

# HYDROCARBON

(Chemical reaction of Alkanes, Alkenes, Alkynes and Benzene)

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### 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.

**Aromatic Hydrocarbon**: 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.

**Aromatic Hydrocarbon**: Electrophilic substitution reactions: halogenation, nitration, sulphonation, Friedel-Crafts alkylation and acylation; Effect of o-, m- and p-directing groups in monosubstituted benzenes.



# HYDROCARBON

## Section (A) : Alkanes

### Physical properties of alkanes :

Alkane molecules are held together by weak Vander waal force which depends upon surface area. On increasing molecular mass surface area increases hence Vander waal forces also increased and thus physical properties are increased.

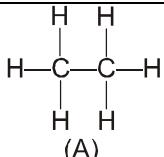
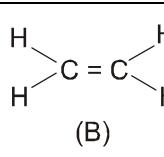
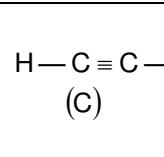
$C_1 - C_4$	$\Rightarrow$	gas
$C_5 - C_{17}$	$\Rightarrow$	liquid
$C_{18} \dots$	$\Rightarrow$	solid

**Note :** (1) On increasing branching surface area tends to be spherical i.e. Vander waal interaction reduced and hence boiling point decreased.

(2) Melting point of alkane having even number of carbon atoms is higher than neighbouring alkanes having odd number of carbon atom. Because in even number of alkanes two ends are facing towards opposite side hence there will be minimum intermolecular repulsion as a result they fit better into crystal lattice.

(3) Density of alkane increases with molecular mass and then acquires a constant value  $0.8 \text{ g/cc}^3$ . Thus also it is clear that alkane is lighter than water.

### Comparative study of alkane, alkene & alkyne :

	Hydrocarbon	 (A)	 (B)	 (C)
		Alkane	Alkene	Alkyne
(i)	C—C Bond distance	$1.54 \text{ \AA}$	$1.34 \text{ \AA}$	$1.20 \text{ \AA}$
(ii)	C—H Bond distance	$1.09 \text{ \AA}$	$1.08 \text{ \AA}$	$1.05 \text{ \AA}$
(iii)	Hybridisation state	$sp^3$	$sp^2$	$sp$
(iv)	Structure	Tetrahedral	Planner	Linear
(v)	Electronegativity $sp^3 < sp^2 < sp$	less than $sp^2/sp$	less than $sp$ , more than $sp^3$	more than $sp^2/sp^3$
(vi)	C—C bond energy	$415 \text{ kJ}$	$615 \text{ kJ}$	$835 \text{ kJ}$
(vii)	density	$0.5 \text{ g/cm}^3$	$0.52 \text{ g/cm}^3$	$0.67 \text{ g/cm}^3$
(viii)	% s-character	25%	33.33 %	50 %

### Lab Test :

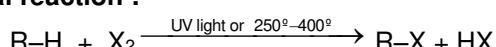
	Hydrocarbon	Alkane	Alkene	Alkyne (Terminal)
(i)	$\text{Br}_2/\text{H}_2\text{O}$ solution	No effect	Decolorise	Decolorise
(ii)	Cold dil. Alkaline + $\text{KMnO}_4$ Solution	No effect	Brown colour	Brown colour
(iii)	Tollen's Reagent	No effect	No effect	White ppt. of silver acetonilide
(iv)	Ammonical cuprous chloride solution	No effect	No effect	Red ppt. of cuprous acetonilide

### Chemical reaction of alkanes (free radical substitution)

#### (a) Halogenation :

Reagents : UV light/hv/high temp. ( $250^\circ$ - $400^\circ\text{C}$ ) / Peroxide +  $X_2$  ( $\text{Cl}_2 + \text{Br}_2$ )

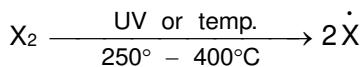
General reaction :-





**Mechanism :** Free radical substitution this reaction is chain reaction which is completed in following three steps.

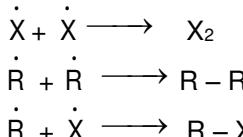
**(i) Chain initiation step :** It is homolytic cleavage of chlorine molecule to give chlorine free radical. It is an endothermic step .



**(ii) Chain propagation step :** The step in which reactant and product, both are having free radical. It is longest step.



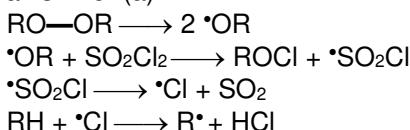
**(iii) Chain Termination step :** It is the step in which any two free radicals combine to give a product without free radical. It is always exothermic step.



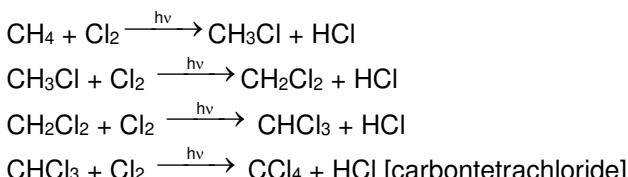
### Remarks :

#### (1) Other halogenating reagent are

- (a) Chlorination :  $\text{SO}_2\text{Cl}_2$ / Peroxide ;      (b) Bromination :  $\text{SO}_2\text{Br}_2$ / Peroxide  
Mechanism for (a)



#### (2) Methane reacts with excess of chlorine in diffused sunlight to give the final product as



#### (3) Reactivity of H = $3^\circ\text{H} > 2^\circ\text{H} > 1^\circ\text{ H}$

#### (4) Reactivity of $X_2$

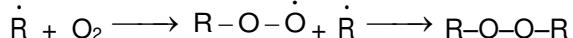
Reactivity of $X_2 = \text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$		
1. Direct fluorination of alkane is not possible because it is very explosive. So $\text{F}_2$ reacts with alkane in dark at room temperature.	Bromination is similar to chlorination but slower in rate.	1. Iodination is reversible reaction since $\text{H-I}$ is formed as a by product, that is strong reducing agent so reduces alkyl iodide back to alkane. Hence iodination can be done only in presence of strong oxidizing agent like $\text{HIO}_3$ , $\text{HNO}_3$ and $\text{HgO}$ etc. which destroy $\text{HI}$ into $\text{I}_2$ . $\begin{aligned} \text{CH}_4 + \text{I}_2 &\longrightarrow \text{CH}_3\text{I} + \text{H-I} \\ \text{HIO}_3 + 5\text{HI} &\longrightarrow 3\text{I}_2 + 3\text{H}_2\text{O} \end{aligned}$
2. Halogen exchange reaction <b>(Swart's Reaction)</b> Reagents : $\text{AgF} + \text{H}_2\text{O}$ (Major) + $\text{C}_2\text{H}_5\text{OH}$ (Minor) Only $\text{AgF}$ is soluble among all silver halides in water. $\text{R-X} \xrightarrow[\text{S}_{\text{N}}1]{\text{AgF}} \text{R}^+ \xrightarrow{\text{F}^-} \text{R-F} + \text{AgX} \downarrow$ $2\text{C}_2\text{H}_5\text{Br} + \text{HgF}_2 \rightarrow 2\text{C}_2\text{H}_5\text{F} + \text{HgBr}_2$		2. Halogen exchange Reactions : <b>(Finkelstein Reaction)</b> Reagents : $\text{NaI} + \text{Acetone}$ $\text{R-X} + \text{NaI} \xrightarrow[\text{S}_{\text{N}}2]{\text{Acetone}} \text{R-I} + \text{NaX} \downarrow$ $(X = \text{Cl}, \text{Br})$ In acetone, $\text{NaI}$ is soluble/Ionised but $\text{NaCl}/\text{NaBr}$ are insoluble. So $\text{NaCl}/\text{NaBr}$ get precipitate out.


**(5) In a chain reaction following reagents are involved :**

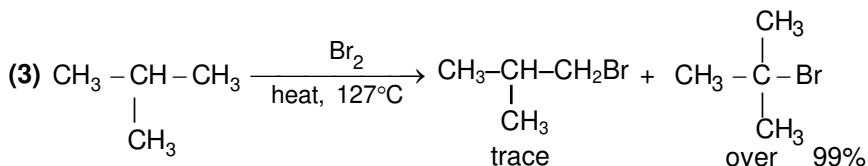
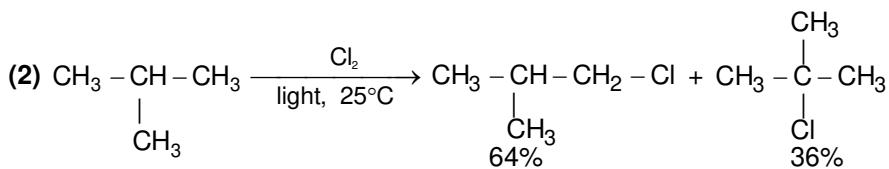
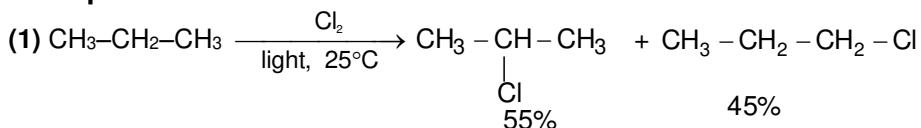
**Initiators** : They initiate the chain reaction, Initiators are peroxide ( $R_2O_2$ ), Perester's etc.

**Inhibitors** : A substance that slows down or stops the reaction is known as inhibitors

For example  $O_2$  is a good inhibitor.



all reactive alkyl free radicals are consumed so reaction stops for a period of time.

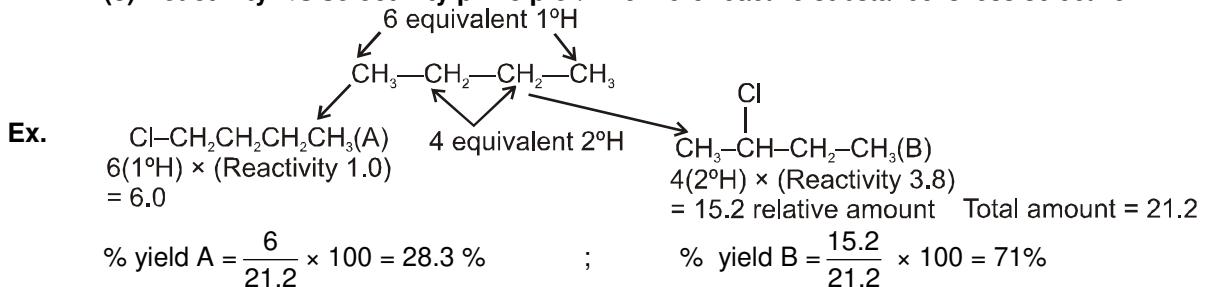
**Examples :**

**Factors affecting the relative yields :**

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

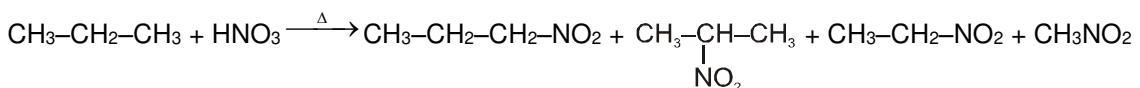
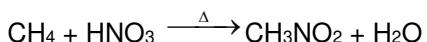
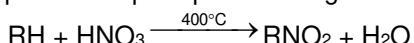
**(2) Reactivity of hydrogen** : The order of reactivity is  $3^\circ > 2^\circ > 1^\circ$  the relative rate per hydrogen atom is found to be :

Primary	Secondary	Tertiary	
1	: 3.8	: 5	For chlorination at $25^\circ C$
1	: 82	: 1600	For bromination at $127^\circ C$

**(3) Reactivity v/s selectivity principle** : The more reactive substance is less selective.


**(b) Nitration of alkane :**

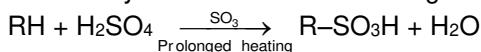
It takes place in vapour phase and gives a mixture of nitroderivatives due to cracking.



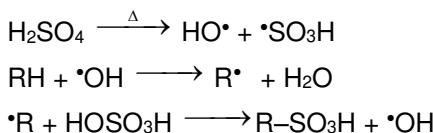
**Note :** Nitration of propane gives a mixture of four nitroderivatives as it has two types of replaceable H-atom ( $1^\circ$  and  $2^\circ$ ) and also it undergoes cracking at high temperature.

**(c) Sulphonation of alkane :**

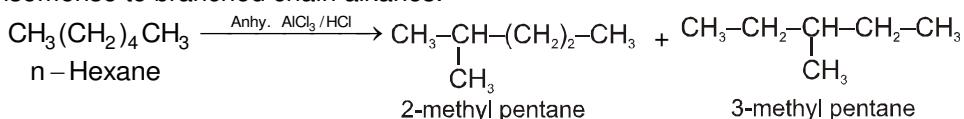
Lower alkanes do not undergo sulphonation easily but higher members (from hexane onward) are sulphonated slowly when treated with fuming acid (oleum) at around 400°C



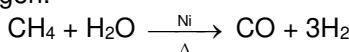
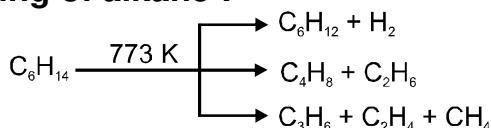
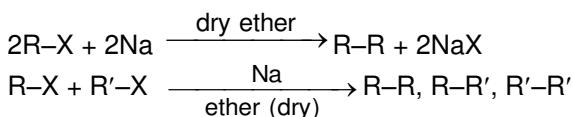
- Note :**
1. Lower members like propane, butane and pentane etc. react with  $\text{SO}_3$  in vapour phase to give corresponding sulphonic acid.
  2. Decreasing order of sulphonation of alkane  
 $3^\circ > 2^\circ > 1^\circ$  H-atom
  3. It follows free radical mechanism as

**(d) Isomerization of alkane :**

n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.

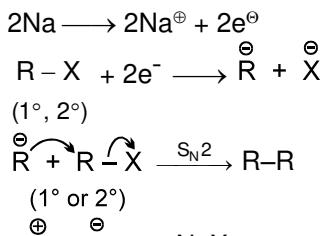
**(e) Reaction with steam :**

Methane reacts with steam at 1273 K in the presence of nickel catalyst to form carbon monoxide and dihydrogen.

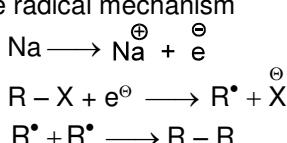
**(f) Cracking of alkane :****(g) By Wurtz reaction :**

**Mechanism :** Two mechanisms are suggested

(a) Ionic mechanism



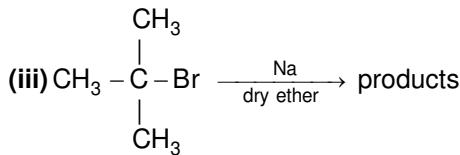
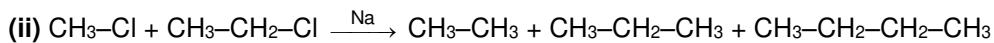
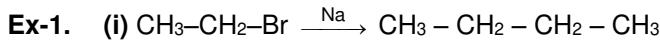
(b) Free radical mechanism



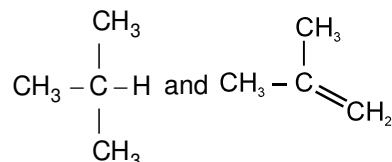


**Note :** The alkyl halide should be  $1^\circ$  or  $2^\circ$ , with  $3^\circ$   $R-X$   $S_N2$  and free radical coupling is not possible due to steric hinderence so in that case elimination or disproportionation is possible.

In the ionic mechanism alkyl sodium ( $R\text{Na}^\ominus$ ) gives strong base as well as nucleophile which gives  $S_N2$  with  $R-X$ , ether should be dry otherwise if moisture is present than  $R\text{Na}^\ominus$  forms  $R-\text{H}$  instead of  $R-R$  with  $H_2O$ .

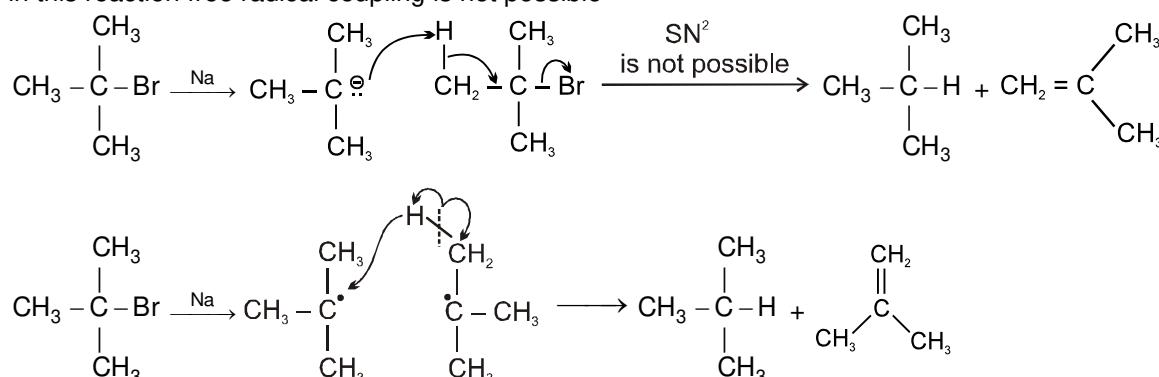


Products will be

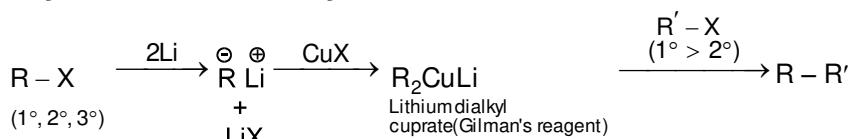


**Ans.**

in this reaction free radical coupling is not possible

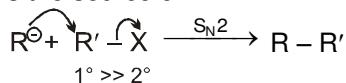


### (h) By Corey House alkane synthesis

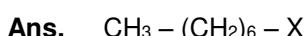
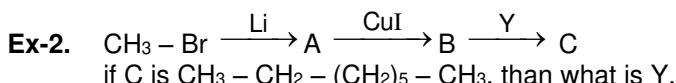


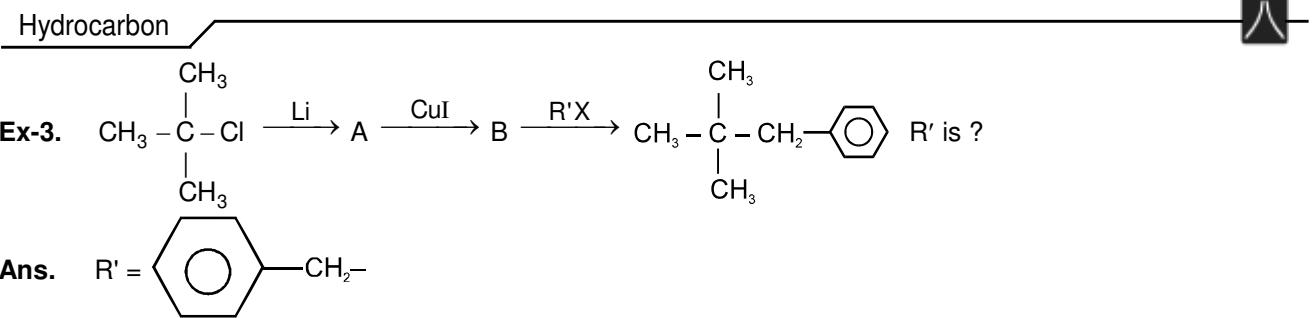
#### Mechanism

$\text{R}_2\text{CuLi}$  is the source of  $\text{R}^\ominus$ .



$\text{R}_2\text{CuLi}$  does not react with  $-\text{NO}_2$ ,  $-\text{CN}$ ,  $>\text{C}=\text{O}$  etc.





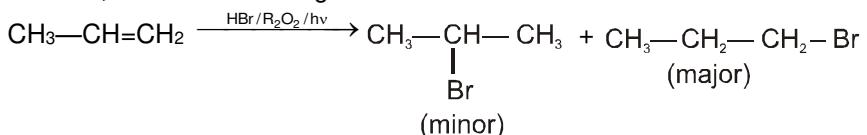
**(I) By Franklands reagent :**



## **Section (B) : Free radical addition and substitution in alkenes / alkynes**

(a) Free Radical Addition of HBr (Kharash Effect or Peroxide Effect) :

**Reagents :** HBr, Peroxide or sunlight



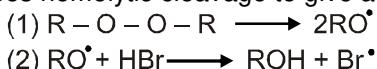
**Remarks :** Anti Markovnikov's Addition; Free radical chain reaction ;

Among all the HX peroxide effect observed with only HBr, not with HF, HCl, HI.

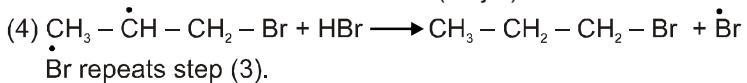
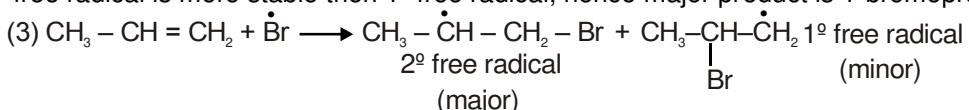
Because HF and HCl are held together by strong electrostatic force. So they can never be broken into free radical. HI will give  $I^-$  but being larger in size  $I^-$  (inspite of going to  $C=C$ ) will combine with another  $I^-$  to give  $I_2$  molecule. Just because of comparable size.

**Mechanism :** Mechanism of this reaction is completed in following three steps.

**(i) Chain initiation step:** This reaction is free radical addition reaction in this reaction peroxide undergoes homolytic cleavage to give a free radical from HBr to give Br<sup>•</sup>.



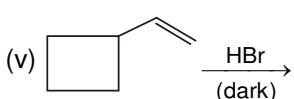
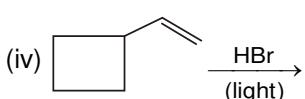
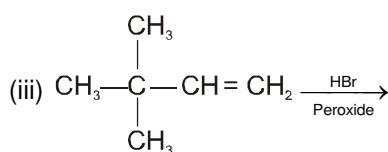
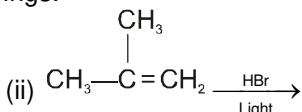
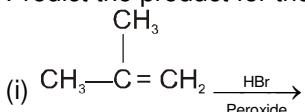
**(ii) Chain propagating step:** This Br<sup>-</sup> will go to either carbon of carbon-carbon double bond of propene to give two type of free radicals.

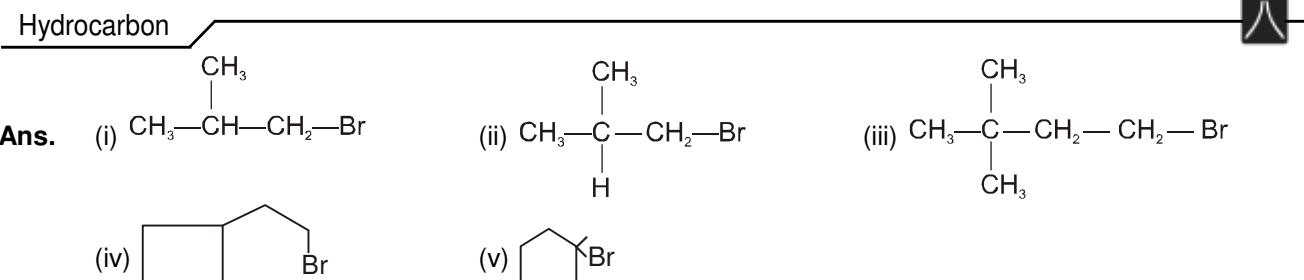


### **(iii) Chain termination step :**

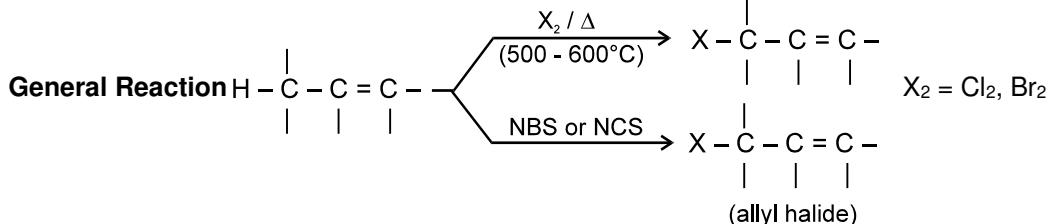


**Q-1.** Predict the product for the followings.

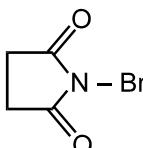




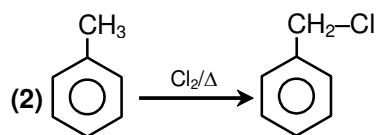
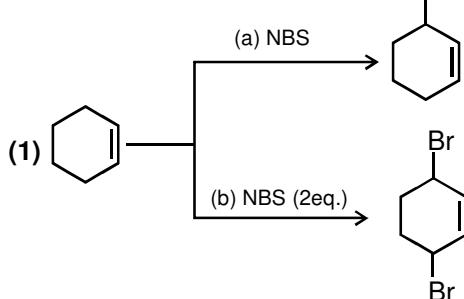
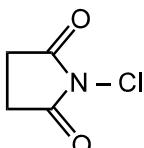
### (b) Allylic or Benzylic substitution by NBS/NCS :



NBS = N-Bromosuccinimide



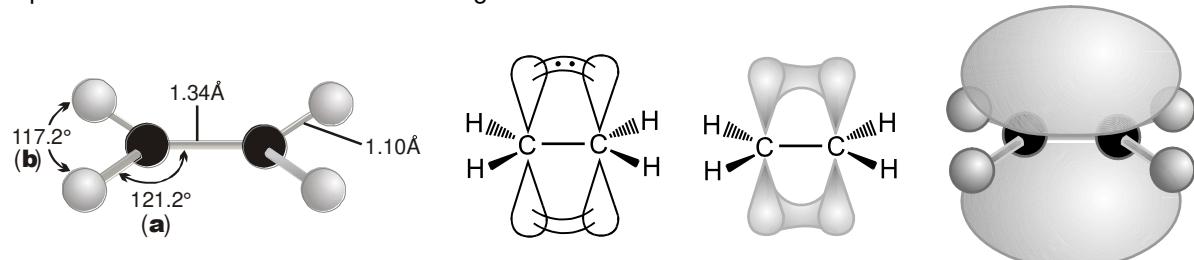
NCS = N-Chlorosuccinimide



## Section (C) : Alkene

### (a) Structure and Bonding :

- (1) Alkenes ( $\text{C}_n\text{H}_{2n}$ ) are unsaturated hydrocarbons having at least one double bond. Alkenes are also known as olefins.
- (2) The  $\pi$  e<sup>-</sup> cloud is present above and below the plane of  $\sigma$ -bonded skeleton.
- (3) These are also known as olefins since ethene, the first member of the homologous series forms oily liquid substance when treated with halogens.



