of light).

$$\dot{X} + R-H \xrightarrow{\text{rds}} \dot{R} + HX$$

$$\dot{R} + X-X \longrightarrow R-X + \dot{X}$$

Formation of alkyl free radical is rate determining step.

(iii) Chain termination → It is always **exothermic.**

$$\dot{X} + \dot{X} \longrightarrow X_2$$

$$\dot{R} + \dot{R} \longrightarrow R-R$$

$$\dot{R} + \dot{X} \longrightarrow R-X$$

(b)

Steps of halogenation	Value of ΔH for each step (Kcal/mole)			
	F	Cl	Br	I
(i) $X_2 \longrightarrow 2\dot{X}$	+ 38	+ 58	+46	+36
(ii) $\dot{X} + CH_4 \longrightarrow \dot{C}H_3 + HX$	– 32	+ 1	+ 16	+ 33
(iii) $\dot{C}H_3 + X_2 \longrightarrow CH_3X + \dot{X}$	– 70	– 26	– 24	– 20

(c) Reactivity

Reactivity of X_2 : $F_2 > Cl_2 > Br_2 > I_2$
Reactivity of H : 3°H > 2°H > 1° H

Rate of halogenation ∝ Order of stability of alkyl free radical

$$Ph_3\dot{C} > Ph_2\dot{C}H > Ph-\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > (CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

Note : **(i)** With F_2 alkanes react so vigorously even in the dark and at room temperature. So, reactant is diluted with an inert gas.

(ii) Iodination is reversible reaction, since HI formed as a by product and it is a strong reducing agent and reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidising agent like HIO_3, HNO_3 or HgO.

$$R–H + I_2 \rightleftharpoons R–I + HI \quad \left[\begin{array}{l} 5HI + HIO_3 \longrightarrow 3H_2O + 3I_2 \\ 2HI + HgO \longrightarrow I_2 + H_2O + Hg \\ 2HI + 2HNO_3 \longrightarrow I_2 + 2H_2O + NO_2 \end{array}\right]$$

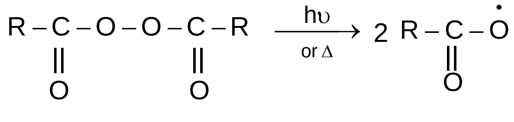
(iii) When equimolar amount of methane and Cl_2 is taken, a mixture of four possible products are formed, but when we take excess of CH_4 then yield of CH_3Cl will be high.

eg.1 $$CH_4 \xrightarrow[h\upsilon]{Cl_2} \underset{HCl}{\underset{+}{CH_3Cl}} \xrightarrow[h\upsilon]{Cl_2} \underset{HCl}{\underset{+}{CH_2Cl_2}} \xrightarrow[h\upsilon]{Cl_2} \underset{HCl}{\underset{+}{CHCl_3}} \xrightarrow[h\upsilon]{Cl_2} \underset{HCl}{\underset{+}{CCl_4}}$$

(d) In a chain reaction following reagents are involved -

(i) Initiators → They initiate the chain reaction. Initiators are peroxide (R_2O_2), peresters, diazo compounds etc.

$$R-O-O-R \xrightarrow[\text{or } \Delta]{h\upsilon} R\dot{O}$$



$$R-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-R \xrightarrow[\text{or } \Delta]{h\upsilon} 2\ R-\underset{\underset{O}{\|}}{C}-\dot{O}$$

(ii) Inhibitors → A substance that slow down or stop the reaction is known as inhibitors.
O_2 and p-benzoquinone are good inhibitors.

$$\dot{R} + O_2 \longrightarrow R-O-\dot{O} + \dot{R} \longrightarrow R-O-O-R$$

All reactive alkyl free radicals are consumed by O_2 so reaction stops for a period of time.

(e) Relative yields

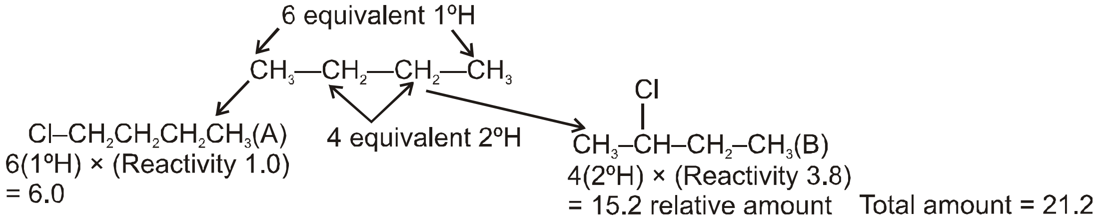
Relative amounts of the various isomers differ remarkably depending upon the halogen used. It is observed that chlorination gives mixture in which no isomer greatly dominates while, in bromination gives a mixture in which one isomer dominates greatly (95% – 99%),

Reactivity v/s selectivity principle → The more reactive is halogen less selective it will be, so the more reactive chlorine free radical is less selective and more influenced by the probability factor and the less reactive bromine radical is more selective and less influenced by the probability factors.
Based on relative reactivity of different types of H, percentage of each in the product mixture can be calculated.

(i) Probability factor : This factor is based on the number of each kind of H atom in the molecule.

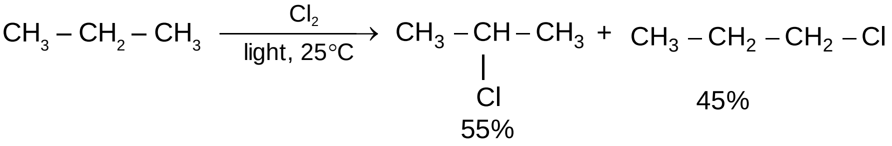
(ii) Relative rate of hydrogen : The order of reactivity is 3° > 2° > 1°, the experimental relative rate per hydrogen atom is

Primary	Secondary	Tertiary	Halogenation
1 :	3.8 :	5	For chlorination at 25°
1 :	82 :	1600	For bromination at 127°C



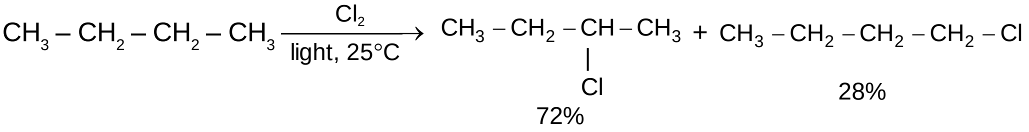
% yield A = $\frac{6}{21.2} \times 100 = 28.3\ \%$; % yield B = $\frac{15.2}{21.2} \times 100 = 71.\%$

eg.2



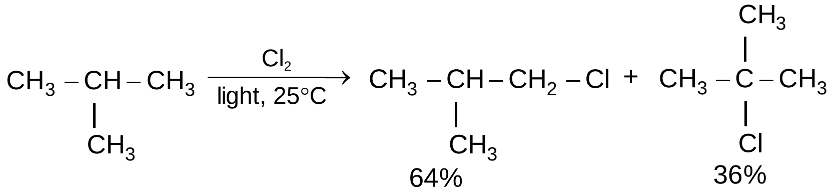
$$CH_3-CH_2-CH_3 \xrightarrow[\text{light, 25°C}]{Cl_2} \underset{\underset{55\%}{Cl}}{CH_3-\underset{|}{CH}-CH_3} + \underset{45\%}{CH_3-CH_2-CH_2-Cl}$$

eg.3



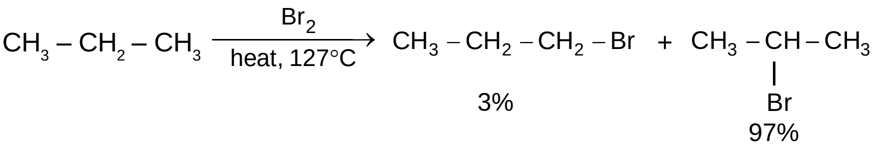
$$CH_3-CH_2-CH_2-CH_3 \xrightarrow[\text{light, 25°C}]{Cl_2} \underset{\underset{72\%}{Cl}}{CH_3-CH_2-\underset{|}{CH}-CH_3} + \underset{28\%}{CH_3-CH_2-CH_2-CH_2-Cl}$$

eg.4



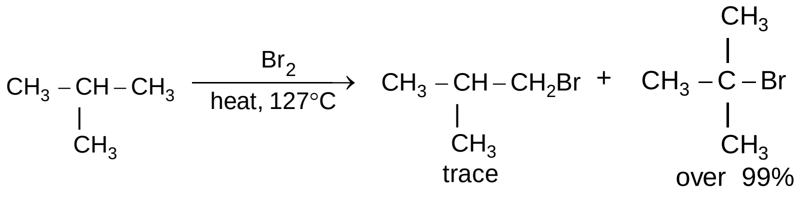
$$\underset{CH_3}{CH_3-\underset{|}{CH}-CH_3} \xrightarrow[\text{light, 25°C}]{Cl_2} \underset{\underset{64\%}{CH_3}}{CH_3-\underset{|}{CH}-CH_2-Cl} + \underset{\underset{36\%}{Cl}}{CH_3-\overset{CH_3}{\underset{|}{\overset{|}{C}}}-CH_3}$$

eg.5



$$CH_3-CH_2-CH_3 \xrightarrow[\text{heat, 127°C}]{Br_2} \underset{3\%}{CH_3-CH_2-CH_2-Br} + \underset{\underset{97\%}{Br}}{CH_3-\underset{|}{CH}-CH_3}$$

eg.6



$$\underset{CH_3}{CH_3-\underset{|}{CH}-CH_3} \xrightarrow[\text{heat, 127°C}]{Br_2} \underset{\underset{\text{trace}}{CH_3}}{CH_3-\underset{|}{CH}-CH_2Br} + \underset{\underset{\text{over 99\%}}{CH_3}}{CH_3-\overset{CH_3}{\underset{|}{\overset{|}{C}}}-Br}$$

1.3.2. Nitration

At ordinary temperature, alkanes do not react with HNO_3, but react with **vapours** of concentrated HNO_3 at 450° C. Since the reaction is carried out at high temperature the C—C bonds of alkanes break during the reaction and a mixture of nitroalkanes is formed.

$$R-H+HO-NO_2 \xrightarrow{400-500^0 C} R-NO_2+H_2O$$

Mechanism : (Free radical substitution)

Step – I $\quad HO-NO_2 \xrightarrow{\Delta} \dot{O}H+\dot{N}O_2$

Step – II $\quad R\text{-}H + \dot{O}H \longrightarrow \dot{R} + H_2O$

$$\dot{R}+HO-NO_2 \longrightarrow \underset{\text{(Product)}}{R-NO_2}+\dot{O}H$$

Step – III $\quad \dot{R}+\dot{N}O_2 \longrightarrow R-NO_2$

$$\dot{R}+\dot{O}H \longrightarrow R-OH \text{ (minor)}$$

$$\dot{O}H+\dot{N}O_2 \longrightarrow HONO_2$$

eg.7 $CH_3–CH_3 + HNO_3 \xrightarrow{450°C} CH_3CH_2NO_2 + CH_3NO_2 + H_2O$

1.3.3. Sulphonation

Alkanes react with fuming H_2SO_4 or oleum ($H_2S_2O_7$) to give alkane sulphonic acid.

$R - H + HO- SO_3H \rightarrow R - SO_3H + H_2O$

Mechanism : (Free Radical substitution)

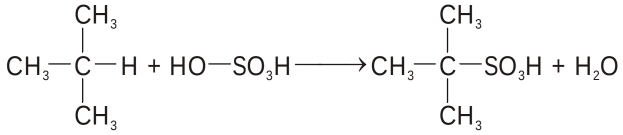
$$HOSO_3H \xrightarrow{400^\circ C} HO^\bullet + \dot{S}O_3H$$

$R–H + {}^\bullet OH \rightarrow R^\bullet + H_2O$

$R^\bullet + {}^\bullet SO_3H \rightarrow R–SO_3H$

$C_3H_8 + SO_3 \longrightarrow C_3H_7–SO_3H$

eg.8



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-H + HO-SO_3H \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-SO_3H + H_2O$$

2–Methylpropane 2–Methylpropane–2–sulphonic acid

1.3.4. Oxidation of alkanes

(a) Complete oxidation or combustion : Burn readily with non-luminous flame in presence of air or oxygen to give CO_2 and water with evolution of heat. Therefore, alkanes are used as fuels.

$$C_nH_{2n+2}+\left(\frac{3n+1}{2}\right)O_2 \longrightarrow nCO_2 + (n+1)\,H_2O + Q;\ (\Delta H = –ve)$$

(b) Incomplete oxidation : In limited supply of air gives carbon black and CO.

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

C–black (used in printing)

(c) Catalytic oxidation :

(i) Alkanes are easily converted to alcohols and aldehydes under controlled catalytic oxidation.

$$2CH_4 + O_2 \xrightarrow[523\,K,100atm]{Cu} 2CH_3OH$$

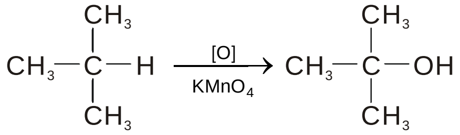
$$CH_4 + O_2 \xrightarrow[230^0C,100atm]{Mo_2O_3} HCHO + H_2O$$

(ii) Alkanes on oxidation in presence of manganese acetate give fatty acids.

$$CH_3(CH_2)_nCH_3 + O_2 \xrightarrow[high\,Temp]{(CH_3COO)_2Mn} CH_3(CH_2)_nCOOH + H_2O$$

(d) Ordinary alkanes resist oxidation but tertiary alkanes are oxidized to give tertiary alcohols by $KMnO_4$.

eg.9

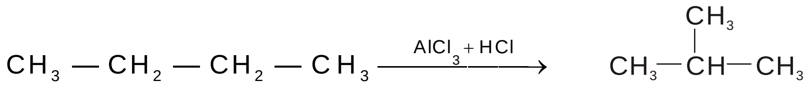


$$CH_3-C(CH_3)_2-H \xrightarrow[KMnO_4]{[O]} CH_3-C(CH_3)_2-OH$$

1.3.5. Isomerisation

Unbranched chain alkanes on heating with anhydrous $AlCl_3$ + HCl / 200^0C are converted in to branched chain alkanes. Branched chain alkanes are converted to more branched alkanes. Isomerisation of alkanes is of great importance in petroleum industry to increase the **octane number** of petrol (gasoline).

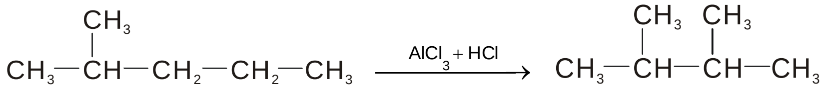
eg.10



$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3+HCl} CH_3-CH(CH_3)-CH_3$$

n-butane Isobutane

eg.11



$$CH_3-CH(CH_3)-CH_2-CH_2-CH_3 \xrightarrow{AlCl_3+HCl} CH_3-CH(CH_3)-CH(CH_3)-CH_3$$

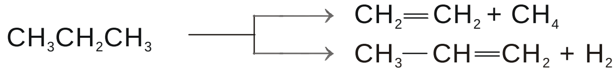
1.3.6. Pyrolysis or cracking or thermal decomposition

When alkanes are heated to 500-700^0C they are decomposed in to lower hydrocarbons. This decomposition is called pyrolysis. The mechanism of pyrolysis occurs via free radicals. In petroleum industry it is also termed as cracking.

eg.12 $CH_4 \xrightarrow{1000°C} C + H_2$

eg.13 $CH_3-CH_3 \xrightarrow[absence\,of\,air]{500°C} CH_2=CH_2 + H_2$

eg.14



$$CH_3CH_2CH_3 \rightarrow CH_2{=}CH_2 + CH_4$$
$$CH_3CH_2CH_3 \rightarrow CH_3-CH{=}CH_2 + H_2$$

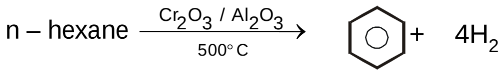
eg.15 n-Butane $\xrightarrow{Cracking}$ 1-Butene + 2–Butene + Ethane + Ethene + Propene + CH_4 + H_2

eg.16 n-hexane $\xrightarrow{773K}$ $(C_6H_{12} + H_2)$ or $(C_4H_8+C_2H_6)$ or $(C_3H_6 + C_2H_4+ CH_4)$

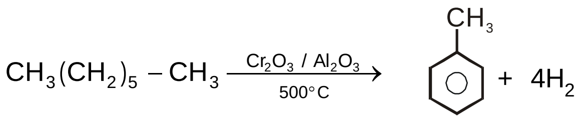
1.3.7. Hydroforming or dehydrogenation or catalytic reforming or aromatization

Unbranched higher alkanes (from 6 to 10 carbon atoms) when heated in presence of oxides of Cr, Mo, V on Al_2O_3 support at 500^0 C aromatic hydrocarbons are formed.

eg.17

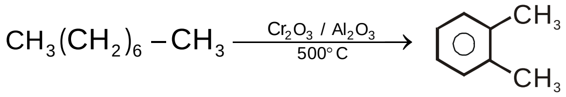


eg.18



n-heptane Toluene

eg.19



n-octane o-xylene

It provides an excellent method of passing from aliphatic to aromatic series.

1.4. Free radical addition & substitutions in alkenes/alkynes

1.4.1 Addition of HBr : Kharasch effect or Peroxide effect

General Reaction : $R-CH=CH_2 \xrightarrow{HBr/R_2O_2/h\nu} R-CH_2-CH_2-Br$

Mechanism :

$$\left.\begin{array}{l}(1)\ R-O-O-R \xrightarrow{h\nu} 2R\dot{O} \\ (2)\ R\dot{O} + HBr \longrightarrow ROH + Br^{\bullet}\end{array}\right] \text{......Chain initiation steps}$$

$$\left.\begin{array}{l}(3)\ R-CH=CH_2 + Br^{\bullet} \longrightarrow \underset{\text{(major)}}{R-\dot{C}H-CH_2-Br\ (2^\circ\dot{R})} + \underset{\text{(minor)}}{R-\underset{\displaystyle Br}{\underset{|}{C}H}-\dot{C}H_2\ (1^\circ\dot{R})} \\ (4)\ R-\dot{C}H-CH_2-Br + HBr \longrightarrow R-CH_2-CH_2-Br + Br^{\bullet} \\ \quad Br^{\bullet}\text{ repeats step (3).}\end{array}\right] \text{......Chain propagating steps}$$

Remarks

(1) When HBr is added to an unsymmetrical alkene in presence of sunlight and peroxide, then mainly an Anti Markovnikov's addition product is obtained.

(2) It is a free radical chain reaction.

(3) In presence of peroxide and sunlight $Br^{\bullet}$ is formed in chain initiation step.

(4) $Br^{\bullet}$ forms more stable alkyl radical by homolysis of C=C π bond.

(5) In the last step alkyl radical abstracts $H^{\bullet}$ from HBr and anti markownikov's product is obtained.

Note : In the presence of peroxide HI, HCl do not react by free radical mechanism because one of the step is endothermic. Overall only HBr will react by free radical mechanism in the presence of peroxide.

Markovnikov's rule

When reagent (asymmetrical HX, H_2O) adds to asymmetrical alkene eg. propene, isobutene etc. the addition occurs such that the nucleophile attaches itself to the carbon atom of the alkene bearing the least number of hydrogen and electrophile adds to the sp^2 carbon that is bonded with the greater number of hydrogen.

Regioselective reaction

A reaction in which two or more constitutional isomers could be formed but one of them predominates is called a regioselective reaction.

eg.20 $\underset{1-\text{Octene}}{n-C_6H_{13}CH=CH_2} \xrightarrow{HBr\ /\ R_2O_2} nC_6H_{13}CH_2-CH_2-Br$

2. Alkenes and Alkynes

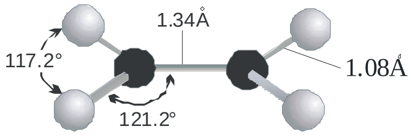
Alkenes

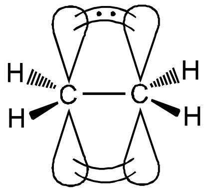
(1) Alkenes are unsaturated hydrocarbons with carbon–carbon double bonds.

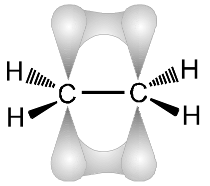
(2) These are represented by general formula C_nH_{2n} (one double bond).

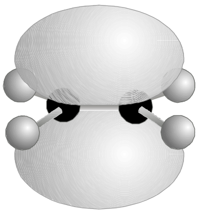
(3) Alkenes are also called as **olefins**, a term derived from olefiant gas, meaning "oil forming gas".

(4) The π e^- cloud is present above and below the plane of σ- bonded skeleton in alkene.









(5) Alkenes are among the most important industrial compounds and many alkenes are also found in plants and animals. Ethylene is the largest–volume industrial organic compound, used to make polyethylene and a variety of other industrial and consumer chemicals.

Alkenes polymerise to give many important polymers.

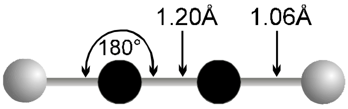
Alkynes

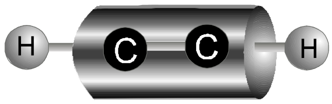
Alkynes are not as common in nature as alkenes, but some plants do use alkynes to protect themselves against disease or predators. Acetylene is by far the most important commercial alkyne. Acetylene is an important industrial feedstock, but its largest use is as the fuel for the oxyacetylene welding torch.

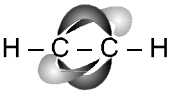
(1) The general formula of alkyne is C_nH_{2n-2}. (one triple bond)

(2) Alkynes are also called acetylenes because they are derivatives of acetylene.

(3) Two π bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** (90°) to each other, forming one π bond with electron density above and below the C – C sigma bond, and the other with electron density in front and in back of the sigma bond. This result in a cylindrical π electron cloud around σ bonded structure.



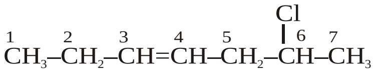
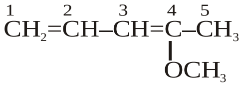
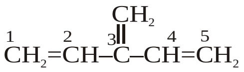
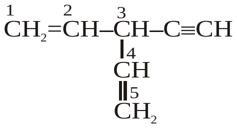
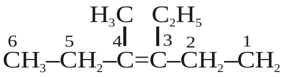
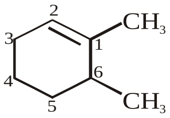
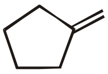
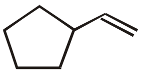
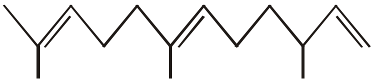
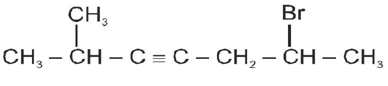




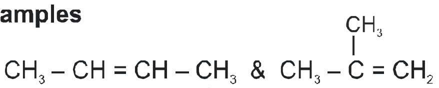
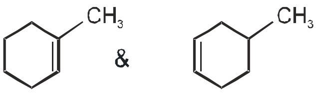
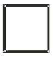
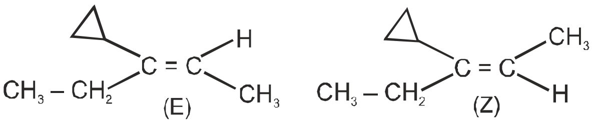
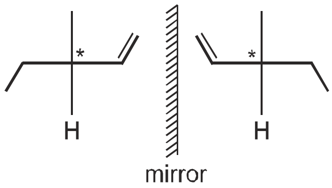
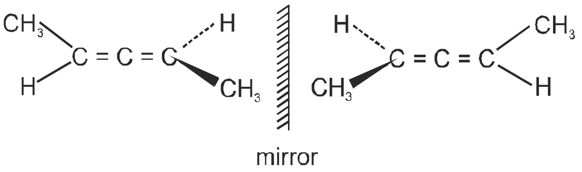
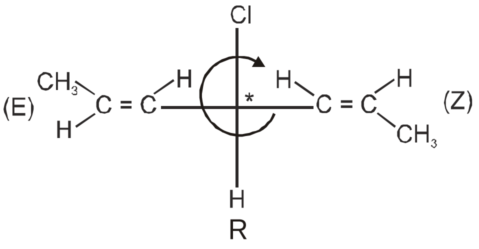
Comparative study of alkanes, alkenes & alkynes

S.No	Properties	Alkanes[CH_3–CH_3]	Alkenes [CH_2=CH_2]	Alkynes[CH≡CH]
1	Shape	Tetrahedral	Planar	Linear
2	Bond length(C-C) Å	1.54	1.32	1.20
3	Bond energy(C-C) ($KJmol^{-1}$)	415	615	835
4	Hybridization	sp^3	sp^2	sp
5	% s character	25%	33%	50%
6	pKa	50	44	25
7	Electronegativity	2.54	2.66	3.25
8	Rate of hydrogenation	–	less	more
9	Rate of electrophilic addition reaction	–	more	less
10	Heat of combustion	C_2H_6 (–373 kcal)	C_2H_4 (–337 kcal)	C_2H_2 (–317 kcal)
11	Density (g/cm^3)	C_3H_8 (0.50)	C_3H_6 (0.52)	C_3H_4 (0.67)

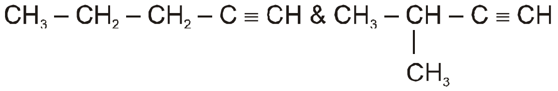
2.1. IUPAC Nomenclature

S.No.	Compound	Name	Type
1.	$(CH_3)C=CH_2$	2–Methylpropene (Isobutylene)	Alkene
2.	$CH_3-CH=CH-CH=CH_2$	Hexa–1, 4–diene	Isolated diene
3.	$CH_2=CH-CH=CH_2$	Buta–1,3–diene	Conjugated diene
4.	$CH_3-CH=C=CH-CH_3$	Penta–2,3–diene	Cumulatd diene
5.	 $\overset{1}{C}H_3-\overset{2}{C}H_2-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_2-\overset{Cl}{\overset{6}{C}}H-\overset{7}{C}H_3$	6–Chlorohept–3–ene	Alkene
6.	 $\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}H=\underset{OCH_3}{\overset{4}{C}}-\overset{5}{C}H_3$	4–Methoxypenta–1,3–ene	Conjugated diene
7.	 $\overset{1}{C}H_2=\overset{2}{C}H-\overset{CH_2}{\overset{\Vert}{\overset{3}{C}}}-\overset{4}{C}H=\overset{5}{C}H_2$	3–Methylenepenta–1,4–diene	Conjugated diene
8.	 $\overset{1}{C}H_2=\overset{2}{C}H-\underset{\underset{\overset{5}{C}H_2}{\overset{4}{C}H}}{\overset{3}{C}H}-C\equiv CH$	3–Ethynylenepenta–1,4–diene	Conjugated diene
9.	 $\overset{6}{C}H_3-\overset{5}{C}H_2-\overset{H_3C}{\overset{4}{C}}=\overset{C_2H_5}{\overset{3}{C}}-\overset{2}{C}H_2-\overset{1}{C}H_2$	3–Ethyl–4–methylhex–3–ene	Alkene
10.		1,6–Dimethylcyclohex–1–ene	Cycloalkene
11.	$CH_2=C=CH_2$	Propadiene (Alkene)	Cumulated diene
12.	$CH_2=C=O$	Ethenone	Alkene
13.		Methylenecyclopentane	Alkene
14.		Cyclopentylethene	Alkene
15.		3,7,11–trimethyldodeca–1,6,10–triene	Isolated triene
16.	 $CH_3-\overset{CH_3}{C}H-C\equiv C-CH_2-\overset{Br}{C}H-CH_3$	6-Bromo-2-methylhept-3-yne	

2.2. Isomerism

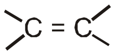
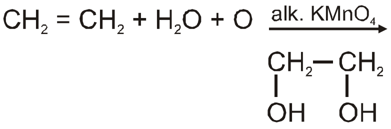
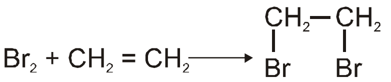
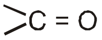
S.N.	Type	Category	Examples
(A)	Structural Isomerism	(i) Chain isomers	 **1.** $CH_3-CH=CH-CH_3$ & $CH_3-\overset{CH_3}{\overset{\mid}{C}}=CH_2$ **2.** 
		(ii) Positional isomers	**1.** $CH_2=CH-CH_2-CH_3$ & $CH_3-CH=CH-CH_3$  **2.** $CH_3-\overset{CH_3}{\overset{\mid}{C}}=CH-CH_3$ & $CH_3-\overset{CH_3}{\overset{\mid}{CH}}-CH=CH_2$ **3.** 
		(iii) Functional isomers	**1.**  & $CH_3-CH=CH-CH_3$ (Ring-chain Functional isomers) **2.** $CH_2=CH-CH=CH_2$ & $CH_3-C\equiv C-CH_3$
(B)	Stereo isomerism	(i) Geometrical Isomers (Geometrical Diastereomers)	**1.**  **2.**  **3.** 
		(ii) Optical isomers	**1.**  (smallest optically active alkene) **2.**  **3.**  configuration – R (since Z > E in priority order)

Any type of stereoisomerism does not arise in acetylenic bond (alkyne) due to linearity of $C \equiv C$ bond.

Type	**Categary**	**Examples**
Structural Isomerism	(i) Chain isomerism	 $CH_3-CH_2-CH_2-C\equiv CH$ & $CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{C}H}-C\equiv CH$
	(ii) Positional isomerism	$CH_3-CH_2-CH_2-C\equiv CH$ & $CH_3-CH_2-C\equiv C-CH_3$
	(iii) Functional isomerism	$CH_3-CH_2-C\equiv C-CH_3$ & $CH_3-CH=C=CH-CH_3$ & 

2.3. Laboratory test

(a) Alkenes

Functional Group	Reagent	Observation	Reaction	Remarks
 $>C=C<$	(1) Bayer's Reagent alk. dil. Cold $KMnO_4$	Pink Colour disappears	 $CH_2=CH_2+H_2O+O \xrightarrow{alk.\ KMnO_4} \underset{\displaystyle OH}{\underset{\vert}{CH_2}}-\underset{\displaystyle OH}{\underset{\vert}{CH_2}}$	Dihydroxylation
	(2) Br_2 / H_2O	Red Colour decolourises	 $Br_2+CH_2=CH_2 \longrightarrow \underset{\displaystyle Br}{\underset{\vert}{CH_2}}-\underset{\displaystyle Br}{\underset{\vert}{CH_2}}$ White ppt	Dibromination
	(3) O_3 (ozone)	 $>C=O$ Compounds	$H_2C=CH_2+O_3 \xrightarrow{Zn / H_2O} 2HCHO$	Ozonolysis

(b) Alkynes

Functional Group	Reagent	Observation	Reaction	Remarks
$-C\equiv C-$	(1) Bayer's Reagent alk. dil. Cold $KMnO_4$	Pink Colour disappears	$HC\equiv CH + H_2O + O \xrightarrow{alk.\ KMnO_4} OHC-CHO$	Hydroxylation
	(2) Br_2 / H_2O	Red Colour decolourises	$Br_2 + HC\equiv CH \longrightarrow CHBr_2-CHBr_2$ White ppt	Bromination
	(3) O_3 (ozone)	Acid Formed	$R-C\equiv C-R' \xrightarrow{O_3} RCOOH + R'COOH$	Ozonolysis

(c) Laboratory test of terminal alkynes [Acidic nature of terminal alkyne]

When triple bond comes at the end of a carbon chain. The alkyne is called a terminal alkyne.

$$\overset{\text{acidic hydrogen}}{\boxed{H}}-C\equiv C-CH_2CH_3$$

But-1-yne, a terminal alkyne

Functional Group	Reagent	Observation	Reaction
R−C≡C−H	(1) Cuprous chloride + NH_4OH	Red ppt.	$R-C\equiv CH + Cu_2Cl_2 \xrightarrow{NH_4OH} R-C\equiv C\,Cu\downarrow$ (red)
	(2)$AgNO_3$ + NH_4OH	White ppt.	$R-C\equiv CH + Ag^+ \longrightarrow R-C\equiv C\,Ag\downarrow$ (white)
	(3) Na in ether	Colourless gas	$HC\equiv CH + 2Na \longrightarrow Na-C\equiv C-Na + H_2\uparrow$

Note. Terminal alkynes are more acidic than other hydrocarbons due to more electronegative sp hybridised carbon. The polarity (acidity) of a C – H bond varies with its hybridization, increasing with the increase in percentage s character of the orbitals : **$sp^3 < sp^2 < sp$.**

Que. Acetylene hydrogens are acidic because:-

(A) Acetylene contains least number of hydrogen atoms.

(B) Acetylene has only one hydrogen atom at each carbon atom.

(C) Acetylene belongs to the class of alkynes with formula C_nH_{2n-2}.

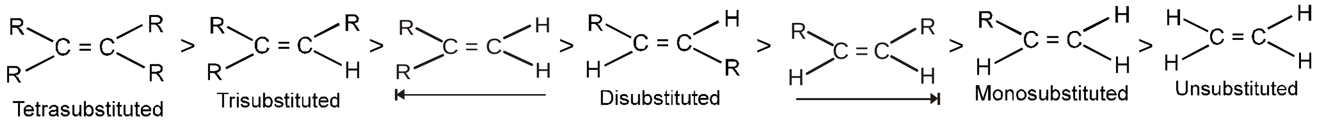
(D) Sigma electron density of C – H bond in acetylene is nearer to a carbon which has 50% s-character.