**Note :** Bond angle a > b since repulsion due to  $\pi$  electrons (double bond - single bond repulsion > single bond - single bond repulsion according to VSEPR theory).



### (b) Physical Properties of Alkene

(i) From C<sub>2</sub>–C<sub>4</sub> they are colourless, odourless gases, from C<sub>5</sub>–C<sub>17</sub> they are colourless liquids, C<sub>18</sub> onwards alkenes are solids.

(ii) Alkenes are practically insoluble in water because they cannot form hydrogen bonds with H<sub>2</sub>O molecules. They dissolve freely in organic solvents like benzene, chloroform, CCl<sub>4</sub> petroleum ether, etc.

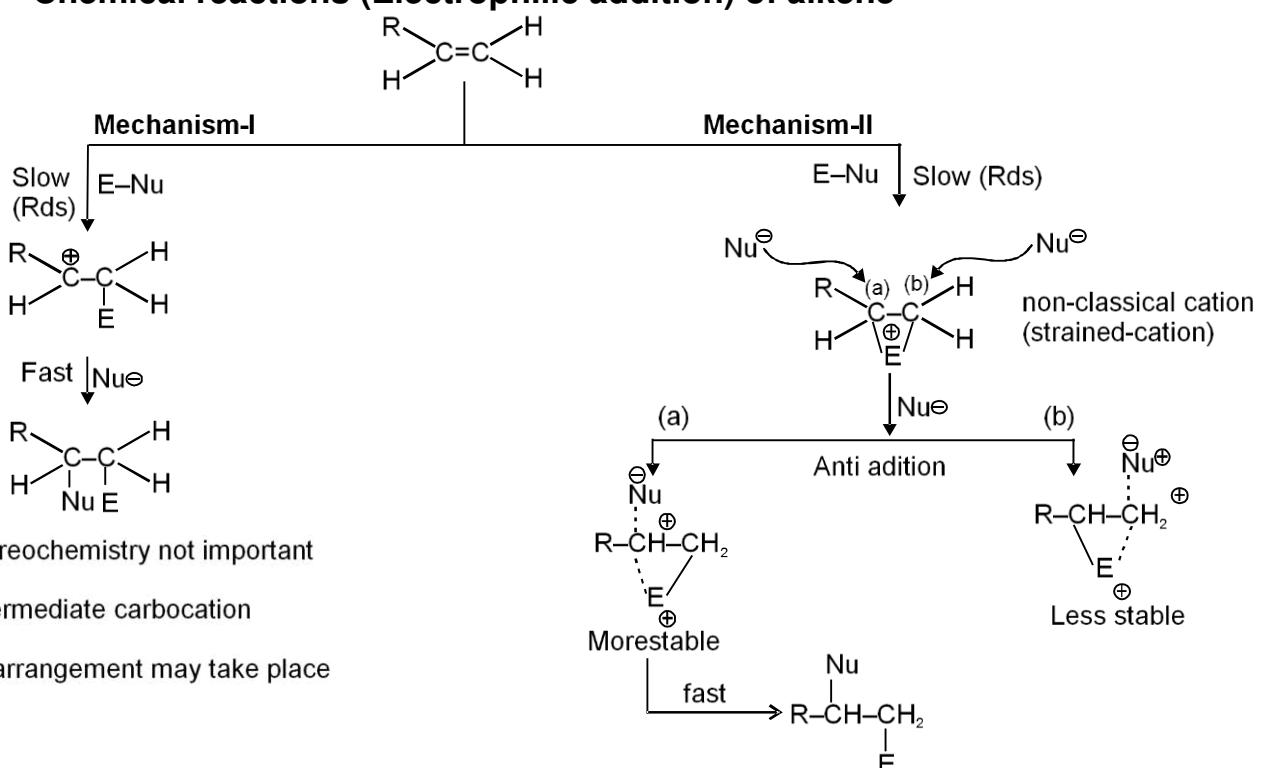
(iii) The boiling and melting points of alkenes are slightly higher than the corresponding alkanes because the intermolecular forces of attraction are stronger due to the presence of easily polarizable  $\pi$  bond. Alkenes are therefore, lesser volatile than the corresponding alkanes.

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

**M.P. and B.P.  $\propto$  mol. wt.**

$$\text{B.P} \propto \frac{1}{\text{branching in alkenes}}$$

### (c) Chemical reactions (Electrophilic addition) of alkene



\*Formation of non classical cation (Bridged cation)

\* Attack of nucleophile on that carbon which have more stable +ve charge

\* Anti addition

\* Stereospecific

\* No Rearrangement

#### Examples of mechanism-I

- (1) Addition of hydrogen halide
- (2) Acid-catalysed hydration.
- (3) Addition of H<sub>2</sub>SO<sub>4</sub>.

#### Examples of mechanism-II

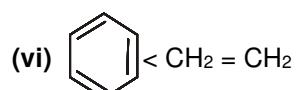
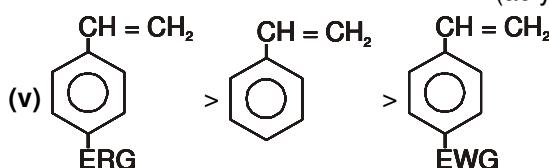
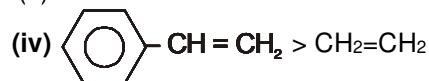
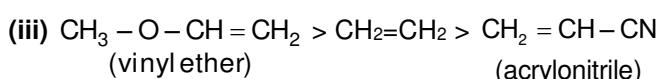
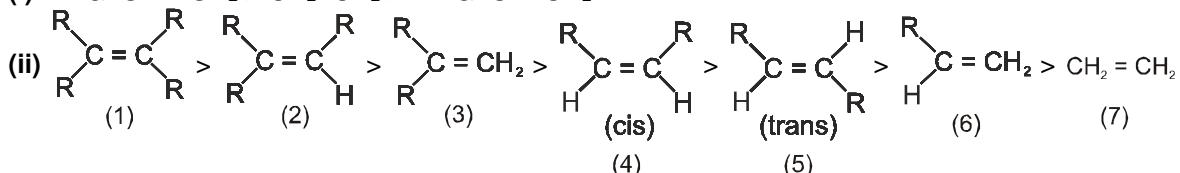
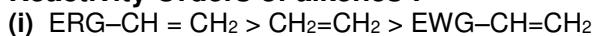
- (1) Addition of halogen.
- (2) Addition of hypohalous acid.
- (3) Oxymercuration-demercuration
- (4) Addition of NOCl

**Markovnikoff rule :** The rule states that negative part of the addendum (adding molecule) or acid reagent gets attached to that carbon atom of unsymmetrical alkene ( $C=C$ ) which possesses lesser number of hydrogen atom.

### Reactivity of an Alkene:

- (1) Presence of electron releasing groups (+M, +I) at  $C=C$  increases electrophilicity and reactivity.
- (2) Presence of ERG stabilises the intermediate carbocation.
- (3) More stable  $C^+$ , more is reactivity.

### Reactivity Orders of alkenes :



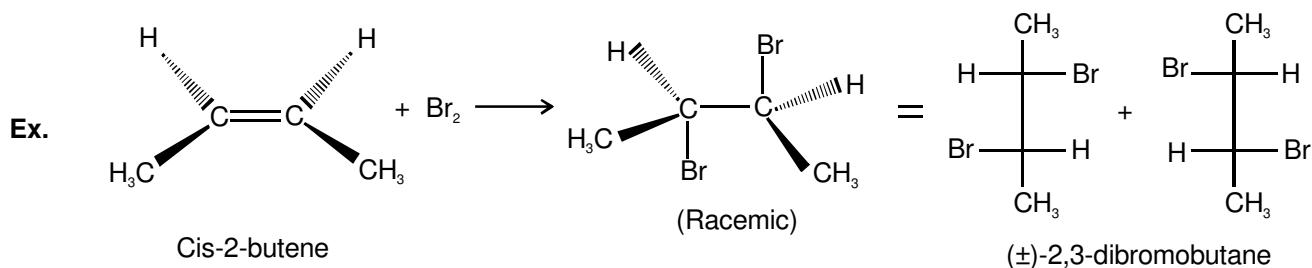
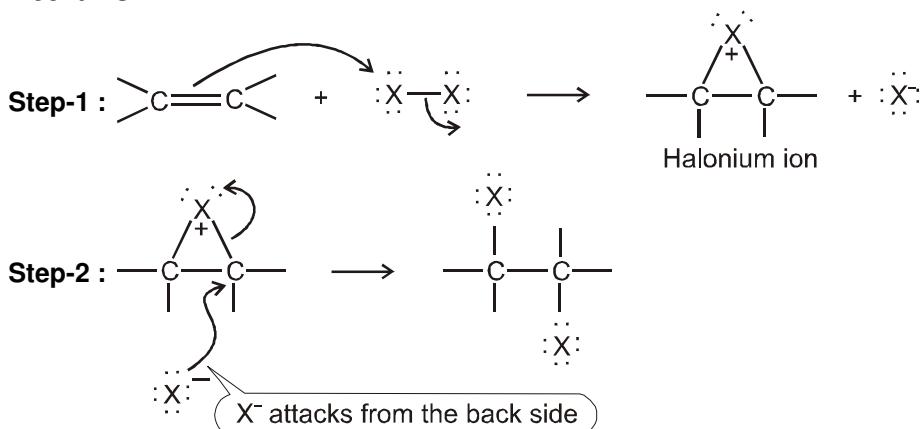
### (i) Additon of halogen (Halogenation) : “Mechanism-II”

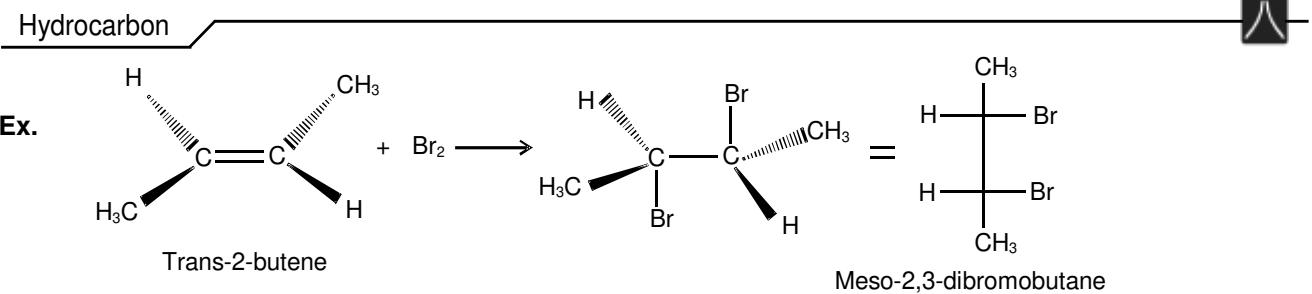
Reagent : ( $X_2 = Cl_2, Br_2$ , but not  $F_2$  and  $I_2$ )

Electrophile :  $X^+$

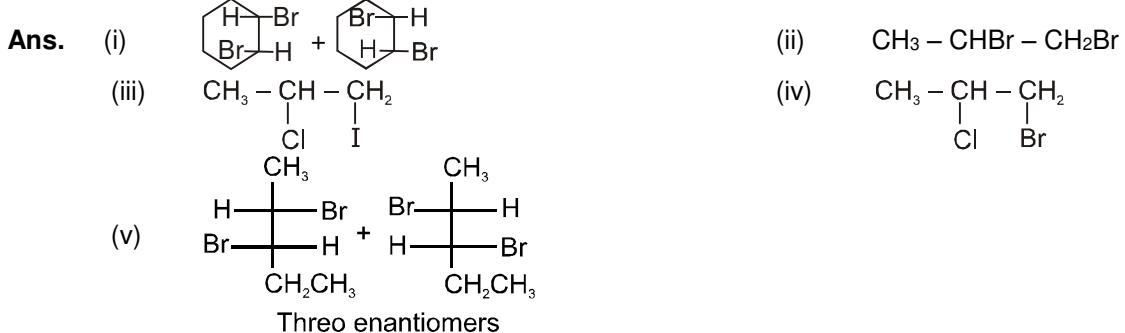
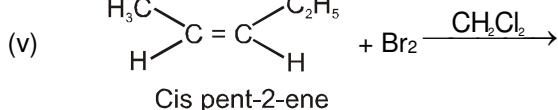
Remarks : Stereospecific anti addition, No rearrangement, Markovnikoff's addition

#### Mechanism :





**Q-2.** Predict the product for the following :-



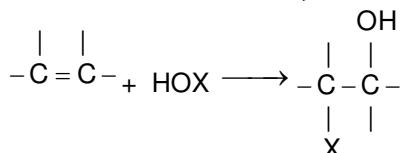
## (ii) Addition of HOX : “Mechanism-II”

**Reagents :** (i) X<sub>2</sub> + H<sub>2</sub>O → HOX + HX or (ii) HOX , H<sup>+</sup>

**Electrophile :** X<sup>+</sup> , Halonium ion :

**Remarks :** Anti addition ; No rearrangement ;

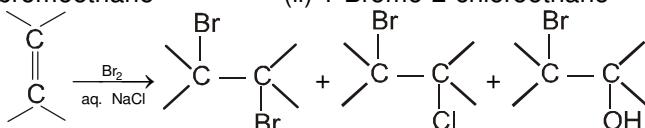
Markovnikoff's addition



### Evidence to support of formation non classical cation :

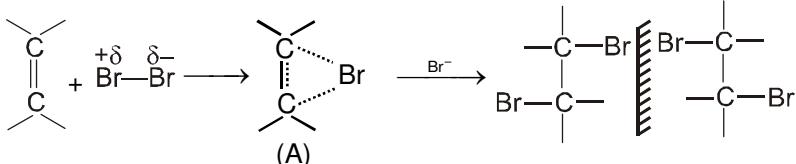
When addition of Br<sub>2</sub> was carried out in the presence of aq. NaCl, we get 3-products.

(i) 1,2-dibromoethane      (ii) 1-Bromo-2-chloroethane      (iii) 2-Bromoethanol

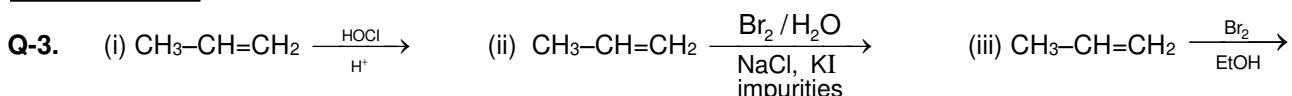


Formation of these three products clearly indicates about intermediate (A) thus addition of bromine water over alkene is electrophilic addition reaction.

**Note :** This addition always takes place in trans manner because of bulky nature of bromine atom in bromonium, which is a cyclic bridge intermediate. Cyclic bridge intermediate is non-classical cation.



### Hydrocarbon



**Ans.** (i)  $\text{CH}_3\text{--CH(OH)--CH}_2\text{--Cl}$  (ii)  $\text{CH}_3\text{--CH}(\text{G})\text{--CH}_2$  4 structural products are formed , G=OH<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, Cl<sup>-</sup>  
 (iii)  $\text{CH}_3\text{--CH(OEt)--CH}_2\text{--Br}$

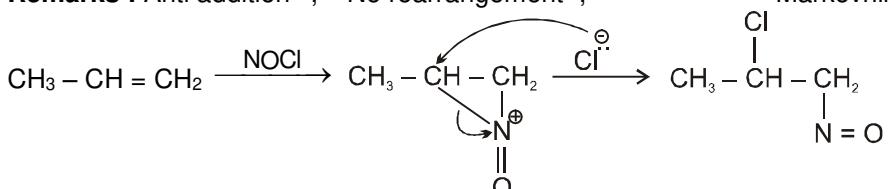
### (iii) Addition of $\text{NOCl}$ :

**Reagents :** NOCl

**Electrophile :**  $\text{NO}^+$

**Remarks :** Anti addition ; No rearrangement ;

## Markovnikoff's addition

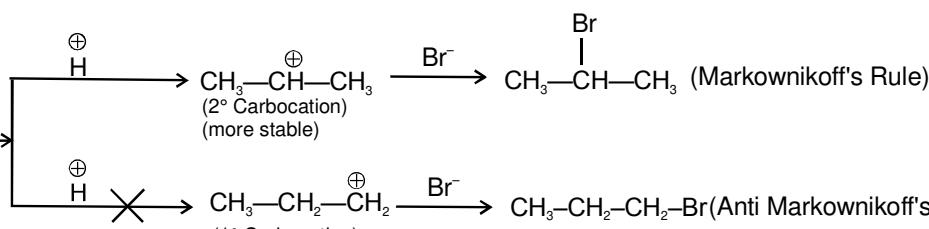
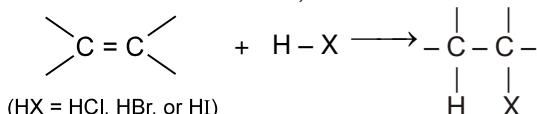


**(iv) Addition of Hydrogen Halides ( $\text{HX}$ ) : “Mechanism-I”**

**Reagents : HX (HI > HBr > HCl)**

## Reagents FIX (1) Electrophile : H<sup>+</sup>

**Remarks :** Markovnikoff addition; Intermediate carbocation; Rearrangement may take place

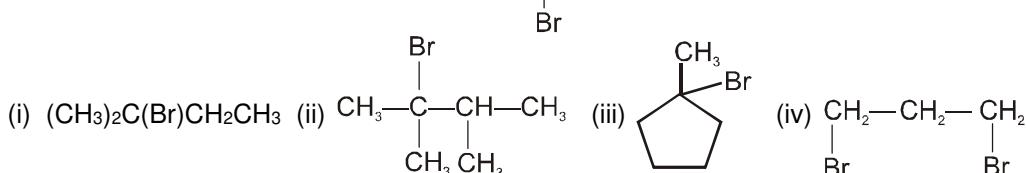
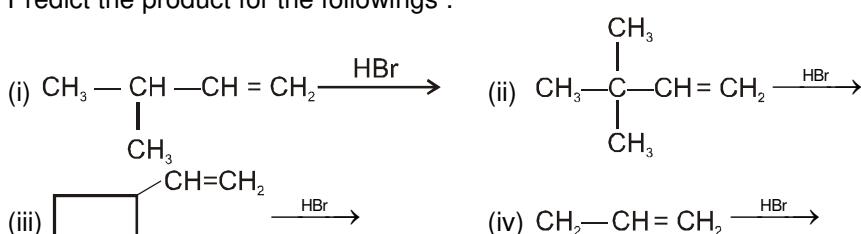


Ex

Above reaction is electrophilic addition reaction hence electrophile will go to that carbon atom of C=C which has more no. of H atoms.

Since  $2^\circ$  carbocation is more stable, hence major product is 2-bromopropane.

**Q-4** Predict the product for the followings :





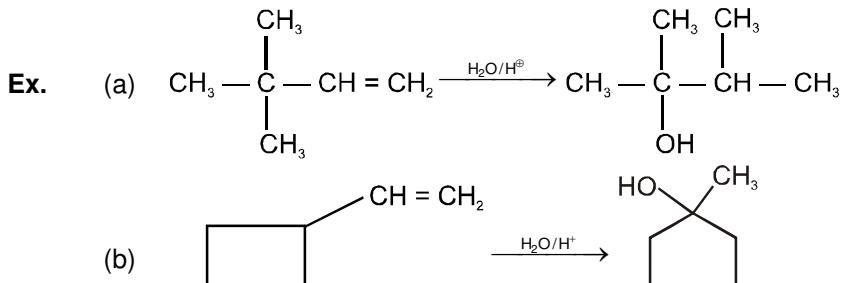
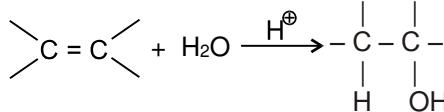
### (v) Addition of H<sub>2</sub>O (Hydration Reaction)

#### (1) Acid-Catalyzed Hydration of Alkenes : "Mechanism-I"

Reagents : Dilute H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>O<sup>+</sup>

Electrophile : H<sup>+</sup>

Remarks : Markovnikoff addition ; Intermediate carbocation ; Rearrangement may take place



#### (2) Oxymercuration-Demercuration : "Mechanism-II"

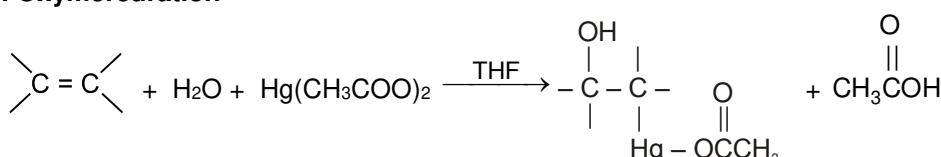
Reagents : (i) Hg(OAc)<sub>2</sub>, H<sub>2</sub>O (ii) NaBH<sub>4</sub>

Electrophile :  $Hg^{+}OAc$

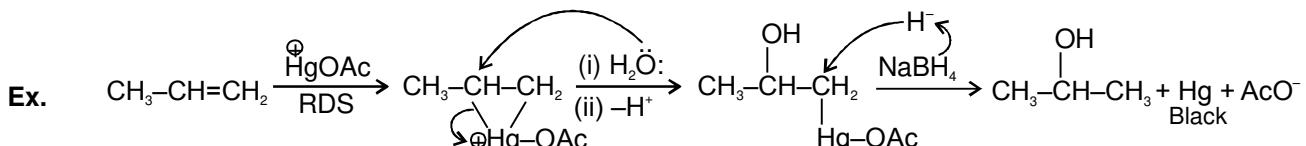
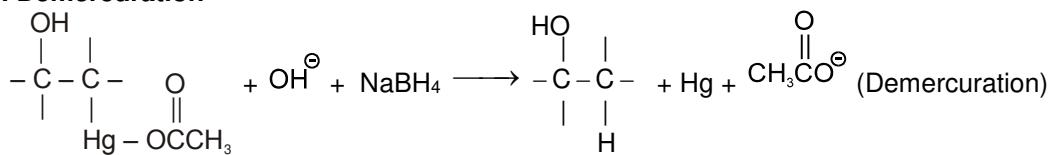
Remarks : No rearrangement ; Markovnikoff's addition

Mechanism :

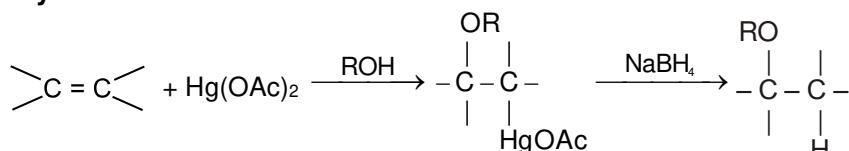
##### Step-1 : Oxymercuration



##### Step-2 : Demercuration



#### (3) Alkoxymercuration - demercuration : "Mechanism-II"



#### (4) Hydroboration-oxidation : (Syn addition)

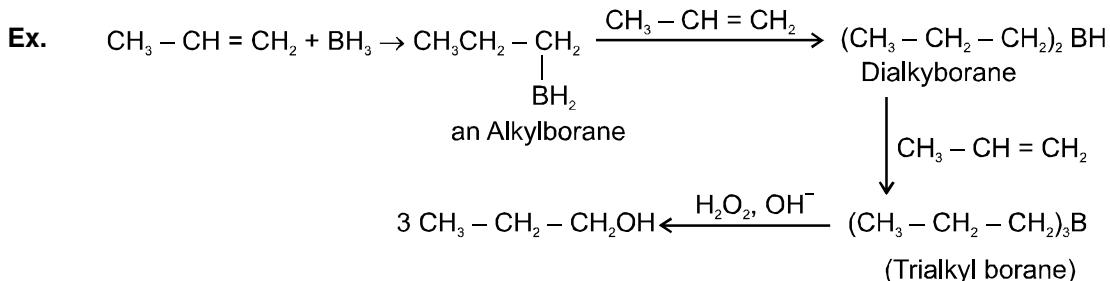
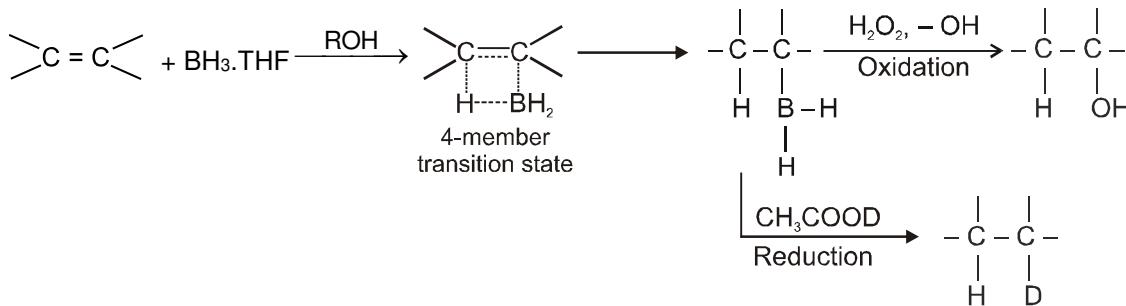
Reagents : (i) BH<sub>3</sub>, THF (ii) H<sub>2</sub>O<sub>2</sub>, -OH

Electrophile : Boron

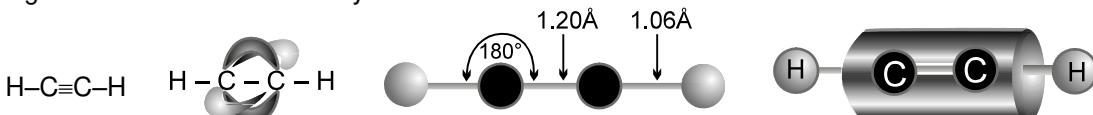
Remarks : Anti Markovnikov's addition, Stereo specific Syn addition.

Less hindered alkene is more reactive.

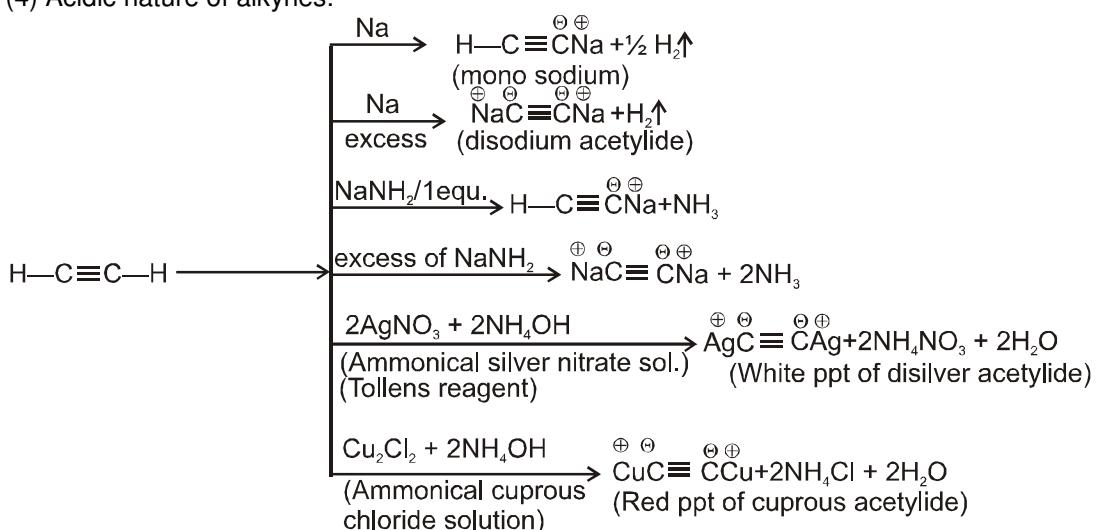
Reaction proceeds through 4-membered transition state.

**Mechanism :****Section (D) : Alkyne****(a) Introduction**

- (1) Alkynes ( $\text{C}_n\text{H}_{2n-2}$ ) are hydrocarbons that contain carbon-carbon triple bond.
- (2) Two  $\pi$  bonds result from overlap of the two remaining unhybridized p orbitals on each carbon atom. These orbitals overlap at **right angles** ( $90^\circ$ ) to each other, forming one  $\pi$  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  $\pi$  electron cloud around  $\sigma$  bonded structure



- (3) Any type of stereoisomerism does not arise in acetylenic bond due to linearity of  $\text{C} \equiv \text{C}$  bond.
- (4) Acidic nature of alkynes.



All these reactions are possible with 1-alkyne or acetylene.

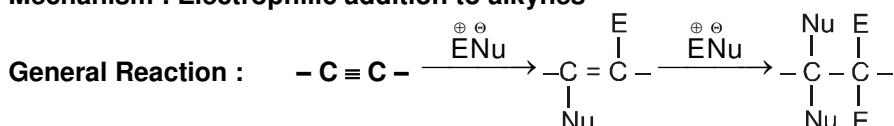
**(b) Physical Properties of Alkyne :**

- (i) Alkynes are colourless, odourless and tasteless.
- (ii) Lower alkynes are partially soluble in  $\text{H}_2\text{O}$ . (It is due to its polarizability)
- (iii) Higher alkynes are insoluble in water due to more % of covalent character.

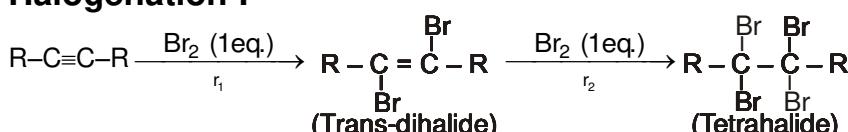
- (iv) Completely soluble in organic solvents.  
 (v) Melting point and boiling point are directly proportional to molecular mass and inversely proportional to number of branches.  
 (vi) Alkynes upto C<sub>4</sub> are gaseous, C<sub>5</sub>–C<sub>11</sub> are liquid, C<sub>12</sub> & above are solids.  
 (vii) Order of Solubility, density, B.P., M.P. and Acidic nature : Alkyne > Alkene > Alkane  
 \* All terminal alkynes are acidic in nature.

### (c) Chemical properties of alkyne :

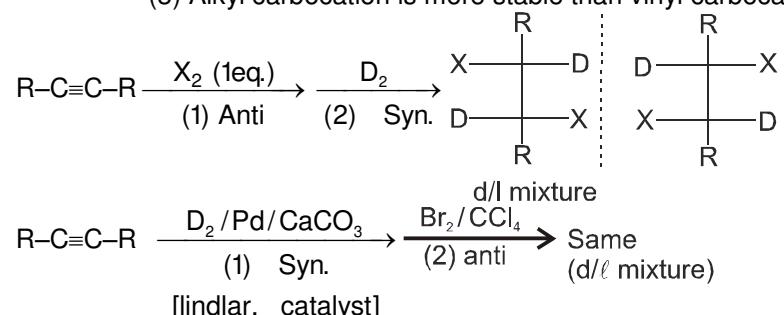
Mechanism : Electrophilic addition to alkynes



#### (i) Halogenation :

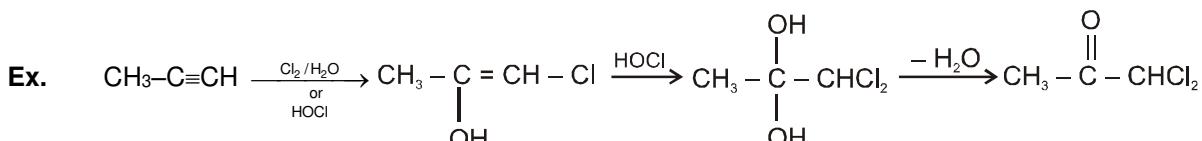
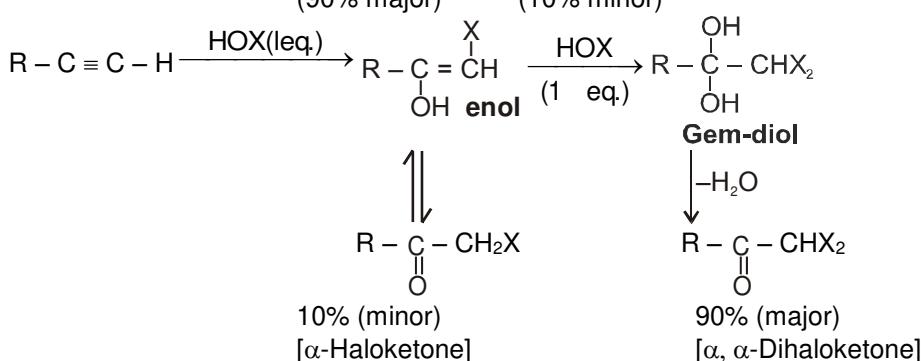


Remarks : (1) Reaction is Anti in both step  
 (2) In above reaction r<sub>2</sub> > r<sub>1</sub>  
 (3) Alkyl carbocation is more stable than vinyl carbocation



#### (ii) Addition of HOX :

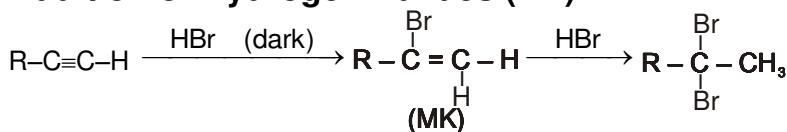
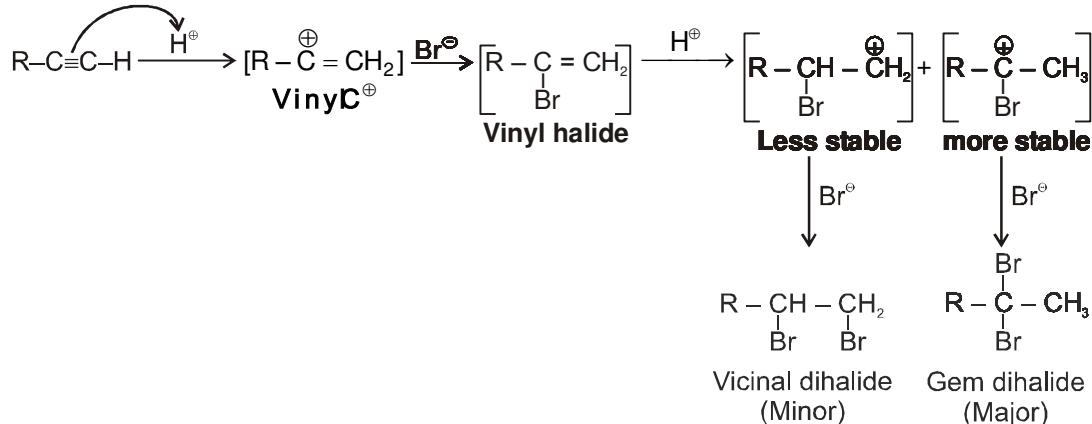
Alkynes + HOX  $\longrightarrow$   $\alpha, \alpha$ -dihaloketone +  $\alpha$ -haloketone  
 (90% major) (10% minor)



Remarks :

- (1) Two molecules of HOX can be added, the end product is  $\alpha, \alpha$ -Dihaloketone.  
 (2) The intermediate product is an enol which gives a minor product  $\alpha$ -haloketone.

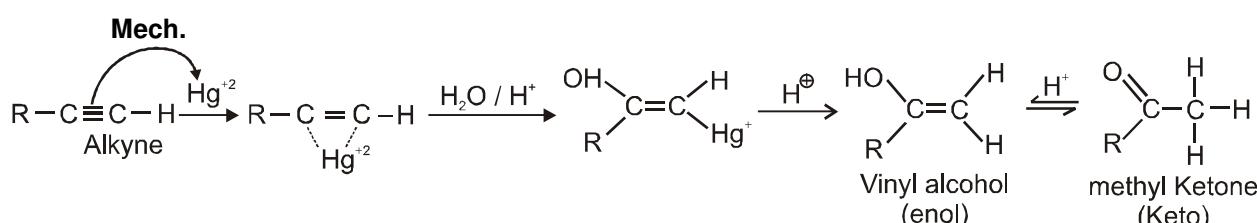
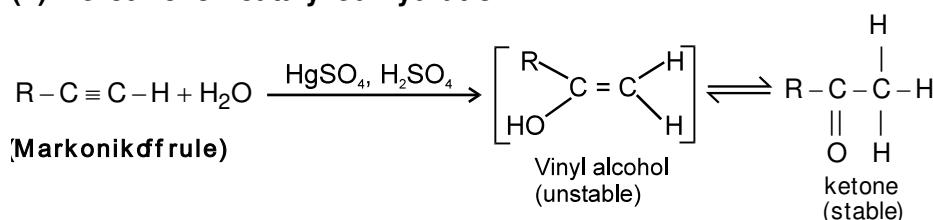
## (iii) Addition of Hydrogen Halides (HX) :

**Mechanism :****Remarks :**

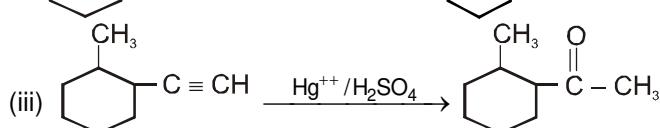
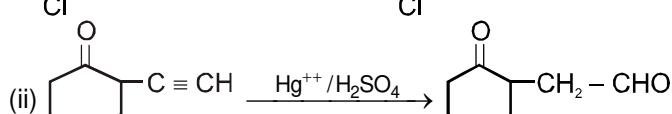
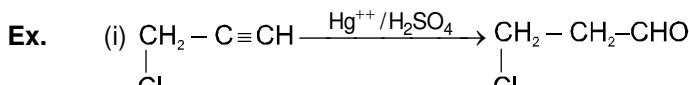
- (1) Markovnikov's Addition in both steps.
- (2) If two moles of HX are added the final product is Gemdihalide.
- (3) **Electrophilic addition to terminal alkyne is regioselective.**

(iv) Addition of H<sub>2</sub>O (Hydration Reaction) :

## (1) Mercuric ion catalyzed hydration :



**Note:** By above reaction it is clear that carbonyl carbon is formed from that carbon of ' $\text{C}\equiv\text{C}$ ' over which nucleophile water attacks.



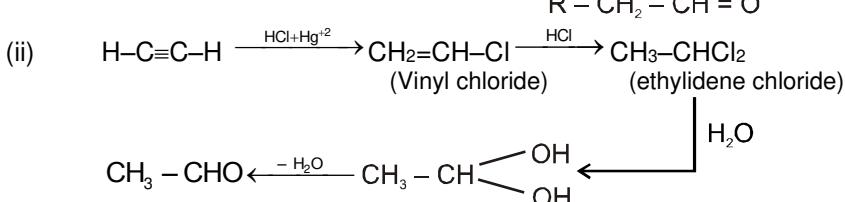
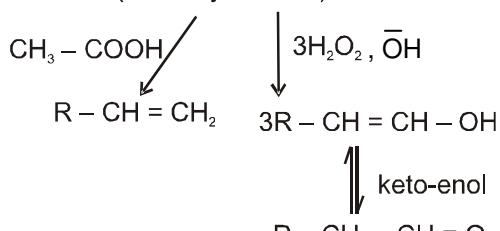
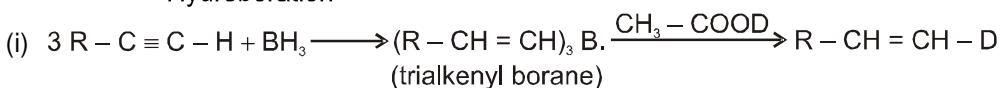
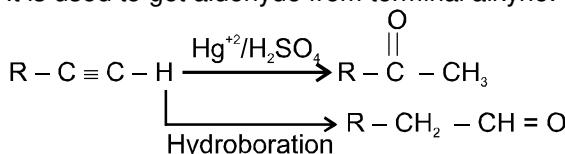
#### Remarks :

- (1) Alkynes add one molecule of water.  
(2) The product enol tautomerises to a carbonyl compound (aldehyde or ketone) and further addition does not take place.  
(3) The reaction is catalysed by  $\text{Hg}^{+2}$  ions.  
(4) The product is Markownikoff Addition of water.  
(5) If hydroboration method is used, then Anti Markownikoff addition of water takes place.

**Important :** The product does not appear to be addition product.

## (2) Hydroboration Oxidation of Alkynes :

It is used to get aldehyde from terminal alkyne.



(v)

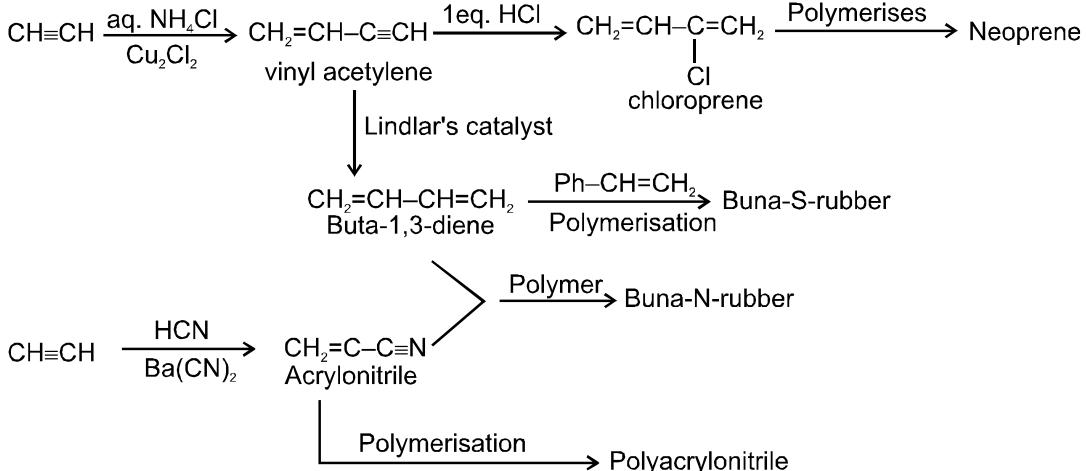
### **Other reactions of Alkynes :**

(v)  
Q-5.

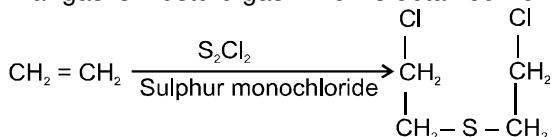
Convert acetylene into Neoprene, Polybutadiene, Buna-S and Buna-N.

Q. 8.

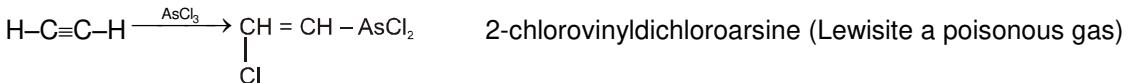
Ans



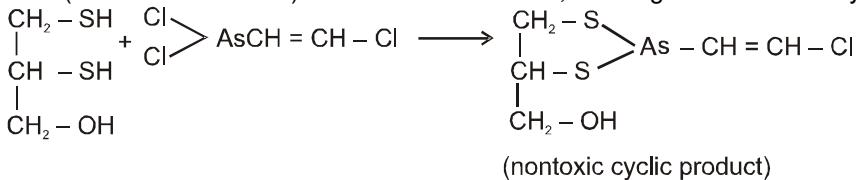
- War gas is mustard gas which is obtained from ethylene as :



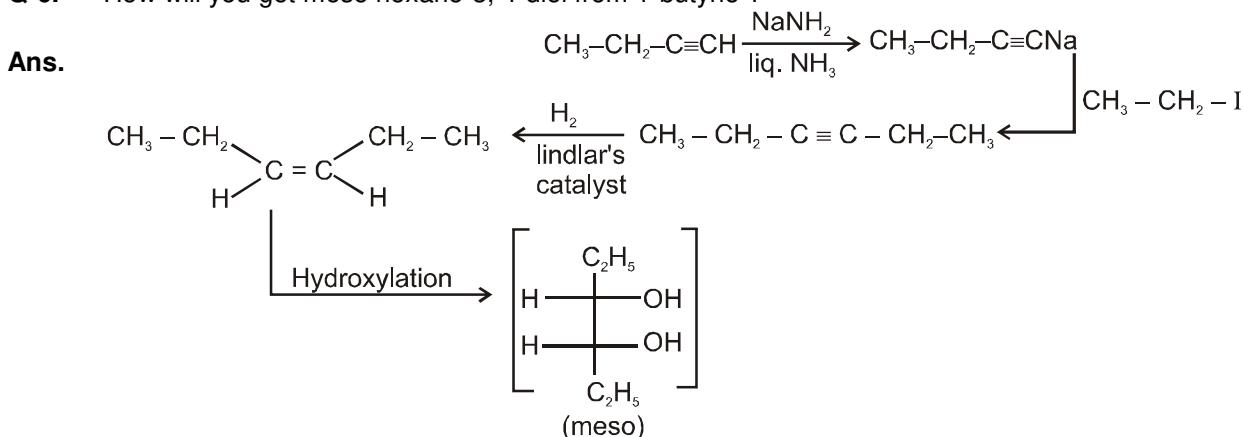
## ■ Preparation of Lewisite



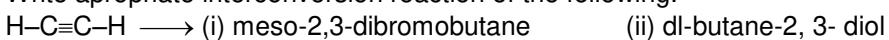
BAL (British anti lewisite) is antidote of lewisite, which gives non-toxic cyclic products.



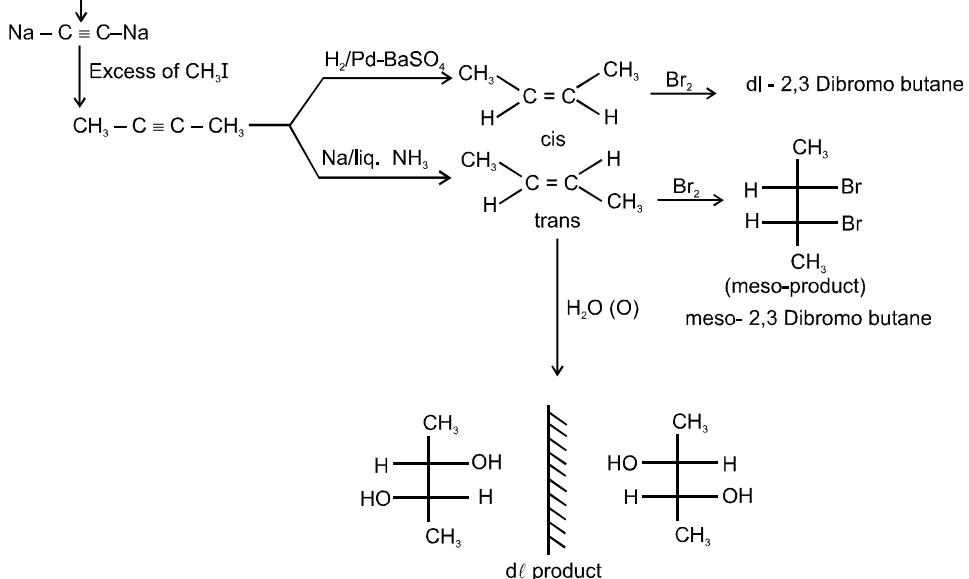
**Q-6.** How will you get meso hexane-3, 4-diol from 1-butyne ?



**Q-7.** Write appropriate interconversion reaction of the following.

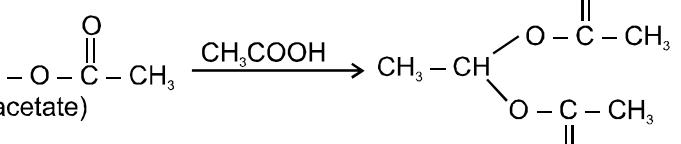
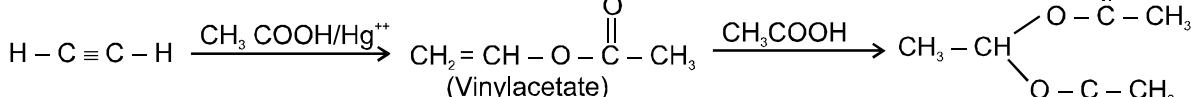


**Ans.**

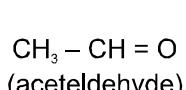




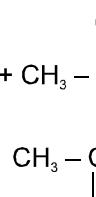
Q-8.



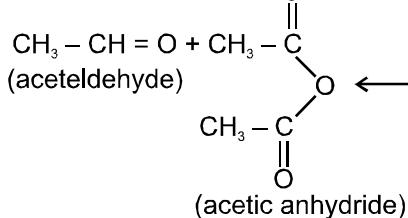
(ethyldene acetate)



(aceteldehyde)



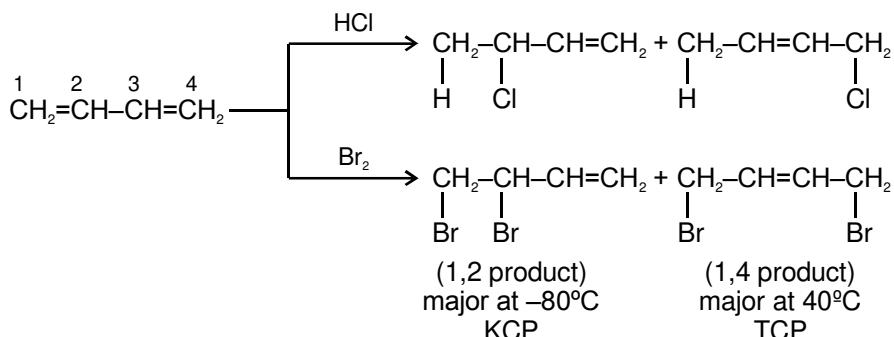
(acetic anhydride)



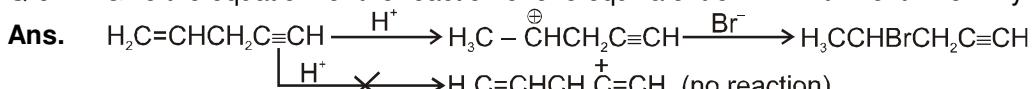
(acetic anhydride)

(acetic anhydride)

## Section (E) : Conjugate addition in Alkadienes



Q-9. Give the equation for the reaction of one equivalent of HBr with Pent -1-en-4-yne



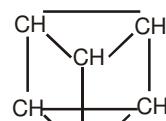
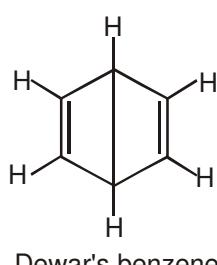
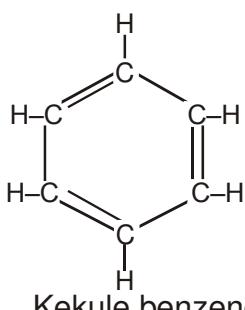
This reaction proceeds through a carbocation. Since the alkyl carbocation from the alkene group is more stable than the vinyl carbocation from the alkyne group.

## Section (F) Aromatic hydrocarbon (Benzene) :

### Introduction :

All organic compounds classify into two broad classes, aliphatic compounds and aromatic compounds. Aromatic compounds are those that resemble with benzene in chemical behaviour.

### Proposed structure of benzene :



[Prism like structure proposed by Albert Ladenberg]

\* Benzene mostly represents by Kekulé structure.



### Huckel's (4n + 2) rule for aromaticity :

An aromatic compound must have cyclic clouds of delocalised ( $4n+2$ )  $\pi$  electrons above and below the plane of the molecule.