Ans. D

2.4. Stability of alkenes

The greater the number of attached alkyl groups (i.e., the highly substituted the carbon atoms of the double bond), the greater is the alkene's stability.

Relative stabilities of alkenes



Another way of measuring the stability of an alkene is the determination of its **heat of hydrogenation** or the **heat of combustion. Both are exothermic reactions**. ($\Delta H = -\,ve$)

$$\Delta H \propto \frac{1}{\text{stability}}$$ (– ve sign indicates the exothermic nature of reaction)

Heat of hydrogenation of alkenes

Alkene	Heat of hydrogenation, kcal/mol	Alkene	Heat of hydrogenation, kcal/mol
Ethene	32.8	cis-2-Butene	28.6
Propene	30.1	trans-2-Butene	27.6
1-Butene	30.3	2-Methyl-2-butene	26.9
1-Pentene	30.1	2-Methyl-1-butene	27.38
Isobutene	27.2	3-Methyl-1-butene	30.23

Combustion of alkenes

Alkene	Heat of combustion kJ / mol
1-Butene	2719
Isobutene	2703
cis-2-Butene	2712
trans-2-Butene	2707

All four butenes may be compared, since all give the same products on combustion viz. $4CO_2 + 4H_2O$.

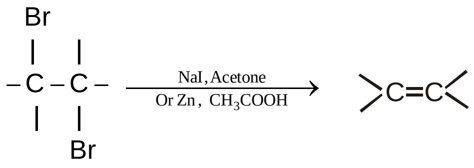
2.5. Methods of preparation of alkenes

2.5.1 By dehalogenation of vicinal dihalides

There are two types of dihalides namely gem (or geminal) dihalides in which the two halogen atoms are attached to the same carbon atom and vicinal dihalides in which the two halogen atoms are attached to the adjacent carbon atoms.

Dehalogenation of vicinal dihalides can be effected either by NaI in acetone or zinc in the presence of acetic acid or ethanol.

General reaction



$$-\overset{\overset{Br}{|}}{\underset{|}{C}}-\overset{|}{\underset{\underset{Br}{|}}{C}}- \xrightarrow[\text{Or Zn, } CH_3COOH]{\text{NaI, Acetone}} \; >C=C<$$

It involves an **antielimination** of halogen atoms

eg.24 $CH_3-CHBr-CH_2Br \xrightarrow[\left(\begin{array}{l}CH_3COOH\text{ or}\\ C_2H_5OH\text{ as solvent}\end{array}\right)]{\text{Zn dust},\Delta} CH_3-CH=CH_2 + ZnBr_2$

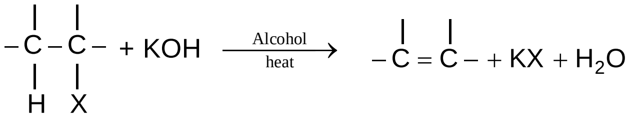
eg.25 $CH_3-CHBr-CHBr-CH_3 \xrightarrow[\text{Acetone}]{\text{NaI}} CH_3-CH=CH-CH_3 + Br + NaBr$

2.5.2 Dehydrohalogenation of alkyl halides

Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene when heated with strong base.

(i) Hot alcoholic solution of KOH(EtO^-/EtOH) or (ii) $NaNH_2$

General reaction :

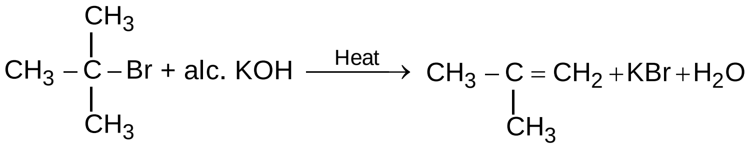


$$-\overset{|}{\underset{\underset{H}{|}}{C}}-\overset{|}{\underset{\underset{X}{|}}{C}}- + KOH \xrightarrow[\text{heat}]{\text{Alcohol}} -\overset{|}{C}=\overset{|}{C}- + KX + H_2O$$

Here β – H is eliminated by base hence called **β elimination** follows.

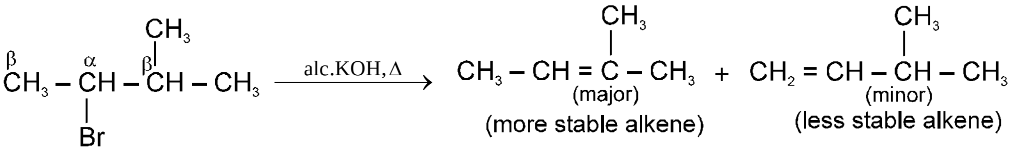
(i.e. **Highly substituted alkene is major product)**. It also involves an anti elimination of HX.

eg.26



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + \text{alc. KOH} \xrightarrow{\text{Heat}} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + KBr + H_2O$$

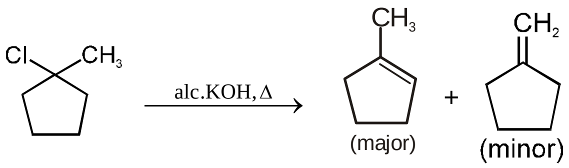
eg.27



$$\overset{\beta}{CH_3}-\overset{\alpha}{\underset{\underset{Br}{|}}{CH}}-\overset{\overset{CH_3}{|}}{\overset{\beta}{CH}}-CH_3 \xrightarrow{\text{alc.KOH},\Delta} CH_3-CH=\overset{\overset{CH_3}{|}}{C}-CH_3 + CH_2=CH-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

(major) (more stable alkene) (minor) (less stable alkene)

eg.28



2.5.3 Dehydration of alcohols

Alcohols when heated in presence of following reagents undergo loss of water molecule and form alkenes. The elimination is β **elimination.**

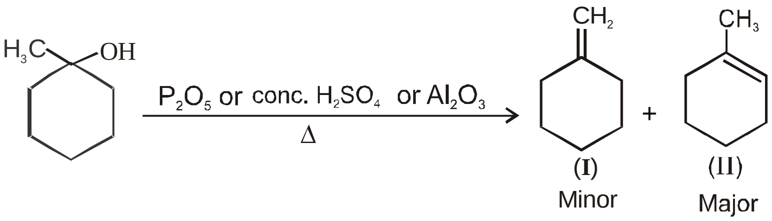
Dehydrating agents

(i) $H_2SO_4 / 160°C$ (ii) H_3PO_4 / Δ

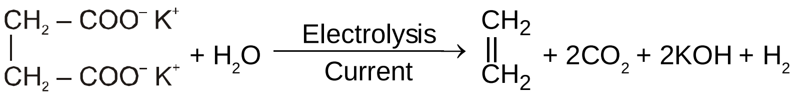
(iii) P_2O_5 / Δ (iv) $Al_2O_3 / 350°C$

General Reaction $RCH_2CH_2OH \xrightarrow[\Delta]{P_2O_5 \text{ or conc. } H_2SO_4 \text{ or } Al_2O_3} R-CH=CH_2 + H_2O$

eg.29



2.5.4 By Kolbe's electrolytic synthesis



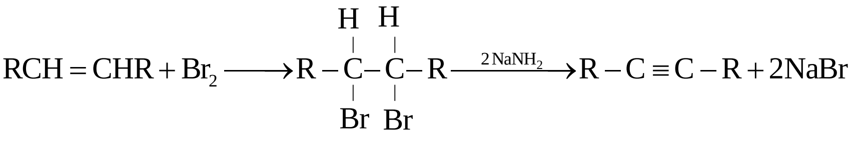
$$\begin{array}{l} CH_2-COO^-K^+ \\ | \\ CH_2-COO^-K^+ \end{array} + H_2O \xrightarrow[\text{Current}]{\text{Electrolysis}} \begin{array}{c} CH_2 \\ \| \\ CH_2 \end{array} + 2CO_2 + 2KOH + H_2$$

2.6. Methods of preparation of alkynes

2.6.1 By Dehydrohalogenation of gem and vic dihalide

The vic-dibromide can be subjected to a double dehydrohalogenation reaction with a strong base to yield an alkyne.

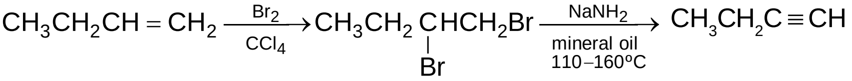
General reaction :



$$RCH=CHR + Br_2 \longrightarrow R-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{Br}{|}}{\overset{\overset{H}{|}}{C}}-R \xrightarrow{2NaNH_2} R-C\equiv C-R+2NaBr$$

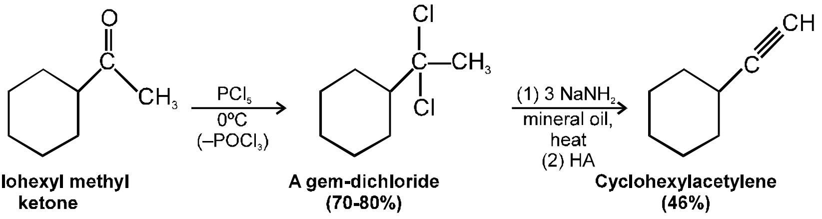
vic – dibromide

eg.30



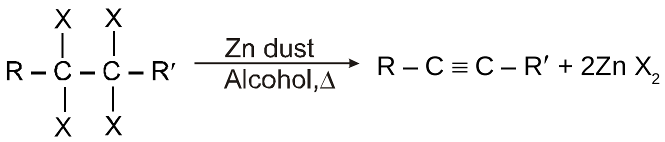
$$CH_3CH_2CH=CH_2 \xrightarrow[CCl_4]{Br_2} CH_3CH_2\underset{\underset{Br}{|}}{C}HCH_2Br \xrightarrow[\substack{\text{mineral oil} \\ 110-160°C}]{NaNH_2} CH_3CH_2C\equiv CH$$

eg.31



2.6.2 By dehalogenation of tetrahaloalkane

General reaction



$$R-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-\underset{\underset{X}{|}}{\overset{\overset{X}{|}}{C}}-R' \xrightarrow[\text{Alcohol},\Delta]{\text{Zn dust}} R-C\equiv C-R' + 2Zn\,X_2$$

2.6.3 Synthesis of higher alkynes

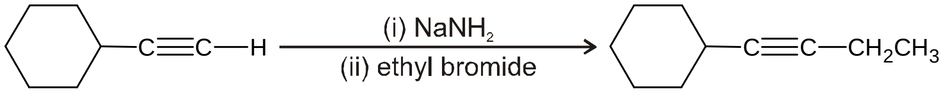
(Replacement of the acetylenic hydrogen atom of terminal alkynes)

General reaction $R-C\equiv CH \xrightarrow{NaNH_2} R-C\equiv\overset{\ominus}{C}: + R'-X \longrightarrow R-C\equiv C-R'$

Sodium ethynide and other sodium alkynides can be prepared by treating terminal alkynes with sodium amide in liquid ammonia :

eg.32 $H-C\equiv C-H \xrightarrow[\text{Liq. }NH_3]{2\text{eq }NaNH_2} Na^+\,C^-\equiv C^-\,Na^+ \xrightarrow{2\text{moles }(CH_3X)} CH_3-C\equiv C-CH_3 + 2NaX$

eg.33 $R-C\equiv C-H \xrightarrow{R'\,MgX} \underset{+\ R'\,H}{R-C\equiv C\,Mg\,X} \xrightarrow{R'X} R-C\equiv C-R' + MgX_2$

eg.34 

Cyclohexyl ethyne

1–Cyclohexyl but-1-yne
(ethylcyclohexyl acetylene)

2.6.4 By Kolbe's electrolytic synthesis

$$\begin{array}{l} CH-COO^-\,K^+ \\ \parallel \\ CH-COO^-\,K^+ \end{array} + H_2O \xrightarrow[\text{Current}]{\text{Electrolysis}} \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2CO_2 + 2KOH + H_2$$

2.6.5 By hydrolysis of carbides

$$CaC_2 + 2HOH \longrightarrow C_2H_2 + Ca(OH)_2$$
$$Mg_2C_3 + 4HOH \longrightarrow CH_3-C\equiv CH + 2Mg(OH)_2$$

2.7 Chemical reactions of alkenes & alkynes

Due to presence of weak π electrons in alkene and alkyne, it will go for electrophilic reaction. Now question **is electrophilic addition or electrophilic substitution ?**

In electrophilic substitution reaction, one σ bond is broken and a new σ- bond between one of the doubly bonded carbon atoms and the electrophile is formed. Since the bond energies of the σ bond broken and the new σ bond formed are not much different therefore **electrophilic substitution** reaction are **not** accompanied by large energy changes.

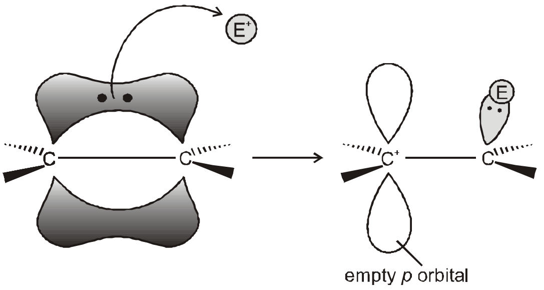
On the other hand in **electrophilic addition** reactions, one weak π-bond (251 KJ mol^{-1}) is broken and two strong σ bonds ($2 \times 347 = 694$ KJ mol^{-1}) are formed. The overall reaction is accompanied by a release of about 694-251 = 443 KJ mol^{-1} of energy. In other words electrophilic addition reactions are energetically more favourable than electrophilic substitution reactions. Thus the typical reactions of alkenes and alkynes are **electrophilic addition reactions** and not the electrophilic substitution reactions.

***Alkenes/alkynes function has nucleophilic nature in addition reaction.**

(a) Electrophilic addition to alkenes

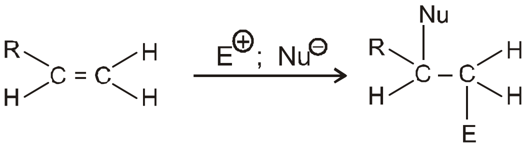
(i) Orbital diagram

The electrons in the pi bond are spread farther from the carbon nuclei and are more loosely held than the sigma electrons.



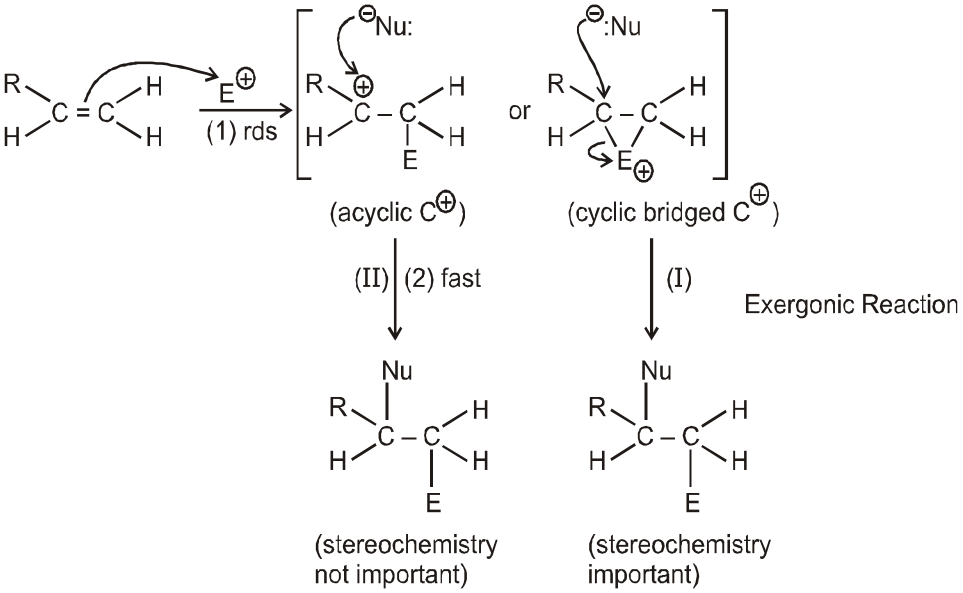
The pi bond acts as a nucleophile. A strong electrophile attracts the electrons out of the pi bond to form a new sigma bond, generating a carbocation. The curved arrow shows the movement of electrons, from the electron-rich pi bond to the electron-poor electrophile.

(ii) General reaction



.... Addition product.

(iii) Mechanism



(iv)

S. No	Reagents	Electrophile	Nucleophile	Mechanism
(1)	HX	(H^+)	X^-	II
(2)	Dilute H_2SO_4	(H^+)	H_2O	II
(3)	H_2SO_4	(H^+)	HSO_4^-	II
(4)	X_2	(X^+)	X^-	I
(5)	HOX	(X^+)	OH^-	I
(6)	$Hg(CH_3COO)_2$ $+ H_2O + NaBH_4$	(Hg^{2+})	H_2O	I
(7)	NOCl	(NO^+)	Cl^-	I

(v) Reactivity of alkenes

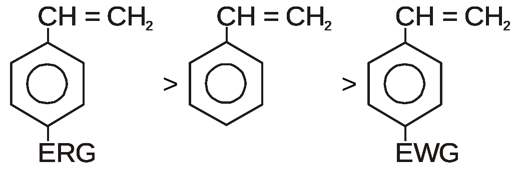
(1) Presence of e^- releasing groups (+M, +I) at C = C increases nucleophilicity and reactivity.

(2) Presence of ERG stabilises the intermediate carbocation.

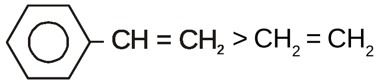
(3) More stable $C^{\oplus}$, more is reactivity.

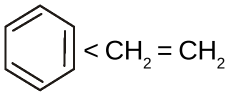
eg.35 (i) $ERG - CH = CH_2 > CH_2 = CH_2 > EWG - CH = CH_2$

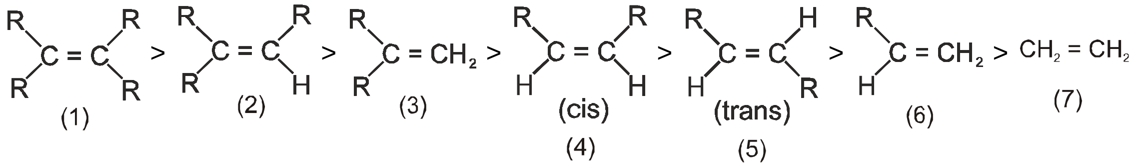
(ii)



(iii) $CH_3-O-CH=CH_2 > CH_2=CH_2 > CH_2=CH-CN$
(vinyl ether) (acrylonitrile)

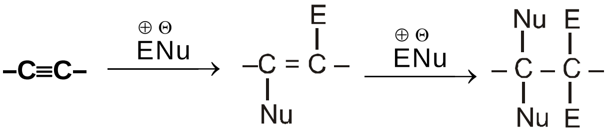
(iv) 
$C_6H_5-CH=CH_2 > CH_2=CH_2$

(v) 
$< CH_2=CH_2$

(vi) 

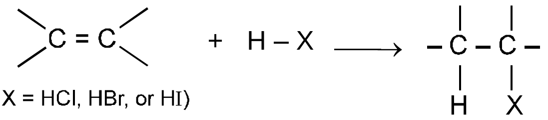
(b) Electrophilic addition to alkynes

Many of the reactions of alkynes are similar to the corresponding reactions of alkenes. We must consider the possibility of a double addition whenever a reagent adds across the triple bond of an alkyne. Some conditions may allow the reaction to stop after a single addition,

General Reaction : 
$$-C\equiv C- \xrightarrow{\overset{\oplus\ \ominus}{ENu}} -\underset{Nu}{C}=\overset{E}{C}- \xrightarrow{\overset{\oplus\ \ominus}{ENu}} -\underset{Nu}{\overset{Nu}{C}}-\underset{E}{\overset{E}{C}}-$$

2.7.1 Addition of hydrogen halides

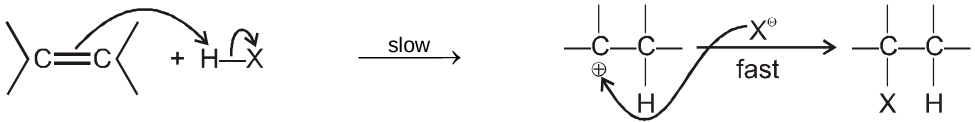
Alkene + HX ⟶ Alkylhalide

(i) General reaction 

(HX = HCl, HBr, or HI)

Markovnikov
orientation
(anti-Markovnikov with
HBr and peroxide)

(ii) Mechanism



The π-electrons of the alkene form a bond with a proton from HX to form a carocation and a halide ion.

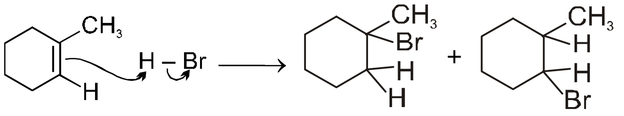
a carbocation intermediate

The halide ion reacts with the carbocation by donating an electron pair, the result is an alkyl halide.

eg.36 $CH_3CH=CH_2 \xrightarrow{HI} CH_3CHICH_3 + CH_3CH_2CH_2I$

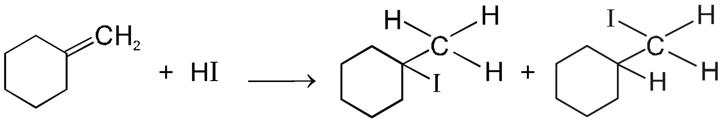
Propene; 2 – Iodopropane (Isopropyl iodide) (major); 1 – Iodopropane (minor)

eg.37



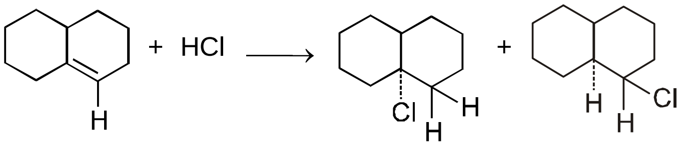
product (major) product (minor)

eg.38



(major) (minor)

eg.39



(major) (minor)

2.7.2. Addition of H_2O (Hydration reaction)

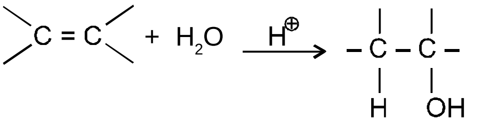
Water is added by three methods :

(a) Acid-catalyzed hydration of alkenes

Alkenes add water in the presence of an acid catalyst to yield alcohols. The addition takes place with Markovnikov regioselectivity. The reaction is reversible, and the mechanism for the acid-catalyzed hydration of an alkene is simply the reverse of that for the dehydration of an alcohol.

The carbocation intermediate may rearrange if a more stable carbocation is possible by hydride or alkanide migration. Thus, a mixture of isomeric alcohol products may result.

(i) General Reaction :

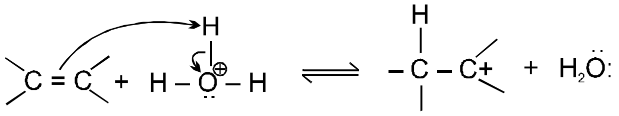


$$>C=C< + H_2O \xrightarrow{H^{\oplus}} -\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

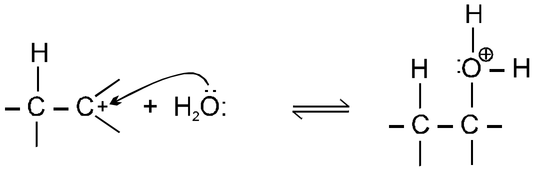
(Markovnikov orientation)

(ii) Mechanism :

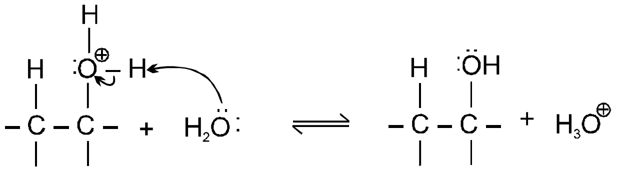
Step 1 : Protonation of the double bond forms a carbocation



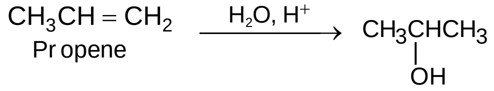
Step 2 : Nucleophilic attack by water



Step 3 : Deprotonation to the alcohol



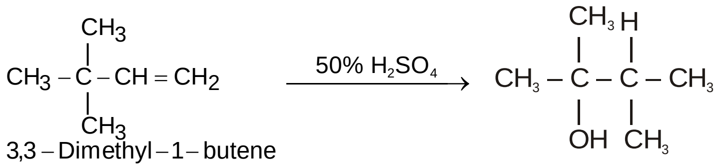
eg.40



$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow{H_2O,\ H^+} \underset{\displaystyle OH}{CH_3\overset{}{C}HCH_3}$$

Isopropyl alcohol

eg.41



$$\underset{\text{3,3-Dimethyl-1-butene}}{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2} \xrightarrow{50\%\ H_2SO_4} CH_3-\underset{OH}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3$$

2, 3-Dimethyl-2-butanol
(major product)

(b) Oxymercuration-Demercuration (OMDM)

In the oxymercuration step, water and mercuric acetate add to the double bond ; in the demercuration step, sodium borohydride reduces the acetoxymercury group and replaces it with hydrogen. The net addition of –H and – OH takes place with Markovnikov regioselectivity and generally takes place without the complication of rearrangements.

Advantage over acid catalysed hydration

(1) No requirement of acidic condition, which is harmful to many organic molecules.
(2) No rearrangement occur.

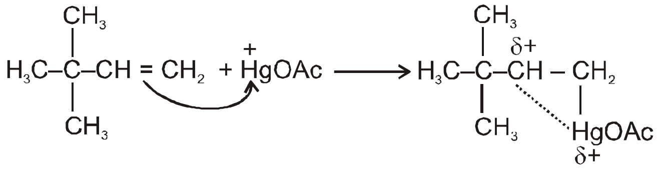
Mechanism : There are two steps

Step I - Oxymercuration : (addition of H_2O & $Hg(CH_3COO)_2$)

(i) Mercuric acetate dissociates to form $\overset{+}{H}gOAC$ cation and an acetate anion.

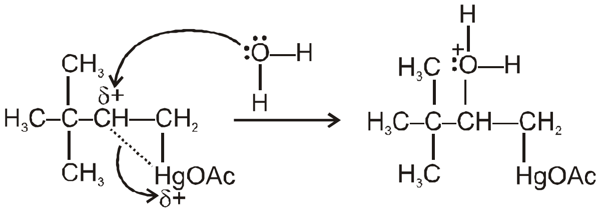
$$Hg(OAc)_2 \rightleftharpoons \overset{+}{H}gOAC + OAc^-$$

(ii) The alkene donates pair of electron to the electrophilic $HgOAc^+$ cation to form a mercury-bridged carbocation. In this carbocation, the positive charge is shared between the 2º (more substituted) carbon atom and mercury atom. The charge on the carbon atom is large enough to account for the Markovnikov's orientation of the addition, but not large enough for rearrangement to occur.

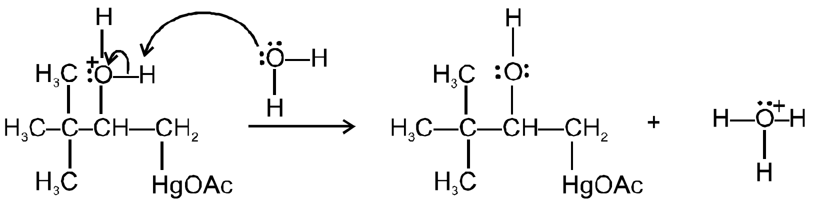


3,3-Dimethyl-1-butene Mercurry-bridged carbocation

(iii) A water molecule attacks the carbon of the bridged mercurinium ion that is better able to bear the partial positive charge.

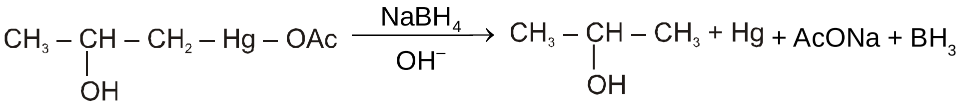


(iv) An acid-base reaction transfers a proton to another water molecule (or to an acetate ion). This step produces the (hydroxyalkyl) mercury compound.



(Hydroxyalkyl)mercury
compound

Step II - Demercuration : $NaBH_4$ converts the carbon mercury bond into a carbon-hydrogen bond. Because the reaction result in the loss of mercury

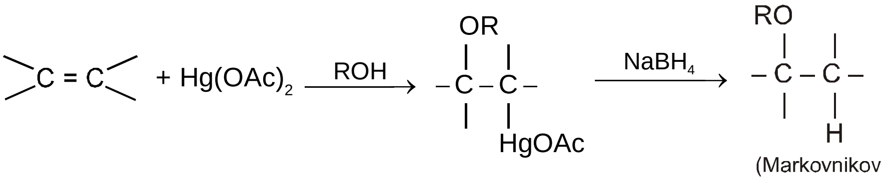


$$\underset{\displaystyle OH}{CH_3-\overset{}{CH}}-CH_2-Hg-OAc \xrightarrow[OH^-]{NaBH_4} \underset{\displaystyle OH}{CH_3-CH}-CH_3 + Hg + AcONa + BH_3$$

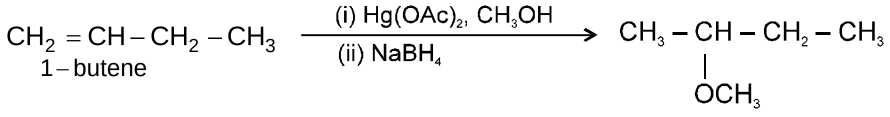
(c) Alkoxymercuration - demercuration

If solvent is alcohol then product will be ether & process is called alkoxymercuration demercuration.

General reaction :



(Markovnikov orientation)

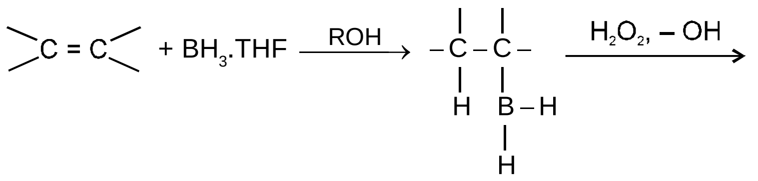
eg.42 

$$\underset{\text{1-butene}}{CH_2=CH-CH_2-CH_3} \xrightarrow[\text{(ii) }NaBH_4]{\text{(i) }Hg(OAc)_2,\ CH_3OH} CH_3-\underset{\displaystyle OCH_3}{CH}-CH_2-CH_3$$

2-Methoxy butane

(d) Hydroboration-oxidation

(i) General reaction :

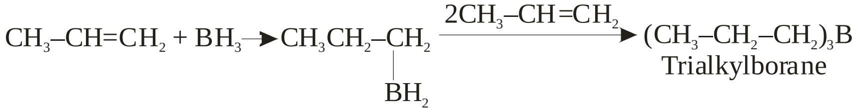


anti-Markovanikov orientation (syn stereochemistry)

(ii) Mechanism : There are two steps :

Step-I - Hydroboration : The addition of electrophilic Borane & the nucleophilic H^- take place in one step (i.e. it is **concerted** reaction).

- No intermediate is formed.

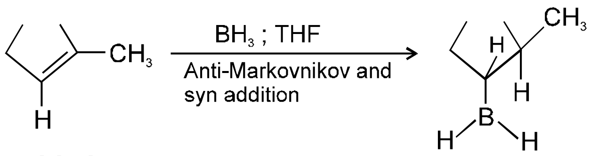


$$CH_3-CH=CH_2 + BH_3 \longrightarrow CH_3CH_2-\underset{\displaystyle BH_2}{CH_2} \xrightarrow{2CH_3-CH=CH_2} \underset{\text{Trialkylborane}}{(CH_3-CH_2-CH_2)_3B}$$

In this way one BH_3 reacts with three molecules of alkene successively to form trialkyl borane.