### Comparison between Aromatic, Anti-aromatic and Non-aromatic compounds :

Characteristics	Aromatic	Anti-aromatic	Non-aromatic
1. Structure	Cyclic	Cyclic	Cyclic or acyclic
2. Shape	Planar	Planar	Planar or non planar
3. Conjugation	Close cyclic	Close cyclic	Any kind of conjugation
4. Hybridization	All atoms of the ring are $sp^2$ or $sp$	All atoms of the ring are $sp^2$	Any kind of hybridization
5. Number of delocalised electrons	$2, 6, 10, 14, \dots, (4n+2) e^-$	$4, 8, \dots, (4n) e^-$	Any number of electrons
6. Resonance energy	High	Zero	Normal

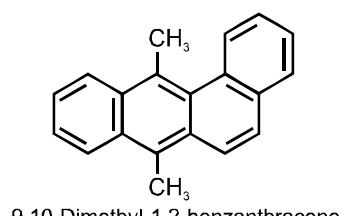
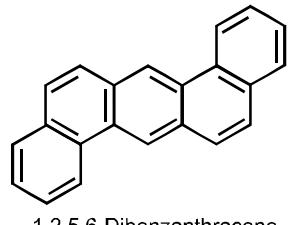
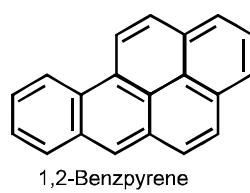
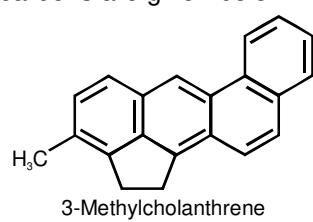
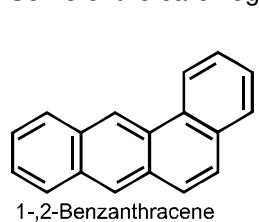
**Stability : aromatic > nonaromatic > antiaromatic**

### Some noteworthy points :

- (1) Some other aromatic species are Pyridine, Furan, Pyrrole, Thiophene, Ferrocene (sandwich compound) Dipotassium cyclooctatetraenide anion, Buckminster fullerene.
- (2) Antiaromatic compounds are paramagnetic in character.
- (3) [10] Annulene is not aromatic, although 1,6-Methano [10] annulene ( $C_{11}H_{12}$ ) is aromatic.
- (4) Aromatic compound has the ability to sustain an induced ring current.
- (5) Azulene is coloured and highly polar although its isomer naphthalene does not have significant zwitter ionic character.
- (6) Fullerene has been called the most symmetrical possible molecule, its buck side salt becomes a super conductor when cooled below 18 K.
- (7) In pyrrole the  $sp^2$  hybridized nitrogen must contribute two electrons to give an aromatic sextet.
- (8) Aromatic hydrocarbons contain higher percentage carbon content so burn with sooty flame.

### Carcinogenicity and Toxicity

Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property. Such polynuclear hydrocarbons are formed on incomplete combustion of organic materials like tobacco, coal and petroleum. They enter into human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below.

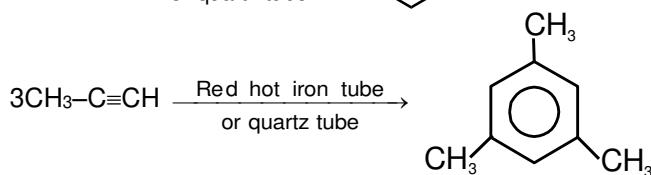
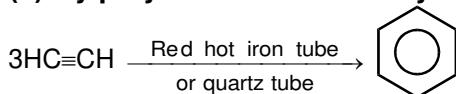




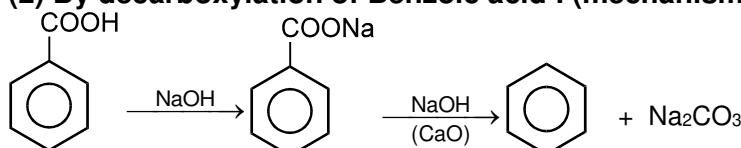
## Preparation and chemical properties of benzene

### (a) Preparation of Benzene

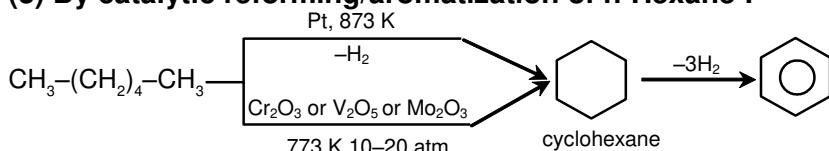
#### (1) By polymerisation of Acetylene :



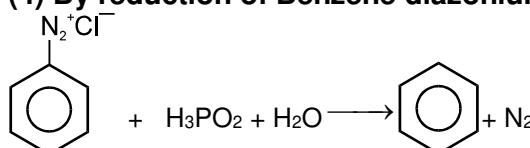
#### (2) By decarboxylation of Benzoic acid : (mechanism S<sub>E1</sub>)



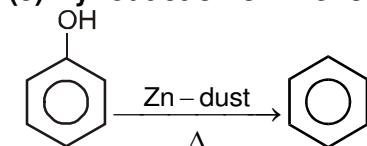
#### (3) By catalytic reforming/aromatization of n-Hexane :



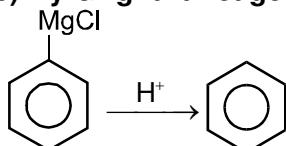
#### (4) By reduction of Benzene diazonium chloride :



#### (5) By reduction of Phenol :

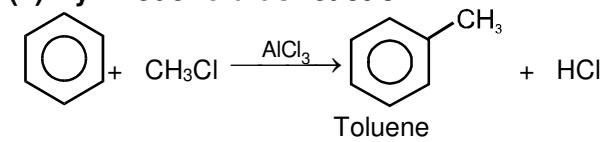


#### (6) By Grignard reagent :



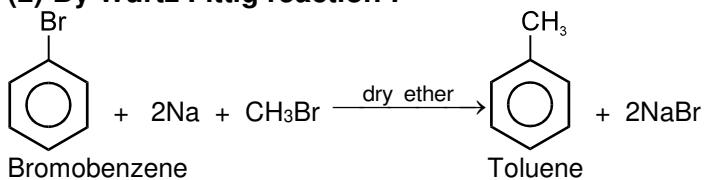
### (b) Preparation of Toluene :

#### (1) By Friedel-craft's reaction :

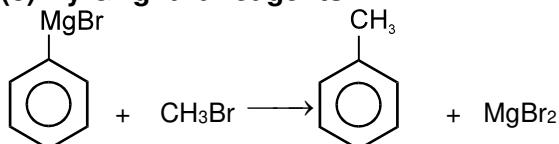


### Hydrocarbon

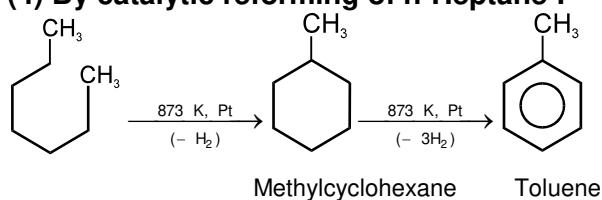
### **(2) By Wurtz Fittig reaction :**



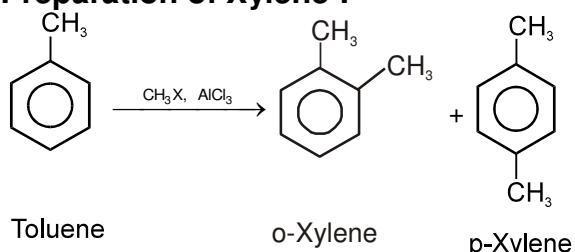
### **(3) By Grignard reagents :**



#### (4) By catalytic reforming of n-Heptane :



### (c) Preparation of Xylene :

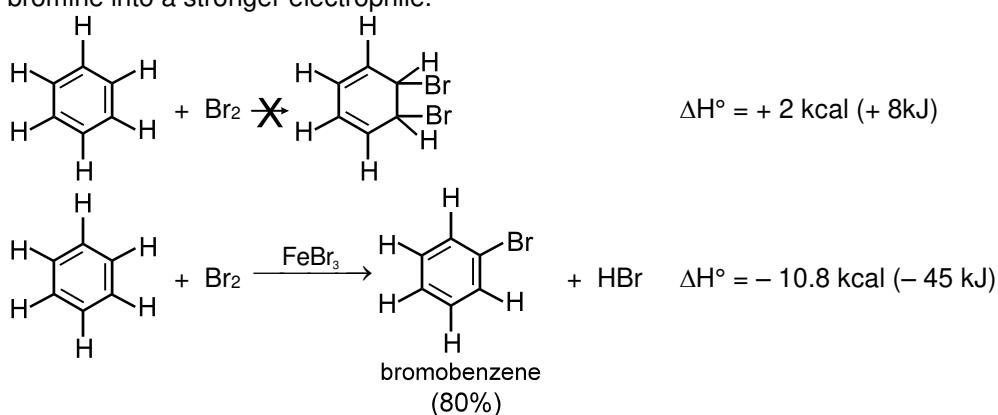


**(d) Comparison of Aromatic compounds with alkenes :**

Benzene is not as reactive as alkenes. Alkene gives addition reaction while benzene gives substitution reaction.



The analogous addition of bromine to benzene is endothermic because it requires the loss of aromatic stability. The addition is not seen under normal circumstances. The substitution of bromine in place of hydrogen atom gives an aromatic product. The substitution requires a Lewis acid catalyst to convert bromine into a stronger electrophile.

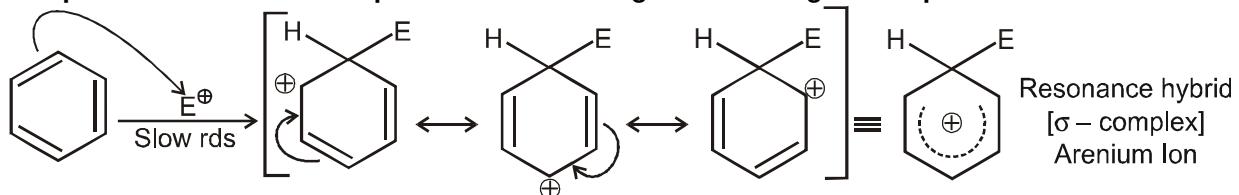




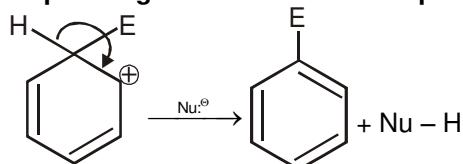
**(e) Aromatic electrophilic substitution ( $\text{ArS}_{\text{E}2}$ ) reactions of benzene**

It is a two step reaction. In 1st step sigma complex is formed in slow step. Formation of the sigma complex is rate determining and the transition state leading to it occupies the highest-energy point on the energy diagram.

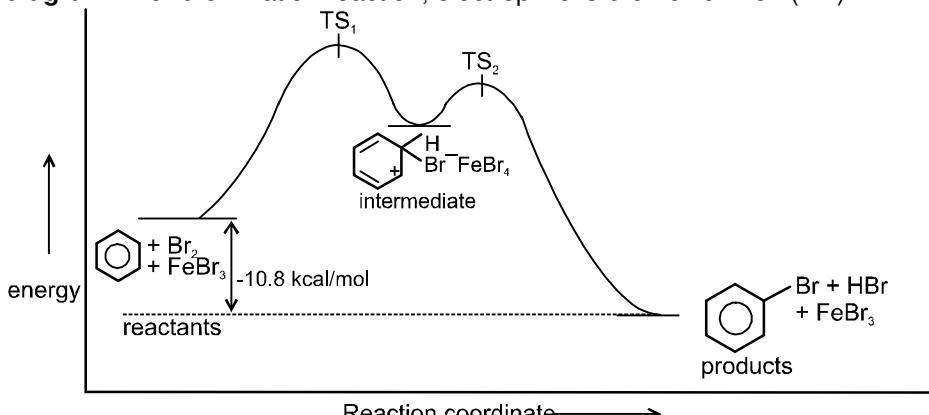
**Step-1 : Attack of an electrophile on benzene ring forms the sigma complex**



**Step-2 : Loss of a proton gives the substitution product.**



**Energy diagram :** For bromination reaction, electrophile is bromonium ion ( $\text{Br}^+$ )



Electrophilic aromatic substitution reaction to overcome the high activation energy that characterizes the first step, the electrophile must be a fairly reactive one. Many of the electrophilic reagents that react rapidly with alkenes do not react at all with benzene. For example peroxy acids and diborane, fall into this category, others such as bromine react with benzene only in presence of catalysts that increases their electrophilicity.

- Note :**
- (1) Aromatic rings have stable pi electrons still they are available to attack on a strong electrophile to give a carbocation.
  - (2) This resonance-stabilized carbocation is called a **sigma complex** because the electrophile is joined to the benzene ring by a new sigma bond.
  - (3) The sigma complex (also called an arenium ion) is not aromatic because the  $\text{sp}^3$  hybrid carbon atom interrupts the ring of p orbitals.
  - (4) This loss of aromaticity contributes to the highly endothermic nature of this first step. The sigma complex regains aromaticity either by a reversal of the first step (returning to the reactants) or by loss of the proton on the tetrahedral carbon atom, leading to the substitution product.
  - (5) The overall reaction is the substitution of an electrophile ( $\text{E}^+$ ) in place of a proton ( $\text{H}^+$ ) on the aromatic ring. (**i.e. electrophilic aromatic substitution**)
  - (6) Electrophilic substitution occurs preferentially in the 5-membered ring of azulene.



### **Effect of substituent groups in monosubstituted benzene :**

(1) **Ortho-para directing and activating groups** : All electron releasing groups (+m, +I) are ortho-para directing groups and activating towards electrophilic reactions.

(2) **Ortho para directing but deactivating groups** : Halogens are deactivating but ortho-para directing groups.

Reactivity of benzene decreases by -I effect of halogens and ortho-para directing nature decided by +m effect of halogens.

(3) **Meta directing and deactivating groups** : Mostly electron withdrawing groups (-m, -I) are meta directing groups and deactivating towards electrophilic reactions.

	Substituent groups	Reactivity (effect on rate)	Directing nature (effect on orientation)
1.	$-O^- > -NH_2 > -NHR > -NR_2 > -OH$	Very strongly activating	Ortho-para directing
2.	$-OR > -NH-C(=O)-R > -O-C(=O)-R$	Strongly activating	Ortho-para directing
3.	$-R, -Ar, -CH=CH_2$	Activating	Ortho-para directing
4.	$-X(F, Cl, Br, I), -N=O, -CH_2X, -CHX_2$	Deactivating	Ortho-para directing
5.	$-CHO, -C(=O)R, -COOH, -COOR, -COCl, -C\equiv N, -SO_3H$	Strongly deactivating	Meta directing
6.	$-NO_2, -NR_3^+, -SR_2^+, -CF_3$	Very strongly deactivating	Meta directing

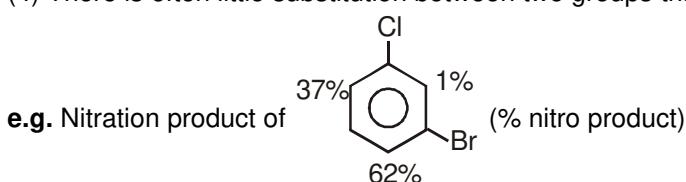
### **Effect of substituent groups in disubstituted benzene :**

(1) If activating and deactivating both groups are present in a system then position of electrophile will be determined by activating group.

(2) If both groups present in a system are deactivator then position of electrophile will be determined by stronger deactivator.

(3) If both the groups are activating group then position of electrophile will be determined by stronger activator.

(4) There is often little substitution between two groups that are meta to each other.



#### **(i) Halogenation**

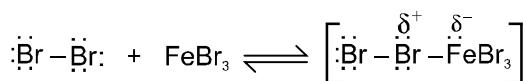
(1) Bromine or chlorine itself is not sufficiently electrophilic to react with benzene so a strong Lewis acid such as  $FeBr_3$  or  $AlCl_3$  catalyzes the reaction.

(2) Iodination takes place in presence of oxidising agents like  $HNO_3$  or  $HIO_3$ . Kinetic isotope effect is also observed in iodination reaction of benzene.

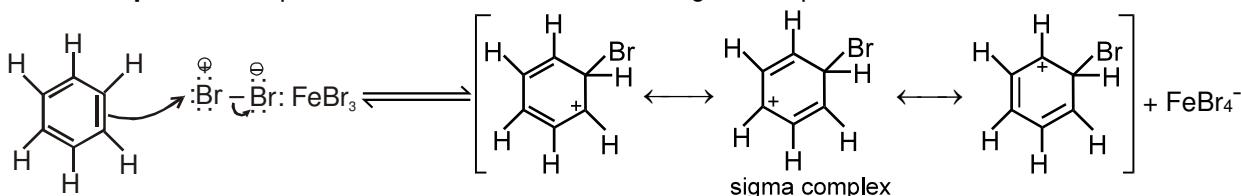
(3) Order of effectiveness :  $Cl_2 > BrCl > Br_2 > ICl > I_2$

(4) Other halogenating agents are  $ICl$ ,  $HOCl$  etc.

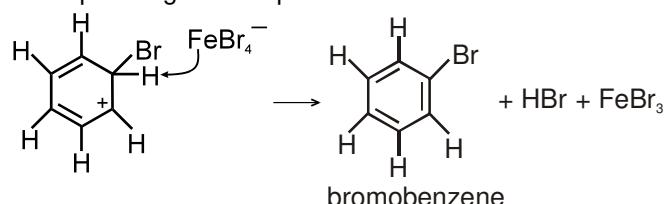
**Step-1 :** Formation of a stronger electrophile.



**Step-2 :** Electrophilic attack and formation of the sigma complex.



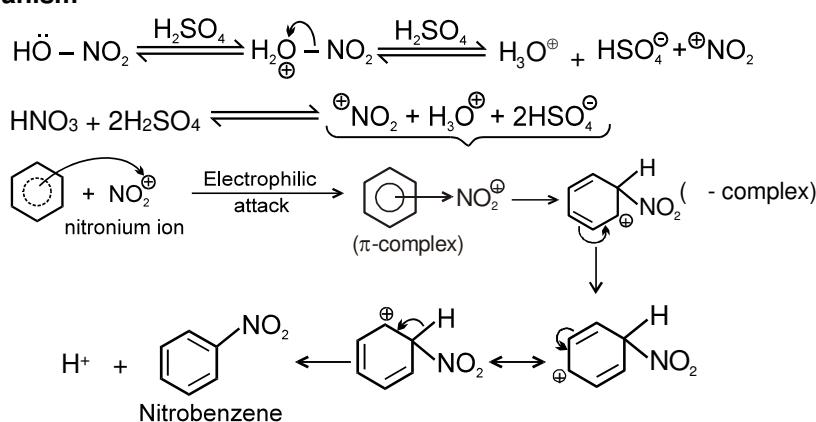
**Step-3 :** Loss of a proton gives the products.



## (ii) Nitration

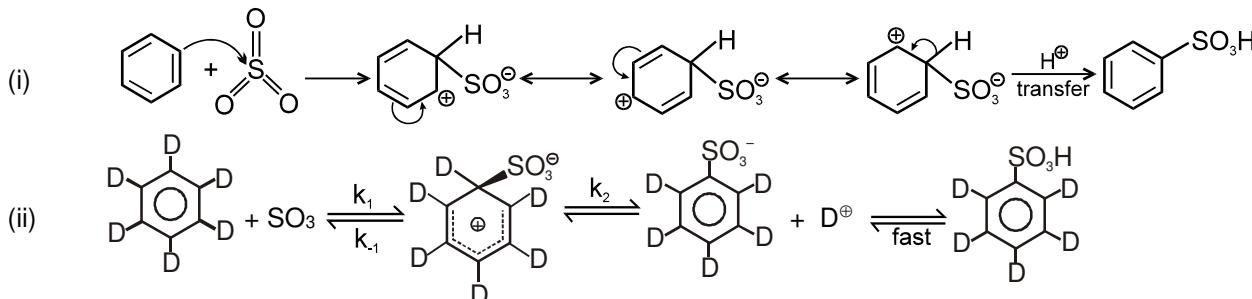
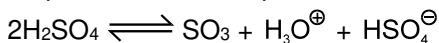
- $\text{HNO}_3$  alone is a weak nitrating agent whereas the mixture of concentrated  $\text{HNO}_3$  and concentrated  $\text{H}_2\text{SO}_4$  is strong nitrating mixture. In this mixture  $\text{HNO}_3$  acts as base.

• Mechanism



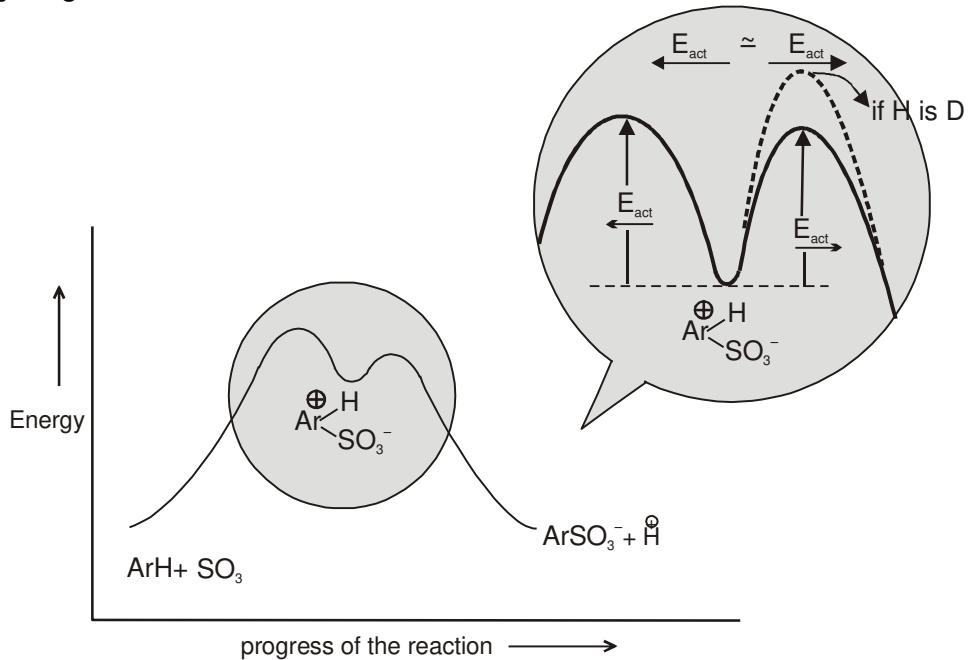
## (iii) Sulphonation

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



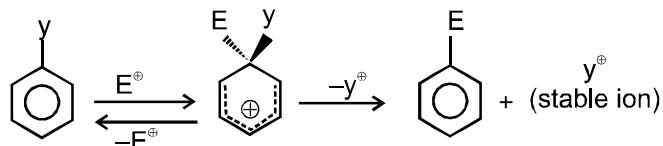
Sulphonation is **reversible** and takes place in concentrated sulphuric acid. ( $K_{-1}K_2$ )

## Energy Diagram



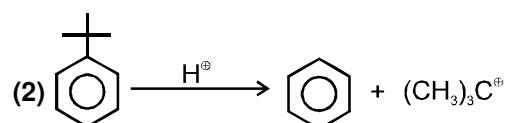
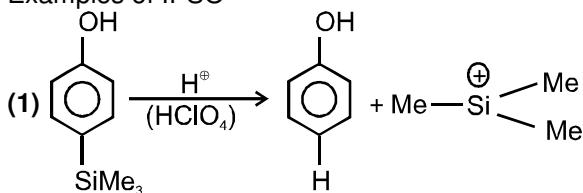
Some  $\text{Ar}-\overset{\oplus}{\text{H}}-\text{SO}_3^-$  or  $\text{Ar}-\overset{\oplus}{\text{D}}-\text{SO}_3^-$  go on to product, some revert to the starting material and decrease the rate of reaction. This effect is known as isotope effect.

## (iv) IPSO Substitution

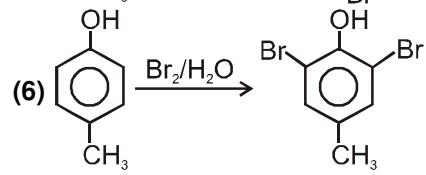
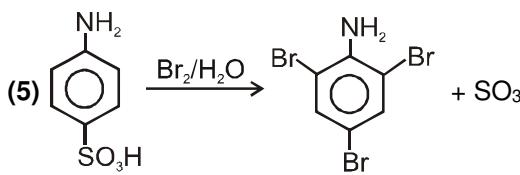
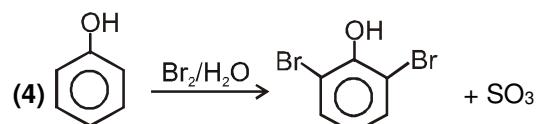
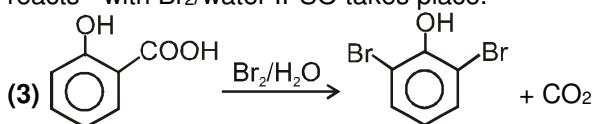


attack at the position bearing the substituent is called IPSO position.

Examples of IPSO



Note : If ortho position or para position of phenol or aniline has presence of  $-\text{COOH}$  or  $-\text{SO}_3\text{H}$  group. When it reacts with Br<sub>2</sub>/water IPSO takes place.

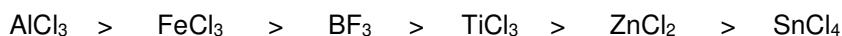




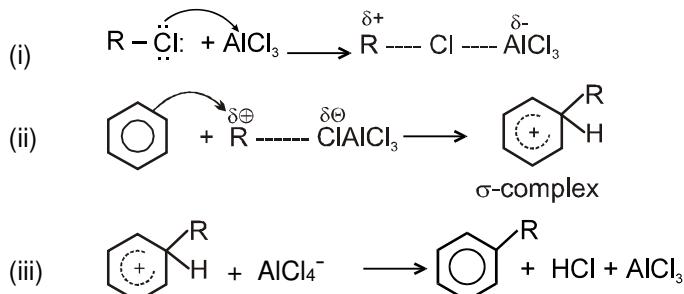
## (v) Friedel Craft reaction

### (a) Alkylation :

- (1) Electrophile is carbocation.
- (2) Alkylating agents are :  $\text{RX} + \text{AlX}_3$  (lewis acid), Alkene in acidic medium and alcohol in acidic medium.
- (3) The order of effectiveness of Lewis acid catalyst has been shown to be



Mechanism :



- Rate law  $\rightarrow$  rate =  $k \cdot [\text{Ar} - \text{H}] \cdot [\text{R} - \text{X}] \cdot [\text{MX}_3]$
- $\text{Me}_3\text{CCH}_2\text{Cl}/\text{FeCl}_3$  on benzene gives wholly the unarranged product  $\text{PhCH}_2\text{CMe}_3$
- On heating p-xylene or o-xylene with  $\text{AlCl}_3/\text{HCl}$  results in the conversion of the majority of it into the more stable meta-xylene.