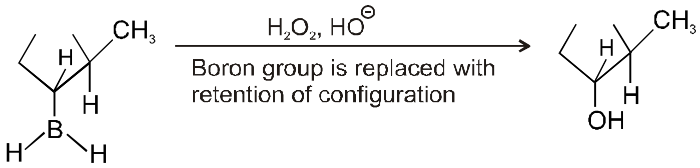
Step-II - Oxidation : (Replacement of B by OH group)

$$(CH_3CH_2CH_2)_3B \text{ or } R_3B \xrightarrow[^-OH]{H_2O_2} 3ROH + BO_3^{3-}$$

eg.43 

\+ enantiomer + dialkyl-and trialkylborane

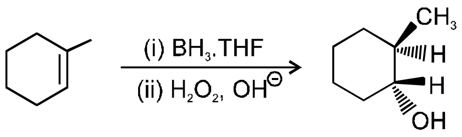
Oxidation



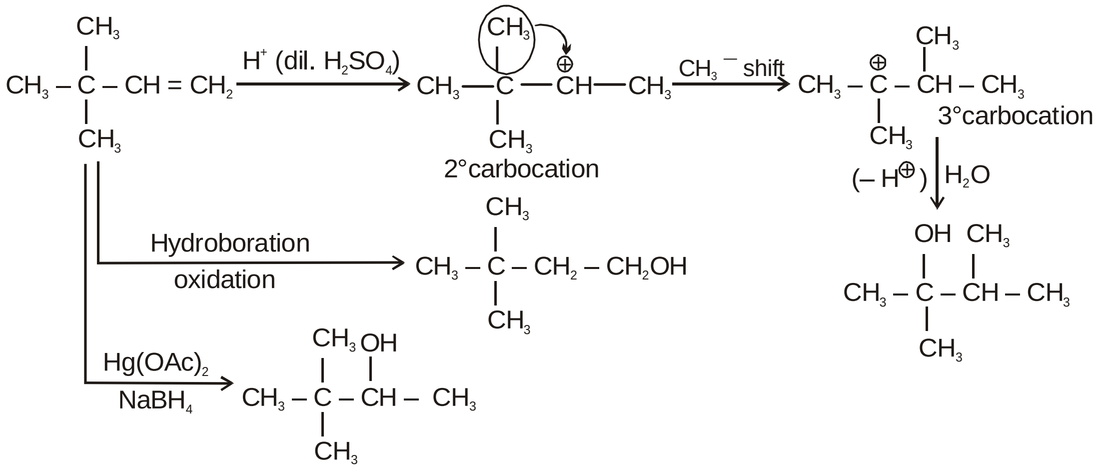
\+ enantiomer

Note : In the first step, boron and hydrogen undergo syn addition to the alkene. In the second step, treatment with hydrogen peroxide and base replaces the boron with – OH with retention of configuration. The net addition of – H and – OH occurs with anti **Markovnikov regioselectivity and syn stereoselectivity**. Hydroboration-oxidation therefore, serves as a useful regiochemical complement to oxymercuration demercuration.

eg.44



eg.45



(i) Hydration with dil. H_2SO_4 proceeds via carbocation rearrangement

(ii) Hydration with $Hg(OAc)_2$, H_2O, followed by $NaBH_4$ proceeds via Markovnikov's rule (no rearrangement).

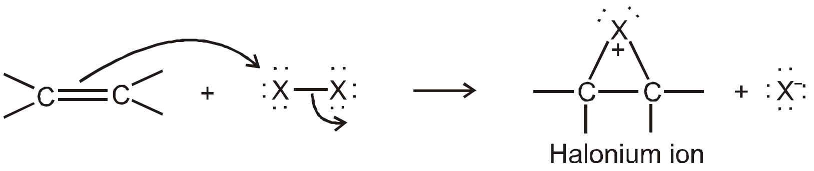
(iii) Hydration with $(BH_3)_2$ followed by H_2O_2 / OH^- proceeds via Anti Markovnikov's rule.

2.7.3. Additon of halogen (Halogenation)

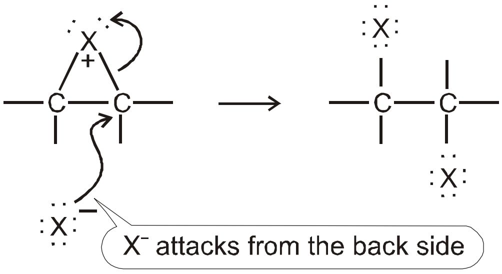
Halogen add to alkenes to form vicinal dihalides.

Mechanism :

Step-I : Electrophilic attack forms a halonium ion.



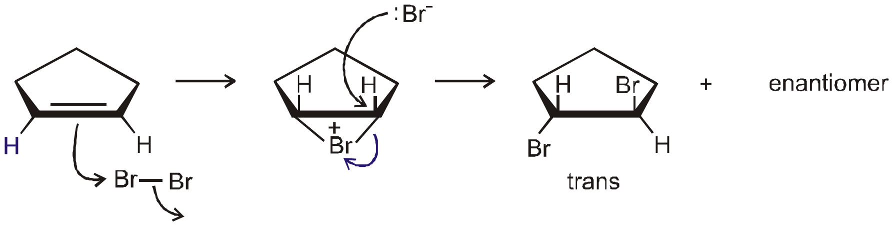
Step-II : The halide ion opens the halonium ion.



Chlorine and bromine commonly add to alkenes by the haloninum ion mechanism. Iodination is used less frequently because diiodide products decompose easily. Any solvents used must be inert to the halogens; methylene chloride (CH_2Cl_2), chloroform ($CHCl_3$), and carbon tetrachloride (CCl_4) are the frequent choices.

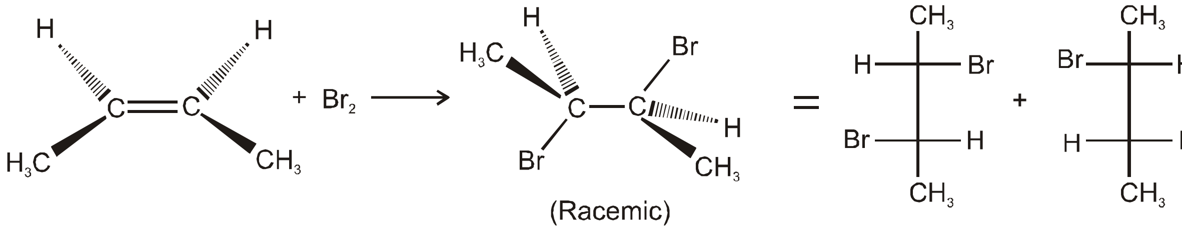
Stereochemistry of halogen addition

The addition of halogen to alkene is a stereospecific **anti addition.**



Halogen addition is another example of a stereospecific reaction, (in which different stereoisomers of the starting meaterial give different stereoisomers of the product).

eg.46

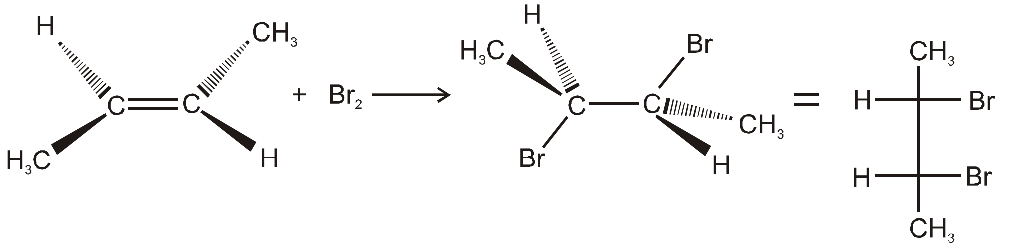


Cis-2-butene

(Racemic)

(±)-2,3-dibromobutane

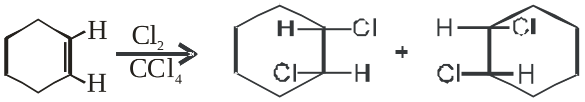
eg.47



Trans-2-butene

Meso-2,3-dibromobutane

eg.48



Racemic trans-1,2-dichlorocyclohexane

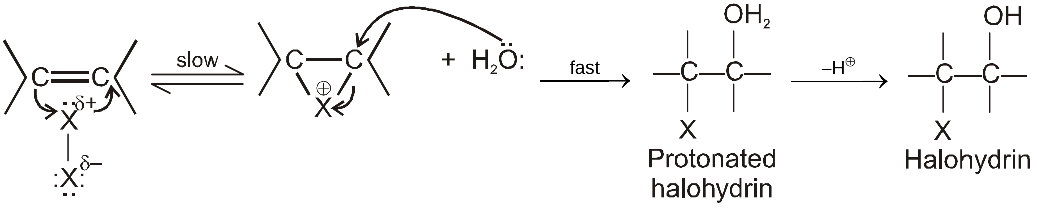
2.7.4. Addition of HOX

General reaction Alkene + HOX ⟶ Halohydrin

Reagents

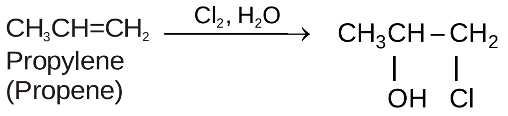
(i) $X_2 + H_2O \rightarrow HOX + HX$ or (ii) HOX

Mechanism : Halohydrin formation from an alkene :



Remarks : Anti adition
No rearrangement
Bridged carbocation

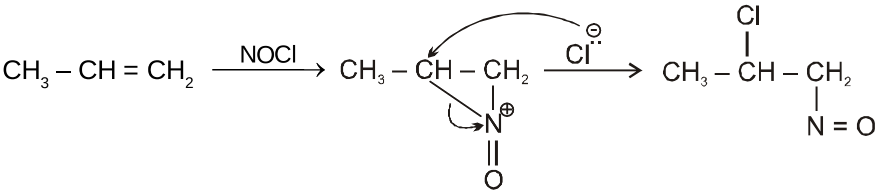
eg.49



$$\underset{\text{Propylene (Propene)}}{CH_3CH{=}CH_2} \xrightarrow{Cl_2,\ H_2O} CH_3\underset{OH}{CH}-\underset{Cl}{CH_2}$$

Propylene chlorohydrin
(1 – Chloro – 2 – propanol)

2.7.5. Addition of NOCl

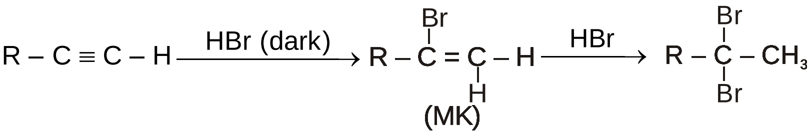


$$CH_3-CH=CH_2 \xrightarrow{NOCl} CH_3-\overset{}{C}H-\underset{\underset{O}{\overset{\oplus}{N}}}{CH_2} \xrightarrow{Cl^{\ominus}} CH_3-\overset{Cl}{CH}-\underset{N=O}{CH_2}$$

2.8. Addition reactions in alkynes

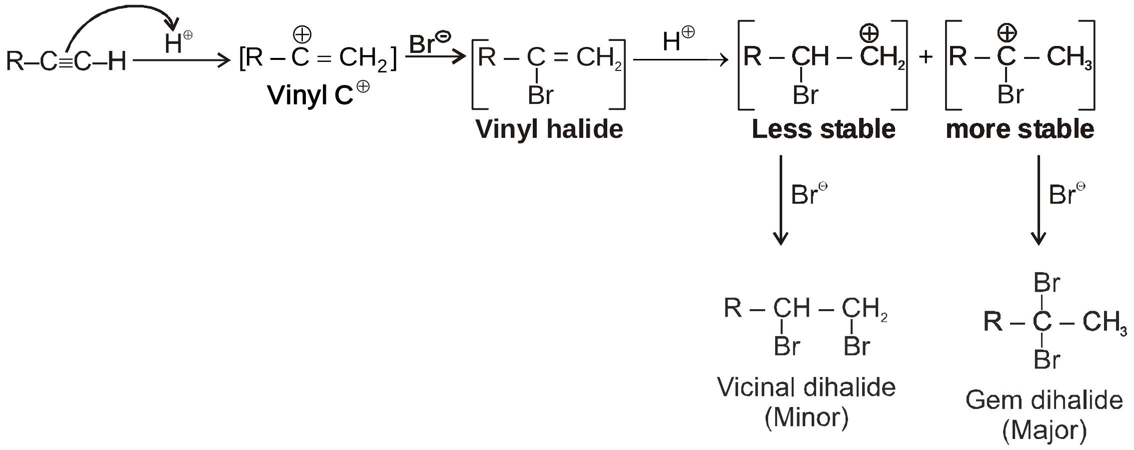
2.8.1. Addition of hydrogen halide

(i) General reaction



$$R-C\equiv C-H \xrightarrow{HBr\ (dark)} \underset{(MK)}{R-\overset{Br}{C}=\underset{H}{C}-H} \xrightarrow{HBr} R-\overset{Br}{\underset{Br}{C}}-CH_3$$

(ii) Mechanism :



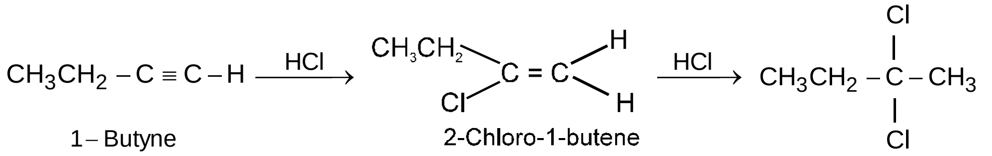
(iii) Remarks :

(1) Markovnikov's Addition in both steps.

(2) If two moles of HX are added the final product is Gemdihalide.

(3) **Electrophilic addition to terminal alkyne is regioselective.**

eg.50

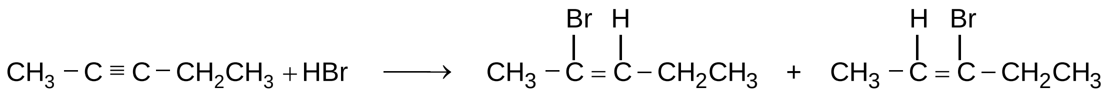


$$CH_3CH_2-C\equiv C-H \xrightarrow{HCl} \text{2-Chloro-1-butene} \xrightarrow{HCl} CH_3CH_2-\overset{Cl}{\underset{Cl}{C}}-CH_3$$

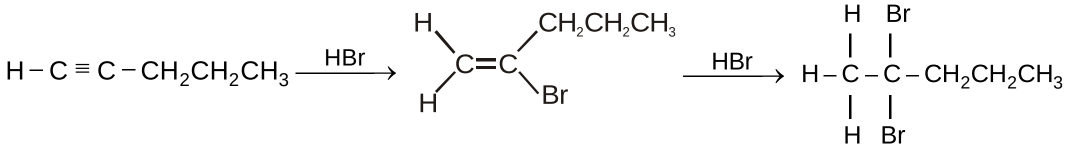
1 – Butyne

2-Chloro-1-butene

2, 2 – Dichlorobu tane

eg.51 

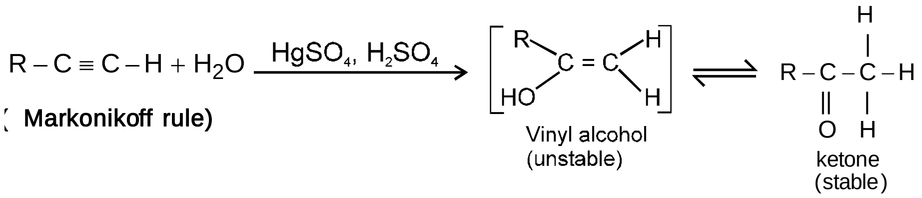
$$CH_3-C\equiv C-CH_2CH_3 + HBr \longrightarrow CH_3-\overset{Br}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_2CH_3 + CH_3-\overset{H}{\overset{|}{C}}=\overset{Br}{\overset{|}{C}}-CH_2CH_3$$

eg.52 

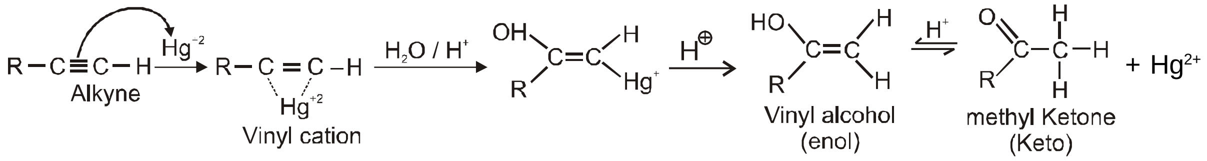
2.8.2. Addition of water (Hydration reaction)

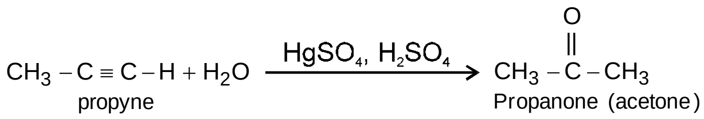
(a) Mercuric ion catalyzed hydration

Alkynes undergo acid–catalyzed addition of water across the triple bond in the presence of mercuric ion as a catalyst. A mixture of mercuric sulfate in aqueous sulfuric acid is commonly used as the reagent.

General reaction 

Electrophilic addition of mercuric ion gives a vinyl cation, which reacts with water and loses a proton to give an organomercurical alcohol. Under the acidic reaction conditions, Hg^{2+} is replaced by proton to give a vinyl alcohol, called an enol.

Mech. 

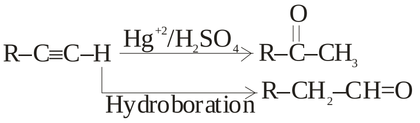
eg.53 

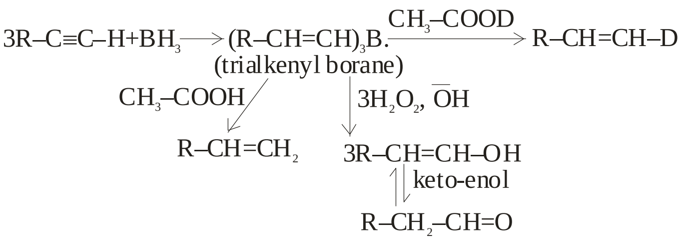
$$\underset{\text{propyne}}{CH_3-C\equiv C-H + H_2O} \xrightarrow{HgSO_4,\ H_2SO_4} \underset{\text{Propanone (acetone)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_3}$$

(b) Hydroboration oxidation of alkynes

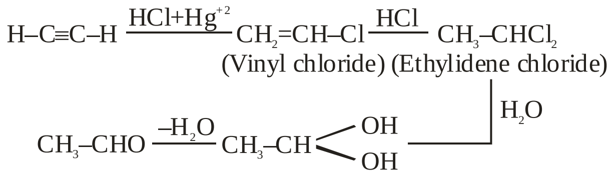
*It is used to get aldehyde from terminal alkyne.

*Anti Markovnikov addition of water with syn stereochemistry



(i) 

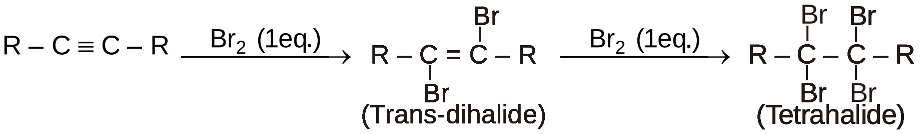
(ii)



$$H{-}C{\equiv}C{-}H \xrightarrow{HCl+Hg^{+2}} \underset{\text{(Vinyl chloride)}}{CH_2{=}CH{-}Cl} \xrightarrow{HCl} \underset{\text{(Ethylidene chloride)}}{CH_3{-}CHCl_2} \xrightarrow{H_2O} CH_3{-}CH(OH)_2 \xrightarrow{-H_2O} CH_3{-}CHO$$

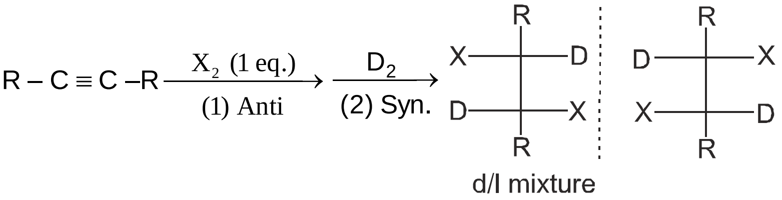
2.8.3. Addition of halogens

$\text{Alkyne} + 2X_2 \longrightarrow \text{Tetrahalide}$



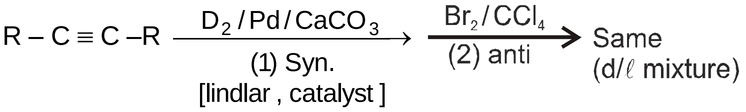
$$R-C\equiv C-R \xrightarrow{Br_2\ (1eq.)} \underset{\text{(Trans-dihalide)}}{R-C(Br)=C(Br)-R} \xrightarrow{Br_2\ (1eq.)} \underset{\text{(Tetrahalide)}}{R-CBr_2-CBr_2-R}$$

Stereochemistry of addition - Anti in both step



$$R-C\equiv C-R \xrightarrow[\text{(1) Anti}]{X_2\ (1\ eq.)} \xrightarrow[\text{(2) Syn.}]{D_2}$$

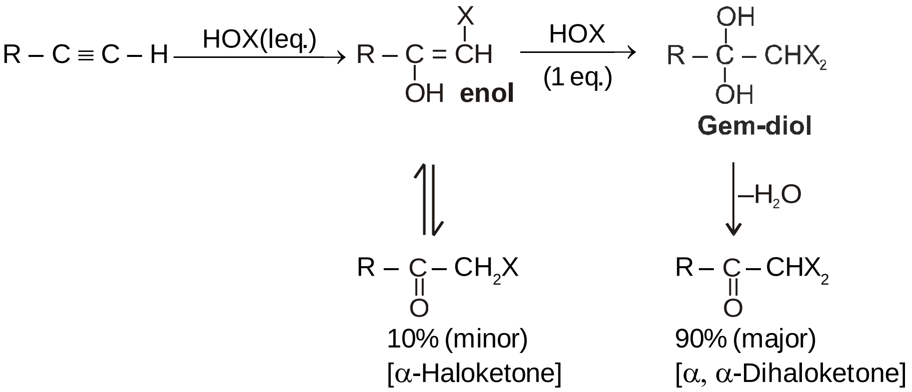
d/l mixture



$$R-C\equiv C-R \xrightarrow[\substack{\text{(1) Syn.}\\ \text{[lindlar , catalyst]}}]{D_2/Pd/CaCO_3} \xrightarrow[\text{(2) anti}]{Br_2/CCl_4} \text{Same (d/}\ell\text{ mixture)}$$

2.8.4. Addition of HOX

$\text{Alkynes} + HOX \longrightarrow \underset{\text{(90\% major)}}{\alpha,\alpha\text{-dihaloketone}} + \underset{\text{(10\% minor)}}{\alpha\text{-haloketone}}$



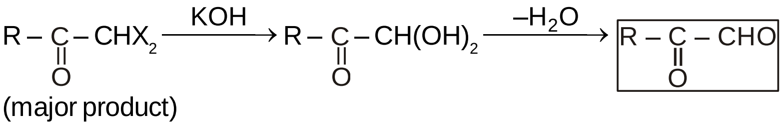
$$R-C\equiv C-H \xrightarrow{HOX(1eq.)} \underset{\textbf{enol}}{R-C(OH)=CH(X)} \xrightarrow[\text{(1 eq.)}]{HOX} \underset{\textbf{Gem-diol}}{R-C(OH)_2-CHX_2} \xrightarrow{-H_2O} \underset{\substack{\text{90\% (major)}\\ [\alpha,\ \alpha\text{-Dihaloketone}]}}{R-CO-CHX_2}$$

$$R-C(OH)=CH(X) \rightleftharpoons \underset{\substack{\text{10\% (minor)}\\ [\alpha\text{-Haloketone}]}}{R-CO-CH_2X}$$

Remarks :

Two molecules of HOX can be added, the end product is α, α-Dihaloketone.
The intermediate product is an enol which gives a minor product α-haloketone.

eg.54



$$\underset{\text{(major product)}}{R-CO-CHX_2} \xrightarrow{KOH} R-CO-CH(OH)_2 \xrightarrow{-H_2O} \boxed{R-CO-CHO}$$

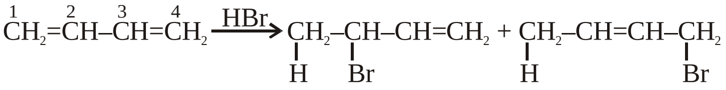
2.9. Alkadienes

Dienes are of three types :
(a) Isolated dienes ($CH_2=CH–CH_2–CH=CH_2$)
(b) Conjugated dienes ($CH_2=CH–CH=CH–CH_3$)
(c) Cumulated dienes ($CH_3–CH=C=CH–CH_3$)

Stability Order : Conjugated > Isolated > Cumulated

Heat of hydrogenation
Cumulated > terminal alkyne > nonterminal alkyne > isolated diene > conjugated diene

General reaction of conjugated dienes
Reaction take place at two position (1, 2) and (1, 4), major product depends on reaction temperature.



$$\overset{1}{C}H_2=\overset{2}{C}H–\overset{3}{C}H=\overset{4}{C}H_2 \xrightarrow{HBr} \underset{H}{CH_2}–\underset{Br}{CH}–CH=CH_2 + \underset{H}{CH_2}–CH=CH–\underset{Br}{CH_2}$$

(1, 2 Product)	(1, 4 Product)
Major at –80ºC	Major at 40ºC
KCP	TCP

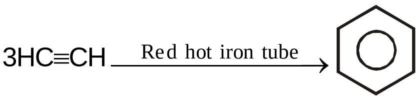
Note : **(1)** Kinetically controlled process (KCP) is governed by stability of intermediate, faster reaction.
(2) Thermodynamically controlled process (TCP) is governed by stability of products.

3. Aromatic Hydrocarbons

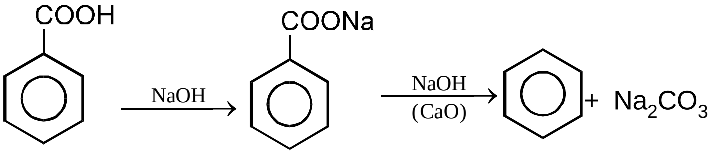
Aromatic hydrocarbons are known generally as arenes. An aryl group is one derived from an arene by removal of a hydrogen atom and its symbol is Ar—. Thus, arenes are designated ArH just as alkanes are designated RH.

3.1. Preparation of arenes

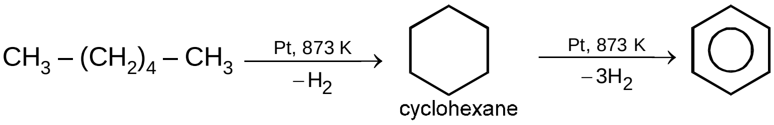
(a) By polymerisation of Acetylene



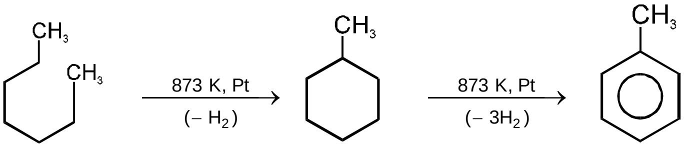
(b) By decarboxylation of benzoic acid



(c) By catalytic reforming of n-Hexane

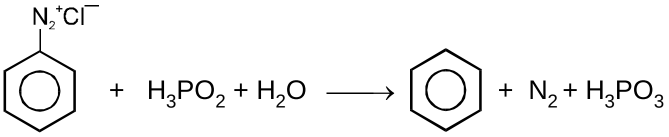


(d) By catalytic reforming of n-Heptane

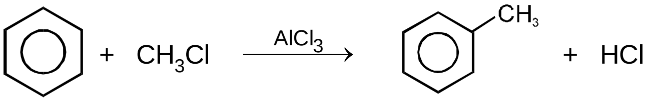


Methylcyclohexane Toluene

(e) By reduction of benzene diazonium chloride

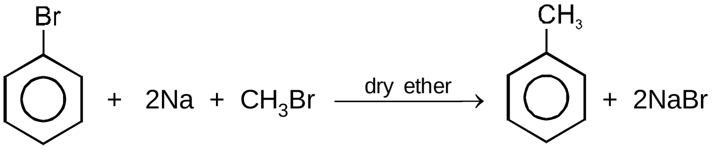


(f) By Friedel-Crafts reaction



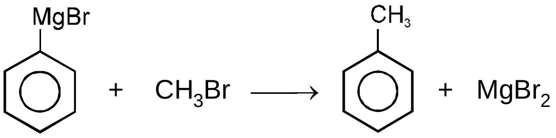
Toluene

(g) By Wurtz fitting reaction

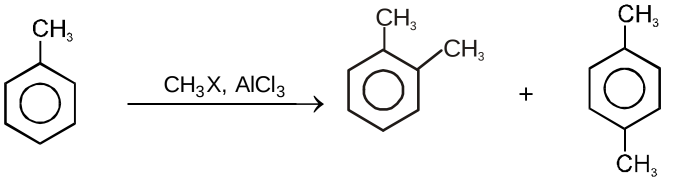


Bromobenzene Toluene

(h) From Grignard reagents



(i) By alkylation of toluene

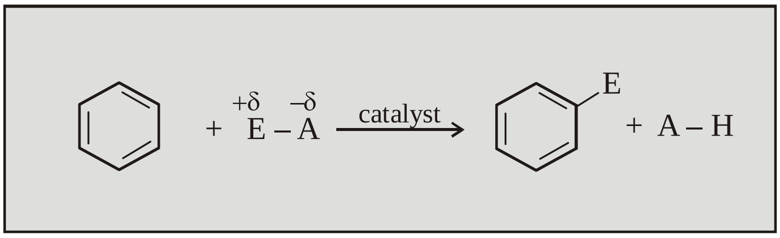


Toluene o-Xylene p-Xylene

3.2. Reaction of aromatic compounds

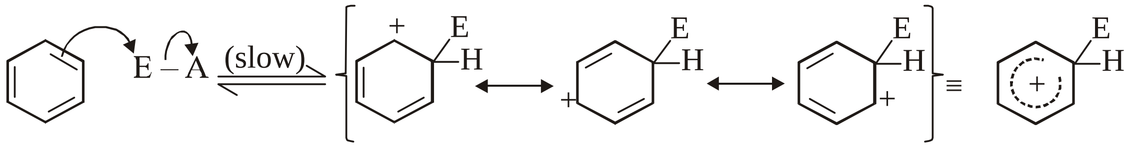
Characteristic reaction of aromatic ring is electrophilic substitution reaction

General reaction



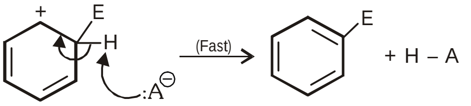
Mechanism for electrophilic substitution

Step-I :

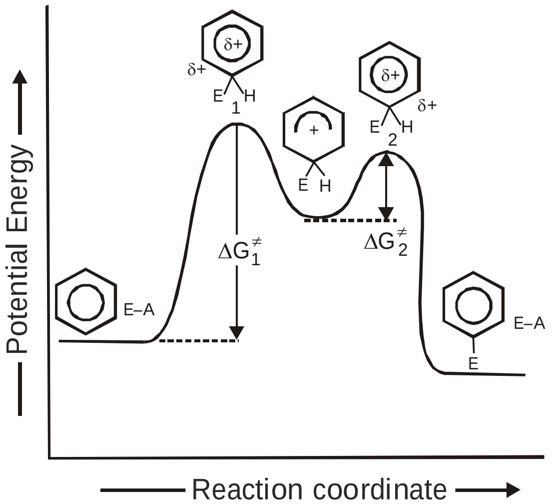


Arenium ion (σ-complex)

Step-II :



Energy diagram



(Figure-1)

3.3. Directing influence

The effects of various substituents on the reactivity of a benzene ring toward electrophilic substituion:

Strong activating groups : $—NH_2$, —NHR, $—NR_2$, —OH, —OR

Moderately activating groups : $—NH\overset{\overset{O}{||}}{C}R$, $—O\overset{\overset{O}{||}}{C}R$

Weakly activating groups : —R, —Ar, $—CH=CR_2$

Weakly deactivating groups : —F, —Cl, —Br, —I , CH_2X

Deactivating groups : —N=O, –CH=CH–COOH, CHX_2

Ortho/para directing

Moderately deactivating groups : —CHO, —COR, —COOR,

: —COOH, —COCl

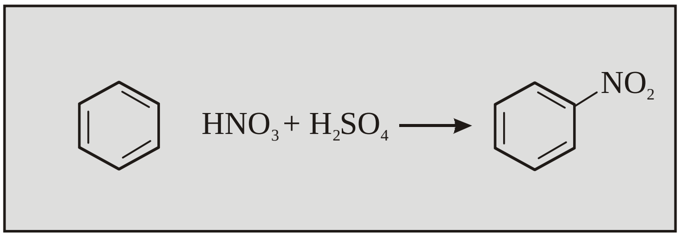
Strong deactivating groups : —C≡N, $—SO_3H$, $—\overset{+}{N}H_3$, $—\overset{+}{N}H_2R$

: $—\overset{+}{N}HR_2$, $—\overset{+}{N}R_3$, $—NO_2$, $–CX_3$

Meta directing

3.4. Nitration

(Electrophile for nitration is NO_2^+)



Reagents

(a) Conc. HNO_3 + Conc. H_2SO_4 (Nitrating mixture)

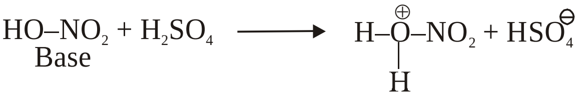
(b) N_2O_5, $NO_2^+BF_4^-$, $NO_2^+PF_6^-$, $NO_2^+SO_3^-$(Nitrating salt) + CCl_4

(c) Conc. HNO_3 only

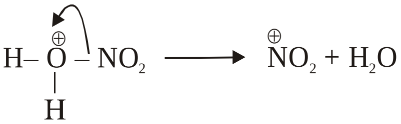
Mechanism

Step-I : Generation of electrophile from nitrating agent

(a) In a mixture of nitric acid and sulphuric acid an acid base reaction takes place in which nitric acid acts as the **base.**



$$\underset{\text{Base}}{HO{-}NO_2} + H_2SO_4 \longrightarrow H{-}\overset{\oplus}{\underset{|\atop H}{O}}{-}NO_2 + HSO_4^{\ominus}$$



$$H{-}\overset{\oplus}{\underset{|\atop H}{O}}{-}NO_2 \longrightarrow \overset{\oplus}{N}O_2 + H_2O$$

$$H_2O + H_2SO_4 \longrightarrow H_3\overset{\oplus}{O} + HSO_4^{\ominus}$$

$$HNO_3 + 2H_2SO_4 \longrightarrow \overset{\oplus}{N}O_2 + H_3\overset{\oplus}{O} + 2\,HSO_4^{\ominus}$$

Purpose of sulphuric acid in the reaction is to increase the concentration of nitronium ion (NO_2^+)

(b) N_2O_5 in CCl_4 when used, results in a spontaneous dissociation reaction.