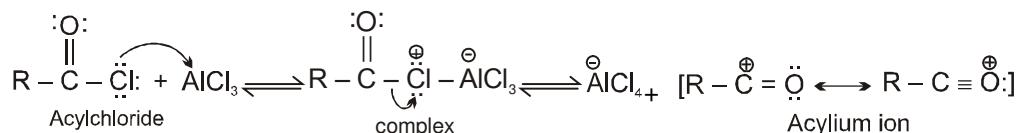
### (b) Acylation :

- (1) Electrophile is acylium ion.

(2) Acylation of benzene may be brought about with acid, acid chlorides or anhydrides in presence of Lewis acids.

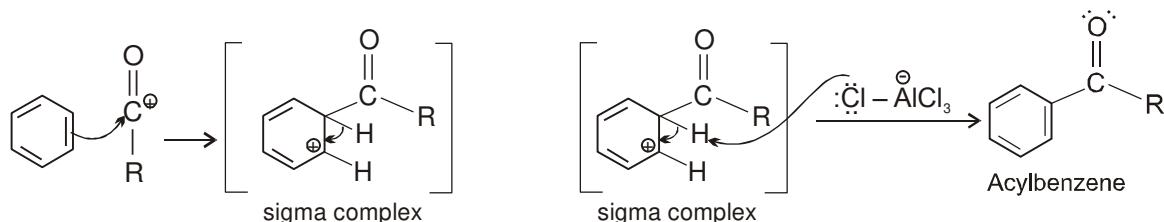
Mechanism :

**Step-1 :** Formation of an acylium ion.

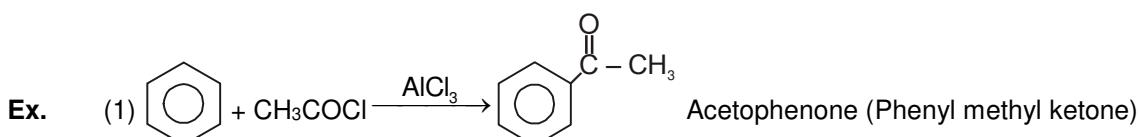


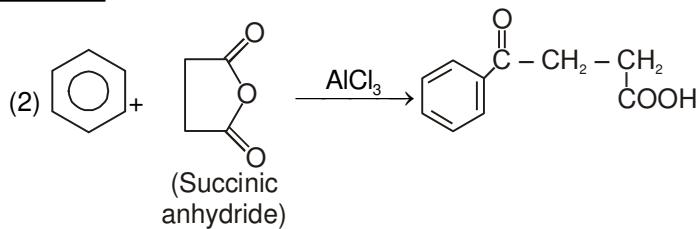
**Step-2 :** Electrophilic attack.

**Step-3 :** Loss of a proton.



- Friedel-Crafts acylations are generally free from rearrangements and multiple substitution. (but decarbonylation can take place)





One significant difference of acylation from alkylation is that in former rather more than one mole of lewis acid is required.

#### (vi) Limitations of Friedel Craft reaction :

**(1) Re-arrangement :** In Friedel craft alkylation carbonium ion can rearrange but in Friedel craft acylation acylium ion can not rearrange.

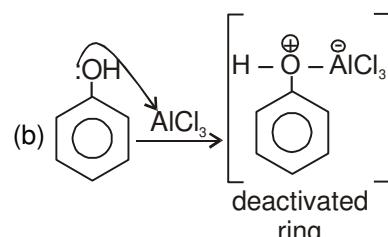
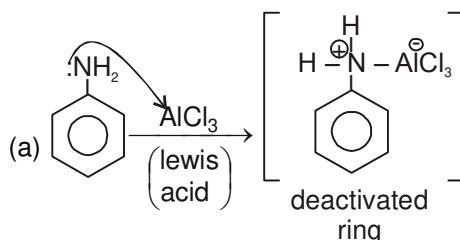
**(2) Polyalkylation** takes place because alkylated benzene is more activated than benzene but **polyacetylation** does not take place because acyl benzene is more deactivated.

**(3) Friedel craft reaction is not possible in presence of following functional groups:-**

(a) If  $-m$  groups are attached to benzene ring.

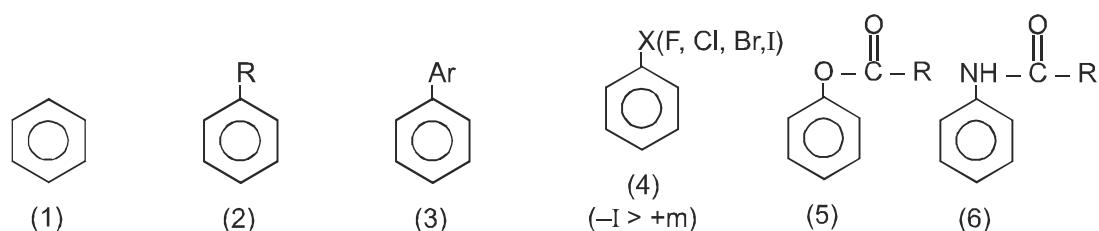
(b) If strong  $+m$  groups are attached to benzene ring.

Ex.



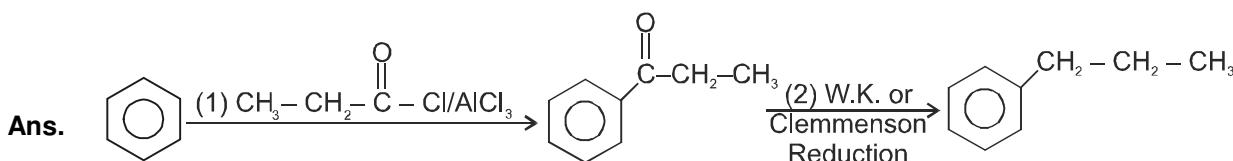
In presence of OH/NH<sub>2</sub> groups Friedel craft reaction is not possible because these groups make coordinate bond with Lewis acid ( $\text{AlX}_3$ ) and the aromatic ring becomes deactivated.

**(4) Friedel craft reaction is Possible in following compounds :**



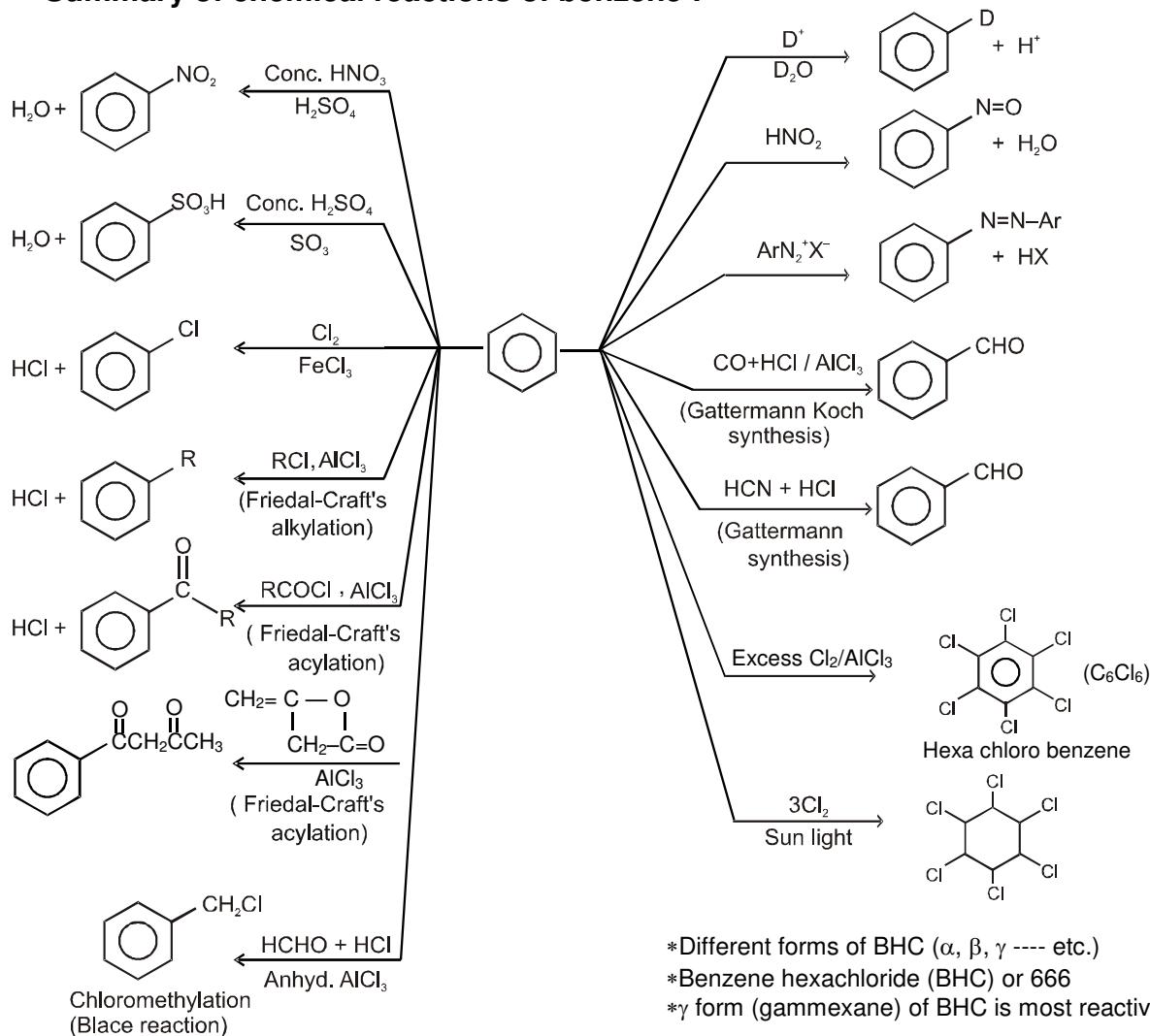
- In acylation rearrangement of R does not takes place, but decarbonylation can take place so the end result is then alkylation.

**Q-10.** How will you get propylbenzene from benzene ?

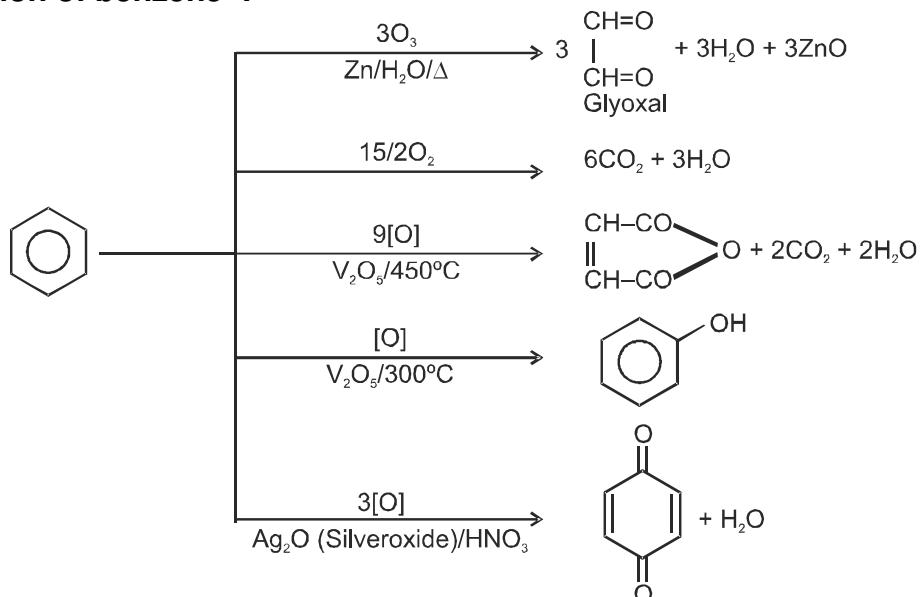




### Summary of chemical reactions of benzene :



### Oxidation of benzene :





## Exercise-1

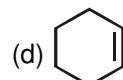
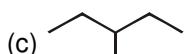
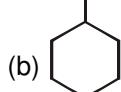
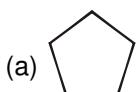
Marked questions are recommended for Revision.

### PART - I : SUBJECTIVE QUESTIONS

#### Section (A) : Alkane

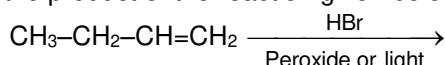
A-1. How do you account for formation of ethane during chlorination of methane ?

A-2. Give the major product of monobromination of following compounds.



#### Section (B) : Free radical addition and substitution in alkenes / alkynes

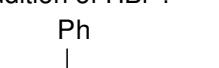
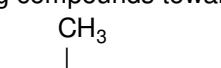
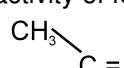
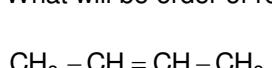
B-1. Predict the product of the reaction given below :



B-2.  $\text{CH}_2=\text{CH--CH}_2\text{--CH}_3 \xrightarrow{\text{NBS}} \text{B} + \text{C}$   
write structure of B and C.

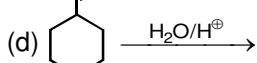
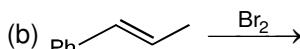
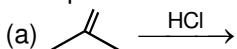
#### Section (C) : Alkene

C-1. What will be order of reactivity of following compounds towards addition of HBr ?



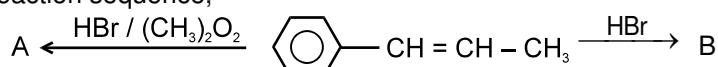
C-2. The acid catalysed hydration follows following order  $(\text{CH}_3)_2\text{C=CH}_2 > \text{CH}_3\text{CH=CH}_2 > \text{CH}_2=\text{CH}_2$   
Explain this order of reactivity.

C-3. Give product of the following reactions.



C-4. What will happen when Br<sub>2</sub>/CCl<sub>4</sub> react with (a) cis But-2-ene (b) trans But-2-ene.

C-5. In the reaction sequence,



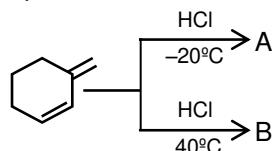
What is the relationship between A & B :

#### Section (D) : Alkyne

D-1. Write all the products when all the isomers of alkynes with molecular formula C<sub>5</sub>H<sub>8</sub> react with excess of Br<sub>2</sub>/CCl<sub>4</sub>.

#### Section (E) : Conjugate addition in Alkadienes

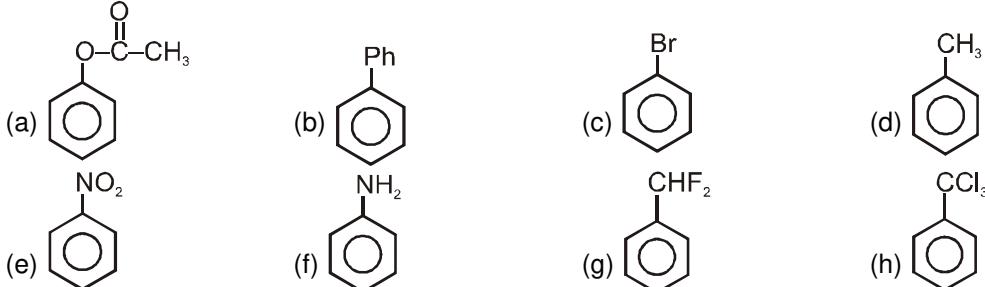
E-1. Write the products in the following reactions;



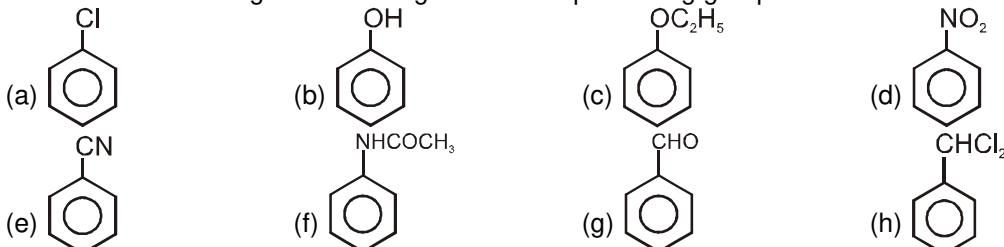
**Section (F) Aromatic hydrocarbon (Benzene)**

F-1. Normally, benzene gives electrophilic substitution reaction rather than electrophilic addition reaction although it has double bonds. Explain why? [JEE 2000]

F-2. Which of the following Benzene rings contain deactivating groups?



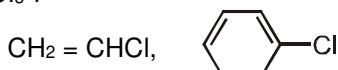
F-3. Which of the following Benzene rings contain o-p directing groups?



F-4. Arrange the following in decreasing order of their reactivity with an electrophile.

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

F-5. Why following organic chlorides will not give a Friedel-Crafts alkylation product when heated with benzene and AlCl<sub>3</sub>?

**PART - II : ONLY ONE OPTION CORRECT TYPE****Section (A) : Alkane**

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<sub>2</sub>?

- |  |   |
|--|---|
| (A) $\text{Cl}_2 \longrightarrow \text{Cl}^\bullet$                                    | (B) $\text{CH}_4 + \text{Cl}^\bullet \longrightarrow \text{CH}_3\text{Cl} + \text{H}^\bullet$ |
| (C) $\text{Cl}^\bullet + \text{CH}_4 \longrightarrow \text{CH}_3^\bullet + \text{HCl}$ | (D) $\text{Cl}^\bullet + \text{CH}_3^\bullet \longrightarrow \text{CH}_3\text{Cl}$            |



**A-3.** A gaseous hydrocarbon 'X' on reaction with bromine in light forms a mixture of two monobromo alkanes and HBr. The hydrocarbon 'X' is :

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

**A-4.** The maximum ease of abstraction of a hydrogen atom by a chlorine atom is shown by :  
 (A)  $(\text{CH}_3)_3\text{C}-\text{CH}_3$       (B)  $(\text{CH}_3)_2\text{CH}_2$       (C)  $\text{C}_6\text{H}_5\text{CH}_3$       (D)  $\text{CH}_2=\text{CHCH}_3$

**A-5.** 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-6.** In which of the following pairs the bromination of first member is easier than the second member ?  
 (A) Isobutane, n-Butane      (B) n-Butane, Isobutane  
 (C) Methane, Ethane      (D) None of these

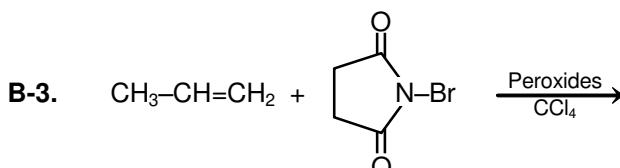
### Section (B) : Free radical addition and substitution in alkenes / alkynes

**B-1.** Anti Markownikoff addition of HBr is not observed in :

- (A) Propene      (B) 1-Butene      (C) But-2-ene      (D) Isobutene

**B-2.**  $\text{CH}_3-\underset{\substack{| \\ \text{CH}_3}}{\text{C}}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{R}_2\text{O}_2}$  Product is :

- (A)  $\text{CH}_3-\underset{\substack{| \\ \text{CH}_3}}{\text{CH}}-\underset{\substack{| \\ \text{Br}}}{\text{CH}_2}$       (B)  $\text{CH}_3-\underset{\substack{| \\ \text{CH}_3}}{\text{C}}-\underset{\substack{| \\ \text{Br}}}{\text{CH}_3}$       (C)  $\text{CH}_3-\underset{\substack{| \\ \text{CH}_3}}{\text{C}}-\underset{\substack{| \\ \text{Br}}}{\text{CH}_2}-\underset{\substack{| \\ \text{Br}}}{\text{CH}_3}$       (D)  $\text{CH}_2-\underset{\substack{| \\ \text{CH}_3}}{\text{C}}=\text{CH}_2-\underset{\substack{| \\ \text{Br}}}{\text{CH}_3}$



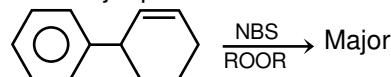
This reaction is classified as

- (A) Electrophilic substitution reaction      (B) Free radical substitution reaction  
 (C) Nucleophilic substitution reaction      (D) Electrophilic addition reaction

**B-4.**  $\xrightarrow{\text{NBS}}$  Product is :

- (A)      (B)      (C)      (D)

**B-5.** Find major product?

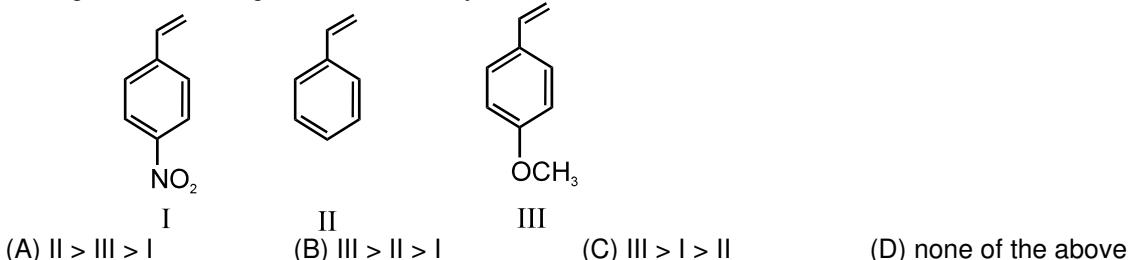


- (A)      (B)      (C)      (D)

**Section (C) : Alkene**

- C-1. What is correct order of acid catalysed hydration of following alkenes ?
- (I)  $\text{CH}_2=\text{CH}_2$       (II)  $\text{CH}_3-\text{CH}=\text{CH}_2$       (III)  $(\text{CH}_3)_2\text{C}=\text{CH}_2$       (IV)  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$   
 (A) III > I > II > IV      (B) III > IV > II > I      (C) II > IV > III > I      (D) I > II > III > IV

- C-2. Arrange in decreasing order of reactivity with HCl :



- C-3.  $\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{C} = \text{CH}_2 + \text{ICl} \longrightarrow \text{P} \text{ (major product)} \end{array}$  Here 'P' is :



- C-4.  $\text{CCl}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{HOCl}} \text{P}$  (Major product),  
 $\text{CCl}_3-\text{CH}=\text{CH}_2 \xrightarrow{\text{HOCl}}$  'P' is :  
 (A)  $\text{CCl}_3\text{CH}(\text{OH})\text{CH}_2\text{Cl}$       (B)  $\text{CCl}_3\text{CH}(\text{Cl})\text{CH}_2\text{OH}$       (C)  $\text{CCl}_3\text{CH}(\text{Cl})\text{CH}_2$       (D)  $\text{CCl}_3\text{CH}(\text{OHOH})\text{CH}_2$

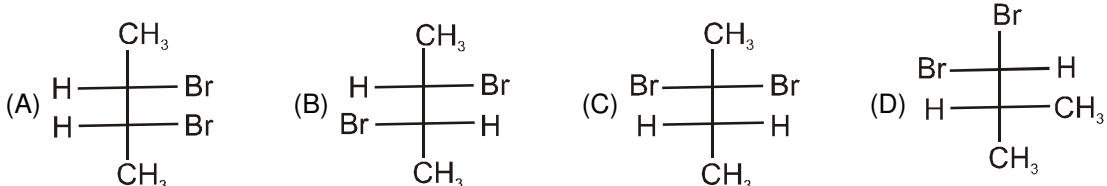
- C-5. In which reaction the product following anti markonikoff rule is observed :



- C-6. Which will form 2, 2-Dibromopropane with HBr ?  
 (A)  $\text{CH}_2=\text{CH}-\text{CH}_3$       (B)  $\text{CH}_3-\text{C}\equiv\text{CH}$       (C)  $\text{CH}_3-\text{C}(\text{Br})=\text{CH}_2$       (D) Both B & C

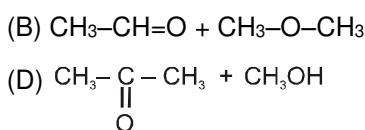
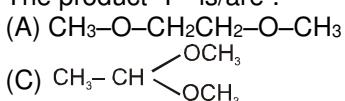
- C-7.  $\text{Ph}-\text{CH}_2-\text{CH}=\text{CH}_2 \xrightarrow{\text{dil. H}_2\text{SO}_4}$  X, 'X' is :  
 (A)  $\text{Ph}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$       (B)  $\text{Ph}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_3$   
 (C)  $\text{Ph}-\text{CH}(\text{OH})-\text{CH}_2-\text{CH}_3$       (D)  $\text{Ph}-\text{CH}_2-\text{OH}$

- C-8.  $\begin{array}{c} \text{H}_3\text{C} \\ | \\ \text{C} = \text{C} \diagup \text{CH}_3 \\ | \quad \diagdown \\ \text{H} \quad \text{H} \end{array} + \text{Br}_2 \xrightarrow{\text{CCl}_4}$  Product is:





The product "P" is/are :

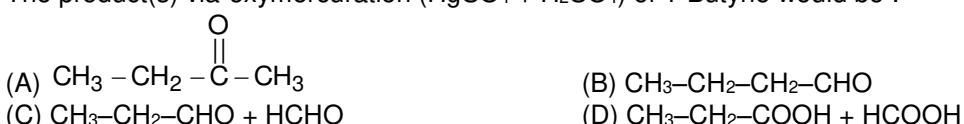


### Section (D) : Alkyne

D-1. What is the product when one mole of Pent-1-yne treated with two moles of HCl ?