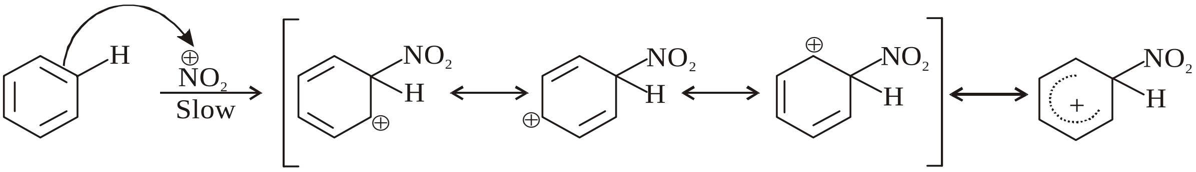
$$N_2O_5 \rightleftharpoons \overset{\oplus}{N}O_2 + NO_3^-$$

(c) With concentrated HNO_3 alone

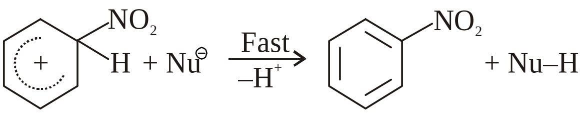
$$2\,HNO_3 \rightleftharpoons NO_2^{\oplus} + NO_3^- + H_2O$$

The electrophile generated in this case is obtained by the behaviour of one molecule of nitric acid as the base and other molecule as the acid, but the equilibrium lies on the reactant side.

Step-II : Attack of electrophile on aromatic system :



Step-III : Transfer of proton to a base/nucleophile



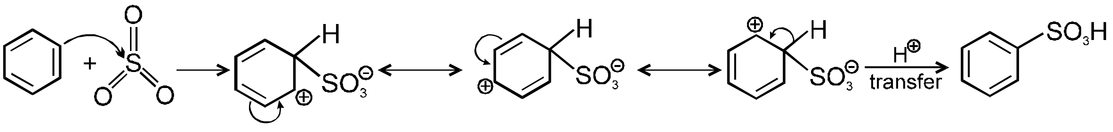
3.5. Sulphonation

(Electrophile for sulphonation is SO_3)

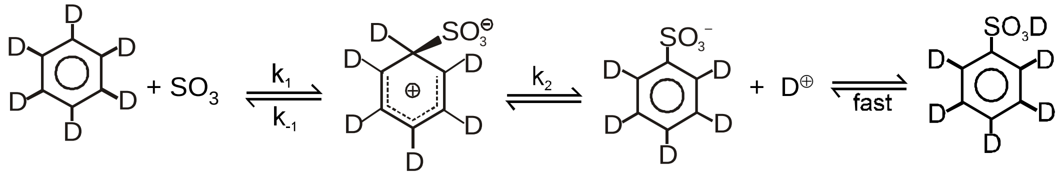
Sulphur trioxide in sulphuric acid is used as the sulphonation agent.

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + HSO_4^{\ominus}$$

(i)

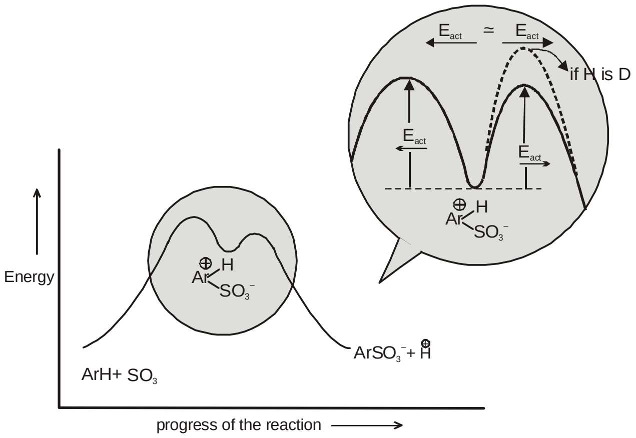


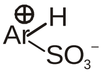
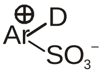
(ii)



Sulphonation, is **reversible** and takes place in concentrated sulphuric acid. ($K_{-1} \simeq K_2$).

Energy diagram



Some  or  go on to product, some revert to the starting material and decrease the rate of reaction. This effect is known as isotope effect.

3.6. Halogenation

(Electrophile for halogenation is X^+)

Catalyst is Lewis acid like $AlCl_3$ or $FeCl_3$

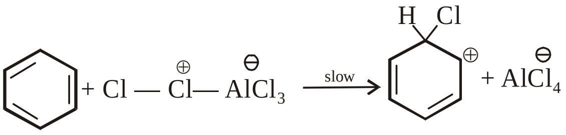
Reagent (a) Cl_2/Br_2+ Lewis acid

(b) IBr/BrCl

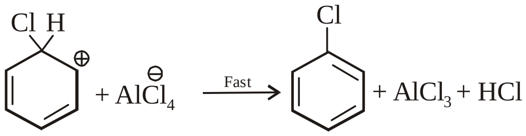
Let us take chlorination as a representative reaction to understand the mechanism of halogenation. Chlorine, in the presence of $AlCl_3$ or $FeCl_3$ forms a complex, $Cl_2—AlCl_3$. This complex can itself be the reactive electrophile or it may dissociate to give Cl^+.

Step-I : $Cl—\ddot{C}l\!: + \underset{\text{(anhydrous)}}{AlCl_3} \rightleftharpoons Cl—\overset{\oplus}{Cl}—\overset{\ominus}{Al}Cl_3$

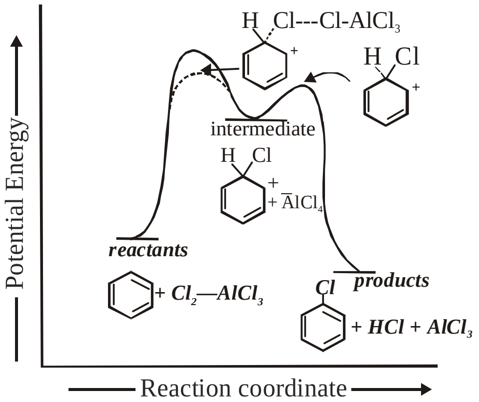
Step-II :



Step-III :



Energy diagram



Schematic potential energy diagram for chlorination of benzene with Cl_2, $AlCl_3$ as the electrophile

(Figure-3)

3.7. Friedel-Craft's alkylation

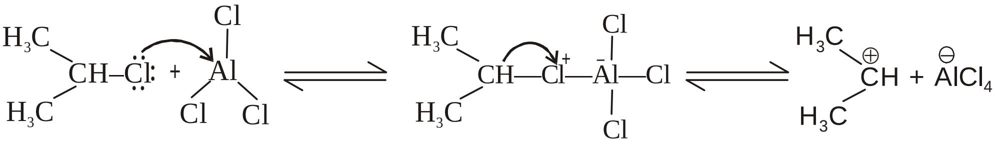
(Electrophile for friedel-craft alkylataion is R^+)

Reagents :

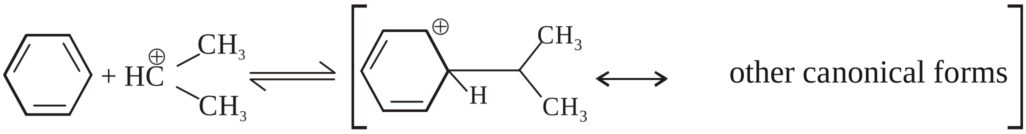
(a) R–X + Lewis acid
(b) R–OH + Lewis acid
(c) Alkene + H^+

Mechanism

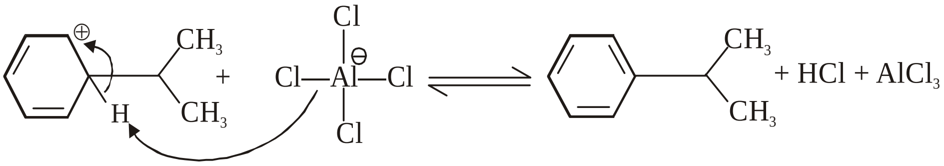
Step-I :



Step-II :

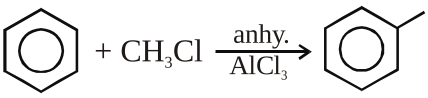


Step III :



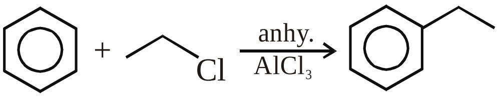
Some examples of Friedel-Craft's alkylation :

eg.55

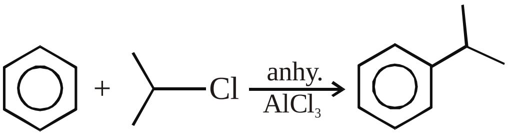


(Toluene)

eg.56

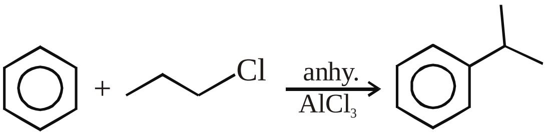


eg.57

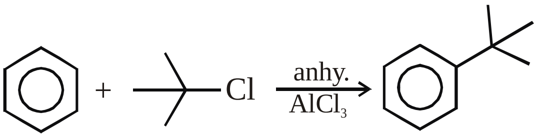


(Cumene)

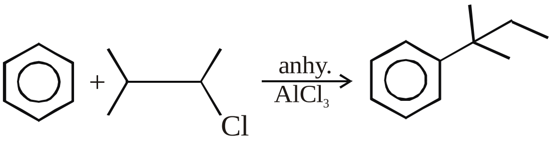
eg.58



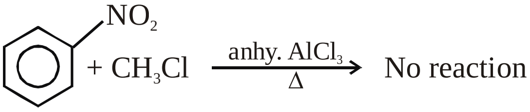
eg.59



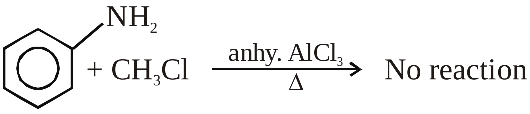
eg.60



eg.61



eg.62

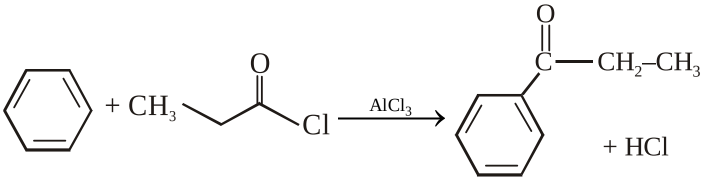


3.8. Friedel-crafts acylation

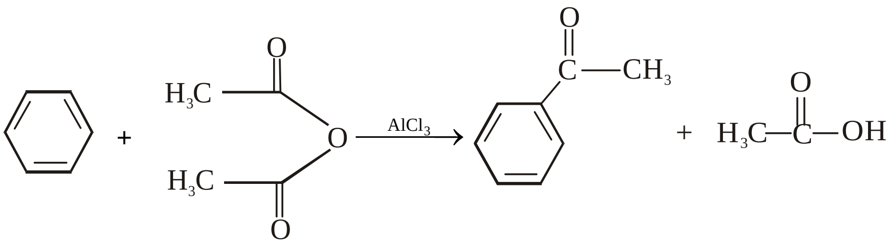
(Electrophile for friedel-craft acylataion is R–C$^+$=O)

Reagents :

(a) RCOX + Lewis acid
(b) $(RCO)_2O$ + Lewis acid
(c) RCOOR' + Lewis acid
(d) RCOOH + Lewis acid



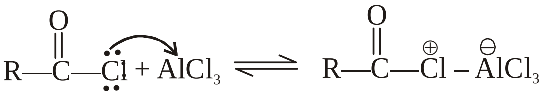
Friedel-Crafts acylations can also be carried out using carboxylic acid anhydrides.



Mechanism :

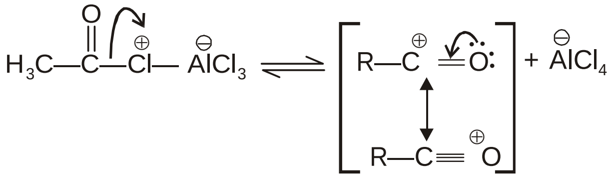
In Friedel-Crafts acylation reactions the electrophile appears to be an acylium ion formed from an acyl halide in the following way.

Step-I :



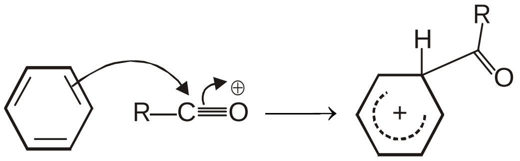
$$R-\overset{O}{\overset{\|}{C}}-\ddot{\underset{\cdot\cdot}{Cl}} + AlCl_3 \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{Cl}-\overset{\ominus}{AlCl_3}$$

Step-II :

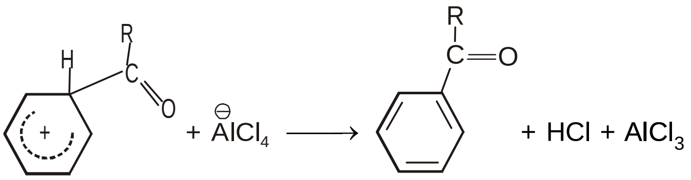


$$H_3C-\overset{O}{\overset{\|}{C}}-\overset{\oplus}{Cl}-\overset{\ominus}{AlCl_3} \rightleftharpoons \left[\begin{array}{c} R-\overset{\oplus}{C}=\ddot{O}: \\ \updownarrow \\ R-C\equiv\overset{\oplus}{O} \end{array}\right] + \overset{\ominus}{AlCl_4}$$

Step-III :

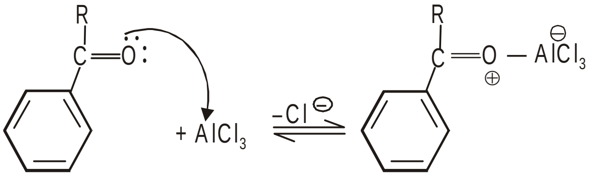


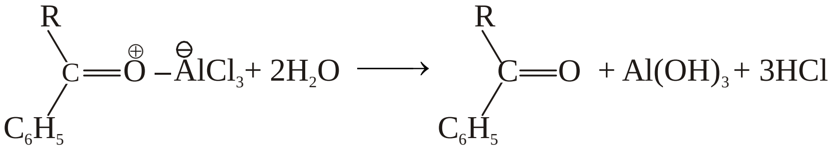
Step-IV :



In the last $AlCl_3$ (a Lewis acid) forms a complex with the ketone (a Lewis base). After the reaction is over, treating the complex with water liberates the ketone.

Step-V :

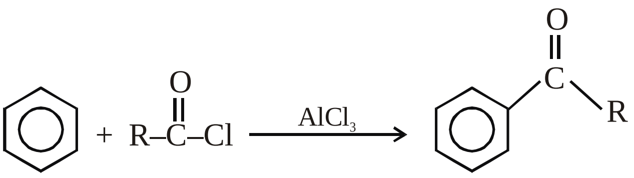




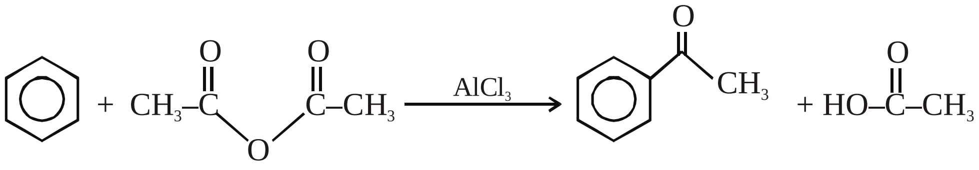
$$\underset{C_6H_5}{\overset{R}{C}}=\overset{\oplus}{O}-\overset{\ominus}{AlCl_3} + 2H_2O \longrightarrow \underset{C_6H_5}{\overset{R}{C}}=O + Al(OH)_3 + 3HCl$$

Some examples of Friedel-Craft's Acylation reaction

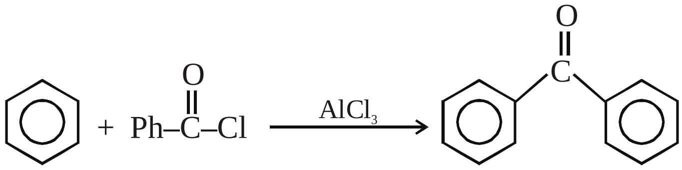
eg.63



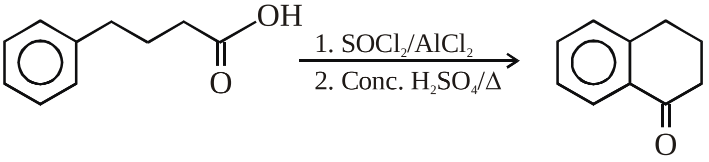
eg.64



eg.65



eg.66



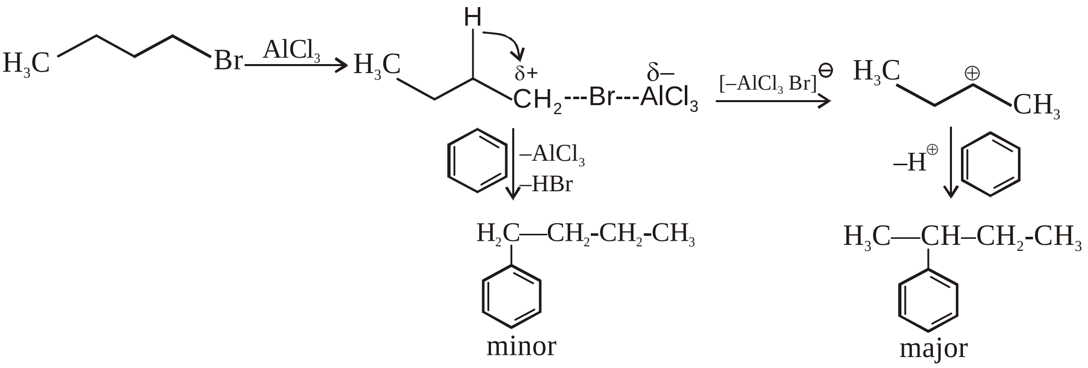
3.9 Limitations of Friedel-Crafts reactions

(a) Rearrangment of alkyl carbocations

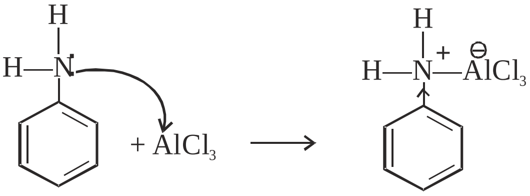
When the carbocation formed from an alkyl halide, alkene, or alcohol can rearrange to a more stable carbocation,

it usually does so and the major product obtained from the reaction is usually the one from the more stable carbocation.

Note : **Rearrangemnt is not possible in Friedel Craft acylation reaction.**

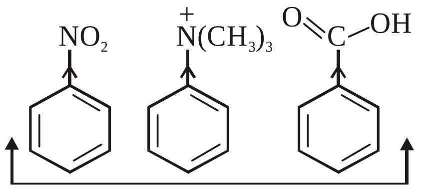


(b) Aromatic ring containing $–NH_2$, –NHR, $–NR_2$, groups do not undergo Friedal-Craft's reaction due to formation of anilinum complex which is meta directing and has more electron withdrawing power than halogen in benzene ring.



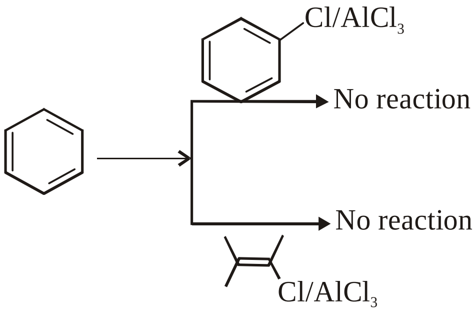
Meta directing group
and does not undergo
Friedal Craft's reaction

(c) Friedel-Crafts reactions (alkylation and acylation) do not occur when powerful electron-withdrawing groups (like $-NO_2$, $-\overset{\oplus}{N}R_3$ etc) are present on the aromatic ring.



These do not undergo Friedel -Crafts reactions

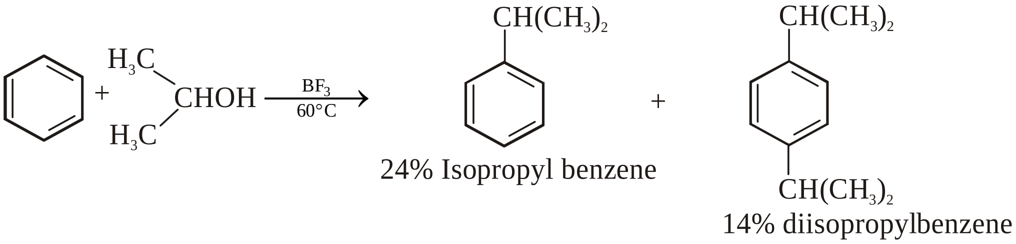
(d) Aryl and vinylic halides can not be used as the halide component because they do not form carbocations readily.



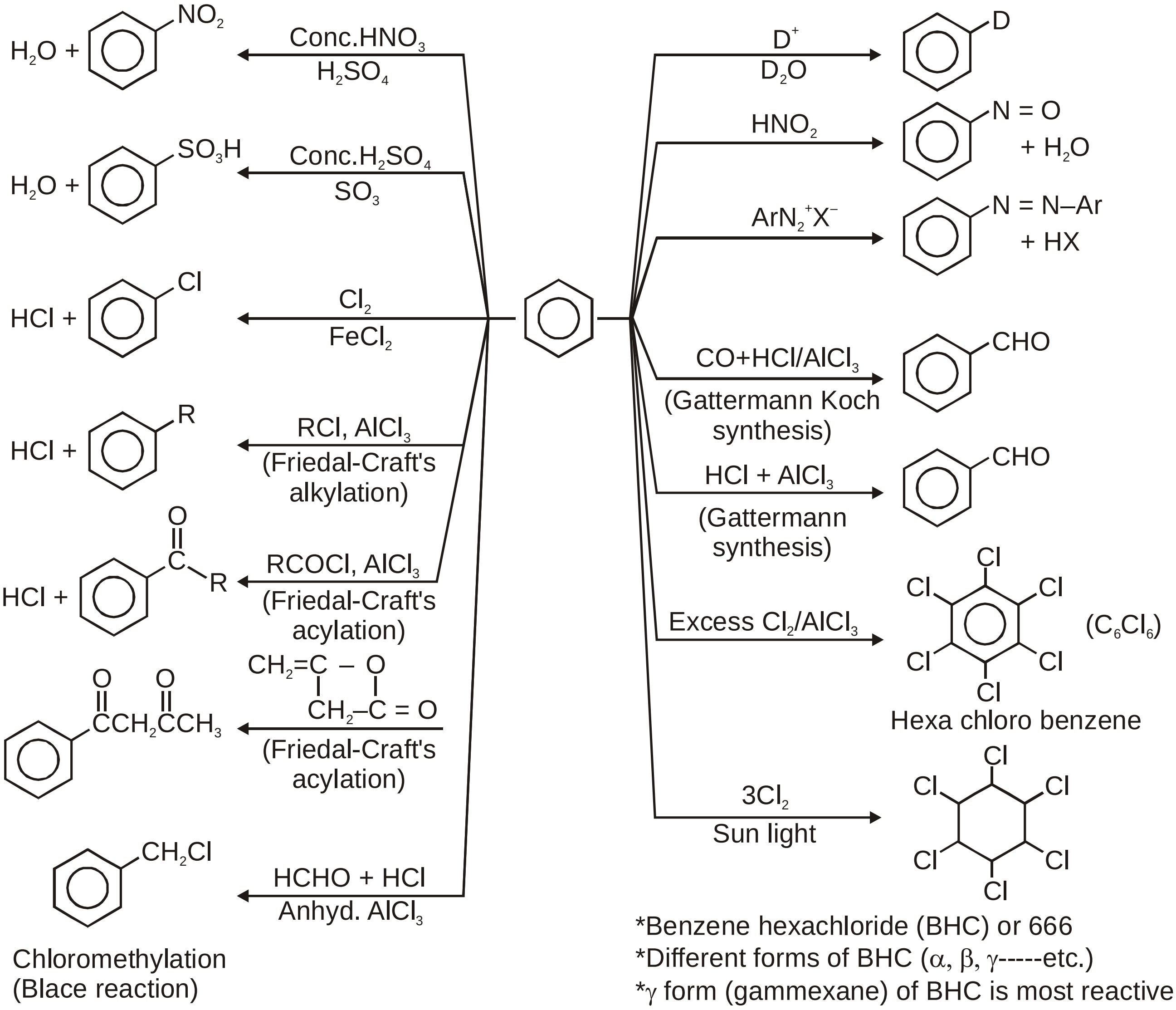
(e) Polyalkylations often occur because alkyl groups are electron releasing groups, and once one is introduced into the benzene ring it activates the ring towards further substitution.

Note : (1) To prepare mono alkyl benzene or n-alkyl benzene acylation is prefer over alkylation reaction.

(2) Polyacylations are not a problem in Friedel-Crafts acylations. The acyl group (RCO–) by itself is an electron-withdrawing group, and when it forms a complex with $AlCl_3$ in the last step of the reaction, it is made even more electron withdrawing. This strongly inhibits further substitution and makes monoacylation easy.



3.9 Summary of chemical reactions of benzene



*Benzene hexachloride (BHC) or 666

*Different forms of BHC (α, β, γ-----etc.)

*γ form (gammexane) of BHC is most reactive

Exercise # 1

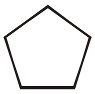
PART-I : SUBJECTIVE QUESTIONS

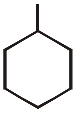
Section (A) : Free radical substitution & free radical addition reaction.

A-1. How do you account for formation of ethane during chlorination of methane ?

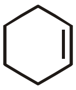
A-2. Calculate the relative amount of 1 and 2-Bromopropane obtained from the bromination of propane. The relative reactivity of 1º : 2º : 3º hydrogen atom towards bromination is 1 : 82 : 1600.

A-3. Give the major product of monobromination of following compounds.

(a) 

(b) 

(c) 

(d) 

A-4. Predict the product of the reaction given below :

$$CH_3–CH_2–CH=CH_2 \xrightarrow[\text{Peroxide or light}]{HBr}$$

A-5. $CH_2 = CH – CH_2 – CH_3 \xrightarrow{NBS} B + C$

write structure of B and C.

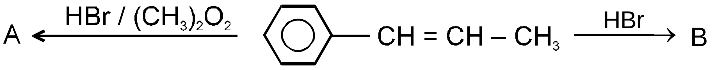
A-6. How many alkanes having molecular weight 100 are chiral ?

Section (B) : Electrophilic addition reaction

B-1. What will be order of reactivity of following compounds towards electrophilic addition reaction?

(I) $CH_2=CH_2$ (II) $CH_3–CH=CH_2$ (III) $(CH_3)_2C=CH_2$ (IV) $CH_3–CH=CH–CH_3$

B-2. In the reaction sequence,



What is the relationship between A & B :

B-3. What will happen when Br_2/CCl_4 react with (a) cis But-2-ene (b) trans But-2-ene.

B-4. How many gram of Br_2 will react with 5 gram of given compounds ?

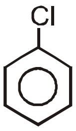
(a) Pent-1-ene (b) Pent-1-yne (c) Pentane + U.V. rays

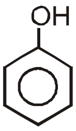
B-5. Give the total isomeric products formed when one equivalent of HBr is added to buta-1, 3-diene ?

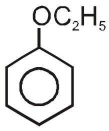
Section (C) : Electrophilic subsitution reaction of aromatic compounds

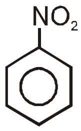
C-1 Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. Explain why?

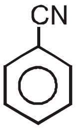
C-2. How many of the following groups on benzene ring are ortho-para director ?

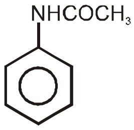
(a) 

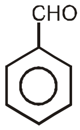
(b) 

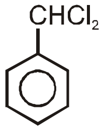
(c) 

(d) 

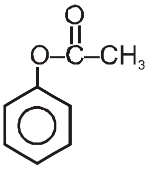
(e) 

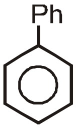
(f) 

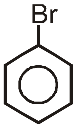
(g) 

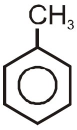
(h) 

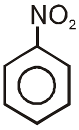
C.3 How many of the following benzene rings contain deactivating groups ?

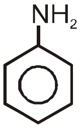
(a) 

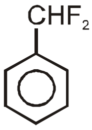
(b) 

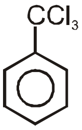
(c) 

(d) 

(e) 

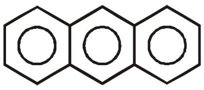
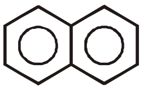
(f) 

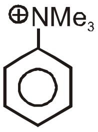
(g) 

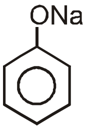
(h) 

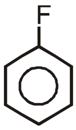
C-4. Arrange the followings in decreasing order of their reactivity with an electrophile.

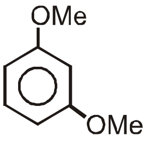
(I) (II) (III)

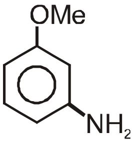
(a)   

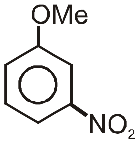
(b) 

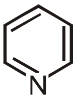


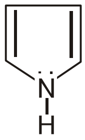


(c) 



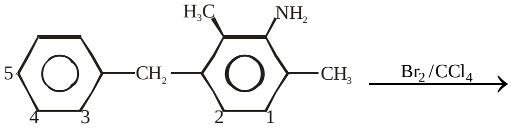


(d)  



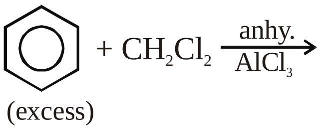
C-5. The number of benzylic hydrogen atom(s) in cumene is :-

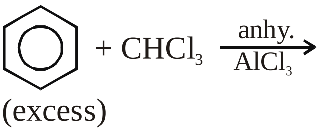
C-6. In the following reaction electrophile attack at which position ?



C-7. Write the product given reactions :

(a)


(b)


(c)


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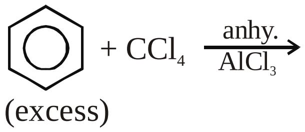

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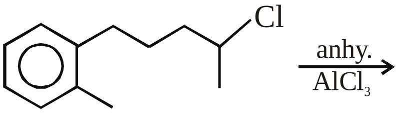
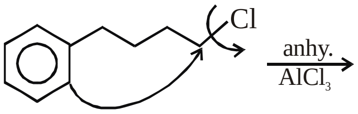


(f)


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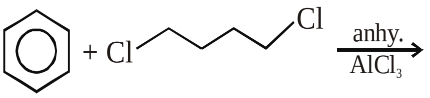

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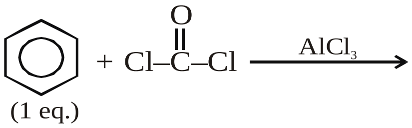
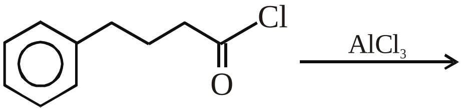


(i)


PART-II : OBJECTIVE QUESTIONS

Section (A) : Free radical substitution & free radical addition reaction

A-1. In the free radical chlorination of methane, the chain initiating step involves the formation of –
(A) Chlorine radical (B) Hydrogen chloride (C) Methyl radical (D) Chloromethyl radical.

A-2. Which of the following cannot be considered as a step of mechanism in chain reaction of methane with Cl_2?

(A) $Cl_2 \longrightarrow 2Cl^{\bullet}$ (B) $CH_4 + Cl^{\bullet} \longrightarrow CH_3Cl + H^{\bullet}$

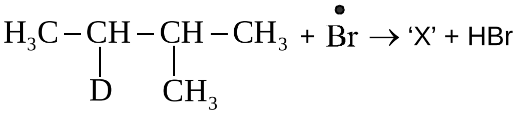
(C) $Cl^{\bullet} + CH_4 \longrightarrow CH_3^{\bullet} + HCl$ (D) $Cl^{\bullet} + CH_3^{\bullet} \longrightarrow CH_3Cl$

A-3. The maximum ease of abstraction of a hydrogen atom by a chlorine atom is shown by –
(A) $(CH_3)_3C–CH_3$ (B) $(CH_3)_2CH_2$ (C) $C_6H_5CH_3$ (D) $CH_2= CHCH_3$

A-4. Methane reacts with excess of chlorine in diffused sunlight to give the final product as
(A) Chloroform (B) Methyl chloride. (C) Methylene chloride (D) Carbon tetrachloride

A-5. What will the chief product obtained when n-butane is treated with Br_2 in the presence of light at 130°C ?
(A) $CH_3 – CH_2 – CHBr – CH_3$ (B) $(CH_3)_2CHCH_2Br$
(C) $(CH_3)_3CBr$ (D) $CH_3 – CH_2 – CH_2 – CH_2 – Br$

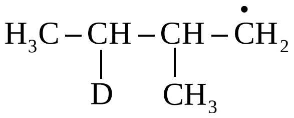
A-6. Consider the following reactions –



$H_3C-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 + \overset{\bullet}{Br} \rightarrow$ 'X' + HBr

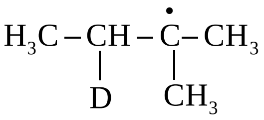
Identify the structure of the major product 'X'

(A)



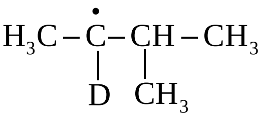
$H_3C-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-\overset{\bullet}{C}H_2$

(B)



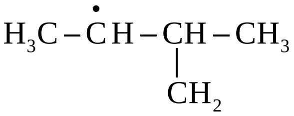
$H_3C-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{\overset{\bullet}{C}}}-CH_3$

(C)



$H_3C-\underset{D}{\underset{|}{\overset{\bullet}{C}}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

(D)



$H_3C-\overset{\bullet}{C}H-\underset{CH_2}{\underset{|}{CH}}-CH_3$

A-7. Which of the following statement is correct in relation to the halogenation of alkane ?

(A) The reactivity of chlorine is less than bromine towards alkanes.

(B) For photochemical chlorination of methane, $\overset{\bullet}{C}l$ is formed in slowest step.

(C) Free radicals are pyramidal intermediate, stabilised by hyperconjugation and resonance.

(D) Bromination has much higher regioselective than chlorination in abstracting 3^0 hydrogen.

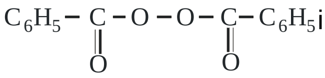
A-8. Which statement is incorrect about free radical halogenation of alkanes ?

(A) The number of product molecules formed by one photon is very high.

(B) If O_2 is added, initially the rate of reaction decreases, then increases.

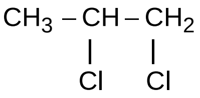
(C) Inhibitors combine with free radical and terminate the chain reaction.

(D) Presence of $C_6H_5-\underset{\underset{O}{\|}}{C}-O-O-\underset{\underset{O}{\|}}{C}-C_6H_5$ inhibits the free radical reaction.



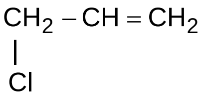
A-9. $CH_3CH = CH_2 \xrightarrow{Cl_2,\ 500°C}$ P, Product P is :

(A)



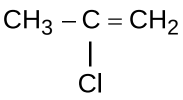
$CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

(B)



$\underset{Cl}{\underset{|}{CH_2}}-CH=CH_2$

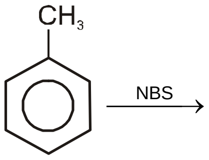
(C)



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

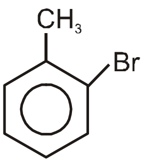
(D) $CH_3-CH=CH-Cl$

A-10.

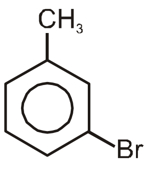


Product is

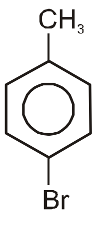
(A)



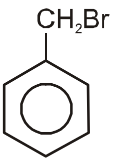
(B)



(C)

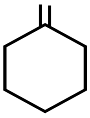


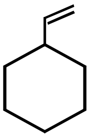
(D)

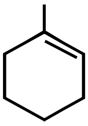


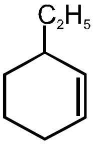
Section (B) : Electrophilic addition reaction

B-1. What is the correct reactivity order of electrophilic addition reactions in the following compounds ?

(I) 

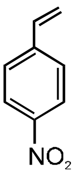
(II) 

(III) 

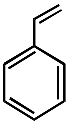
(IV) 

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

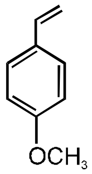
B-2. Arrange the following in decreasing order of reactivity with HBr :



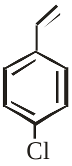
I



II



III



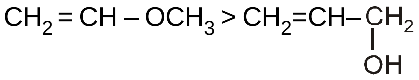
IV

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

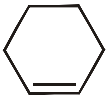
B-3. The correct order of alkenes reactivity towards an electrophile is mentioned in-

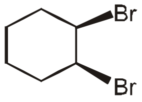
(A) $CH_2=CH–Cl > CH_2=CH–OCH_3$ (B) $CH_2=CHCl < CH_2=CCl_2$

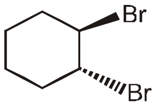
(C) ethene > propene

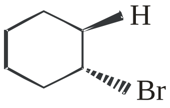
(D) 

$CH_2 = CH – OCH_3 > CH_2=CH–\underset{\large OH}{\underset{|}{CH_2}}$

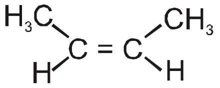
B-4.  + Br_2 ⟶ P, P will have configuration :

(A) 

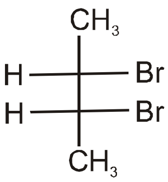
(B) 

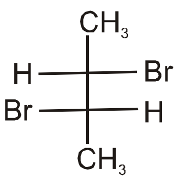
(C) 

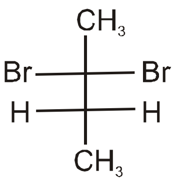
(D) none is true

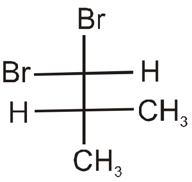
B-5. 

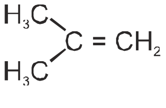
$+ Br_2 \xrightarrow{CCl_4}$ Product is :

(A) 

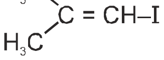
(B) 

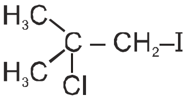
(C) 

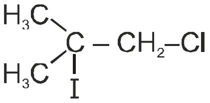
(D) 

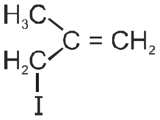
B-6. 

+ ICl ⟶ P (major product), Here 'P' is :

(A) 

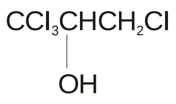
(B) 

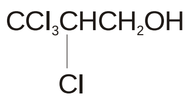
(C) 

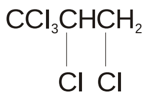
(D) 

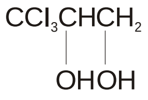
B-7. $CCl_3CH{=}CH_2 \xrightarrow{Cl_2 + H_2O} P$

Identify major product 'P'.

(A) 
$CCl_3\underset{\underset{OH}{|}}{C}HCH_2Cl$

(B) 
$CCl_3\underset{\underset{Cl}{|}}{C}HCH_2OH$

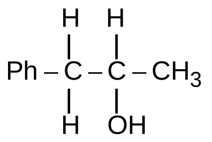
(C) 
$CCl_3\underset{\underset{Cl}{|}}{C}H\underset{\underset{Cl}{|}}{C}H_2$

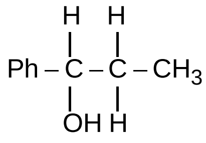
(D) 
$CCl_3\underset{\underset{OH}{|}}{C}H\underset{\underset{OH}{|}}{C}H_2$

B-8. $Ph-CH_2-CH=CH_2 \xrightarrow{\text{dil. } H_2SO_4} X,$

Identify major product 'X' is :

(A) $Ph-CH_2-CH_2-CH_2-OH$

(B) 
$Ph-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$

(C) 
$Ph-\overset{\overset{H}{|}}{\underset{\underset{OH}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-CH_3$

(D) $Ph-CH_2-OH$

B-9. In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti–Markovnikov addition to alkene because –

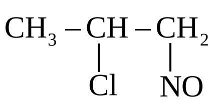
(A) both are highly ionic
(B) one is oxidising and the other is reducing
(C) one of the step is endothermic in both the cases
(D) all the steps are exothermic in both cases

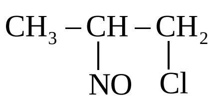
B-10. The reaction of propene with HOCl proceeds via the addition of –

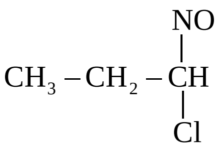
(A) H^+ in first step
(B) Cl^+ in first step
(C) OH^- in first step
(D) Cl^+ and OH^- in single step

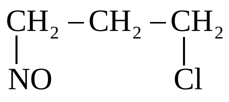
B-11. $CH_3{-}CH{=}CH_2 + NOCl \rightarrow$ Major product

Identify the product.

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

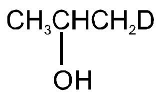
(B) 
$CH_3-\underset{\underset{NO}{|}}{CH}-\underset{\underset{Cl}{|}}{CH_2}$

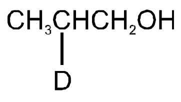
(C) 
$CH_3-CH_2-\overset{\overset{NO}{|}}{\underset{\underset{Cl}{|}}{CH}}$

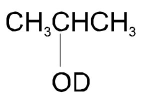
(D) 
$\underset{\underset{NO}{|}}{CH_2}-CH_2-\underset{\underset{Cl}{|}}{CH_2}$

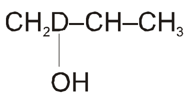
B-12. $CH_3CH{=}CH_2 \xrightarrow[H_2O_2/OH^-]{BD_3/\,THF} X,$

Identify product X is :

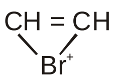
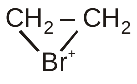
(A) 
$CH_3\underset{\underset{OH}{|}}{C}HCH_2D$

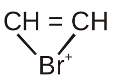
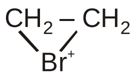
(B) 
$CH_3\underset{\underset{D}{|}}{C}HCH_2OH$

(C) 
$CH_3\underset{\underset{OD}{|}}{C}HCH_3$

(D) 
$CH_2D{-}\underset{\underset{OH}{|}}{CH}{-}CH_3$

B-13. Alkynes are less reactive than alkenes towards addition of Br_2 because :

(A) 
$\underset{Br^+}{\underset{\diagdown\;\diagup}{CH=CH}}$ is less stable than 
$\underset{Br^+}{\underset{\diagdown\;\diagup}{CH_2-CH_2}}$

(B) 
$\underset{Br^+}{\underset{\diagdown\;\diagup}{CH=CH}}$ is more stable than 
$\underset{Br^+}{\underset{\diagdown\;\diagup}{CH_2-CH_2}}$

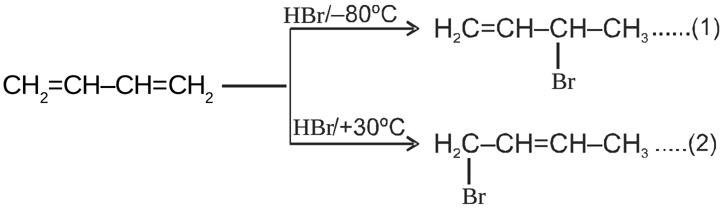
(C) Both are equally stable
(D) Original statement is incorrect

B-14. $R \xleftarrow[H_2O_2/OH^-]{BH_3/THF} P \xrightarrow[H_2SO_4]{HgSO_4} Q$

Q & R are identical when P is –

(A) HC≡CH (B) CH_3–C≡CH (C) CH_3–C≡C–CH_3 (D) Both A and C

B-15.

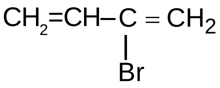


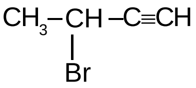
At given temperature, these reactions tell about control of reaction which is :

(1)	(2)
(A) Kinetic	Thermodynamic
(B) Thermodynamic	Kinetic
(C) Kinetic	Kinetic
(D) Thermodynamic	Thermodynamic

B-16. The reaction of one equivalent of HBr with CH_2=CH–C≡CH gives :

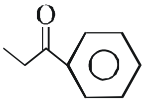
(A) CH_2=CH–C≡CBr

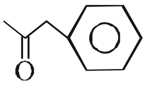
(B) 
$CH_2=CH-\underset{Br}{C}=CH_2$

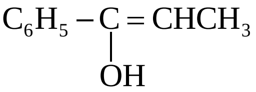
(C) 
$CH_3-\underset{Br}{CH}-C\equiv CH$

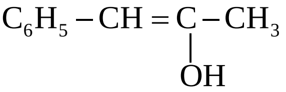
(D) CH_2=CH–CH=CHBr

B-17. $C_6H_5-C\equiv C-CH_3 \xrightarrow[H_2SO_4]{HgSO_4}$ Product is :

(A) 

(B) 

(C) 
$C_6H_5-\underset{OH}{C}=CHCH_3$

(D) 
$C_6H_5-CH=\underset{OH}{C}-CH_3$

Section (C) : Electrophilic substitution reaction of aromatic compounds

C-1. Which can be used to generate NO_2^+ in nitration of benzene ring ?

(A) $HNO_3 + H_2SO_4$ (B) $HNO_3 + HClO_4$ (C) Solid N_2O_5 (D) All

C-2. For the electrophilic substitution reaction involving nitration, which of the following sequence regarding the rate of reaction is true?

(A) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (B) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$

(C) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (D) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

C-3. For the electrophilic substitution reaction involving sulphonation, which of the following sequence regarding the rate of reaction is true?

(A) $k_{C_6H_6} > k_{C_6D_6} > k_{C_6T_6}$ (B) $k_{C_6H_6} < k_{C_6D_6} < k_{C_6T_6}$

(C) $k_{C_6H_6} = k_{C_6D_6} = k_{C_6T_6}$ (D) $k_{C_6H_6} > k_{C_6D_6} < k_{C_6T_6}$

C-4. Reaction of SO_3 is easier in –

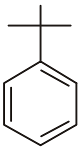
(A) benzene (B) toluene (C) nitrobenzene (D) chlorobenzene

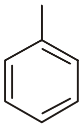
C-5. Which order is correct for the decreasing reactivity to ring monobromination of the following compounds ?

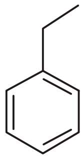
(I) $C_6H_5CH_3$ (II) C_6H_5COOH (III) C_6H_6 (IV) $C_6H_5NO_2$

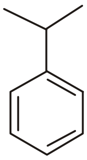
(A) I > II > III > IV (B) I > III > II > IV (C) II > III > IV > I (D) III > I > II > IV

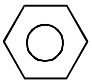
C-6. Which of the following will undergo sulphonation at the fastest rate ?

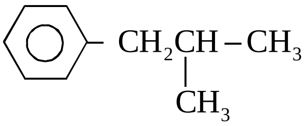
(A) 

(B) 

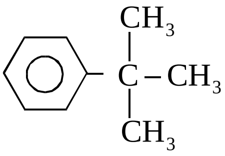
(C) 

(D) 

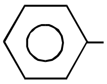
C-7.  + $CH_3CH_2CH_2CH_2Cl \xrightarrow{AlCl_3}$ hydrocarbon (X), major product X is:

(A) 

$C_6H_5-CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_3$

(B) 

$C_6H_5-\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle CH_3}{\underset{|}{C}}}}-CH_3$

(C)  $CH_2CH_2CH_2CH_3$

(D) None is correct

C-8. o/p Ratio is highest for nitration of which of the following compound ?

(A) Ethyl benzene (B) Toluene

(C) Isopropyl benzene (D) Tertiarybutyl benzene

C-9. $C_6H_6 \xrightarrow[AlCl_3]{CH_3COCl} A \xrightarrow[HCl]{Zn-Hg} B$

The end product in the above sequence is:

(A) toluene (B) ethyl benzene (C) benzophenone (D) acetophenone

C-10. For preparing monoalkyl benzene, acylation process is preferred than direct alkylation because

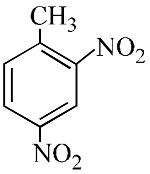
(A) In alkylation, a poisonous gas is evolved

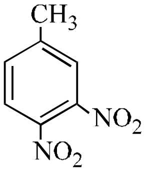
(B) In alkylation, large amount of heat is evolved

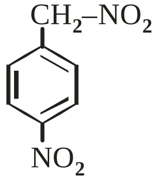
(C) In alkylation, polyalkylated product is formed

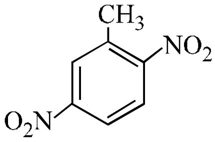
(D) Alkylation is very costly

C-11. p-Nitrotoluene on further nitration gives:

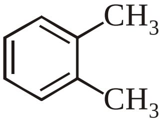
(A) 

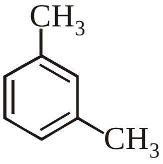
(B) 

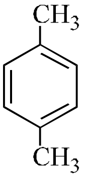
(C) 

(D) 

C-12. Ring nitration of dimethyl benzene results in the formation of only one nitro dimethyl benzene. The dimethyl benzene is:

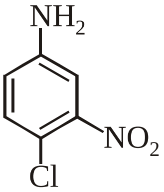
(A) 

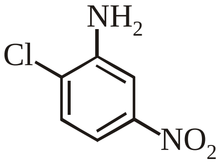
(B) 

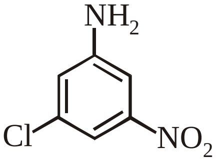
(C) 

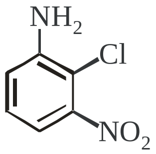
(D) None of these

C-13 If meta-nitroaniline is chlorinated, the major product is:

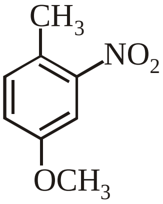
(A) 

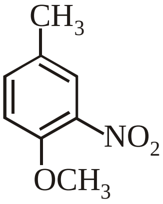
(B) 

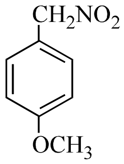
(C) 

(D) 

C-14. If p-methoxy toluene is nitrated, the major product is:

(A) 

(B) 

(C) 

(D) No reaction

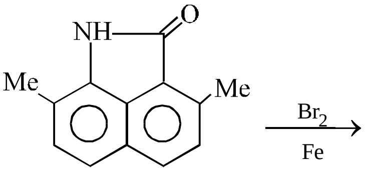
C-15. The highest yield of m-product is possible by the electrophilic substitution, in which of the following ?

(A) $C_6H_5CH_3$

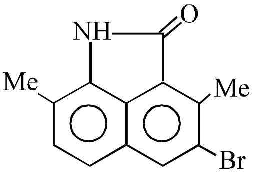
(B) $C_6H_5CH_2COOC_2H_5$

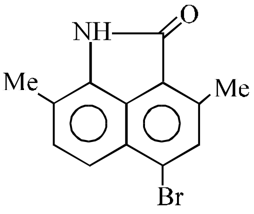
(C) $C_6H_5CH(COOC_2H_5)_2$

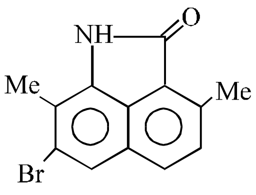
(D) $C_6H_5C(COOC_2H_5)_3$

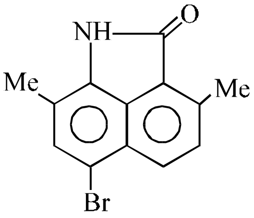
C-16. 

Major product of above reaction is:

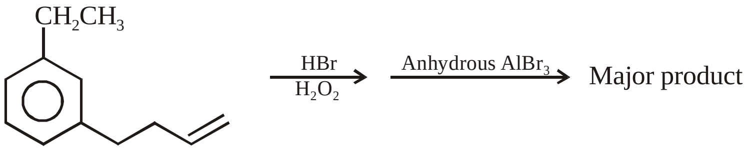
(A) 

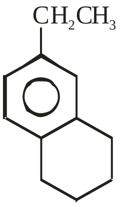
(B) 

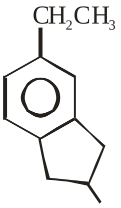
(C) 

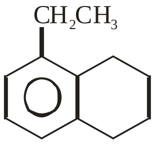
(D) 

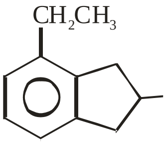
C-17.



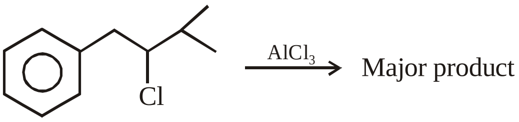
(A)


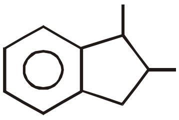
(B)


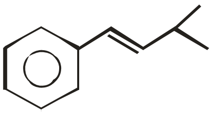
(C)


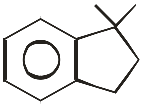
(D)


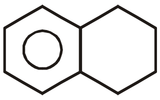
C-18.



(A)


(B)


(C)


(D)


PART-III : MATCH THE COLUMN

1. Match List-I with List-II.

List-I (Reaction)	**List-II (Reagents)**
(A) CH_3–CH=CH_2→CH_3–CHBr–CH_3	(P) HBr
(B) CH_3–CH=CH_2→CH_3–CH_2–CH_2Br	(Q) Br_2 / CCl_4
(C) CH_3–CH=CH_2→BrCH_2–CH=CH_2	(R) HBr / Peroxide
(D) CH_3–CH=CH_2→CH_3–CHBr–CH_2Br	(S) NBS

2. Match List I (reactions) with List II (type of mechanisms) and select the correct answer using the code given below the lists :

List - I	**List- II**
(A) $Ph–CH_2–CH_3 \xrightarrow{Br_2/h\nu}$	(P) Electrophilic substitution
(B) $Ph–CH=CH_2 \xrightarrow{dil.H_2SO_4}$	(Q) Electrophilic addition
(C) $Ph–CH=CH_2 \xrightarrow{HBr/R_2O_2}$	(R) Free radical substitution
(D) $Ph–CH_2–CH_3 \xrightarrow{Br_2/Fe}$	(S) Free radical addition

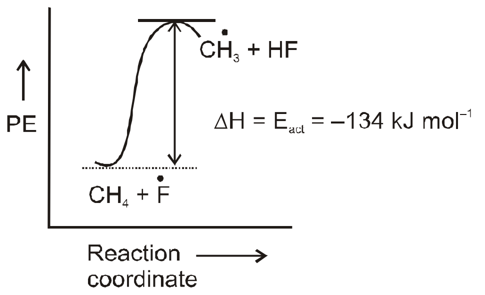
Exercise # 2

PART - I : OBJECTIVE QUESTIONS

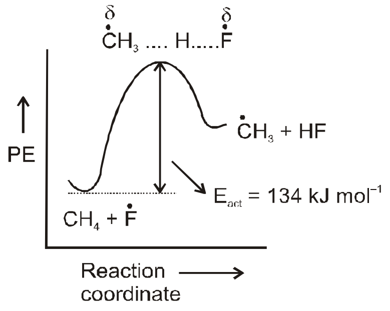
1. Which of the following is correct potential energy diagram for the given chain propagation step ?

$$\underset{\text{B.E.} = 435}{CH_3-H} + \dot{F} \longrightarrow \dot{C}H_3 + \underset{\text{B.E.} = 569}{H-F} \qquad \Delta H^o = -134\ kJ/mol$$

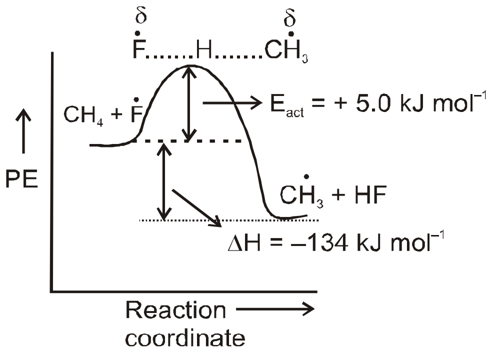
(A)



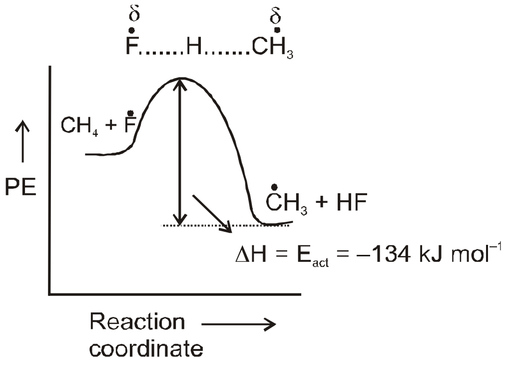
(B)



(C)



(D)

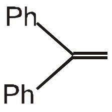


2. Which statement is correct about photochemical bromination of butane ?

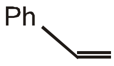
$$CH_3-CH_2-CH_2-CH_3 \xrightarrow{Br_2,\ h\upsilon}$$

(A) 1-Bromobutane and 2-bromobutanes are formed in equal amounts.
(B) 2-Bromobutane is formed with faster rate than 2-chlorobutane in the other experiment of chlorination.
(C) The major product is an equimolar mixture of two compounds
(D) Homolysis of C – H bond has lower activation energy than homolysis of Br – Br bond.

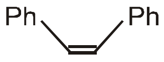
3.



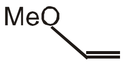
(I)



(II)



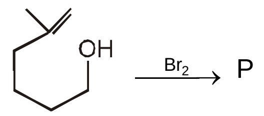
(III)



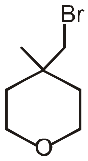
(IV)

Order of rate of electrophilic addition reaction with HBr will be :
(A) IV> I > III > II (B) I > II > III > IV (C) I > III > II > IV (D) IV > I > II > III

4.



Identify the major product 'P'.

(A)


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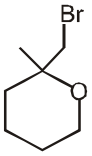
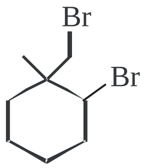
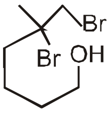
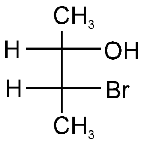


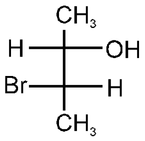
(C)


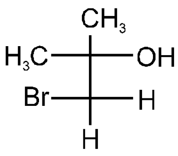
(D)


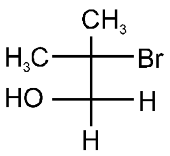
5. cis-2-Butene $\xrightarrow{HOBr}$ P,

Identify the product 'P'.

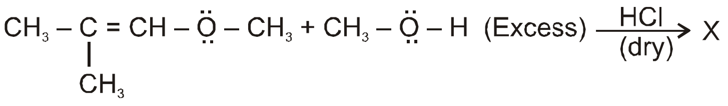
(A)


(B)


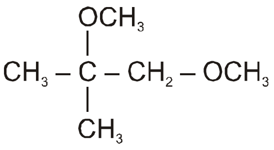
(C)


(D)


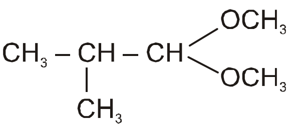
6. In the given reaction major product 'X' will be :



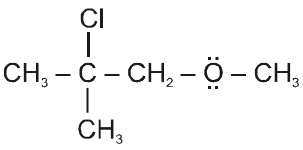
$CH_3-\underset{\underset{CH_3}{|}}{C}=CH-\ddot{\underset{..}{O}}-CH_3+CH_3-\ddot{\underset{..}{O}}-H$ (Excess) $\xrightarrow[\text{(dry)}]{HCl}$ X

(A)


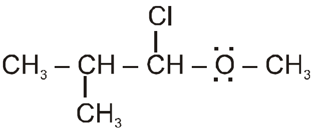
$CH_3-\overset{\overset{OCH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-OCH_3$

(B)


$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH\begin{array}{l}OCH_3\\OCH_3\end{array}$

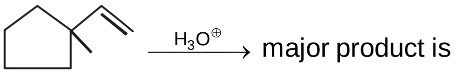
(C)


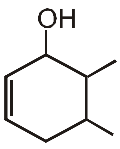
$CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\ddot{\underset{..}{O}}-CH_3$

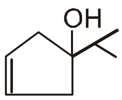
(D)


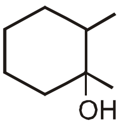
$CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{Cl}{|}}{CH}-\ddot{\underset{..}{O}}-CH_3$

7.



(A)


(B)


(C)


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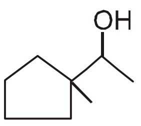
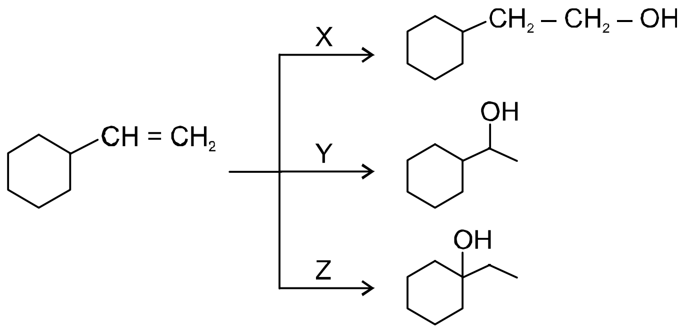


8. 

X, Y, Z reaction are respectively.

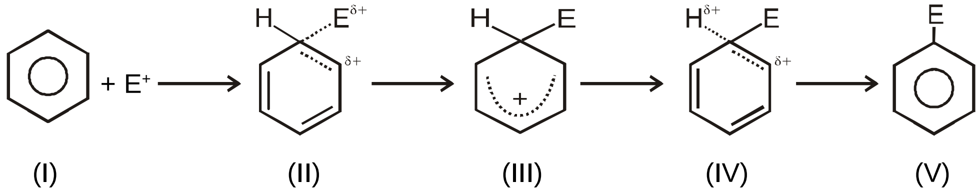
(A) Simple hydration reactions.

(B) Hydroboration oxidation, hydration and oxymercuration demercuration.

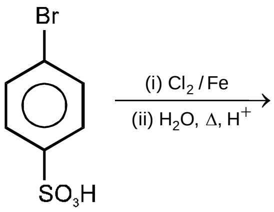
(C) Hydroboration oxidation, oxymercuration demercuration and hydration.

(D) Oxymercuration demercuration, hydroboration oxidation and hydration.

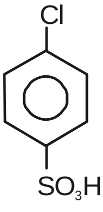
9. Which of the following species is expected to have maximum enthalpy in an electrophilic aromatic substitution reaction ?

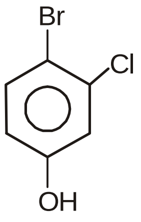


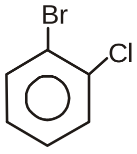
(A) Species (II) (B) Species (III) (C) Species (IV) (D) Species (V)

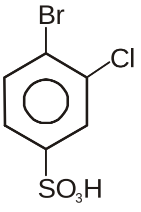
10. 

Identify the product

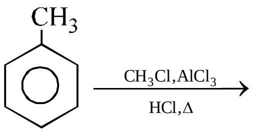
(A) 

(B) 

(C) 

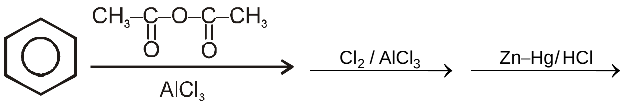
(D) 

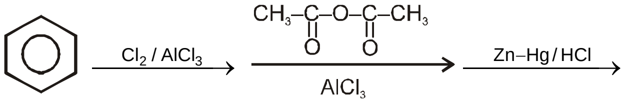
11. Major product of this reaction will be :

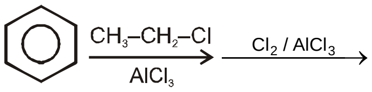


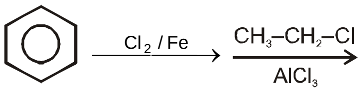
(A) o-Xylene (B) p-Xylene (C) both A and B (D) m-Xylene

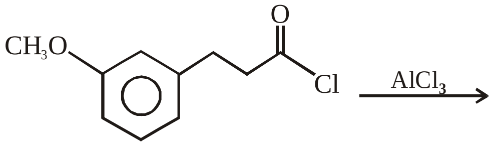
12. Which step is used to produce 1–Chloro–3–ethylbenzene ?

(A) 

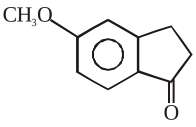
(B) 

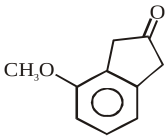
(C) 

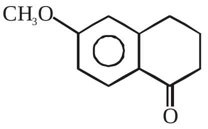
(D) 

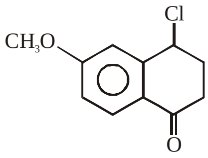
13. 