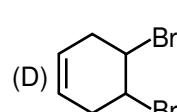
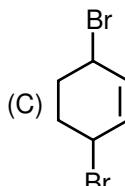
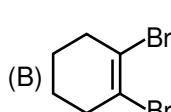
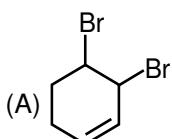
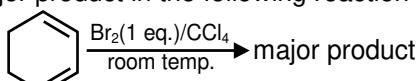
- (A) 1,2-Dichloropentane      (B) 2,3-Dichloropentane  
 (C) 1,1-Dichloropentane      (D) 2,2-Dichloropentane

D-2. The product(s) via-oxymercuration ( $\text{HgSO}_4 + \text{H}_2\text{SO}_4$ ) of 1-Butyne would be :



### Section (E) : Conjugate addition in Alkadienes

E-1. The major product in the following reaction is

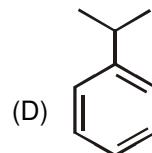
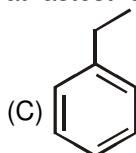
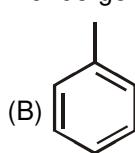
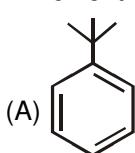


### Section (F) Aromatic hydrocarbon (Benzene)

F-1. The reagent used for Friedel-Craft's reaction is :

- (A) Dry ether      (B)  $\text{AlCl}_3$       (C) Anhydrous  $\text{AlCl}_3$       (D)  $\text{P}_2\text{O}_5$

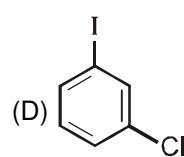
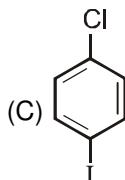
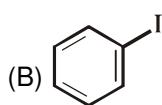
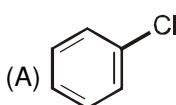
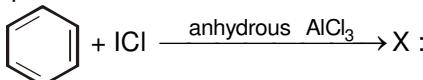
F-2. Which of the following will undergo sulphonation at fastest rate ?



F-3. Which among the following is deactivating group ?

- (A)  $-\text{Cl}$       (B)  $-\text{OR}$       (C)  $-\text{NH}_2$       (D)  $-\text{NHR}$

F-4. The compound X in the reaction is :

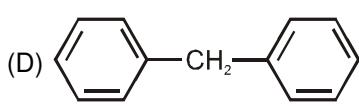
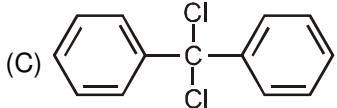
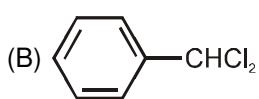
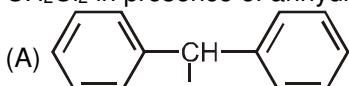


F-5. Toluene is o/p orienting with respect to an electrophilic substitution reaction due to

- (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.



**F-6.** Which of the following structures correspond to the product expected, when excess of  $C_6H_6$  reacts with  $CH_2Cl_2$  in presence of anhydrous  $AlCl_3$ :



**F-7.** 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.

**F-8.** Chlorobenzene is o,p-directing in electrophilic substitution reaction. The directing influence is explained by:

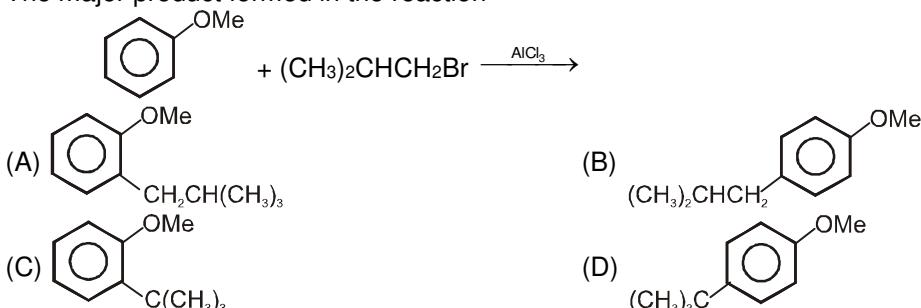
(A) +m of Ph

(B) +I of Cl

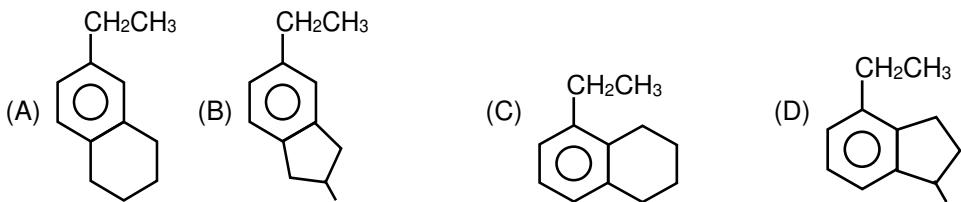
(C) +m of Cl

(D) +I of Ph

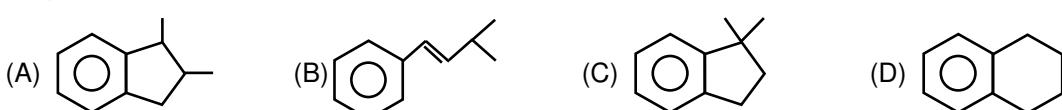
**F-9.** The major product formed in the reaction



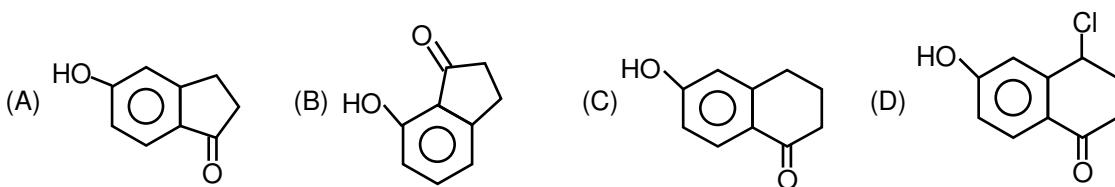
**F-10.**



**F-11.**



**F-12.**



**PART - III : MATCH THE COLUMN**

1. Match List I (Reaction) with List II (Type of reaction) and select the correct answer using the code given below the lists :

	<b>List I</b>		<b>List II</b>
(P)	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CH}_3 + \text{Br}_2 \xrightarrow{\text{h}\nu}$	(1)	Electrophilic addition
(Q)	$\text{CH}_3\text{--CH=CH--CH}_3 + \text{Br}_2 \xrightarrow{\text{CCl}_4}$	(2)	Nucleophilic addition
(R)	 + $\text{Br}_2 \xrightarrow{\text{Fe}}$	(3)	Free radical substitution
(S)	$\text{CH}_3\text{--CH}_2\text{--CH}_2\text{--CHO} + \text{LiAlH}_4 \xrightarrow{\text{H}_2\text{O}}$	(4)	Electrophilic substitution

Codes:

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

2. Match the column-I with column-II :

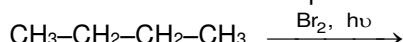
	<b>Column-I</b>		<b>Column-II</b>
	<b>Group</b>		<b>Nature</b>
(A)	$-\text{Cl}$	(p)	Activating
(B)	$-\text{CH}_3$	(q)	deactivating
(C)	$-\text{OH}$	(r)	<i>o,p</i> -directing
(D)	$-\text{NO}_2$	(s)	<i>m</i> -directing

**Exercise-2**

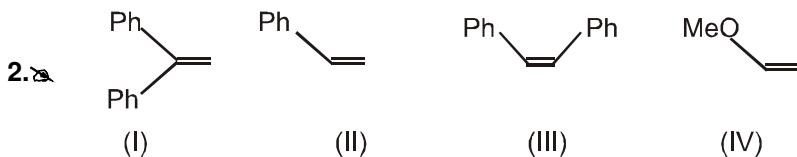
Marked questions are recommended for Revision.

**PART - I : ONLY ONE OPTION CORRECT TYPE**

1. Which statement is correct about photochemical bromination of Butane ?



- (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) Major product is formed by more stable carbocation.

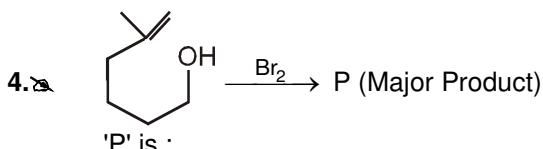


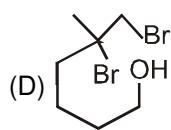
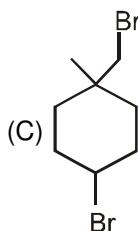
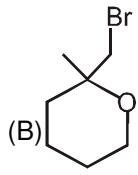
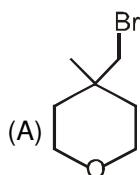
Order of rate of electrophilic addition reaction with HBr will be :

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

3. The correct order of reactivity of alkene towards an electrophile is mentioned in :

- (A)  $\text{CH}_2=\text{CH}-\text{Cl} > \text{CH}_2=\text{CH}-\text{OCH}_3$       (B)  $\text{CH}_2=\text{CHCl} < \text{CH}_2=\text{CCl}_2$   
 (C)  $\text{CH}_2=\text{CH}_2 > \text{CH}_3\text{--CH=CH}_2$       (D)  $\text{CH}_2=\text{CH}-\text{OCH}_3 > \text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$





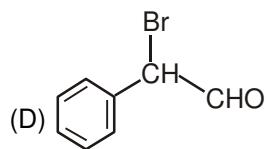
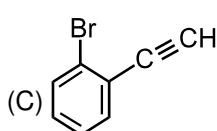
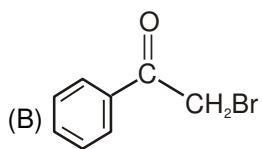
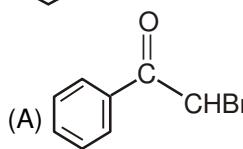
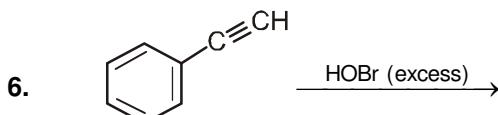
5. Alkenes are less reactive than alkynes towards addition of  $\text{Br}_2$  because :

(A)  $\begin{array}{c} \text{CH} = \text{CH} \\ | \\ \text{Br}^+ \end{array}$  is less stable than  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{Br}^+ \end{array}$

(B)  $\begin{array}{c} \text{CH} = \text{CH} \\ | \\ \text{Br}^+ \end{array}$  is more stable than  $\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ | \\ \text{Br}^+ \end{array}$

(C) Both are equally stable

(D) Original statement is incorrect





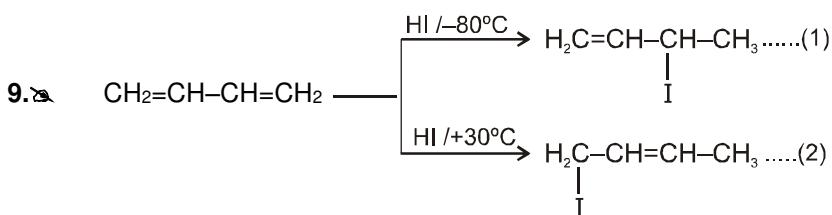
- 8.** The reaction of one equivalent of HBr with  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$  gives :

(A)  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CBr}$

(B)  $\text{CH}_2=\text{CH}-\text{C}(\text{Br})=\text{CH}_2$

(C)  $\text{CH}_3-\underset{\text{Br}}{\text{CH}}-\text{C}\equiv\text{CH}$

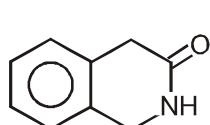
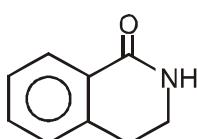
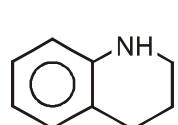
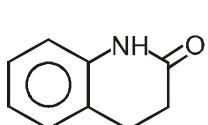
(D)  $\text{CH}_2=\text{CH}-\text{CH}=\text{CHBr}$



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

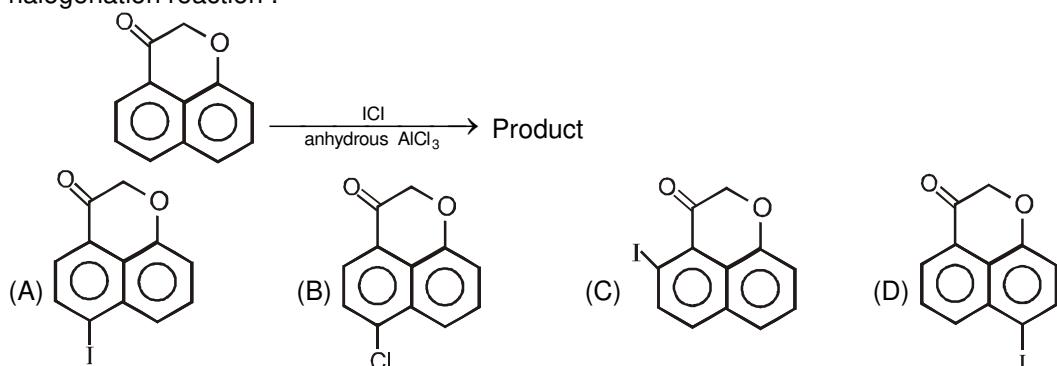
	(1)	(2)
(A)	Kinetic	Thermodynamic
(B)	Thermodynamic	Kinetic
(C)	Kinetic	Kinetic
(D)	Thermodynamic	Thermodynamic

- 10.** Order of rate of electrophilic substitution reaction is :

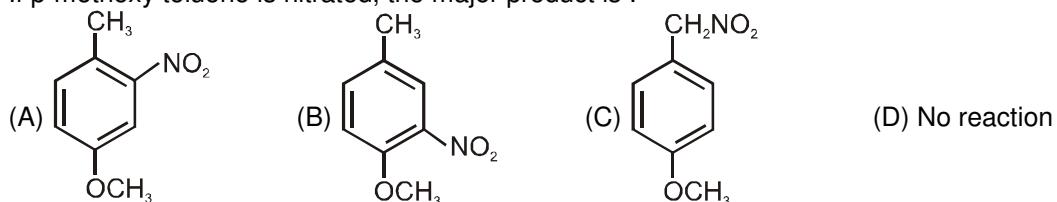


- (A) Q > P > S > B      (B) Q > P > B > S      (C) P > Q > S > B      (D) P > Q > B > S

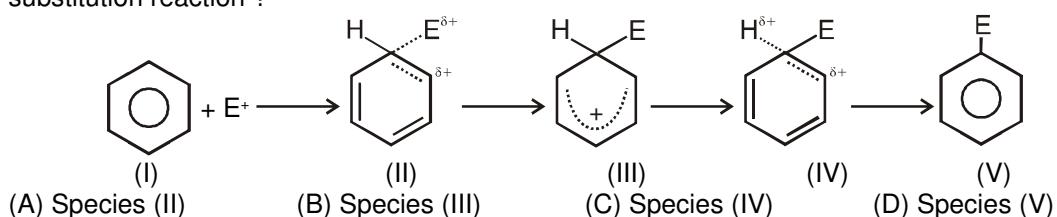
11. Benzene ring can be halogenated by using interhalogens. Identify the product of the following halogenation reaction :



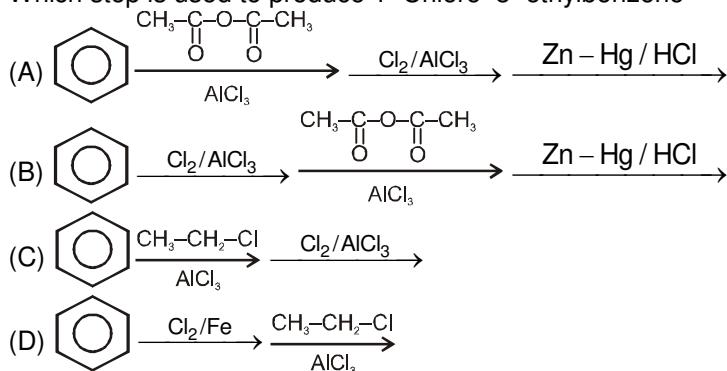
12. If p-methoxy toluene is nitrated, the major product is :



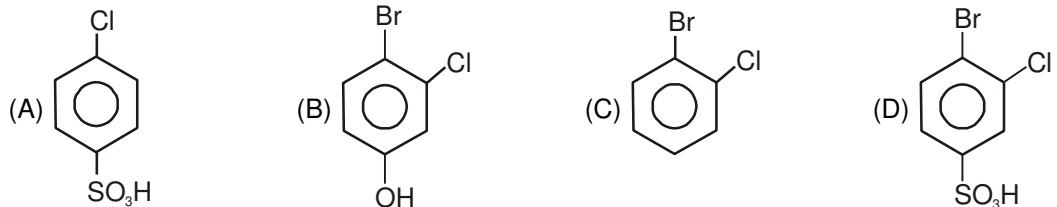
13. Which of the following species is expected to have maximum enthalpy in an electrophilic aromatic substitution reaction ?



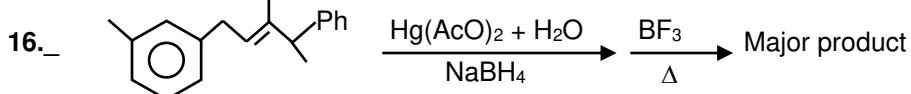
14. Which step is used to produce 1-Chloro-3-ethylbenzene



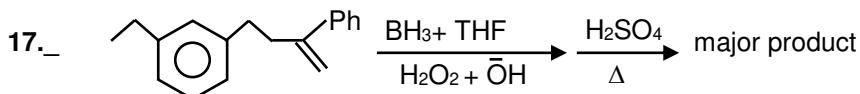
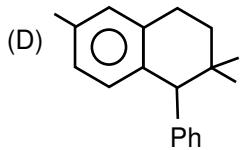
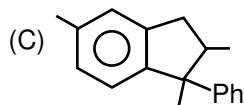
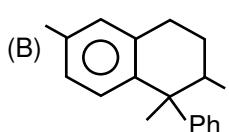
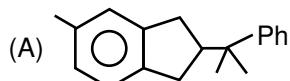
15.  $\xrightarrow[\text{(ii) H}_2\text{O, } \Delta, \text{ H}^+]{\text{(i) Cl}_2 / \text{Fe}}$  Identify the product.



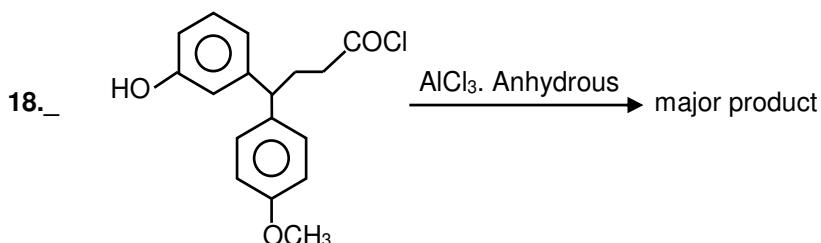
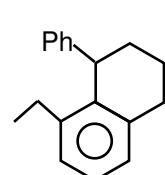
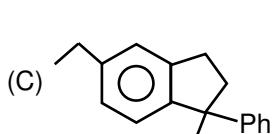
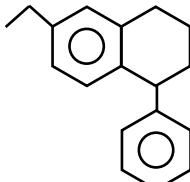
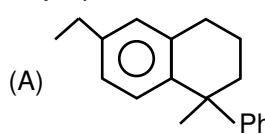
Hydrocarbon



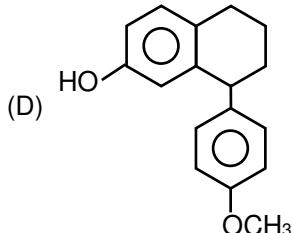
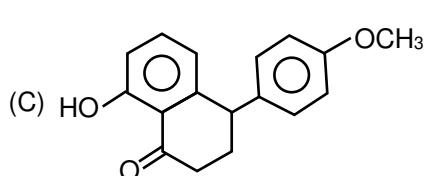
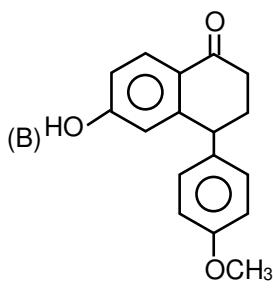
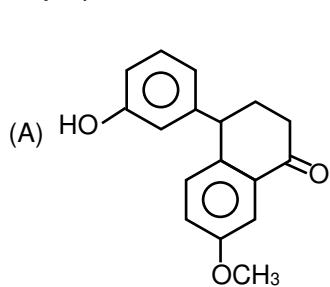
Major product will be -



Major product will be -



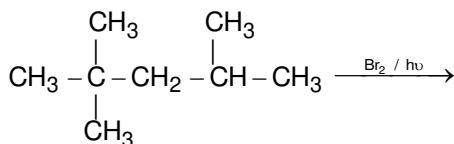
Major product will be -



## PART - II : NUMERICAL VALUE QUESTIONS

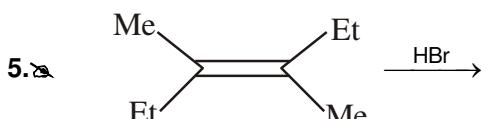
1. The number of possible enantiomer pairs that can be produced during monochlorination of 2-Methylbutane is :

2. For the given reaction how many products are optically active (all isomers) :



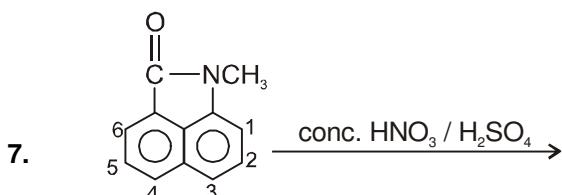
3. Number of structural isomers which can be obtained on monochlorination of 2-Methylbutane is :

4. Find the total number of products formed by dichlorination of butane.

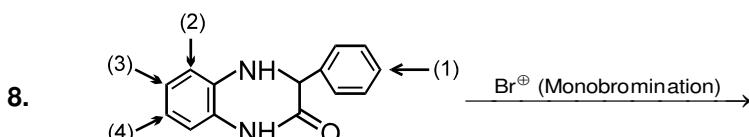


How many product will be formed in above reaction.

6. When trans-2-butene reacts with  $\text{Br}_2/\text{CCl}_4$ , X number of products are formed. Whereas when trans-2-butene reacts with HBr Y number of products are formed. Report your answer as  $\boxed{Y} \boxed{X}$ .



At which position nitration mainly takes place ?

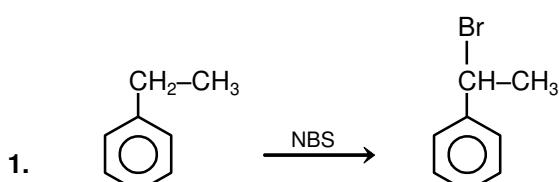


The substitution will mainly take place at position :

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

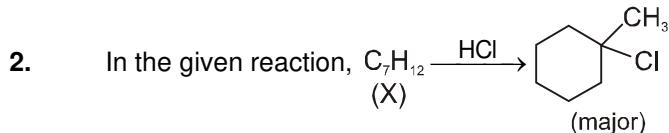
10. Find total number of products when all alkene isomers with molecular formula  $\text{C}_4\text{H}_8$  react with excess of  $\text{Br}_2/\text{CCl}_4$ .

### PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

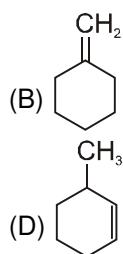
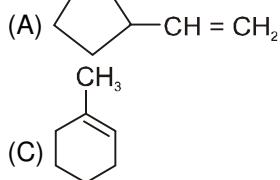


Which of the following statements are correct for above reaction.

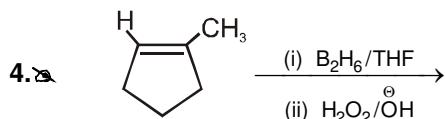
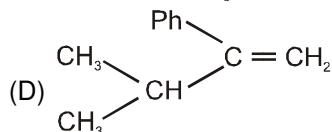
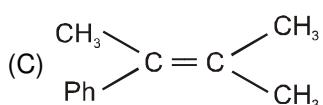
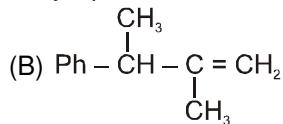
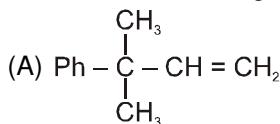
- (A) Reaction intermediate is carbocation.
- (B) Product is mixture of two enantiomers.
- (C) Reaction intermediate is stabilized by +I, hyperconjugation & resonance.
- (D)  $\text{Br}_2$  at high temperature also give same product in the place of NBS.



Structure of X can be :



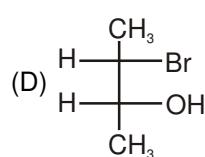
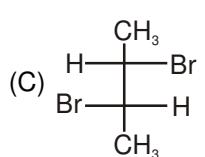
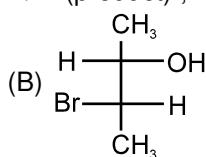
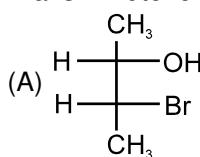
3. Which of the following compounds will give same major product on acid catalysed hydration ?



True statement about above reaction :

- (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.

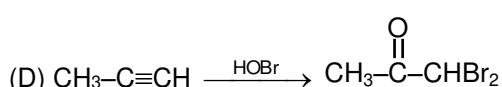
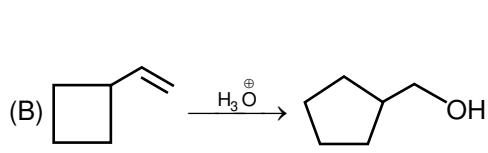
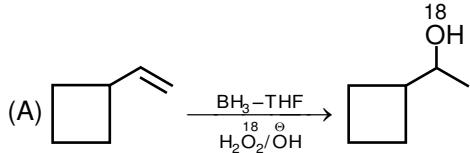
5. Trans-2-Butene  $\xrightarrow{HOBr}$  P (product) ; 'P' is :

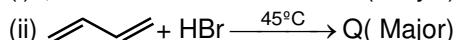


6. Identify the incorrect statement(s):

- (A) Alkynes are more reactive than alkenes towards electrophilic addition reaction
- (B) Alkynes are less reactive than alkenes towards electrophilic addition reaction
- (C) Alkynes decolourise  $Br_2$  water
- (D) Addition of HBr to alkynes in presence of peroxide proceeds via Markownikoff's addition

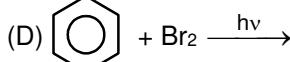
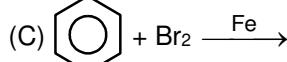
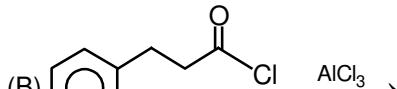
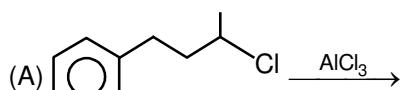
7. Choose the correct options for major product.