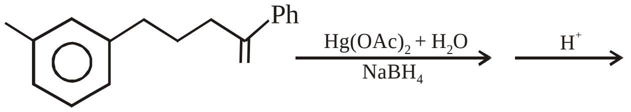
Major product

(A) 

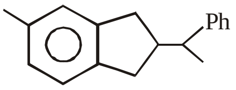
(B) 

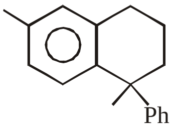
(C) 

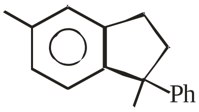
(D) 

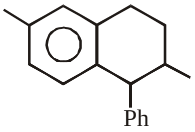
14. 

Major product

(A) 

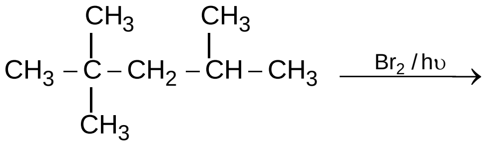
(B) 

(C) 

(D) 

PART - II : NUMERICAL TYPE QUESTIONS

1. For the given reaction how many products (consider all isomers) are optically active ?



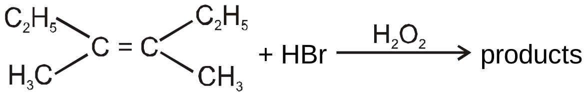
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow{Br_2/h\upsilon}$$

2. The number of possible enantiomeric pairs that can be produced during monochlorination of 2-methylbutane is

3. How many products are formed when 1,5-dimethylcyclopentene react with HBr in presence of peroxide ?

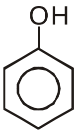
4. How many dibromo derivatives are formed when bromine is added to 3-methylcyclohexene in presence of CCl_4 ?

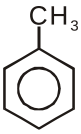
5. Mixture of one mole each of ethene and propyne on reaction with Na will form H_2 gas at S.T.P. Amount of H_2 (in litre) gas will be –

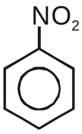
6. 

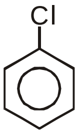
How many total products will be formed in the above reaction ?

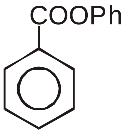
7. How many of following compounds are less reactive than benzene for sulphonation by conc. H_2SO_4 ?

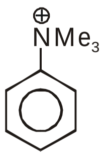


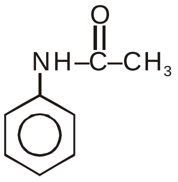


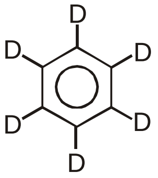


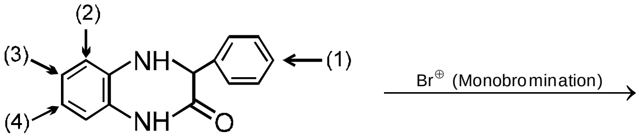








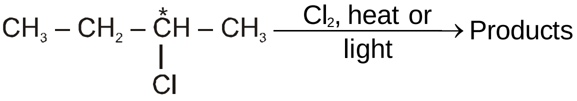


8. 

The substitution will mainly take place at which position ?

9. When ortho dibromobenzene is subjected to mononitration, X number of product are formed and when meta dibormobenzene is subjected to mononitration, Y number of products are formed. Report your answer as XY.

PART - III : ONE OR MORE THAN ONE OPTION CORRECT TYPE

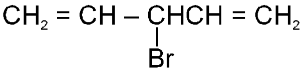
1. 
$CH_3 - CH_2 - \overset{*}{C}H(Cl) - CH_3 \xrightarrow[\text{light}]{Cl_2,\ \text{heat or}} \text{Products}$

Sec-butylchloride

Which statement is/are correct ?

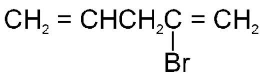
(A) One of the product exist as three stereoisomers
(B) Only two pair of diastereomers are obtained
(C) Only one meso stereoisomer is obtained
(D) Two pair of enantiomers are obtained

2. $CH_2 = CHCH_2CH = CH_2 \xrightarrow{NBS}$ Product is/are

(A) 
$CH_2 = CH - \underset{Br}{C}HCH = CH_2$

(B) $CH_2 = CH - CH = CH - CH_2 - Br$

(C) $CH_2 = CHCH_2CH = CHBr$

(D) 
$CH_2 = CHCH_2\underset{Br}{C} = CH_2$

3. In which reaction the product follows anti Markovnikov's rule ?

(A) $CF_3CH{=}CH_2 \xrightarrow{HCl}$

(B) $ClCH{=}CH_2 \xrightarrow{HCl}$

(C) $CH_3OCH{=}CH_2 \xrightarrow{HCl}$

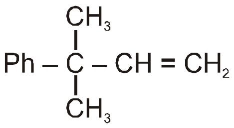
(D) $Ph{-}CH{=}CH_2 \xrightarrow{HCl}$

4. Which of the following will give same product with HBr in presence or absence of peroxide ?

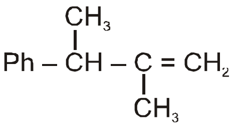
(A) Cyclohexene (B) 1-Methylcyclohexene

(C) 1,2-Dimethylcyclohexene (D) 1-Butene

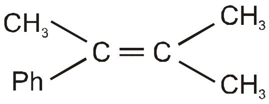
5. Which of the following compounds will give same major product on acid catalysed hydration ?

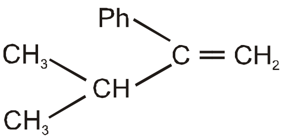
(A)


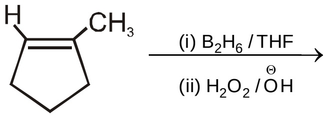
$Ph-C(CH_3)_2-CH=CH_2$

(B)


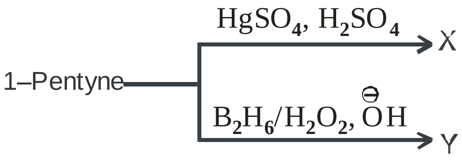
$Ph-CH(CH_3)-C(CH_3)=CH_2$

(C)


(D)


6.


True statement(s) about above reaction is/are -
(A) Reagent involve stereospecific syn addition of H and OH species.
(B) Product obtained is trans isomer.
(C) Boron atom acts as electrophile.
(D) Two stereoisomers are obtained as product.

7.


X and Y can be distinguished by :
(A) Silver-mirror test (B) Iodoform test (C) 2,4-DNP (D) Fehling solution

8. In which of the following reaction t-butylbenzene is formed ?

(A) Benzene + iso-butyl chloride $\xrightarrow{AlCl_3}$ (B) Benzene + $(CH_3)_2C=CH_2$ $\xrightarrow{BF_3.HF}$

(C) Benzene + t-butyl alcohol $\xrightarrow{H_2SO_4}$ (D) Benzene + $(CH_3)_2$ C= CH_2 $\xrightarrow{H^{\oplus}}$

9. The replacement of a hydrogen atom in benzene by alkyl group can be brought about with which of the following reagents ?
(A) Alkyl chloride and $AlCl_3$ (B) Alkene and $AlCl_3$
(C) Alkanol and alkali (D) Alkanol and acid

10. A good method for converting benzene into n-propyl benzene is:
(A) $C_6H_6 + CH_3CH_2CH_2Cl$ + Anhyd. $AlCl_3$
(B) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with Zn/Hg/HCl
(C) $C_6H_6 + CH_3CH_2COCl$ + Anhyd. $AlCl_3$ and then treatment with H_2/Ni
(D) $C_6H_6 + CH_2=CH-CH_2Cl$ + Anhyd. $AlCl_3$ + H_2/Ni

11. Which of the following statements is/are not true?

(A) All ortho-para directing groups activates the ring towards electrophilic substitution.

(B) Halobenzene is ortho para directing but deactivating in nature.

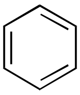
(C) All meta-directing groups must have π-bond on the atom directly attached to the ring.

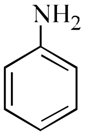
(D) All meta directing groups are deactivating.

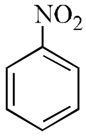
12. Which of the following is not an ortho-para directing group?

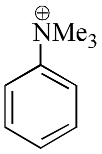
(A) CF_3 (B) CCl_3 (C) –CH=CH–COOH (D) $-\mathrm{N}\overset{\rightarrow}{\equiv}\mathrm{C}$

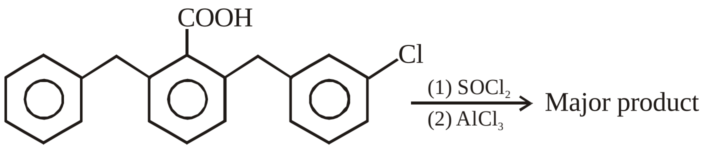
13. Which of the following does not give Friedel-Craft's reaction?

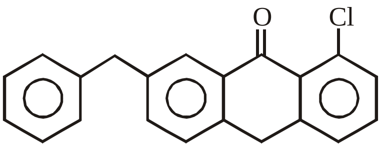
(A) 

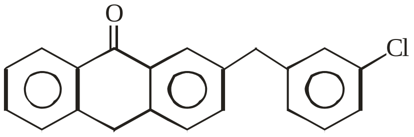
(B) 

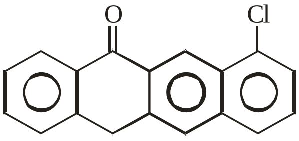
(C) 

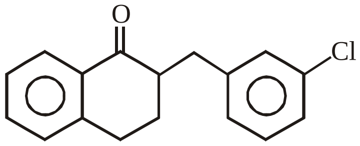
(D) 

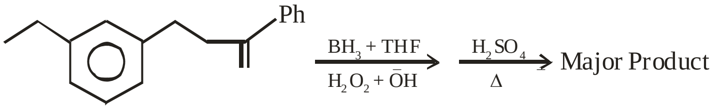
14. 

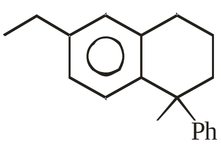
(A) 

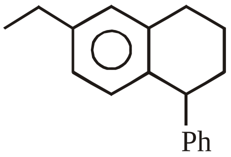
(B) 

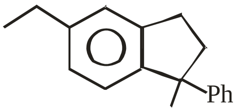
(C) 

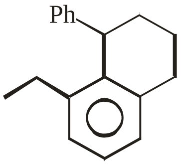
(D) 

15. 

(A) 

(B) 

(C) 

(D) 

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Three acyclic alkenes (x, y, z) on catalytic hydrogenation give same alkane. On reaction with HCl, (x, y, z) form same major tertiary halide product. Reductive ozonolysis of mixture of (x, y, z) gives a mixture of two moles of $CH_2=O$ one moles of $CH_3CH=O$ one mole of acetone, one mole of butanone and one mole of 2-methyl propanal. x, y and z do not have any stereoisomers.

1. Alkene x, y, z are

(A) chain isomers (B) Position isomers (C) Geometrical isomers (D) Optical isomers

2. (x, y, z) $\xrightarrow{H_3O^+}$ addition product. The correct statement is -

(A) All three alkenes will give 3 different major hydration products

(B) Three alkenes will give same major hydration product

(C) Two alkenes form same product but one alkene forms different major product.

(D) Addition of HCl and H_3O^+ both are following different regioselectivity.

3. What is true about x, y, z ?

(A) These have molecular formula C_3H_6

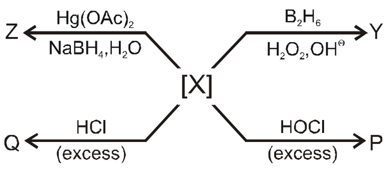
(B) x, y, z on catalytic hydrogenation give chiral alkanes.

(C) These are unbranched alkenes.

(D) These form same carbocation intermediate on reaction with HCl to give the major product.

Comprehension # 2

A Hydrocarbon X (M.F. C_4H_6) produces an aldehyde Y through Hydroboration-Oxidation and a ketone Z through Oxymercuration-Demercuration. Y and Z are functional isomers. X gives P when treated with excess of HOCl and Q when treated with excess of HCl.



4. The structure of X is :

(A) $CH_3–C≡C–CH_3$ (B) $CH_3–CH_2C≡CH$ (C) $CH_2=CH–CH=CH_2$ (D) $CH_2=CH–C≡CH$

5. The correct statement is :

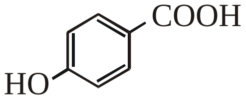
(A) P and Q are positional isomers. (B) Q is 1,2-Dichlorobutane.

(C) P is 1,1-Dichlorobutan-2-one. (D) P and Q are identical.

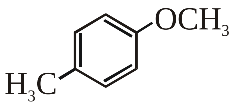
Exercise # 3

PART- I : JEE ADVANCE PROBLEMS (PREVIOUS YEARS)

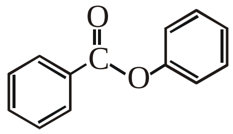
1. The compounds P, Q and S **[JEE 2010]**



P



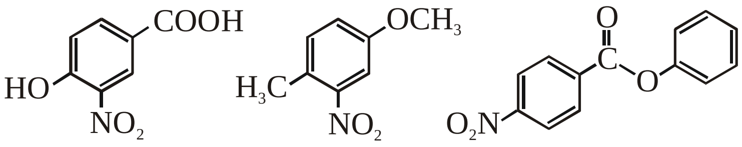
Q



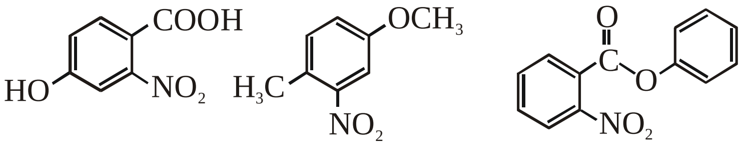
S

were separately subjected to nitration using HNO_3 / H_2SO_4 mixture. The product formed in each case respectively, is

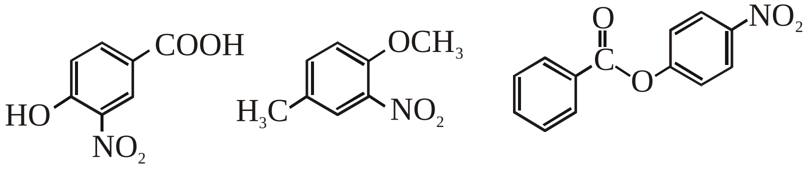
(A)



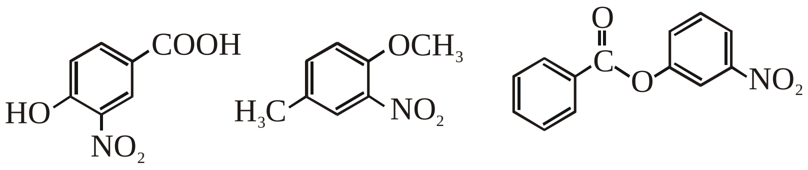
(B)



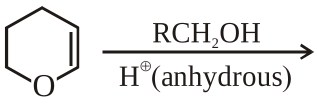
(C)



(D)



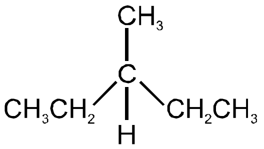
2. The major product of the following reaction is **[JEE 2011]**



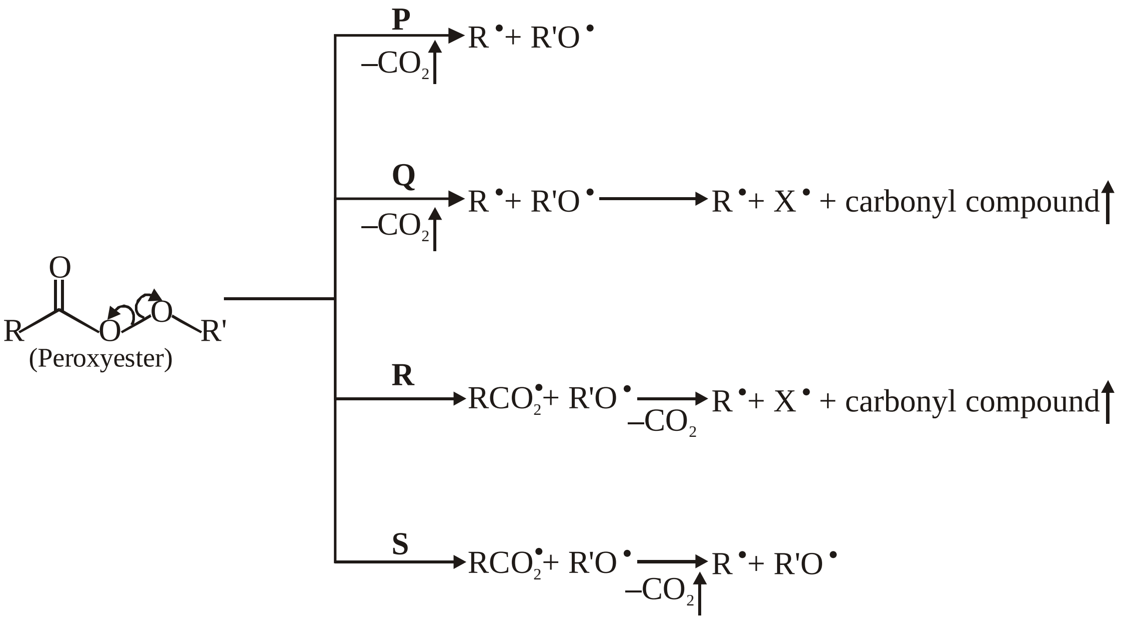
(A) a hemiacetal (B) an acetal

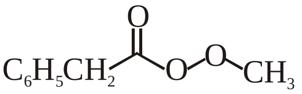
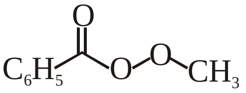
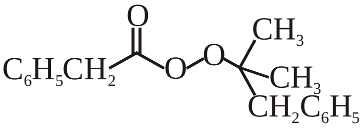
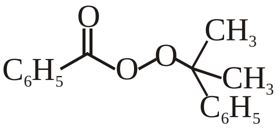
(C) an ether (D) an ester

3. The maximum number of isomers (including stereoisomers) that are possible on monochlorination of the following compound, is : **[JEE-2011, 4/160]**



4. Different possible **thermal** decomposition pathways for peroxyesters are shown below. Match each pathway from List-**I** with an appropriate structure from List-**II** and select the correct answer using the code given below the lists. **[JEE 2014]**

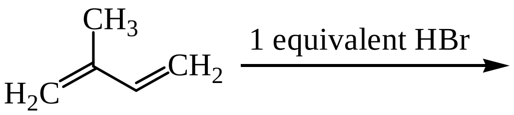


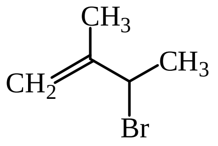
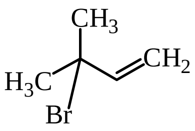
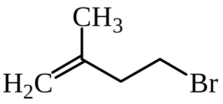
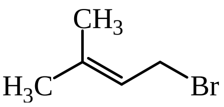
List-I		**List-II**
(P) Pathway **P**	(1)	
(Q) Pathway **Q**	(2)	
(R) Pathway **R**	(3)	
(S) Pathway **S**	(4)	

Code :

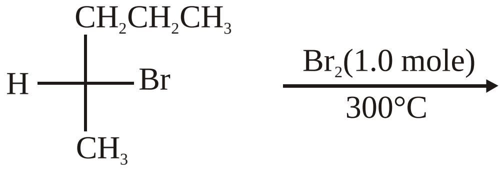
	P	Q	R	S
(A)	1	3	4	2
(B)	2	4	3	1
(C)	4	1	2	3
(D)	3	2	1	4

5. In the following reaction, the major product is -



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

6. In the following monobromination reaction, the number of possible chiral products is **[JEE 2016]**

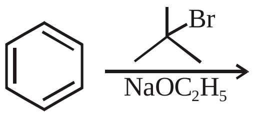


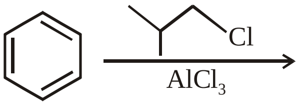
(1.0 mole)

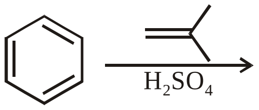
(enantiomerically pure)

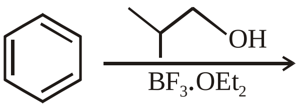
7. Among the following reaction(s) which give(s) tert-butyl benzene as the major product is(are)

[JEE 2016]

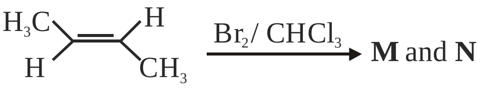
(A) 

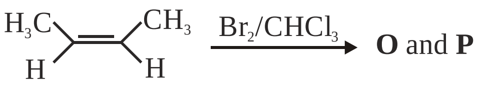
(B) 

(C) 

(D) 

8. The correct statement(s) for the following addition reactions is(are) **[JEE 2017]**

(i) 

(ii) 

(A) (**M** and **O**) and (**N** and **P**) are two pairs of enantiomers.

(B) Bromination proceeds through *trans*-addition in both the reactions.

(C) **O** and **P** are identical molecules.

(D) (**M** and **O**) and (**N** and **P**) are two pairs of diastereomers.

PART - II : JEE MAIN PROBLEMS (PREVIOUS YEARS)

1. How many chiral compounds are possible on monochlorination of 2-methylbutane?

[AIEEE-2012, 4/120]

(1) 8 (2) 2 (3) 4 (4) 6

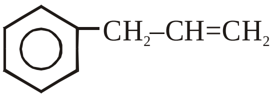
2. Which branched chain isomer of the hydrocarbon with molecular mass 72u gives only one isomer of mono substituted alkyl halide ? **[AIEEE-2012, 4/120]**

(1) Tertiary butyl chloride (2) Neopentane

(3) Isohexane (4) Neohexane

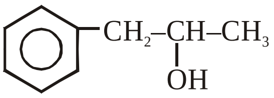
3. In the hydroboration - oxidation reaction of propene with diborane, H_2O_2 and NaOH, the organic compound formed is : **[JEE MAIN ONLINE 2014]**

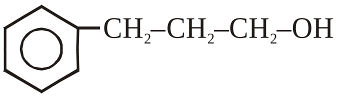
(1) $CH_3CH_2CH_2OH$ (2) $(CH_3)_3COH$ (3) $CH_3CHOHCH_3$ (4) CH_3CH_2OH

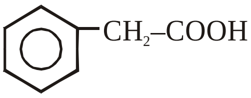
4. 

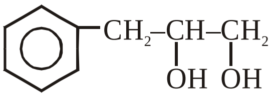
on mercuration- demercuration produces the major product :-

[JEE Main online 2014]

(1) 

(2) 

(3) 

(4) 

5. The major product obtained in the photo catalysed bromination of 2-methylbutane is :-

[JEE Main online 2014]

(1) 2-Bromo-2-methylbutane (2) 2-Bromo-3-methylbutane

(3) 1-Bromo-2-methylbutane (4) 1-Bromo-3-methylbutane

6. In the presence of peroxide, HCl and HI do not give anti-Markownikoff s addition to alkenes because

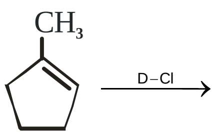
(1) All the steps are exothermic in HCl and HI **[JEE Main online 2014]**

(2) One of the steps is endothermic in HCl and HI

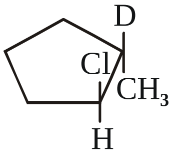
(3) HCl is oxidizing and the HI is reducing

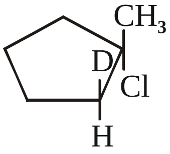
(4) Both HCl and HI are strong acids

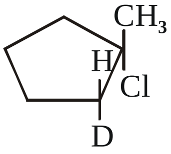
7. What is the major product expected from the following reaction ? **[JEE Main On Line 2015]**

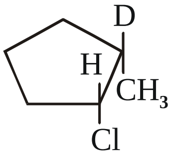


Where D is an isotope of hydrogen.

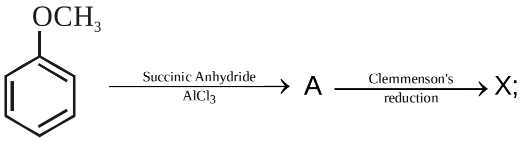
(1) 

(2) 

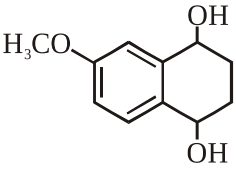
(3) 

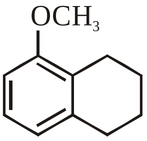
(4) 

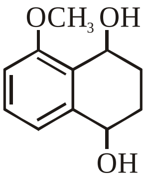
8. Consider the reaction sequence below : **[JEE Main On Line 2016]**

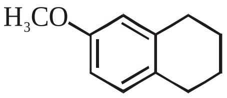


X is :

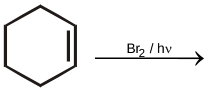
(1) 

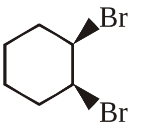
(2) 

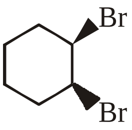
(3) 

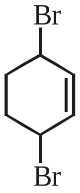
(4) 

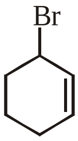
9. Bromination of cyclohexene under conditions given below yields : **[JEE Main On Line 2016]**



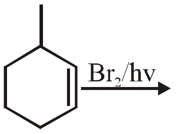
(1) 

(2) 

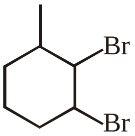
(3) 

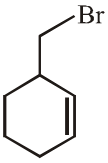
(4) 

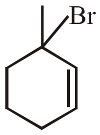
10. The major product of the following reaction is:-

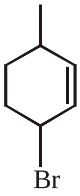


[JEE(Main)-2017(ONLINE)]

(1) 

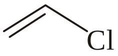
(2) 

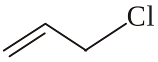
(3) 

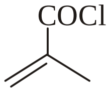
(4) 

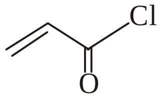
11. Which of the following compounds will not undergo Friedel Craft's reaction with benzene ?

[JEE(Main)-2017(ONLINE)]

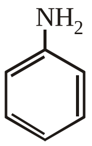
(1) 

(2) 

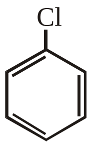
(3) 

(4) 

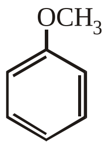
12. The increasing order of nitration of the following compound is :- **[JEE(Main)-2018(ONLINE)]**



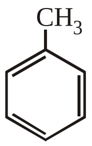
(a)



(b)



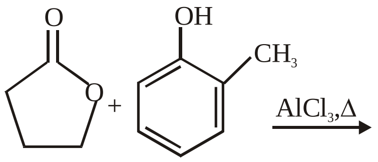
(c)

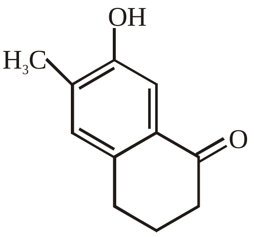


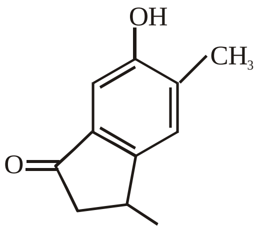
(d)

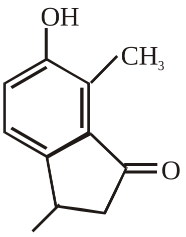
(1) (b) < (a) < (c) < (d)
(2) (b) < (a) < (d) < (c)
(3) (a) < (b) < (c) < (d)
(4) (a) < (b) < (d) < (c)

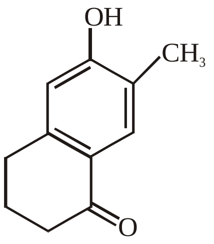
13. The major product of the following reaction is: **[JEE-Mains (JAN)-2019]**



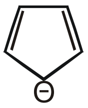
(1)


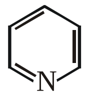
(2)


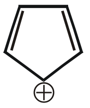
(3)


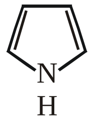
(4)


14. Which of the following compounds is not aromatic ? **[JEE-Mains (JAN)-2019]**

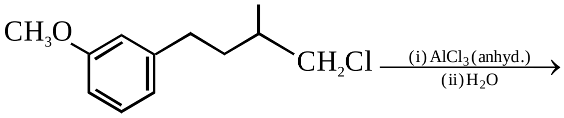
(1)


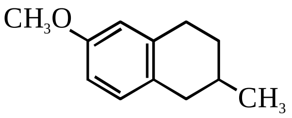
(2)


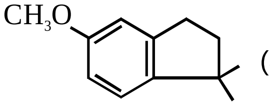
(3)


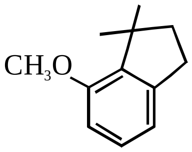
(4)


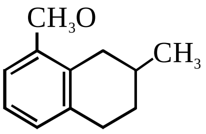
15. The major product of the following reaction is: **[JEE-Mains (JAN)-2019]**



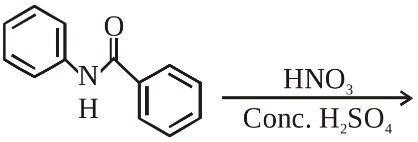
(1)


(2)


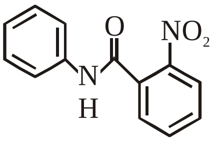
(3)


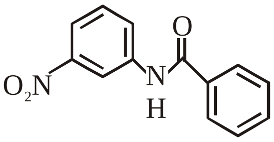
(4)


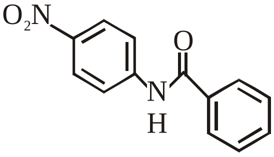
16. What will be the major product in the following mononitration reaction ?

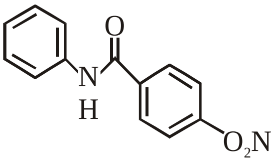


[JEE-Mains (JAN)-2019]

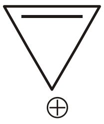
(1)


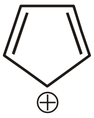
(2)


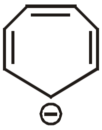
(3)


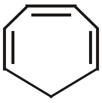
(4)


17. Which compound(s) out of the following is/are not aromatic ? **[JEE-Mains (JAN)-2019]**


(A)

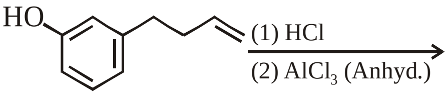

(B)

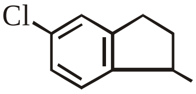

(C)


(D)

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

18. The major product of the following reaction is :- **[JEE-Mains (JAN)-2019]**



(1)


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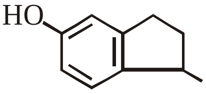
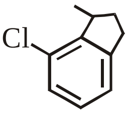
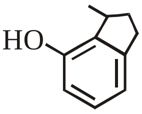
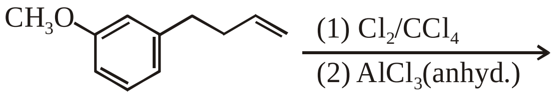
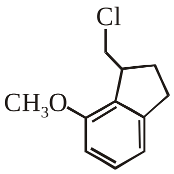


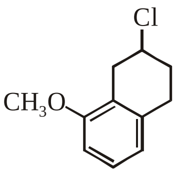
(3)


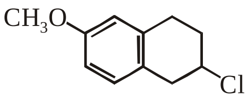
(4)


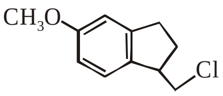
19. The major product of the following reaction is : **[JEE-Mains (JAN)-2019]**



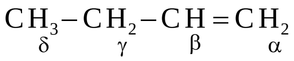
(1) 

(2) 

(3) 

(4) 

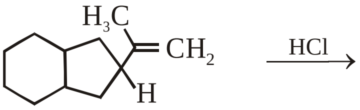
20. Which hydrogen in compound (E) is easily replacable during bromination reaction in the presence of light ? **[JEE Main (Jan) 2019]**

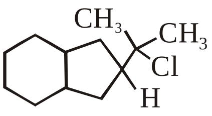


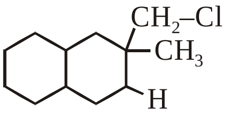
$$\underset{\delta}{CH_3}-\underset{\gamma}{CH_2}-\underset{\beta}{CH}=\underset{\alpha}{CH_2}$$

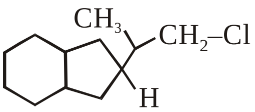
(1) β – hydrogen (2) γ – hydrogen (3) δ – hydrogen (4) α – hydrogen

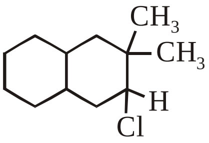
21. The major product of the following reaction is: **[JEE Main (Jan) 2019]**



(1) 

(2) 

(3) 

(4) 

ANSWER KEY

EXERCISE # 1

PART-I

A-1. Chlorination of methane is a free radical reaction which occurs by the following mechanism

Initiation $Cl-Cl \xrightarrow{\text{Homolytic Fission}} 2\dot{C}l$

Propagation $CH_3-H + Cl \longrightarrow \dot{C}H_3 + HCl$

$\dot{C}H_3 + Cl-Cl \longrightarrow CH_3-Cl + \dot{C}l$

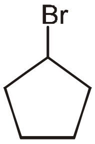
Termination $\dot{C}H_3 + \dot{C}H_3 \longrightarrow CH_3-CH_3$ (Ethane)

$\dot{C}H_3 + \dot{C}l \longrightarrow CH_3-Cl$

$\dot{C}l + \dot{C}l \longrightarrow Cl-Cl$

A-2. 2-Bromopropane = 96.5 %

1-Bromopropane = 3.5 %

A-3. (a)


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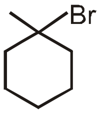

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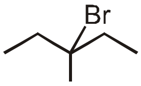

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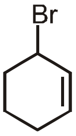
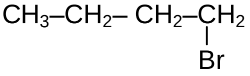
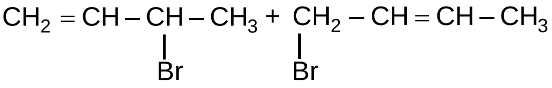


A-4.


$CH_3-CH_2-CH_2-CH_2Br$

A-5.


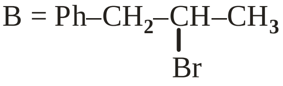
$CH_2=CH-CH(Br)-CH_3 + CH_2(Br)-CH=CH-CH_3$

A-6. 4

B-1. III > IV > II > I

B-2. Positional isomers

A = $Ph-CH_2-CH_2-CH_2-Br$



B = $Ph-CH_2-CH(Br)-CH_3$

B-3. (a) Racemic mixture of 2,3-Dibromobutane (b) Meso 2,3-Dibromobutane

B-4. (a) 11.43g Br_2 ; (b) 23.53 g Br_2; (c) 11.11 g Br_2

B-5. 4

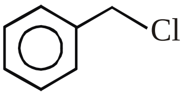
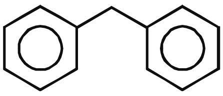
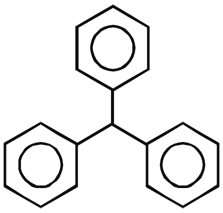
C-1 Benzene has resonance stabilization due to delocalisation of π-electrons and during electrophilic addition reactions, it looses its aromaticity. In electrophilic substitution reaction aromaticity is retained.

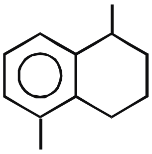
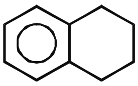
C-2. 5 (a , b , c , f , h)

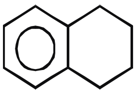
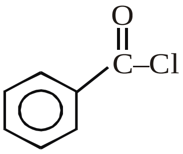
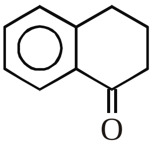
C.3 **4** (c, e , g , h)

C-4. (a) (I) > (II) > (III) (b) (II) > (III) > (I) (c) (II) > (I) > (III) (d) (III) > (I) > (II)

C-5. **1** **C-6.** **2**

C-7. (a)  (b)  (c) 

(d) $Ph_3C–Cl$ (e)  (f) 

(g)  (h)  (i) 

PART-II

A-1.	(A)	**A-2.**	(B)	**A-3.**	(C)	**A-4.**	(D)	**A-5.**	(A)	**A-6.**	(B)	**A-7.**	()
A-8.	()	**A-9.**	(B)	**A-10.**	(D)	**B-1.**	(C)	**B-2.**	(B)	**B-3.**	(D)	**B-4.**	(B)
B-5.	(B)	**B-6.**	(B)	**B-7.**	(B)	**B-8.**	(C)	**B-9.**	(C)	**B-10.**	(B)	**B-11.**	(A)
B-12.	(B)	**B-13.**	(A)	**B-14.**	(D)	**B-15.**	(A)	**B-16.**	(B)	**B-17.**	(A)	**C-1.**	(D)
C-2.	(C)	**C-3.**	(A)	**C-4.**	(B)	**C-5.**	(B)	**C-6.**	(B)	**C-7.**	(D)	**C-8.**	(B)
C-9.	(B)	**C-10.**	(C)	**C-11.**	(A)	**C-12.**	(C)	**C-13**	(B)	**C-14.**	(B)	**C-15.**	(D)
C-16.	(D)	**C-17.**	(A)	**C-18.**	(C)								

PART-III

1. (A) → P ; (B)→R ; (C)→S ; (D)→Q **2.** (A)→R ; (B)→Q ; (C)→S ; (D)→P

EXERCISE # 2

PART - I

1.	(C)	**2.**	(C)	**3.**	(D)	**4.**	(B)	**5.**	(B)	**6.**	(B)	**7.**	(C)
8.	(C)	**9.**	(A)	**10.**	(C)	**11.**	(D)	**12.**	(A)	**13.**	(A)	**14.**	(B)

PART - II

1. 4 **2.** 2 **3.** 8 **4.** 4 **5.** 11.2 L **6.** 4 **7.** **4**
8. 4 **9.** 23

PART - III

1. (ABC) **2.** (AB) **3.** (A) **4.** (AC) **5.** (ABCD) **6.** (ABCD)

7. (ABD) **8.** (ABCD) **9.** (ABD) **10.** (B,D) **11.** (A,C) **12.** (A,B,D)

13. (B,C,D) **14.** (B) **15.** (C)

PART - IV

1. (B) **2.** (B) **3.** (D) **4.** (B) **5.** (C)

EXERCISE # 3

PART- I

1. (C) **2.** (B) **3.** 8 **4.** (A) **5.** (D) **6.** 5 **7.** (BCD)

8. (BD)

PART - II

1. (3) **2.** (2) **3.** (1) **4.** (1) **5.** (1) **6.** (2) **7.** (2)

8. (4) **9.** (2) **10.** (3) **11.** (1) **12.** (4) **13.** (1) **14.** (3)

15. (2) **16.** (3) **17.** (2) **18.** (2) **19.** (4) **20.** (2) **21.** (1)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Reliable students.

PART- 1 : PAPER JEE (MAIN) PATTERN

SECTION–I : (Maximum Marks : 80)

- This section contains **TWENTY** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :
  Full Marks : +4 If only the bubble corresponding to the correct option is darkened.
  Zero Marks : 0 If none of the bubbles is darkened.
  Negative Marks : –1 In all other cases

1. Which reagent is the most useful for distinguishing compound I from the rest of the compounds ?

$CH_3CH_2C{\equiv}CH$	$CH_3C{\equiv}CCH_3$	$CH_3CH_2CH_2CH_3$	$CH_3CH{=}CH_2$
I	II	III	IV

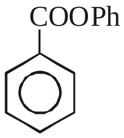
(A) Alk. $KMnO_4$ (B) Br_2/CCl_4 (C) Br_2/CH_3COOH (D) Ammonical $AgNO_3$

2. A mixture of CH_4, C_2H_4 and C_2H_2 gaseous are passed through a Wolf bottle containing ammonical cuprous chloride. The gas coming out is/are -

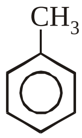
(A) Methane (B) Acetylene

(C) Mixture of methane and ethylene (D) original mixture

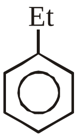
3 . Decide the correct order of reactivity of following compounds towards halogenation with ($Cl_2 + AlCl_3$).



I



II



III

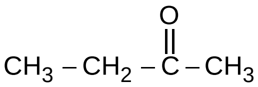

IV

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

4. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO_3 and conc. H_2SO_4. In the nitrating mixture HNO_3 acts as a:

(A) Base (B) Acid (C) Reducing agent (D) Catalyst

5. The product(s) via-oxymercuration ($HgSO_4 + H_2SO_4$) of 1-butyne would be :

(A) 
$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

(B) $CH_3-CH_2-CH_2-CHO$

(C) $CH_3-CH_2-CHO + HCHO$ (D) $CH_3-CH_2-COOH + HCOOH$

6. What is the product formed when acetylene reacts with hypochlorous acid ?

(A) CH_3COCl (B) $ClCH_2CHO$ (C) Cl_2CHCHO (D) $ClCH_2COOH$

7. Reaction of one molecule of HBr with one molecule of 1,3–butadiene at 40°C gives predominantly

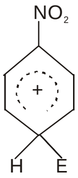
(A) 1–Bromo–2–butene under thermodynamically controlled conditions.
(B) 3–Bromobutene under kinetically controlled conditions.
(C) 1–Bromo–2–butene under kinetically controlled conditions.
(D) 3–Bromobutene under thermodynamically controlled conditions.

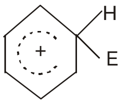
8. Which of the following reactions will yield, 2, 2-dibromopropane **?**

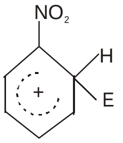
(A) $CH_3—C{\equiv}CH + 2HBr \longrightarrow$ (B) $CH_3CH{=}CHBr + HBr \longrightarrow$

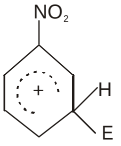
(C) $CH{\equiv}CH + 2HBr \longrightarrow$ (D) $CH_3—CH{=}CH_2 + HBr \longrightarrow$

9. The electrophile, $E^{\oplus}$ attacks the benzene ring to generate the intermediate σ–complex. Of the followings, which σ–complex is of lowest energy ?

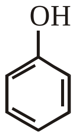
(A) 

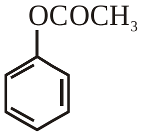
(B) 

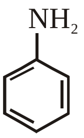
(C) 

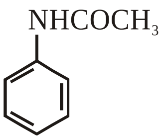
(D) 

10. Which of the following compounds will give significant amount of meta product during mono-nitration reaction ?

(A) 

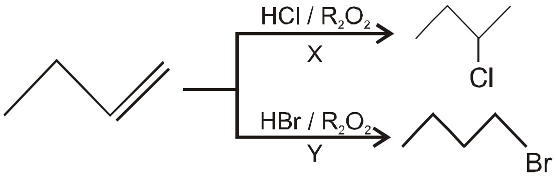
(B) 

(C) 

(D) 

11. Which of these will not react with acetylene ?

(A) NaOH (B) ammonical $AgNO_3$ (C) Na (D) HCl

12. 

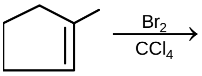
Which is correct statement about X and Y.

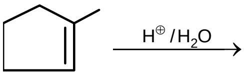
(1) X is product of ionic reaction and Y is product of radical reaction.
(2) X and Y both are product of ionic reaction.
(3) X and Y both are product of radical reaction.
(4) X is product of radical reaction and Y is product of ionic reaction.

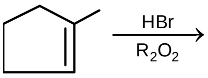
13. The chlorination of toluene in presence of ferric chloride gives predominatly:

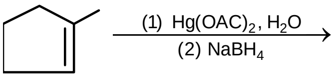
(A) Benzyl chloride (B) m-Chlorotoluene (C) Benzal chloride (D) *o*-and *p*-Chlorotoluene

14. Which of the following reactions is not an electrophilic addition reaction ?

(A) 

(B) 

(C) 

(D) 

15. Which of the following is the best reagent to convert 1-Methylcyclohexene into 2-Methylcyclohexanol ?

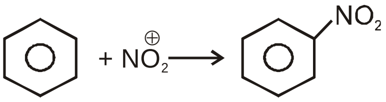
(A) Dil H_2SO_4

(B) Hg $(OAc)_2$ / $NaBH_4$, H_2O

(C) $B_2H_6/H_2O_2, \overset{\ominus}{O}H$

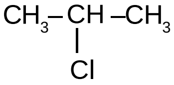
(D) Conc. H_2SO_4

16. Which of the following is free radical addition reaction ?

(A) 

(B) $CH_2=CH_2 + HBr \longrightarrow CH_3–CH_2–Br$

(C) $CH_3–CH=CH_2 + HBr \xrightarrow{R_2O_2} CH_3–CH_2–CH_2–Br$

(D) $CH_3–CH=CH_2 + HCl \longrightarrow$ 
$CH_3–\underset{\substack{|\\Cl}}{CH}–CH_3$

17. Among the following statements on the nitration of aromatic compounds, the false one is:

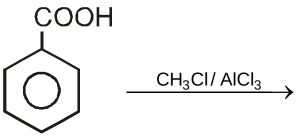
(A) The rate of benzene is almost the same as that of hexadeuterobenzene.

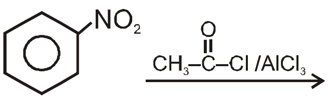
(B) The rate of nitration of toluene is greater than that of benzene.

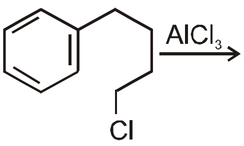
(C) The rate of nitration of benzene is greater than that of hexadeuterobenzene.

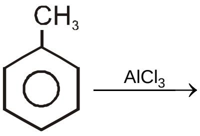
(D) Nitration is an electrophilic substitution reaction.

18. Which of the following reaction is feasible ?

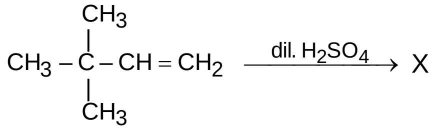
(A) 

(B) 

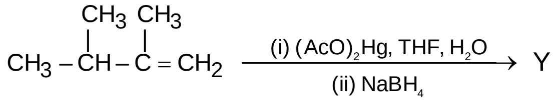
(C) 

(D) 

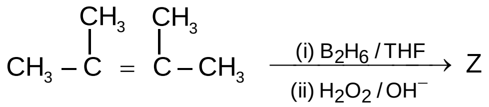
19.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{\text{dil. } H_2SO_4} X$$



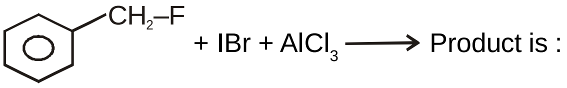
$$CH_3-\overset{\overset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{(ii) } NaBH_4]{\text{(i) } (AcO)_2Hg,\ THF,\ H_2O} Y$$

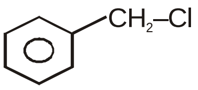


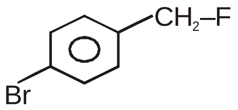
$$CH_3-\overset{\overset{CH_3}{|}}{C}=\overset{\overset{CH_3}{|}}{C}-CH_3 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6/THF} Z$$

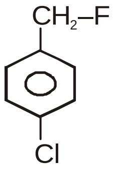
(A) All three products (X, Y, Z) are different.
(B) X and Y are identical but Z is different.
(C) Y and Z are identical but X is different.
(D) All three products (X, Y, Z) are identical.

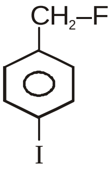
20.



(A) 

(B) 

(C) 

(D) 

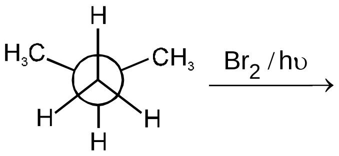
SECTION-II : (Maximum Marks: 20)

- This section contains **FIVE** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (If the numerical value has more than two decimal places, **truncate/round-off** the value to **TWO** decimal places; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

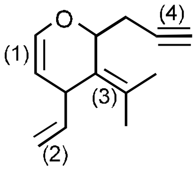
  Full Marks : +4 If ONLY the correct numerical value is entered as answer.

21.



Number of products

22. The most reactive C=C / C≡C bond towards $Br^{\oplus}$ is :

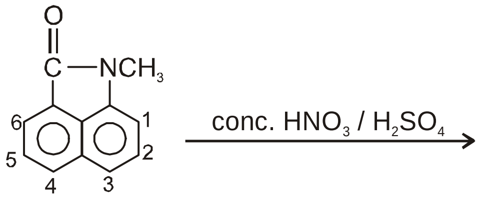


23. An isomer of C_5H_{12} gives total six isomeric products on monochlorination. Calculate the percentage yield of the primary monochloride which is chiral. Consider the following relative reactivity of C – H bonds for chlorination.

Degree of C – H	1° C – H	2° C – H	3° C – H
Relative reactivity for chlorination (RR)	1	3	5

24. When Buta-1,3-diene react with one equivalent of Br_2 at room temperature then how many products are formed?

25.



At which position nitration mainly takes place ?

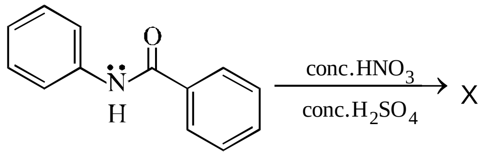
PART 2 : PAPER JEE (ADVANCED) PATTERN

SECTION-I : (Maximum Marks : 12)

- This section contains **FOUR** questions.
- Each question has **FOUR** options (A), (B), (C) and (D). **ONLY ONE** of these four options is correct.
- For each question, darken the bubble corresponding to the correct option in the ORS.
- For each question, marks will be awarded in one of the following categories :

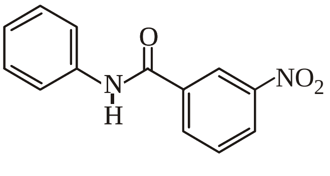
Full Marks : +3 If only the bubble corresponding to the correct option is darkened.
Zero Marks : 0 If none of the bubbles is darkened.
Negative Marks : –1 In all other cases

1. In the following reaction,

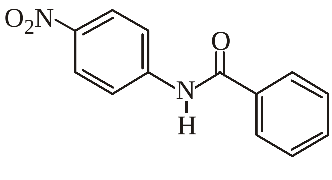


the structure of the major product 'X' is

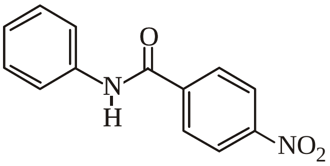
(A)



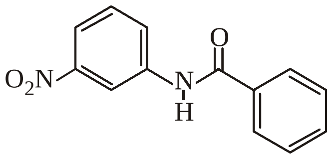
(B)

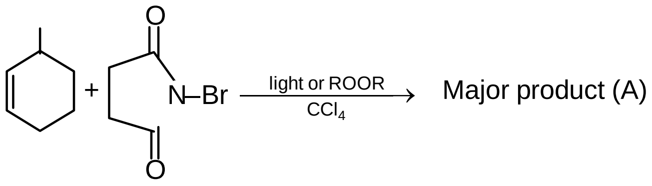


(C)

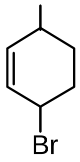


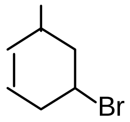
(D)

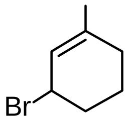


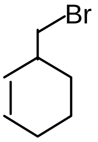
2. 

A is

(A) 

(B) 

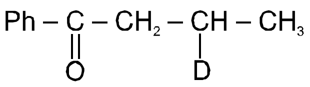
(C) 

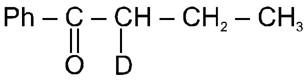
(D) 

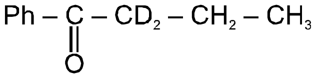
3. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y' Thus, 'X' and 'Y' are

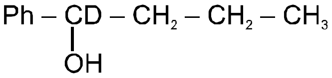
(A) X = Benzyl chloride, Y = m-Chlorotoluene
(B) X = Benzal chloride, Y = o-Chlorotoluene
(C) X = m-Chlorotoluene, Y = p-Chlorotoluene
(D) X = o- and p-Chlorotoluene, Y = Trichloromethyl benzene

4. $Ph-C\equiv C-CH_2-CH_3 \xrightarrow[D_2SO_4/D_2O]{Hg^{2+}/D^{\oplus}}$ A, A is :

(A) 
$Ph-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{D}{|}}{C}H-CH_3$

(B) 
$Ph-\underset{\underset{O}{\|}}{C}-\underset{\underset{D}{|}}{C}H-CH_2-CH_3$

(C) 
$Ph-\underset{\underset{O}{\|}}{C}-CD_2-CH_2-CH_3$

(D) 
$Ph-\underset{\underset{OH}{|}}{C}D-CH_2-CH_2-CH_3$

SECTION-II : (Maximum Marks: 32)

- This section contains **EIGHT** questions.
- Each question has **FOUR** options for correct answer(s). **ONE OR MORE THAN ONE** of these four option(s) is (are) correct option(s).
- For each question, choose the correct option(s) to answer the question.
- Answer to each question will be evaluated according to the following marking scheme:

Full Marks : +4 If only (all) the correct option(s) is (are) chosen.
Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.
Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct options.
Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.
Zero Marks : 0 If none of the options is chosen (i.e. the question is unanswered).
Negative Marks : –1 In all other cases.

- **For Example :** If first, third and fourth are the **ONLY** three correct options for a question with second option being an incorrect option; selecting only all the three correct options will result in +4 marks. Selecting only two of the three correct options (e.g. the first and fourth options), without selecting any incorrect option (second option in this case), will result in +2 marks. Selecting only one of the three correct options (either first or third or fourth option), without selecting any incorrect option (second option in this case), will result in +1 marks. Selecting any incorrect option(s) (second option in this case), with or without selection of any correct option(s) will result in –1 marks.

5. In the chlorination of methane which of the following reaction involve in the chain termination step.

(A) $Cl-Cl \longrightarrow 2\overset{\bullet}{Cl}$

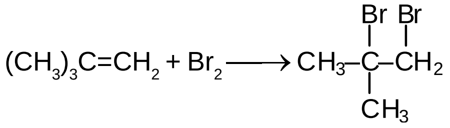
(B) $\overset{\bullet}{Cl} + \overset{\bullet}{Cl} \longrightarrow Cl-Cl$

(C) $\overset{\bullet}{C}H_3 + \overset{\bullet}{Cl} \longrightarrow CH_3-Cl$

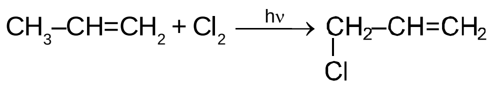
(D) $\overset{\bullet}{C}H_3 + Cl-Cl \longrightarrow CH_3-Cl + \overset{\bullet}{Cl}$

6. Which of the following reactions are completed through free radical intermediate?

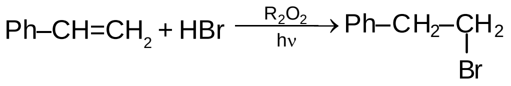
(A) $(CH_3)_3CH + Br_2 \xrightarrow{h\nu} (CH_3)_3CBr + HBr$

(B) 

$(CH_3)_3C=CH_2 + Br_2 \longrightarrow CH_3-\underset{CH_3}{\overset{Br}{C}}-\overset{Br}{CH_2}$

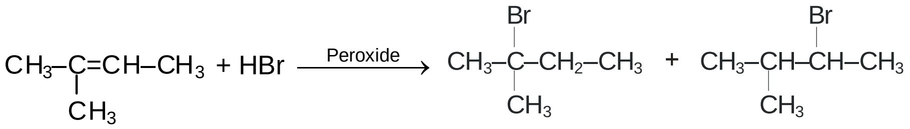
(C) 

$CH_3-CH=CH_2 + Cl_2 \xrightarrow{h\nu} \underset{Cl}{CH_2}-CH=CH_2$

(D) 

$Ph-CH=CH_2 + HBr \xrightarrow[h\nu]{R_2O_2} Ph-CH_2-\underset{Br}{CH_2}$

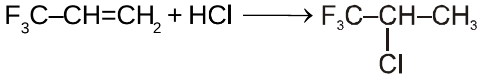
7. Which of the following statements are correct for give reaction?



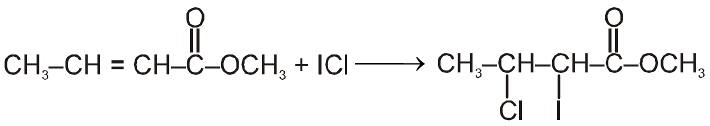
$$CH_3-\underset{CH_3}{C}=CH-CH_3 + HBr \xrightarrow{\text{Peroxide}} CH_3-\underset{CH_3}{\overset{Br}{C}}-CH_2-CH_3 + CH_3-\underset{CH_3}{CH}-\overset{Br}{CH}-CH_3$$

(A) Major product is mixture of two enantiomers.
(B) Less stable carbocation give major product.
(C) Less stable free radical give major product.
(D) More stable free radical give major product.

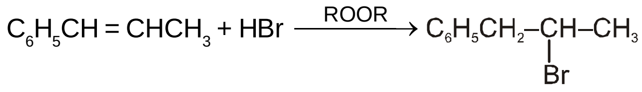
8. In which of the following reaction reactants and products are correctly matched ?

(A) 

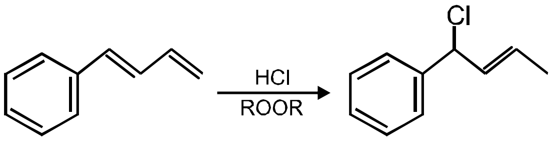
$F_3C-CH=CH_2 + HCl \longrightarrow F_3C-\underset{Cl}{CH}-CH_3$

(B) 

$CH_3-CH = CH-\overset{O}{\overset{\|}{C}}-OCH_3 + ICl \longrightarrow CH_3-\underset{Cl}{CH}-\underset{I}{CH}-\overset{O}{\overset{\|}{C}}-OCH_3$

(C) 

$C_6H_5CH = CHCH_3 + HBr \xrightarrow{ROOR} C_6H_5CH_2-\underset{Br}{CH}-CH_3$

(D) 

9. When nitrobenzene is treated with Br_2 in presence of $FeBr_3$ the major product formed is m-Bromonitrobenzene. Correct statements are :

(A) The electron density on meta carbon is more than that on ortho and para position.

(B) The intermediate carbonium ion formed after initial attack of Br^+ at the meta position is least destabilized.

(C) Loss of aromaticity when Br^+ attacks at the ortho and para positions and not at meta position.

(D) Easier loss of H^+ to regain aromaticity form the meta position than from ortho and para position.

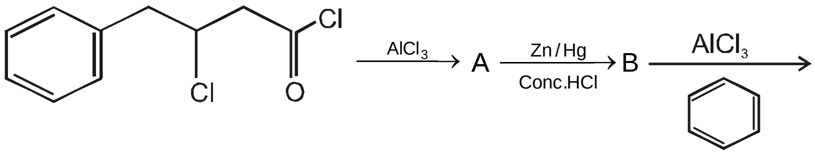
10. Which of the following statement(s) is/are incorrect ?

(A) Nitrobenzene will give meta-nitrotoluene on reaction with $CH_3Cl/AlCl_3$.

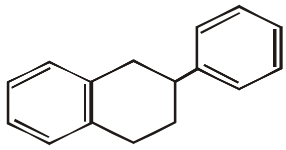
(B) Chlorobenzene will give meta-substituted product on electrophilic substitution since it exerts –I > + M effect.

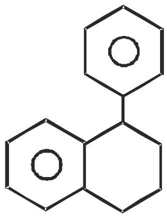
(C) n-Propyl benzene can be easily obtained on Friedal crafts alkylation of benzene with n-propyl chloride.

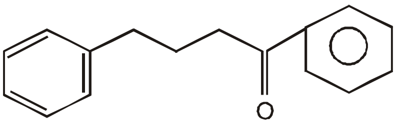
(D) Toluene can be obtained in better yield when excess of benzene will react with $CH_3Cl/AlCl_3$.

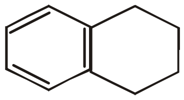
11. 

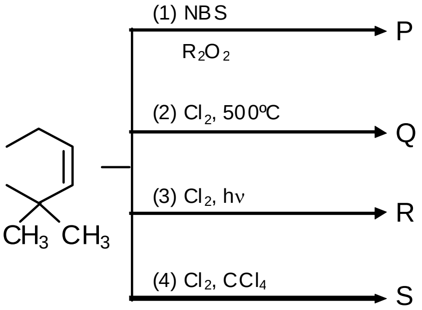
C, The product C is :

(A) 

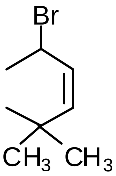
(B) 

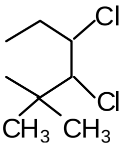
(C) 

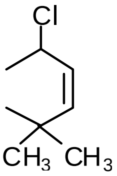
(D) 

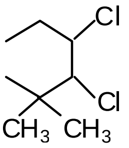
12. 

For the above reactions, which is/are the expected major product mentioned in the options given below :

(A) P is 

(B) Q is 

(C) R is 

(D) S is 

SECTION-III : (Maximum Marks: 18)

- This section contains **SIX** questions.
- The answer to each question is a **NUMERICAL VALUE**.
- For each question, enter the correct numerical value (in decimal notation, truncated/rounded-off to the **second decimal place**; e.g. 6.25, 7.00, –0.33, –.30, 30.27, –127.30, if answer is 11.36777..... then both 11.36 and 11.37 will be correct) by darken the corresponding bubbles in the ORS.

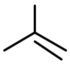
  For Example : If answer is –77.25, 5.2 then fill the bubbles as follows.
- Answer to each question will be evaluated according to the following marking scheme:

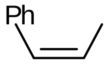
Full Marks	: +3	If ONLY the correct numerical value is entered as answer.
Zero Marks	: 0	In all other cases.

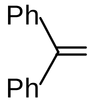
13. $CH_3{-}C{\equiv}CH \xrightarrow{\text{Red hot iron tube}} A \xrightarrow[AlCl_3]{CO + HCl} B \xrightarrow[\text{(ii)} NH_4Cl]{\text{(i)} CH_3MgBr} C$

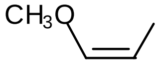
Mass percentage of oxygen in the final product (C) is :

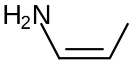
14. How many alkenes react faster than propene with dil.H_2SO_4?

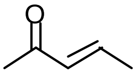
(a) 

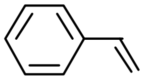
(b) 

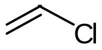
(c) 

(d) 

(e) 

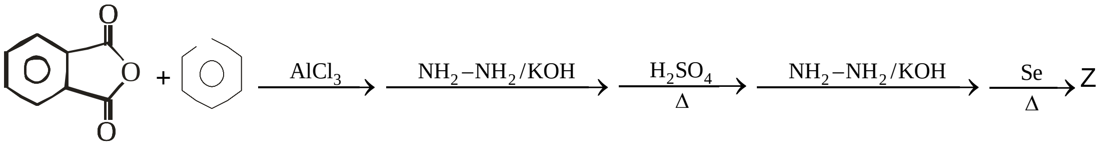
(f) 

(g) 

(h) 

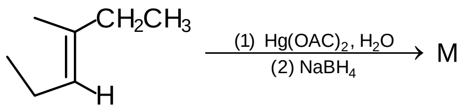
15. $(CH_3)_2CH - CH_2CH_3 \xrightarrow{Cl_2 / h\upsilon} [N] \xrightarrow[\text{distillati on}]{\text{Fractional}} [P]$

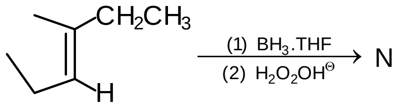
The sum of number of possible isomers [N] and number of fractions [P] are

16. 

Find the sum of P + Q in product Z where P is the number of valid resonance structures and Q is the number of p-orbitals participate in resonance ?

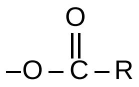
17. In the given reactions M is the number of major products obtained in Ist reaction and N number of major products obtained in IInd reaction. Report your answer as $\boxed{M}\boxed{N}$.

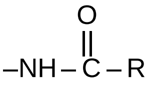
(i) 

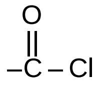
(ii) 

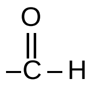
18. How many of the following substituents can cause aromatic electrophilic substitution faster than benzene?

(a) $-NH_2$ (b) $-NR_2$ (c) $-NO_2$ (d) $-\overset{+}{N}H_3$

(e) 
$-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$

(f) 
$-NH-\overset{\overset{\displaystyle O}{\|}}{C}-R$

(g) 
$-\overset{\overset{\displaystyle O}{\|}}{C}-Cl$

(h) 
$-\overset{\overset{\displaystyle O}{\|}}{C}-H$

(i) $-SO_3H$ (j) $-CH_3$ (k) $-CH = CR_2$

PART - 3 : OLYMPIAD (PREVIOUS YEARS)

STAGE - I (NATION STANDARD EXAMINATION IN CHEMISTRY (NSEC))

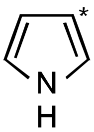
1. The peroxide effect occurs by : **[NSEC-2001]**

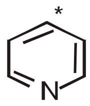
(A) ionic mechanism (B) heterolytic fission of double bond
(C) heterolytic fission of double bond (D) free radical mechanism

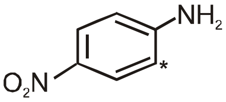
2. The number of structural and configurational isomers of a bromo compound formed by the addition of HBr to 2-hexene are respectively **[NSEC-2002]**

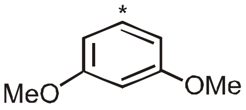
(A) 1 and 2 (B) 4 and 2 (C) 2 and 4 (D) 2 and 1

3. The most favourable position (indicated by) for an electrophilic attack is **[NSEC-2003]**

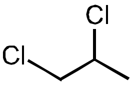
(A) 

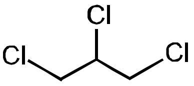
(B) 

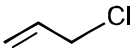
(C) 

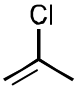
(D) 

4. In the reaction of chlorine with propene at 450°C, the major product is **[NSEC-2003]**

(A) 

(B) 

(C) 

(D) 

5. In the nitration of an aromatic compound using a mixture of concentrated nitric acid and sulphuric acid, the acids respectively function as **[NSEC-2003]**

(A) an oxidising agent and an acid
(B) a Bronsted and a Lewis acid
(C) a base and an acid
(D) an acid and an oxidising agent.

6. Toluene is o/p orienting with respect to an electrophilic substitution reaction due to **[NSEC-2004]**

(A) + I effect of the methyl group
(B) +I as well as + M effect of the methyl group
(C) hyperconjugation between the methyl group and the phenyl ring
(D) + M effect to the methyl group.

7. Select the major product obtained from the addition of HBr to 1-methylcyclohexene. **[NSEC-2005]**

(A) 1-bromo-2-methylcyclohexane
(B) 6-bromo-1-methylcyclohex-l-ene
(C) 3-bromo-1-methylcyclohex-1-ene
(D) 1-bromo-1-methylcyclohexane.

8. Reaction of benzene with isobutylchloride ($CH_3CH(CH_3)CH_2Cl$) in the presence of anhydrous $AlCl_3$ yields

(A) tert-butylbenzene (B) iso-butylbenzene (C) n-butylbenzene (D) chlorobenzene.**[NSEC-2005]**

9. The reagent system for preparing propan - 1-ol from propene is **[NSEC-2006]**

(A) $Hg(OAc)_2/H_2O$ followed by $NaBH_4$
(B) H_2SO_4/H_2O
(C) B_2H_6 followed by H_2O_2
(D) HCO_2H/H_2SO_4.

10. In Friedel - Craft acylation, the amount of $AlCl_3$ that must be taken is **[NSEC-2006]**

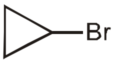
(A) in catalytic amount
(B) one equivalent
(C) more than one equivalent
(D) amount does not matter.

11. For a Friedel - Craft reaction using $AlCl_3$, which compound can be used as solvent, benzene or nitrobenzene?

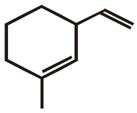
(A) nitrobenzene but not benzene
(B) benzene but not nitrobenzene **[NSEC-2006]**
(C) both benzene and nitrobenzene
(D) neither benzene nor nitrobenzene.

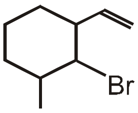
12. The major product of the following reaction is **[NSEC-2006]**

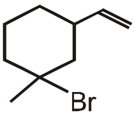
$$CH_3{-}CH = CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2}$$

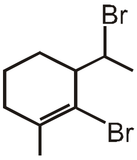
(A) $CH_3{-}CH_2{-}CH_2{-}Br$
(B) $CH_3{-}CH(Br){-}CH_3$
(C) $BrCH_2{-}CH = CH_2$
(D) 

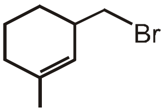
13. The major product formed upon addition of 1 mole of HBr in the following reactions is : **[NSEC-2007]**

 $\xrightarrow{\text{HBr(1mole)}}\xrightarrow{\text{HBr(1 eky)}}$ Major product

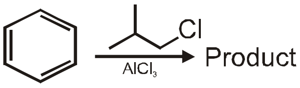
(A) 

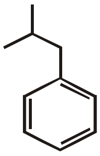
(B) 

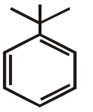
(C) 

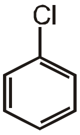
(D) 

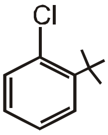
14. Predict the product formed in the following reaction **[NSEC-2007]**



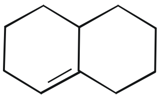
(A) 

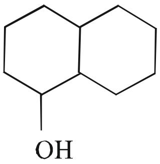
(B) 

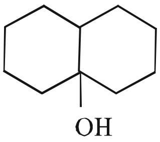
(C) 

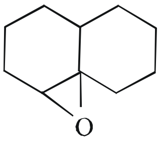
(D) 

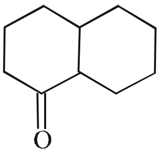
15. The major product in the following reaction is **[NSEC-2008]**

 $\xrightarrow[\text{2. NaOH, } H_2O_2\text{,} H_2O]{\text{1. } BH_3\text{, THF}}$?

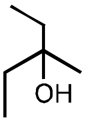
(A) 

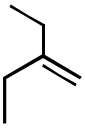
(B) 

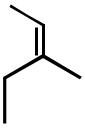
(C) 

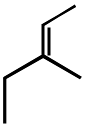
(D) 

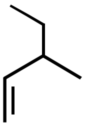
16. Identify the alkene which will not provide the following alcohol upon oxymercuration demercuration. **[NSEC-2008]**



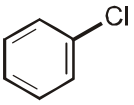
(A) 

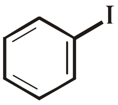
(B) 

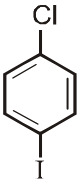
(C) 

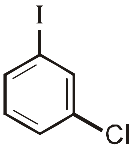
(D) 

17. The compound X in the reaction,  + ICl $\xrightarrow{\text{anhydrous AlCl}_3}$ X is : **[NSEC-2009]**

(A) 

(B) 

(C) 

(D) 

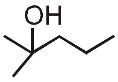
18. Cyclohexene reacts with limited amount of bromine in the presence of light to form product X (C_6H_9Br). The statement correct about X is : **[NSEC-2010]**

(A) It is a racemate.
(B) It is a product of an addition reaction.
(C) It is formed through a cationic intermediate.
(D) It is optically active.

19. The major product of the following reaction is : **[NSEC-2010]**

$(CH_3)_2C{=}CH{-}CH_2{-}CH_3 \xrightarrow{\text{(i) } B_2H_6\text{, ether (ii) } H_2O_2\text{, NaOH}}$

(A)



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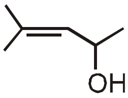
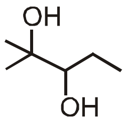
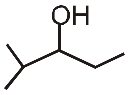


(C)



(D)



20. The compound which does not react with bromine easily at room temperature is **[NSEC-2010]**

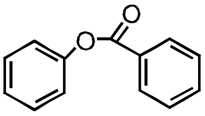
(A) phenol
(B) 2-butyne
(C) chlorobenzene
(D) 1-pentene

21. The product obtained from the following sequence of reactions is **[NSEC-2011]**

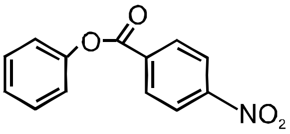
$H_3C-C\equiv CH \xrightarrow[H_2SO_4]{HgSO_4} A \xrightarrow{NaBH_4} B$

(A) Propanal
(B) 2-Propanol
(C) 1-Propanol
(D) Propane

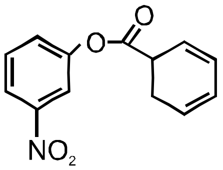
22. Major product of mononitration of the following compound is **[NSEC-2011]**



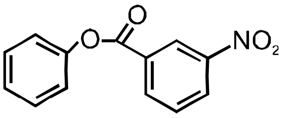
(A)



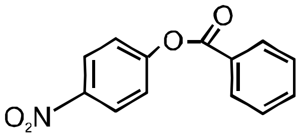
(B)



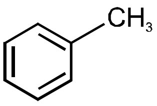
(C)



(D)

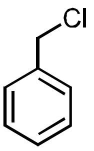


23. The product (P) of the following reaction is **[NSEC-2011]**

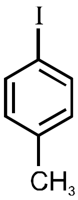


$+ \text{ ICl} \xrightarrow{\text{Lewis acid}} P$

(A)



(B)



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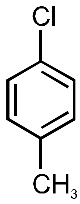
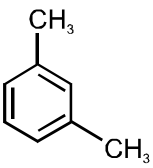
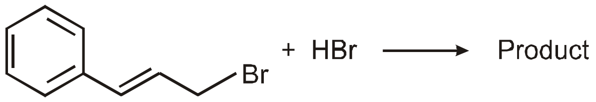


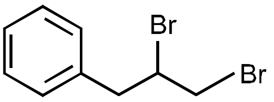
(D)

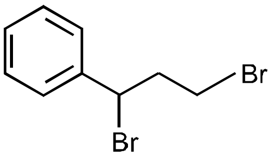


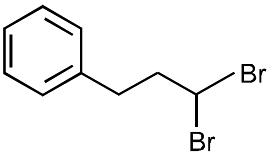
24. 

[NSEC-2012]

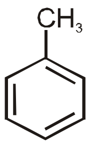
The ‘product’ in the above reaction is :

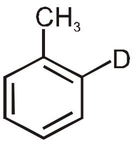
(A) 

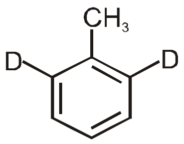
(B) 

(C) 

(D) This reaction cannot take place

25. 
I

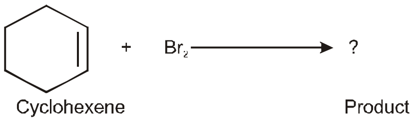

II


III

[NSEC-2012]

The rate of o-nitration of the above compounds, (I) toluene, (II) 2-D-toluene and (III) 2, 6-D_2-toluene are is in the following order

(A) I > II > III
(B) II > I > III
(C) III > I > II
(D) The rate is the same for all the three compounds.

26. 

[NSEC-2013]

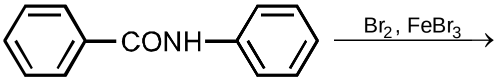
The correct name of the product obtained is

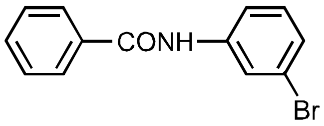
(A) cis-1,2-dibromocyclohexane
(B) cis-1,4-dibromocyclohexane
(C) trans-1,2-dibromocyclohexane
(D) trans-1,4-dibromocyclohexane

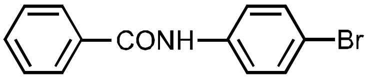
27. Which of the following statements is correct ? **[NSEC-2013]**

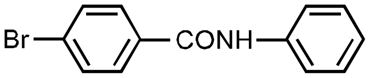
(A) $-NO_2$ group activates the benzene ring for attack of electrophile at ortho and para position.
(B) $-NH_2$ group activates the benzene ring for attack of electrophile at ortho and para position.
(C) Both$-NO_2$ group as well as $-NH_2$ group activate the benzene ring for attack of electrophile at ortho and para position.
(D) Neither $-NO_2$ group nor $-NH_2$ group activate the benzene ring for attack of electrophile at ortho and para position.

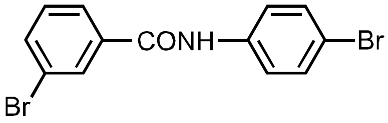
28. The major product of the following reaction is **[NSEC-2014]**



(A) 

(B) 

(C) 

(D) 

29. 1,3-Pentadiene and 1,4-pentadiene are compared with respect to their intrinsic stability and reaction with HI. The correct statement is: **[NSEC-2015]**

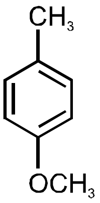
(A) 1,3-Pentadiene is more stable and more reactive than 1,4-Pentadiene.

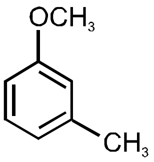
(B) 1,3-Pentadiene is less stable and less reactive than 1,4-Pentadiene.

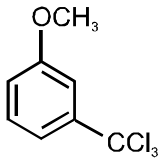
(C) 1,3-Pentadiene is more stable but less reactive than 1,4-Pentadiene.

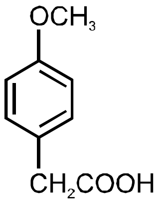
(D) 1,3-Pentadiene is less stable but more reactive than 1,4-Pentadiene.

30. The order of reactivity of the following compounds in electrophilic monochlorination at the most favorable position is **[NSEC-2015]**

(I) 

(II) 

(III) 

(IV) 

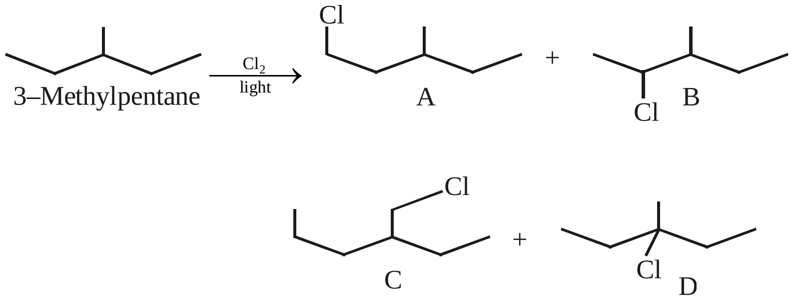
(A) I < II < IV < III (B) III < IV < I < II (C) IV < III < II < I (D) III < II < IV < I

31. The reaction of 1–phenylpropene with limited amount of chlorine in the presence of light gives mainly. **[NSEC-2016]**

(A) 4–Chloropropylbenzene (B) 1–Chloro–1–phenylpropane

(C) 3–Chloro–1–phenylpropane (D) 2–Chloro–1–phenylpropane

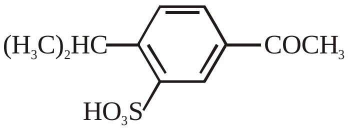
32. 3–Methylpentane on monochlorination gives four possible products. The reaction follows free radical mechanism. The relative reactivities for replacement of –H are 3º : 2 º : 1º = 6 : 4 : 1 .



Relative amounts of A, B, C and D formed are **[NSEC-2016]**

(A) 6/31, 16/31, 6/31, 3/31
(B) 16/31, 6/31, 6/31, 3/31
(C) 6/31, 16/31, 3/31, 6/31
(D) 6/31, 3/31, 6/31, 16/31

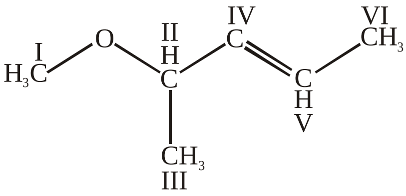
33. The best sequence of reactions for preparation of the following compound from benzene is



[NSEC-2016]

(A) (i) $CH_3COCl/AlCl_3$ (ii) Oleum (iii) $(CH_3)_2CH–Cl$ (1 mole)/$AlCl_3$
(B) (i) $(CH_3)_2CH–Cl$(1 mole)/$AlCl_3$ (ii) $CH_3COCl/AlCl_3$(iii) Oleum
(C) (i) Oleum (ii) $CH_3COCl/AlCl_3$(iii) $(CH_3)_2CH–Cl$(1 mole)/$AlCl_3$
(D)(i) $(CH_3)_2CH–Cl$(1 mole)/$AlCl_3$ (ii) Oleum (iii) $CH_3COCl/AlCl_3$

34. In the given compound the order of case with hydrogen atom can be abstracted from carbons I to VI is :



[NSEC-2017]

(A) I > VI > IV = V > I > III
(B) II > I > VI > III > IV = V
(C) II > I > III > VI > IV = V
(D) IV > II > I > III > IV = V

35. Addition of bromine to cis–3–hexene give **[NSEC-2017]**

(A) racemic dibromide
(B) a mixture of diastereomeric dibromides
(C) optically active dibromide
(D) meso dibromide

RRP ANSWER KEY

PART- 1

1.	(D)	**2.**	(C)	**3 .**	(A)	**4.**	(A)	**5.**	(A)	**6.**	(C)	**7.**	(A)
8.	(A)	**9.**	(B)	**10.**	(C)	**11.**	(A)	**12.**	(A)	**13.**	(D)	**14.**	(C)
15.	(C)	**16.**	(C)	**17.**	(C)	**18.**	(C)	**19.**	(D)	**20.**	(D)	**21.**	2
22.	1	**23.**	30	**24.**	4	**25.**	3						

PART - 2

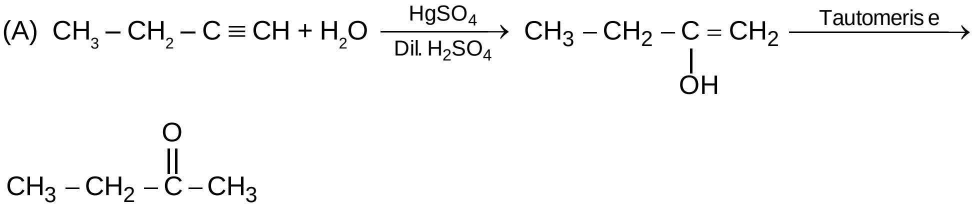
1.	(D)	**2.**	(C)	**3.**	(D)	**4.**	(C)	**5.**	(BC)	**6.**	(ACD)	**7.**	(AD)
8.	(BCD)	**9.**	(AB)	**10.**	(ABC)	**11.**	(B)	**12.**	(ACD)	**13.**	9.75 to 9.76		
14.	6 (a, b , c ,d , e , g)			**15.**	10	**16.**	18	**17.**	12	**18.**	6 (a , b , e, f , j , k)		

PART - 3

1.	(D)	**2.**	(C)	**3.**	(C)	**4.**	(C)	**5.**	(C)	**6.**	(C)	**7**.	(D)
8.	(A)	**9.**	(C)	**10.**	(C)	**11.**	(A)	**12.**	(A)	**13.**	(B)	**14.**	(B)
15.	(A)	**16.**	(D)	**17.**	(B)	**18.**	(A)	**19.**	(D)	**20.**	(C)	**21.**	(B)
22.	(D)	**23.**	(B)	**24.**	(B)	**25.**	(D)	**26.**	(C)	**27.**	(B)	**28.**	(B)
29.	(A)	**30.**	(B)	**31.**	(B)	**32.**	(C)	**33.**	(B)	**34.**	(B)	**35.**	(A)

RRP SOLUTIONS

PART- 1

5. 

$$(A)\ CH_3-CH_2-C\equiv CH + H_2O \xrightarrow[\text{Dil. } H_2SO_4]{HgSO_4} CH_3-CH_2-\underset{\underset{OH}{|}}{C}=CH_2 \xrightarrow{\text{Tautomerise}}$$

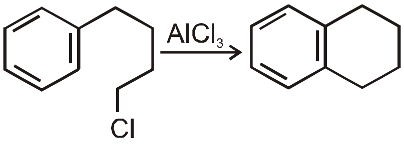
$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_3$$

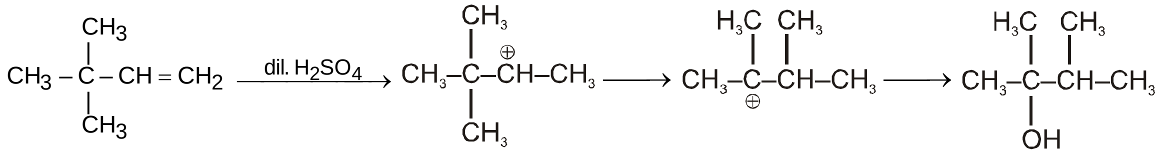
(Because keto form is more stable than enol form)

12. In the presence of peroxide, HBr undergoes free radical addition and HCl undergoes electrophilic addition, because of H–Cl bond have high bond energy.

14. Reaction 3 is free radical addition reaction and rest all are electrophilic addition reactions.

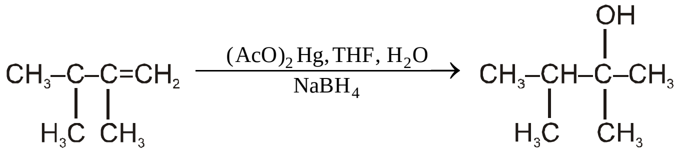
18. Reaction is possible in option (3) only.



19. 

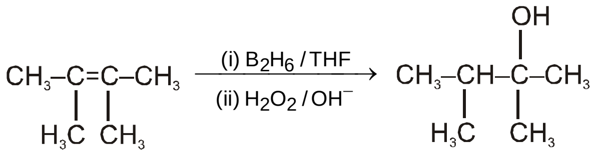
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2 \xrightarrow{dil.\ H_2SO_4} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\oplus}{C}H-CH_3 \longrightarrow CH_3-\underset{\oplus}{\overset{\overset{H_3C}{|}}{C}}-\overset{\overset{CH_3}{|}}{C}H-CH_3 \longrightarrow CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H_3C}{|}}{C}}-\overset{\overset{CH_3}{|}}{C}H-CH_3$$

(X)



$$CH_3-\underset{\underset{H_3C}{|}}{C}-\underset{\underset{CH_3}{|}}{C}=CH_2 \xrightarrow[NaBH_4]{(AcO)_2Hg,\ THF,\ H_2O} CH_3-\underset{\underset{H_3C}{|}}{C}H-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

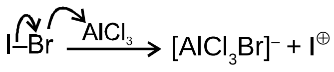
(Y)



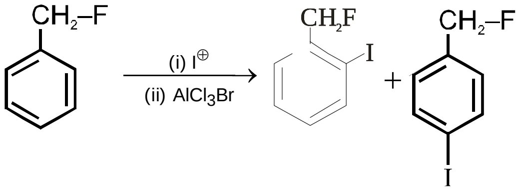
$$CH_3-\underset{\underset{H_3C}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3 \xrightarrow[\text{(ii) } H_2O_2/OH^-]{\text{(i) } B_2H_6/THF} CH_3-\underset{\underset{H_3C}{|}}{C}H-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$

(Z)

All products are identical.

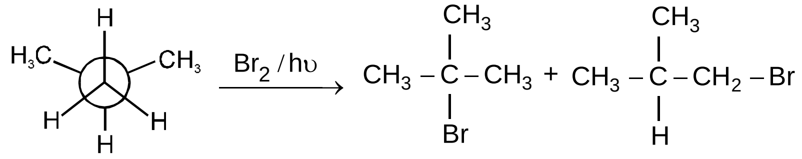
20. 

$$I-Br \xrightarrow{AlCl_3} [AlCl_3Br]^- + I^{\oplus}$$



Minor Major

21.



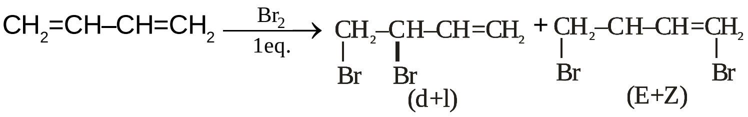
22. C=C at position 1 is more reactive towards electrophile $Br^{\oplus}$ as this is adjacent to O atom to provide +M effect. C=C at position 3 is more substituted as compared to C=C at position 2. Alkyne is less reactive towards $Br^{\oplus}$ as compared to alkene.

23. Primary monochloride can be

(i) 6 (1^o H) × 1 = 6 (ii) (2^o H) × 3 = 6 (iii) (3^o H) × 5 = 10

% yield of 1^oChiral mono chloro product $= \frac{6}{20} \times 100 = 30\%$

24.

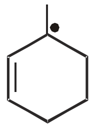


$$CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{1eq.}]{Br_2} \underset{Br}{CH_2}{-}\underset{Br}{CH}{-}CH{=}CH_2 \; (d+l) + \underset{Br}{CH_2}{-}CH{-}CH{=}\underset{Br}{CH_2} \; (E+Z)$$

25. Electrophile attack on that ring which have maximum electron density.

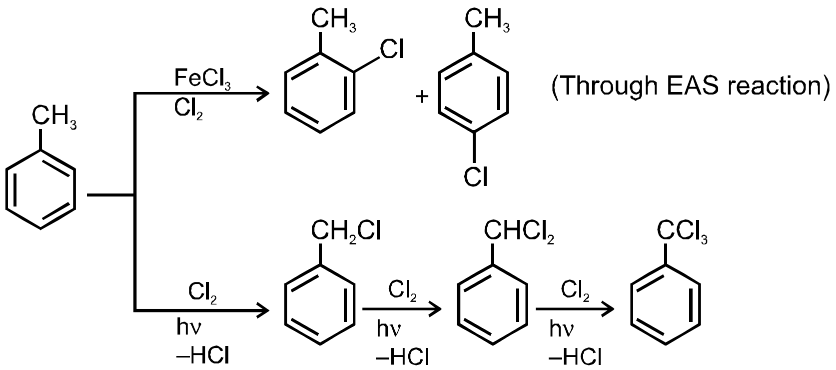
PART - 2

2. The given reaction occur via free radical substitution mechanism. Major product will depend on the stability of free radical.



Most stable free radical

3.



5. Option ‘D’ is chain propagating step.

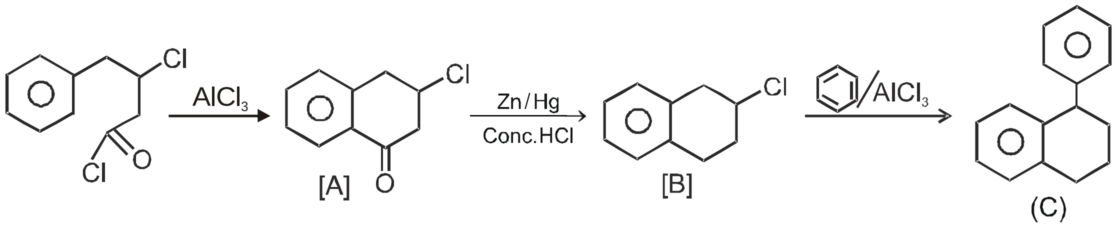
10. (A) In highly de-activated ring Friedal Crafts reaction is not possible.

(B) Chloro group is ortho-para director.

(C) In Friedal Craft reaction the electrophile carbocation rearranges.

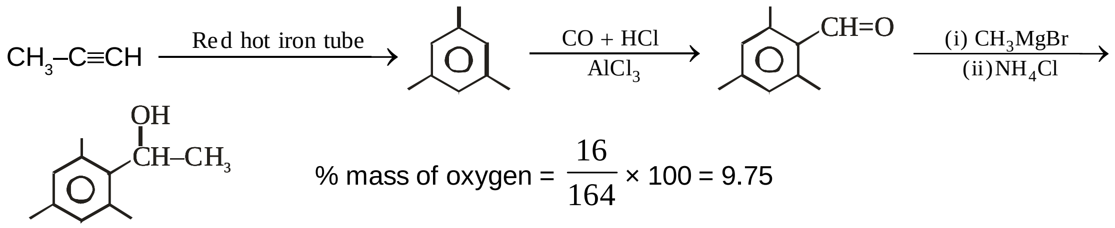
(D) To avoid polyalkylation aromatic substrate is taken in excess.

11.



12. Reaction-1 is free radical substitution. ; Reaction-2 is free radical substitution.
Reaction-3 is free radical substitution. ; Reaction-4 is Electrophilic addition reaction.

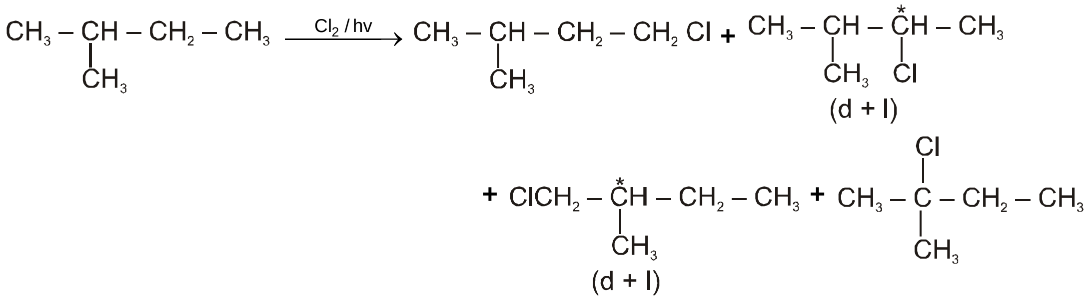
13.



$$\% \text{ mass of oxygen} = \frac{16}{164} \times 100 = 9.75$$

14. rate of Electrophilic addition $\propto$ stability of cation

15.



$$CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_2-CH_3 \xrightarrow{Cl_2/h\nu} CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_2-CH_2Cl + CH_3-\underset{CH_3}{\underset{|}{C}}H-\underset{Cl}{\underset{|}{\overset{*}{C}}}H-CH_3$$

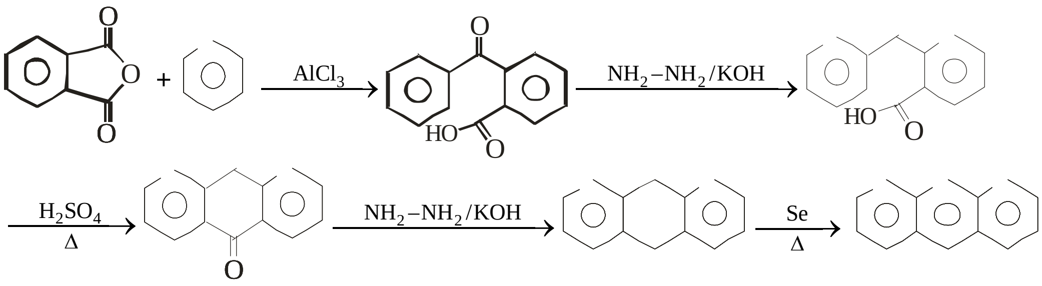
(d + l)

$$+\ ClCH_2-\underset{CH_3}{\underset{|}{\overset{*}{C}}}H-CH_2-CH_3 + CH_3-\underset{CH_3}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_2-CH_3$$

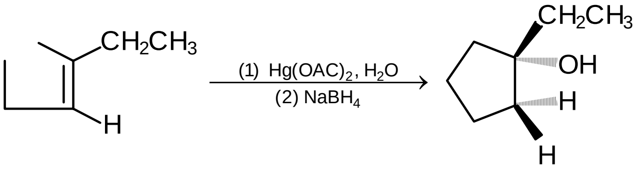
(d + l)

N = 6 , P = 4

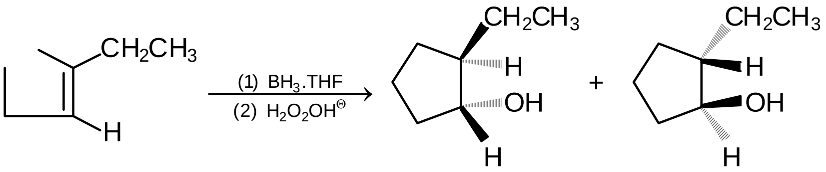
16.



17.



Single product
m = 1

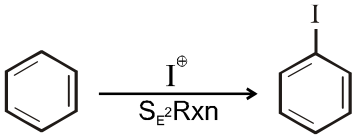


n = 2

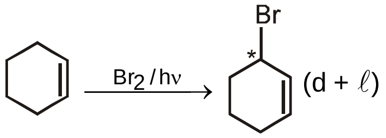
18. 6 (a , b , e, f , j , k)

PART - 3

17.



18.

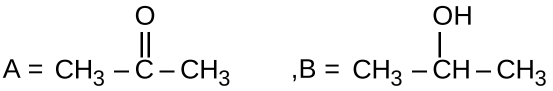


It is a free radical allylic substitution reaction.

19. It is example of anti Markovnikov hydration reaction using hydroboration-oxidation.

20. Chlorobenzene has π bond in aromatic ring.

21.



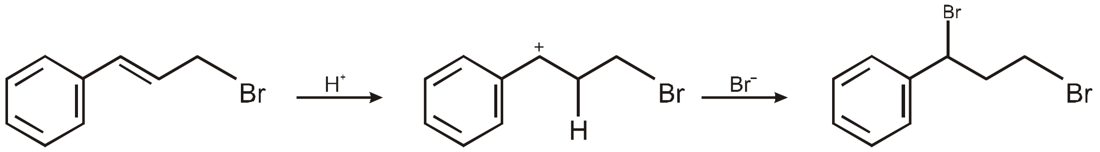
$A = CH_3 - \overset{\overset{O}{||}}{C} - CH_3$,$B = CH_3 - \overset{\overset{OH}{|}}{CH} - CH_3$

Step 1 is Markovnikov addition of water and Step 2 is reduction of ketone formed in step-I to 2-propanol.

22. Nitration takes place at activated benzene ring.

23. It is simple example of electrophilic aromatic substitution.

24.

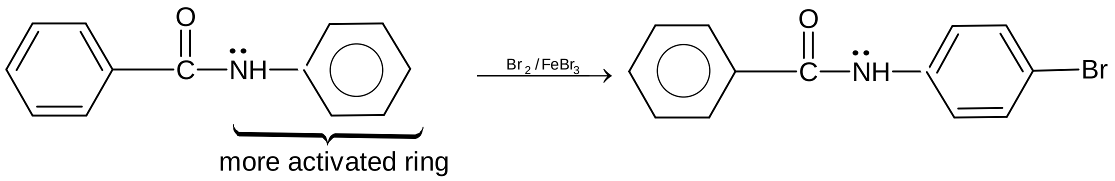


25. Nitration reaction is independent of leaving group ability hence all the three have nearly equal rate.

26. Addtion of bromine is anti. The product is trans-1,2-dibromocyclohexane.

27. $-NO_2$ group is strong electron withdrawing due to –M whereas $-NH_2$ group is strong electron donating group due to +M effect.

28.



Para w.r.t to activating group will be major due to steric hindrance at ortho.

29. Conjugated alkene are more stable and more reactive

30. Because of +M effect of OCH_3 group and +Hyperconjugation effect of CH_3 group.