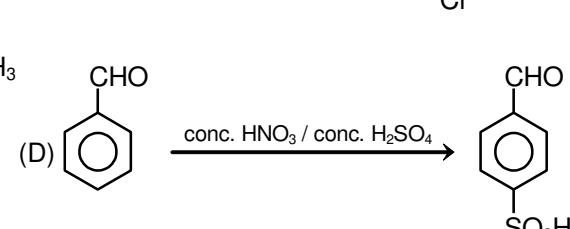
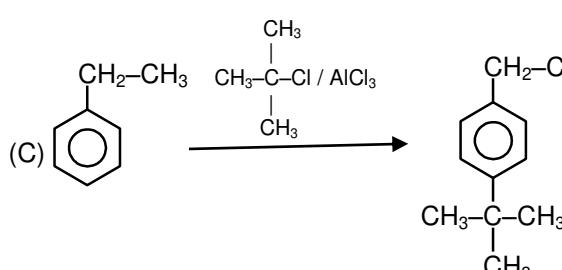
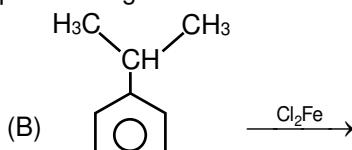
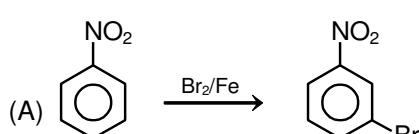


- (A) Major product P is kinetic product formed by 1,2-addition  
 (B) Major product Q is Thermodynamic product formed by 1,4-addition  
 (C) Reaction intermediate of both (i) & (ii) reaction is carbocation.  
 (D) P is 1-Bromobut-2-ene & Q is 3-Bromobut-1-ene.

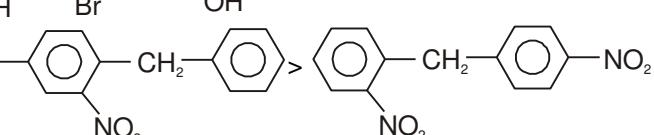
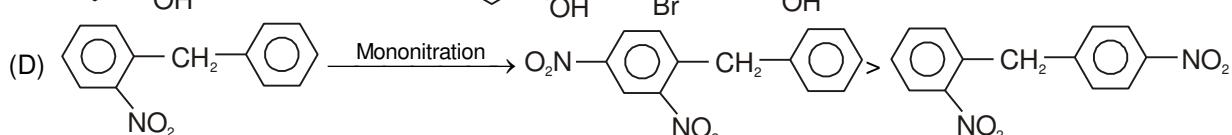
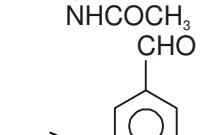
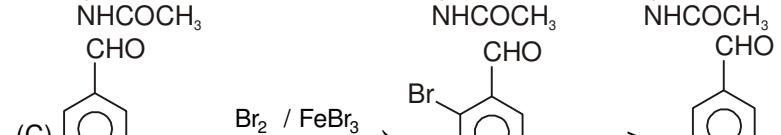
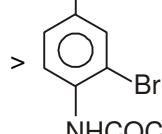
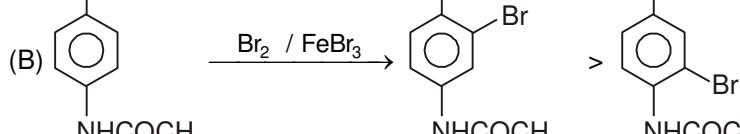
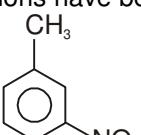
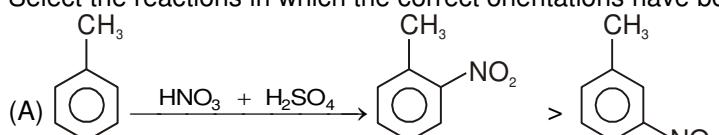
9. Electrophilic aromatic substitution can be seen in which of the following cases ?



10. In which of the following reactions correct major product is given ?

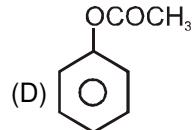
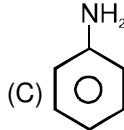
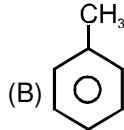
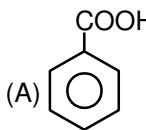


11. Select the reactions in which the correct orientations have been mentioned in the major products.





12. Friedel-Crafts acylation is simply observed in :



13. Choose the correct statements :

- (A) Benzene reacts with electrophile to form reaction intermediate known as sigma complex (arenium ion)
- (B) Formation of carbon-electrophile bond is rate-determining step in nitration of benzene.
- (C) Breaking of C-H bond is rate-determining step in nitration of benzene.
- (D) Sulphonation of benzene is a reversible reaction

## 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  $\text{CH}_2=\text{O}$  one moles of  $\text{CH}_3\text{CH}=\text{O}$  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.  $x$ ,  $y$ ,  $z$  are

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

2.  $(x, y, z) \xrightarrow{\text{H}_3\text{O}^+}$  addition product. The correct statement is

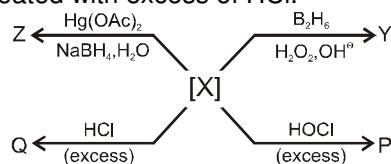
- (A) All three alkenes will give 3 different major hydration products
- (B) Three alkenes will give same hydration major product
- (C) Two alkenes form same product but one alkene forms different major product.
- (D) Addition of HCl and  $\text{H}_3\text{O}^+$  both are following different regioselectivity.

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

- (A) These have molecular formula  $\text{C}_3\text{H}_6$
- (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.  $\text{C}_4\text{H}_6$ ) 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)  $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$
- (B)  $\text{CH}_3-\text{CH}_2\text{C}\equiv\text{CH}$
- (C)  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$
- (D)  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}$

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.



## **Comprehension # 3**

**Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.**

Observe the three columns in which column-1 represents reactants, column-2 represents reagent while column-3 represents reaction conditions.

While Column 3 represents reaction conditions.			
Column 1	Column 2	Column 3	
(I) $\text{Ph}-\text{C}\equiv\text{CH}$	(i) $\text{Hg}^{++}/\text{H}_3\text{O}^+$	(P) Electrophilic substitution	
(II) 	(ii) $\text{Cl}_2/\text{h}\nu$	(Q) Electrophilic addition	
(III) 	(iii) $\text{CH}_3-\overset{\text{O}}{\underset{\text{  }}{\text{C}}}-\text{H}/\text{H}^+$	(R) Carbocation intermediate	
(IV) 	(iv) $\text{H}^+/\text{H}_2\text{O}$	(S) Radical intermediate	

6. Ketone is formed by the reaction  
(A) (I) (i) (Q)                    (B) (IV) (iii) (R)                    (C) (III) (iv) (Q)                    (D) (II) (iii) (P)

7. Which of the following is non correct for substitution reaction.  
(A) (II) (iii) (R)                    (B) (IV) (ii) (S)                    (C) (III) (iv) (R)                    (D) (IV) (iii) (P)

8. Arenium ion is formed in the reaction.  
(A) (I) (iv) (P)                    (B) (II) (iii) (P)                    (C) (III) (iv) (R)                    (D) (IV) (ii) (S)

## **Exercise-3**

**\* Marked Questions may have more than one correct option.**

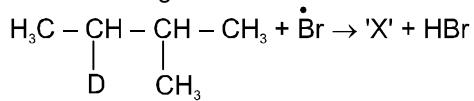
**PART - I : JEE (ADVANCED) / IIT(JEE)-PROBLEMS (PREVIOUS YEARS)**

- 1.** In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because : [IIT(JEE)-2001(S), 3/135]  
(A) both are highly ionic (B) one is oxidising and the other is reducing  
(C) one of the steps is endothermic in both the cases (D) all the steps are exothermic in both the cases.

**2.** The reaction of propene with HOCl proceeds via the addition of [IIT(JEE)-2001(S), 3/135]  
(A) H<sup>+</sup> in the first step (B) Cl<sup>+</sup> in the first step  
(C) OH<sup>-</sup> in the first step (D) Cl<sup>+</sup> and OH<sup>-</sup> in a single step

**3.** **Assertion :** Addition of bromine to trans-2-butene yields meso-2, 3-dibromobutane.  
**Reason :** Addition of bromine to an alkene is an electrophilic addition. [IIT(JEE)-2001(S), 3/135]  
(A) Both Assertion and Reason are true and Reason is the correct explanation of Assertion.  
(B) Both Assertion and Reason are true but Reason is not correct explanation of Assertion.  
(C) Assertion is true but Reason is false.  
(D) Assertion is false but Reason is true.

**4.** Consider the following reaction



Identify the structure of the major product 'X'.

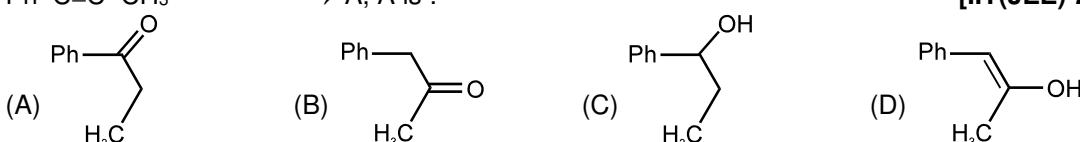
- (A)  $\text{H}_3\text{C} - \underset{\text{D}}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \overset{\bullet}{\text{CH}_2}$

(B)  $\text{H}_3\text{C} - \underset{\text{D}}{\text{CH}} - \overset{\bullet}{\underset{\text{CH}_3}{\text{C}}} - \text{CH}_3$

(C)  $\text{H}_3\text{C} - \overset{\bullet}{\underset{\text{D}}{\text{C}}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$

(D)  $\text{H}_3\text{C} - \overset{\bullet}{\text{CH}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_3$

5.  $\text{Ph}-\text{C}\equiv\text{C}-\text{CH}_3 \xrightarrow{\text{Hg}^{2+} / \text{H}^+}$  A, A is : [IIT(JEE)-2003, 3/144]



6. The number of chiral compounds produced upon monochlorination of 2-methylbutane is : [IIT(JEE)-2004, 3/144]

- (A) 2 (B) 4 (C) 6 (D) 8

7. The major product obtained on acid-catalysed hydration of 2-phenylpropene is [IIT(JEE)-2004, 3/144]

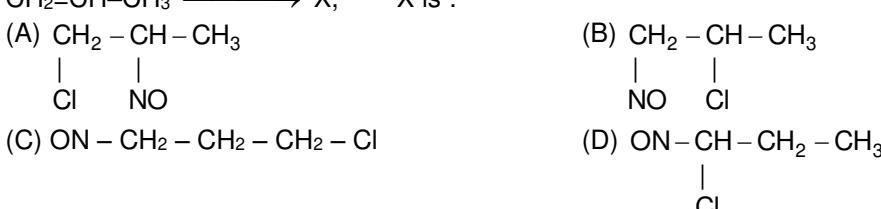
- (A) 2-Phenylpropan-2-ol (B) 2-Phenylpropan-1-ol  
(C) 3-Phenylpropan-2-ol (D) 1-Phenylpropan-1-ol

8.  $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{CH}_3 \xrightarrow{\text{Cl}_2 / \text{h}\nu}$  [N]  $\xrightarrow[\text{distillation}]{\text{Fractional}}$  [P]

The number of possible isomers [N] and number of fractions [P] are : [IIT(JEE)-2006, 5/184]

- (A) (6, 6) (B) (6, 4) (C) (4, 4) (D) (3, 3)

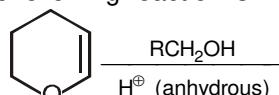
9.  $\text{CH}_2=\text{CH}-\text{CH}_3 \xrightarrow{\text{NOCl}}$  X, X is : [IIT(JEE)-2006, 3/184]



10. The number of stereoisomers obtained by bromination of trans-2-butene is : [IIT(JEE)-2007, 3/162]

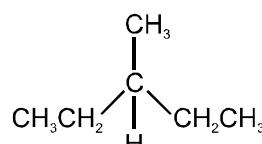
- (A) 1 (B) 2 (C) 3 (D) 4

11. The major product of the following reaction is [IIT(JEE)-2011, 3/160]

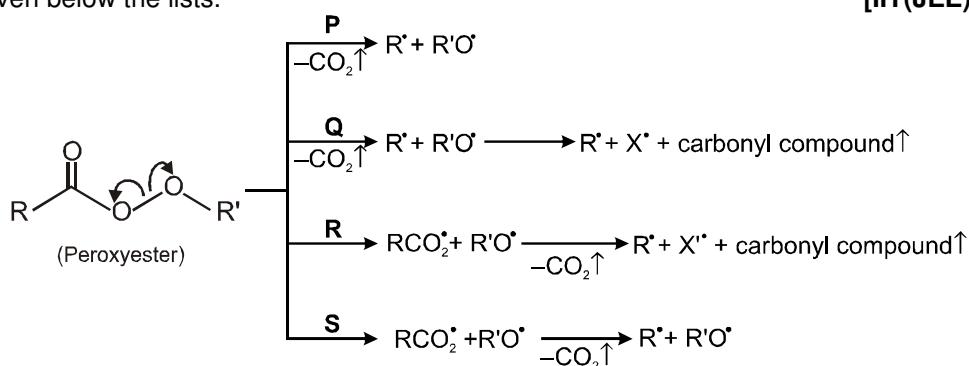


- (A) a hemiacetal (B) an acetal (C) an ether (D) an ester

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



13. 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. [IIT(JEE)-2014, 3/160]



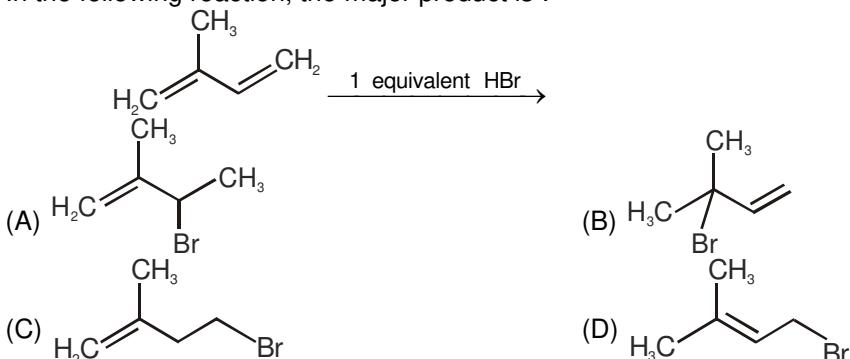
	List-I		List-II
P.	Pathway P	1.	
Q.	Pathway Q	2.	
R.	Pathway R	3.	
S.	Pathway S	4.	

Code :

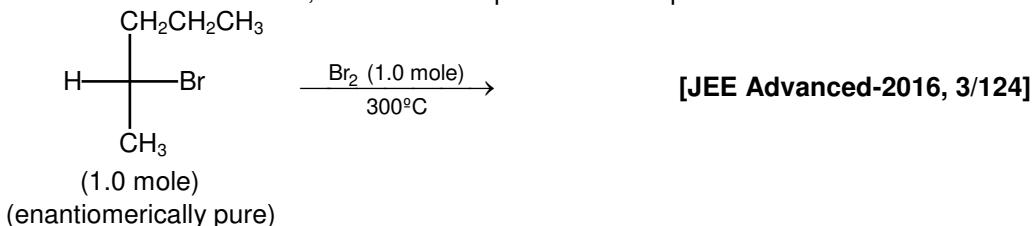
	P	Q	R	S		P	Q	R	S	
(A)	1	3	4	2		(B)	2	4	3	1
(C)	4	1	2	3		(D)	3	2	1	4

14. In the following reaction, the major product is :

[IIT(JEE)-2015, 4/168]



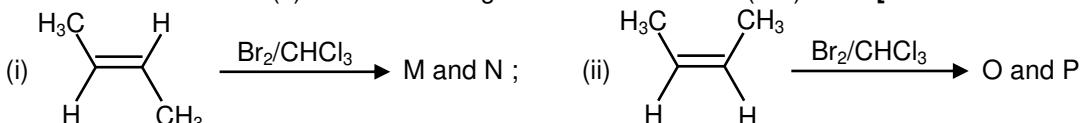
15. In the following monobromination reaction, the number of possible chiral products is



[JEE Advanced-2016, 3/124]

- 16.\* The correct statement(s) for the following addition reactions is (are)

[JEE Advanced-2017, 4/122]

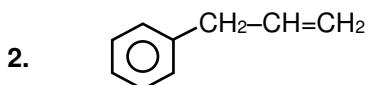


- (A) (M and O) and (N and P) are two pairs of enantiomers  
 (B) Bromination proceeds through trans-addition in both the reactions  
 (C) O and P are identical molecules  
 (D) (M and O) and (N and P) are two pairs of diastereomers

## PART - II : JEE (MAIN) ONLINE PROBLEMS (PREVIOUS YEARS)

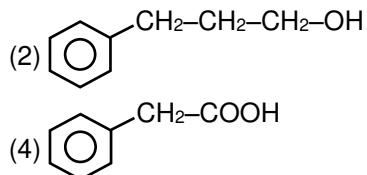
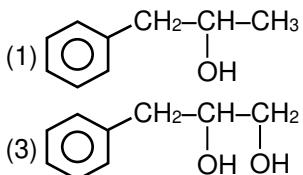
1. In the hydroboration-oxidation reaction of propene with diborane,  $\text{H}_2\text{O}_2$  and  $\text{NaOH}$ , the organic compound formed is :  
 (1)  $\text{CH}_3\text{CH}_2\text{OH}$       (2)  $\text{CH}_3\text{CHOHCH}_3$       (3)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$       (4)  $(\text{CH}_3)_3\text{COH}$

[JEE(Main) 2014 (09-04-14), 4/120]



on mercuration-demercuration produces the major product.

[JEE(Main) 2014 (12-04-14), 4/120]



3. In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition to alkenes because:  
 [JEE(Main) 2014 (12-04-14), 4/120]

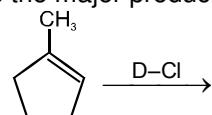
- (1) One of the steps is endothermic in HCl and HI.
- (2) Both HCl and HI are strong acids.
- (3) HCl is oxidizing and the HI is reducing.
- (4) All the steps are exothermic in HCl and HI.

4. The major product obtained in the photo catalyzed bromination of 2-methylbutane is :

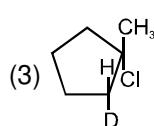
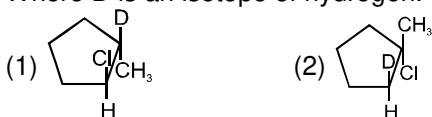
[JEE(Main) 2014 (12-04-14), 4/120]

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

- 5\*. What is the major product expected from the following reaction ?

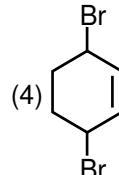
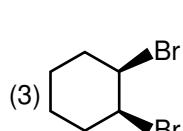
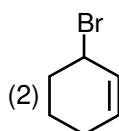
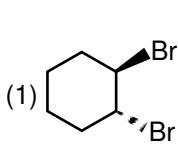
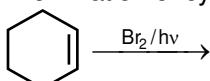


Where D is an isotope of hydrogen.



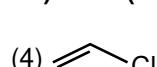
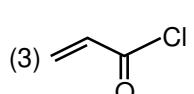
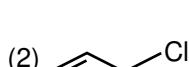
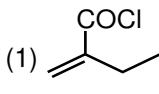
[JEE(Main) 2015 (11-04-15), 4/120]

6. Bromination of cyclohexene under conditions given below yields: [JEE(Main) 2016 (10-04-16), 4/120]



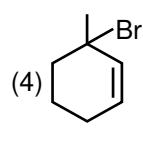
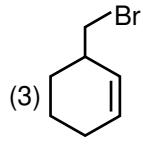
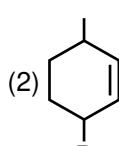
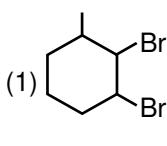
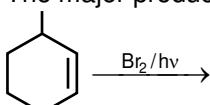
7. Which of the following compounds will not undergo Friedel Craft's reaction with benzene ?

[JEE(Main) 2017 (08-04-17), 4/120]



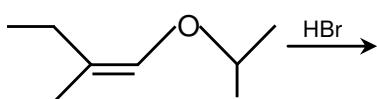
8. The major product of the following reaction is :

[JEE(Main) 2017 (09-04-17), 4/120]



9. The total number of optically active compounds formed in the following reaction is :

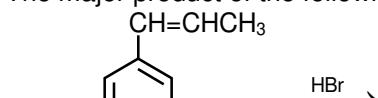
[JEE(Main) 2018 (15-04-18), 4/120]



- (1) Two      (2) Four      (3) Six      (4) Zero

10. The major product of the following reaction is :

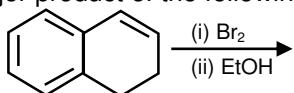
[JEE(Main) 2018 (15-04-18), 4/120]



- (1)      (2)      (3)      (4)

11. The major product of the following reaction is :

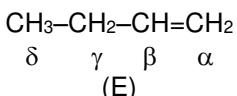
[JEE(Main) 2019 (09-01-19), 4/120]



- (1)      (2)      (3)      (4)

12. Which hydrogen in compound (E) is easily replaceable during bromination reaction in presence of light?

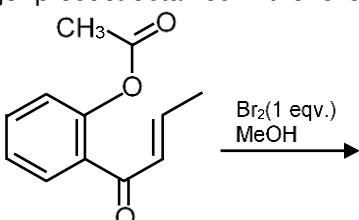
[JEE(Main) 2019 (10-01-19), 4/120]



- (1)  $\alpha$ -hydrogen      (2)  $\gamma$ -hydrogen      (3)  $\beta$ -hydrogen      (4)  $\delta$ -hydrogen

13. The major product obtained in the following conversion is:

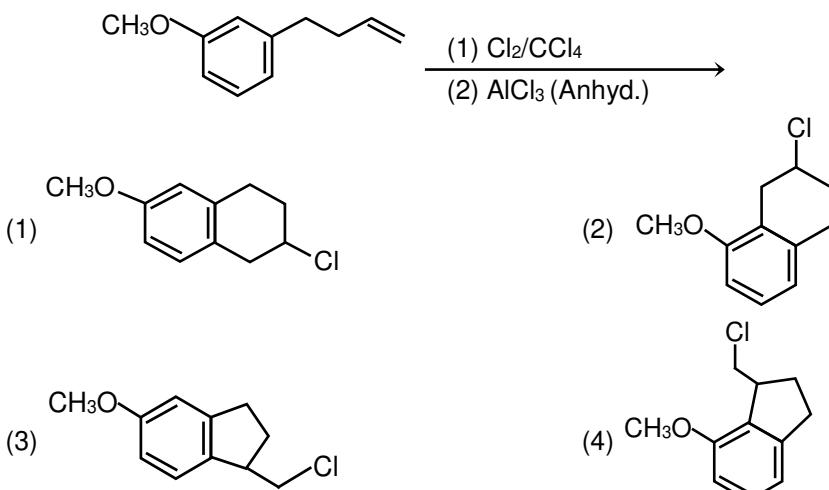
[JEE(Main) 2019 (11-01-19), 4/120]



- (1)      (2)      (3)      (4)

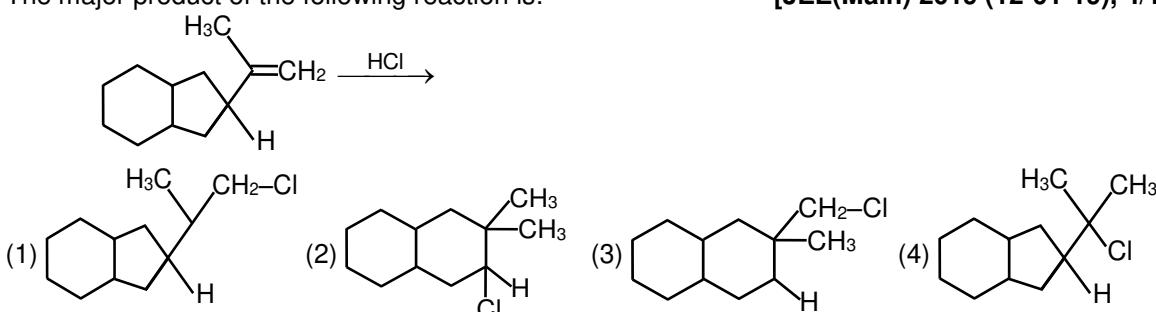
14. The major product of the following reactions is :

[JEE(Main) 2019 (12-01-19), 4/120]



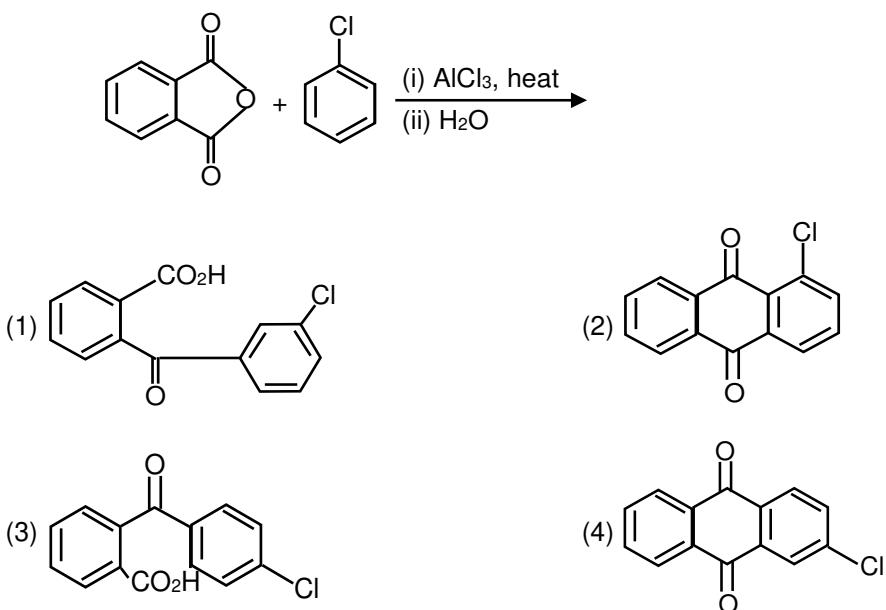
15. The major product of the following reaction is:

[JEE(Main) 2019 (12-01-19), 4/120]



16. The major product of the following reaction is :

[JEE(Main) 2019 (08-04-19), 4/120]



17. Which one of the following alkenes when treated with HCl yields majorly an anti-Markovnikov product?

[JEE(Main) 2019 (08-04-19), 4/120]

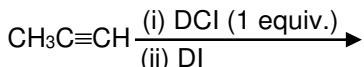
- (1)  $\text{CH}_3\text{O}-\text{CH}=\text{CH}_2$       (2)  $\text{Cl}-\text{CH}=\text{CH}_2$       (3)  $\text{H}_2\text{N}-\text{CH}=\text{CH}_2$       (4)  $\text{F}_3\text{C}-\text{CH}=\text{CH}_2$

18. Polysubstitution is a major drawback in :

[JEE(Main) 2019 (08-04-19), 4/120]

- (1) Friedel-Crafts acylation  
(2) Reimer-Tiemann reaction  
(3) Friedel-Crafts alkylation  
(4) Acetylation of aniline

19. The major product of the following reaction is :

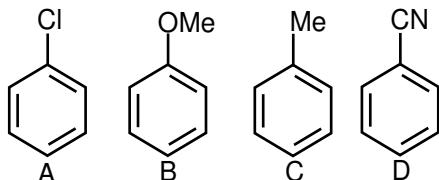


- (1)  $\text{CH}_3\text{C}(\text{I})(\text{Cl})\text{CHD}_2$     (2)  $\text{CH}_3\text{CD}(\text{Cl})\text{CHD}(\text{I})$     (3)  $\text{CH}_3\text{CD}_2\text{CH}(\text{Cl})(\text{I})$     (4)  $\text{CH}_3\text{CD}(\text{I})\text{CHD}(\text{Cl})$

[JEE(Main) 2019 (09-04-19), 4/120]

20. The increasing order of reactivity of the following compounds towards aromatic electrophilic substitution reaction is :

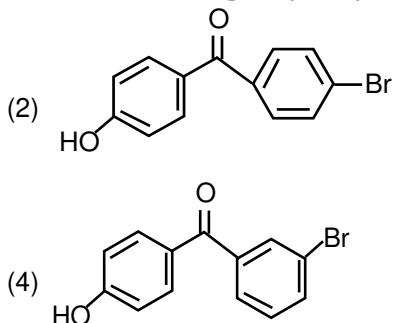
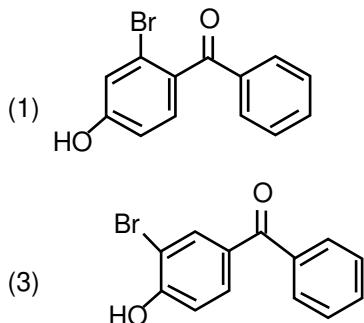
[JEE(Main) 2019 (09-04-19), 4/120]



- (1)  $D < A < C < B$     (2)  $A < B < C < D$     (3)  $D < B < A < C$     (4)  $B < C < A < D$

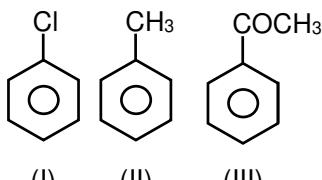
21. p-Hydroxybenzophenone upon reaction with bromine in carbon tetrachloride gives:

[JEE(Main) 2019 (09-04-19), 4/120]



22. The increasing order of the reactivity of the following compounds towards electrophilic aromatic substitution reactions is :

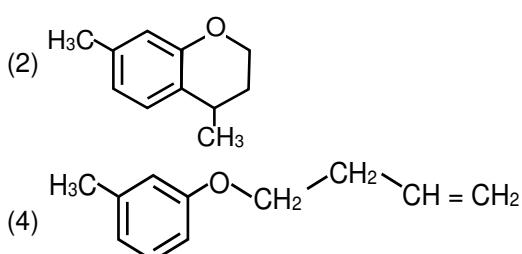
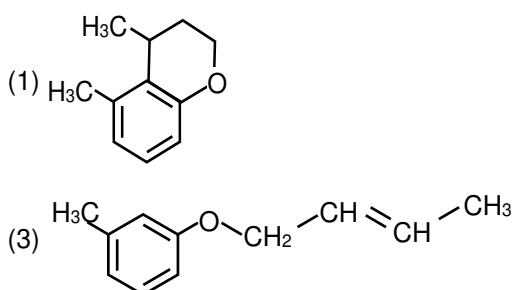
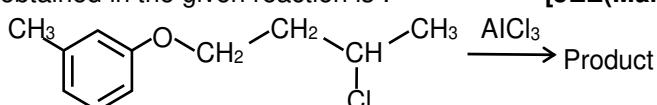
[JEE(Main) 2019 (10-04-19), 4/120]



- (1)  $\text{II} < \text{I} < \text{III}$     (2)  $\text{III} < \text{I} < \text{II}$     (3)  $\text{III} < \text{II} < \text{I}$     (4)  $\text{I} < \text{III} < \text{II}$

23. The major product obtained in the given reaction is :

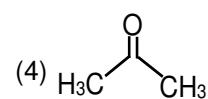
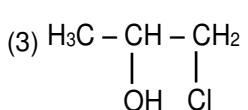
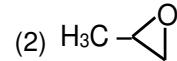
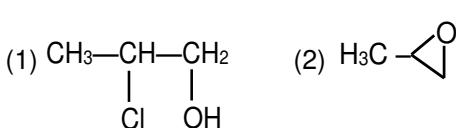
[JEE(Main) 2019 (10-04-19), 4/120]



Hydrocarbon



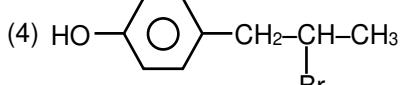
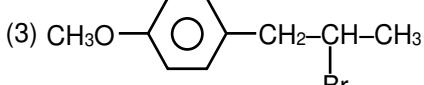
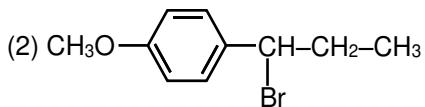
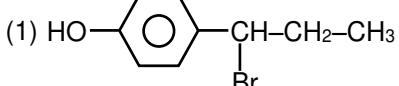
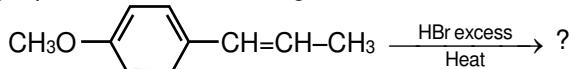
24. The major product of the following addition reaction is:



[JEE(Main) 2019 (12-04-19), 4/120]

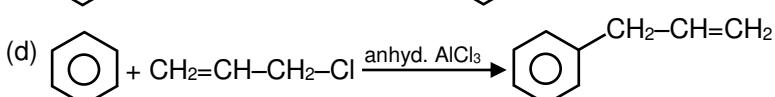
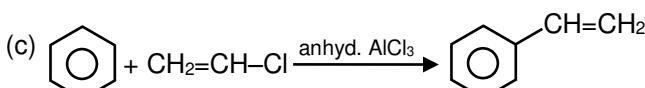
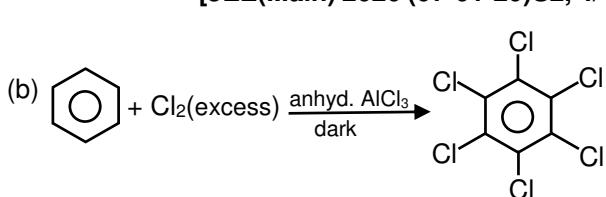
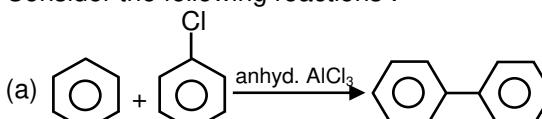
25. The major product in the following conversion is:

[JEE(Main) 2019 (12-01-19), 4/120]



26. Consider the following reactions :

[JEE(Main) 2020 (07-01-20)S2, 4/100]



Which of these reactions are possible?

- (1) (a) and (d)      (2) (a) and (b)      (3) (b) and (d)      (4) (b), (c) and (d)

27. Arrange the following compounds in increasing order of C-OH bond length :

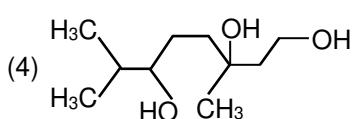
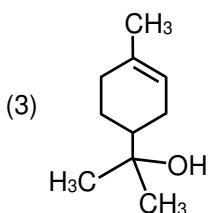
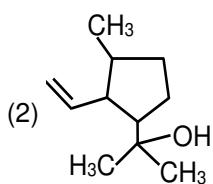
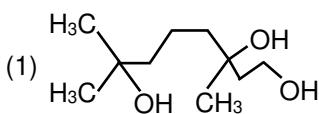
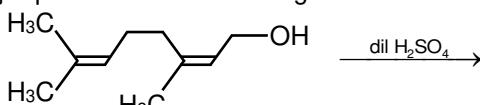
Methanol, phenol, p-ethoxyphenol

[JEE(Main) 2020 (08-01-20)S1, 4/100]

- (1) methanol < phenol < p-ethoxyphenol      (2) phenol < methanol < p-ethoxyphenol  
 (3) phenol < p-ethoxyphenol < methanol      (4) methanol < p-ethoxyphenol < phenol

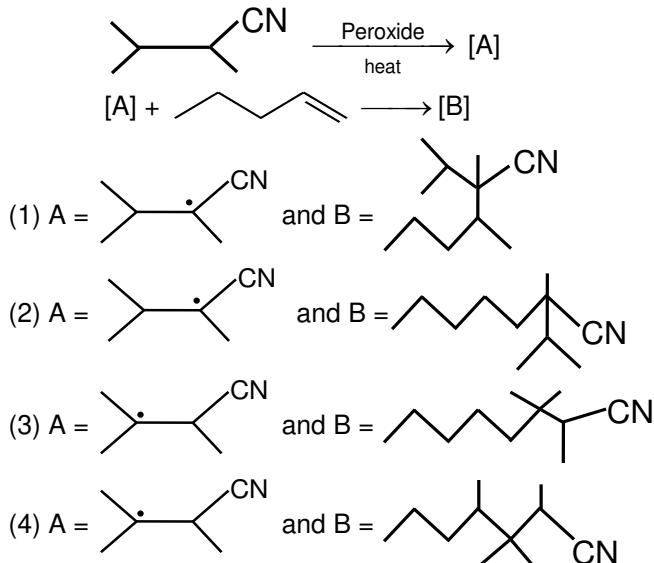
28. The major product of the following reaction is :

[JEE(Main) 2020 (08-01-20)S1, 4/100]



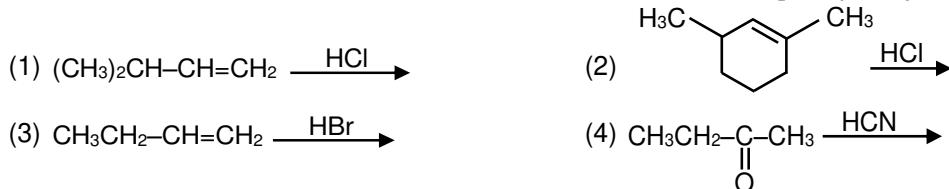
29. The major products A and B in the following reactions are :

[JEE(Main) 2020 (08-01-20)S1, 4/100]



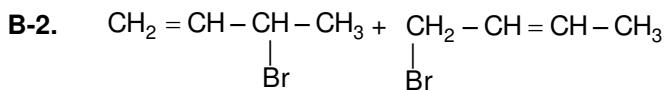
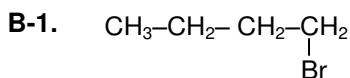
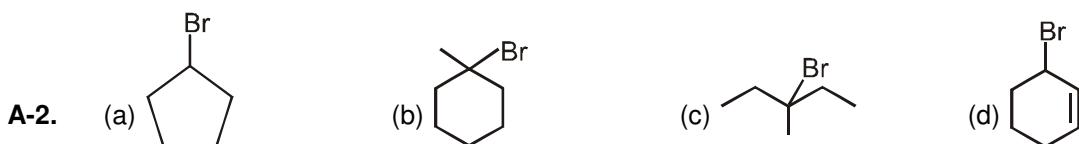
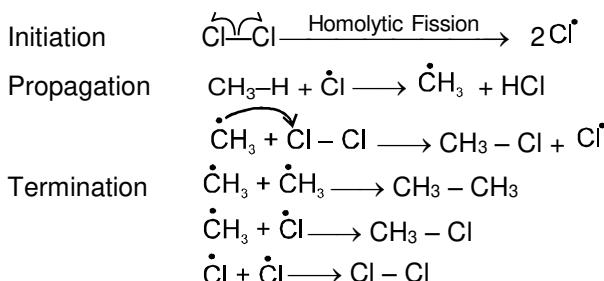
30. Which of the following reactions will not produce a racemic product?

[JEE(Main) 2020 (09-01-20)S2, 4/100]



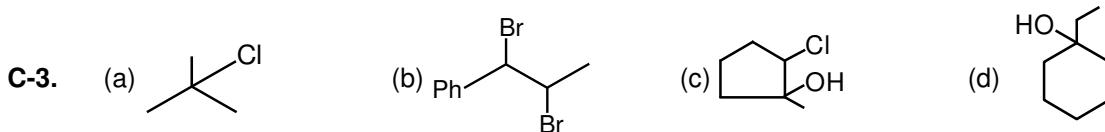
**Answers****EXERCISE - 1****PART - I**

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



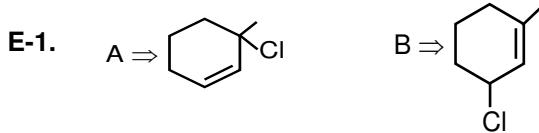
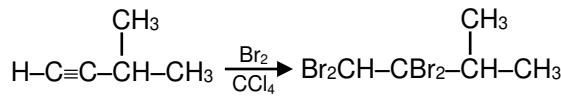
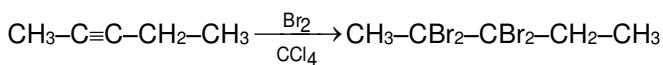
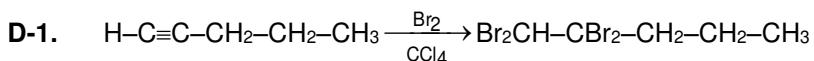
**C-1.** IV > III > II > I

- C-2.** Reactivity is based on stability of intermediate carbocation.  
 $3^{\circ}$  carbocation >  $2^{\circ}$  carbocation >  $1^{\circ}$  carbocation (stability order)



- C-4.** (a) Racemic mixture of 2,3-Dibromobutane      (b) Meso 2,3-Dibromobutane

**C-5.** Positional isomers



- F-1.** Benzene has resonance stabilization due to delocalisation of  $\pi$ -electrons and during electrophilic addition reactions, it loses its aromaticity. In electrophilic substitution reaction aromaticity is retained.
- F-2.** c, e, g, h
- F-3.** a, b, c, f, h
- F-4.** (a) (I) > (II) > (III)      (b) (II) > (III) > (I)      (c) (II) > (I) > (III)      (d) (III) > (I) > (II)
- F-5.** In vinyl chloride and chloro benzene lone pair on Cl atom takes part in conjugation. So, partial double bond character between C–Cl bond is developed.

**PART – II**

- |                 |                 |                  |                  |                  |
|-----------------|-----------------|------------------|------------------|------------------|
| <b>A-1.</b> (A) | <b>A-2.</b> (B) | <b>A-3.</b> (C)  | <b>A-4.</b> (C)  | <b>A-5.</b> (D)  |
| <b>A-6.</b> (A) | <b>B-1.</b> (C) | <b>B-2.</b> (A)  | <b>B-3.</b> (B)  | <b>B-4.</b> (D)  |
| <b>B-5.</b> (B) | <b>C-1.</b> (B) | <b>C-2.</b> (B)  | <b>C-3.</b> (B)  | <b>C-4.</b> (B)  |
| <b>C-5.</b> (A) | <b>C-6.</b> (D) | <b>C-7.</b> (C)  | <b>C-8.</b> (B)  | <b>C-9.</b> (C)  |
| <b>D-1.</b> (D) | <b>D-2.</b> (A) | <b>E-1.</b> (C)  | <b>F-1.</b> (C)  | <b>F-2.</b> (B)  |
| <b>F-3.</b> (A) | <b>F-4.</b> (B) | <b>F-5.</b> (C)  | <b>F-6.</b> (D)  | <b>F-7.</b> (C)  |
| <b>F-8.</b> (C) | <b>F-9.</b> (D) | <b>F-10.</b> (A) | <b>F-11.</b> (C) | <b>F-12.</b> (C) |

**PART – III**

- 1.** (D)      **2.** (A - q, r) ; (B - p, r) ; (C - p, r) ; (D - q, s)

**EXERCISE - 2****PART – I**

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

**PART – II**

- |              |             |             |              |              |
|--------------|-------------|-------------|--------------|--------------|
| <b>1.</b> 2  | <b>2.</b> 4 | <b>3.</b> 4 | <b>4.</b> 10 | <b>5.</b> 4  |
| <b>6.</b> 21 | <b>7.</b> 3 | <b>8.</b> 4 | <b>9.</b> 23 | <b>10.</b> 6 |

**PART – III**

- |                 |                  |                  |                  |                  |
|-----------------|------------------|------------------|------------------|------------------|
| <b>1.</b> (BCD) | <b>2.</b> (ABCD) | <b>3.</b> (ABCD) | <b>4.</b> (ABCD) | <b>5.</b> (AD)   |
| <b>6.</b> (AD)  | <b>7.</b> (CD)   | <b>8.</b> (ABC)  | <b>9.</b> (ABC)  | <b>10.</b> (ABC) |
| <b>11.</b> (AC) | <b>12.</b> (BD)  | <b>13.</b> (ABD) |                  |                  |

**PART – IV**

- |               |               |               |               |               |
|---------------|---------------|---------------|---------------|---------------|
| <b>1.</b> (B) | <b>2.</b> (B) | <b>3.</b> (D) | <b>4.</b> (B) | <b>5.</b> (C) |
| <b>6.</b> (A) | <b>7.</b> (C) | <b>8.</b> (B) |               |               |

**EXERCISE - 3****PART – I**

- |             |      |            |     |            |     |            |     |            |     |
|-------------|------|------------|-----|------------|-----|------------|-----|------------|-----|
| <b>1.</b>   | (C)  | <b>2.</b>  | (B) | <b>3.</b>  | (B) | <b>4.</b>  | (B) | <b>5.</b>  | (A) |
| <b>6.</b>   | (B)  | <b>7.</b>  | (A) | <b>8.</b>  | (B) | <b>9.</b>  | (B) | <b>10.</b> | (A) |
| <b>11.</b>  | (B)  | <b>12.</b> | 8   | <b>13.</b> | (A) | <b>14.</b> | (D) | <b>15.</b> | 5   |
| <b>16.*</b> | (BD) |            |     |            |     |            |     |            |     |

**PART – II**

- |            |     |            |     |            |     |            |     |            |       |
|------------|-----|------------|-----|------------|-----|------------|-----|------------|-------|
| <b>1.</b>  | (3) | <b>2.</b>  | (1) | <b>3.</b>  | (1) | <b>4.</b>  | (4) | <b>5.</b>  | (2,3) |
| <b>6.</b>  | (2) | <b>7.</b>  | (4) | <b>8.</b>  | (4) | <b>9.</b>  | (2) | <b>10.</b> | (2)   |
| <b>11.</b> | (1) | <b>12.</b> | (2) | <b>13.</b> | (2) | <b>14.</b> | (3) | <b>15.</b> | (4)   |
| <b>16.</b> | (3) | <b>17.</b> | (4) | <b>18.</b> | (3) | <b>19.</b> | (1) | <b>20.</b> | (1)   |
| <b>21.</b> | (3) | <b>22.</b> | (2) | <b>23.</b> | (2) | <b>24.</b> | (3) | <b>25.</b> | (1)   |
| <b>26.</b> | (3) | <b>27.</b> | (3) | <b>28.</b> | (3) | <b>29.</b> | (2) | <b>30.</b> | (1)   |



## Additional Problems for Self Practice (APSP)

Marked questions are recommended for Revision.

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

### PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

**Max. Marks: 100**

**Max. Time : 1 Hour**

**Important Instructions:**

**A. General :**

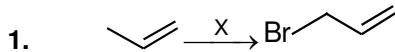
1. The test paper is of **1** hour duration.
2. The Test Paper consists of **25** questions and each question carries **4** Marks. Test Paper consists of **Two Sections**.

**B. Test Paper Format and its Marking Scheme:**

1. Section-1 contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **ONE** is correct. For each question in Section-1, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. In all other cases, minus one (**-1**) mark will be awarded.
2. Section-2 contains **5** questions. The answer to each of the question is a **Numerical Value**. For each question in Section-2, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. No negative marks will be answered for incorrect answer in this section. In this section answer to each question is **NUMERICAL VALUE** with two digit integer and decimal upto two digit. If the numerical value has more than two decimal places **truncate/round-off** the value to **TWO** decimal placed.

#### SECTION-1

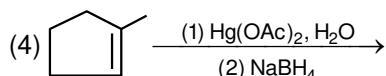
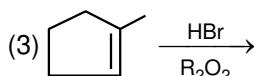
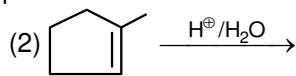
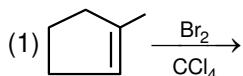
This section contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **Only ONE** option is correct.



x is :

- (1) Br<sub>2</sub> / H<sub>2</sub>O      (2) HBr      (3) HBr / Peroxide      (4) NBS

2. Which of the following reactions is not an electrophilic addition reactions –



3. Nitrobenzene can be prepared from benzene by using a mixture of conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub>. In the nitrating mixture HNO<sub>3</sub> acts as a :

- (1) Base      (2) Acid      (3) Reducing agent      (4) Catalyst

4. Ethylbenzene + Cl<sub>2</sub> major product is :

- (1) o- & p-chloroethylbenzene      (2) 1-Chloroethylbenzene  
 (3) 2-Chloroethylbenzene      (4) m-Chloroethylbenzene

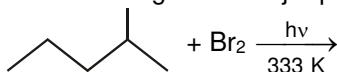
5. The relative rates of mononitration of R-C<sub>6</sub>H<sub>5</sub>, where R=CH<sub>3</sub>, -NO<sub>2</sub>, -OH, -Cl are :

- (1) CH<sub>3</sub> > OH > NO<sub>2</sub> > Cl      (2) OH > Cl > CH<sub>3</sub> > NO<sub>2</sub>  
 (3) OH > CH<sub>3</sub> > NO<sub>2</sub> > Cl      (4) OH > CH<sub>3</sub> > Cl > NO<sub>2</sub>

6. In the free radical chlorination of Methane, the chain initiating step involves the formation of

- (1) Chlorine radical      (2) Hydrogen chloride      (3) Methyl radical      (4) Chloromethyl radical.

7. Which of the following is the major product for the given reaction ?

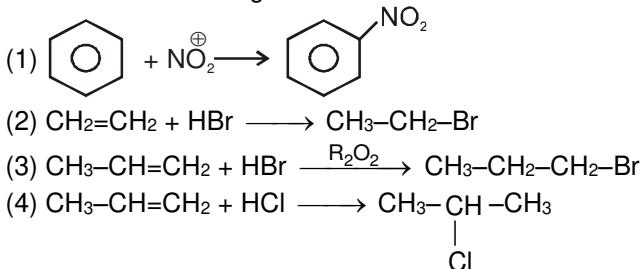


- (1) 2-Bromo-2-methylpentane  
 (2) 1-Bromo-2-methylpentane  
 (3) 4-Bromo-2-methylpentane  
 (4) 3-Bromo-2-methylpentane

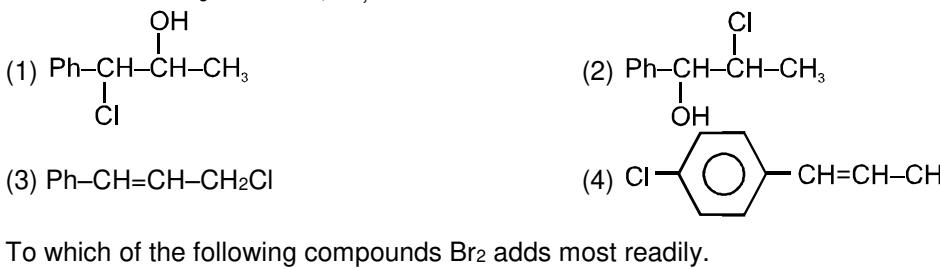
8. Allylic bromination of an olefin is :

- (1) Nucleophilic substitution  
 (2) Electrophilic substitution  
 (3) Free radical substitution  
 (4) Electrophilic addition.

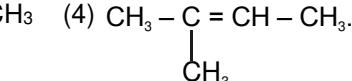
9. Which of the following is free radical addition reaction ?



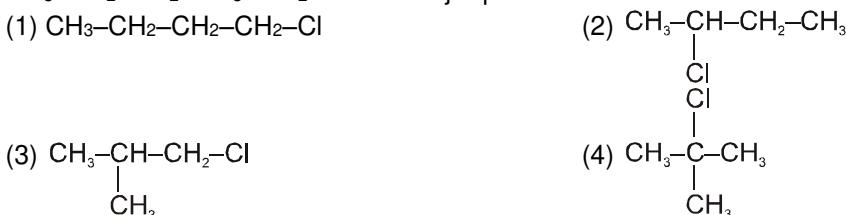
10. Ph-CH=CH-CH3 → X, X is :

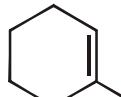


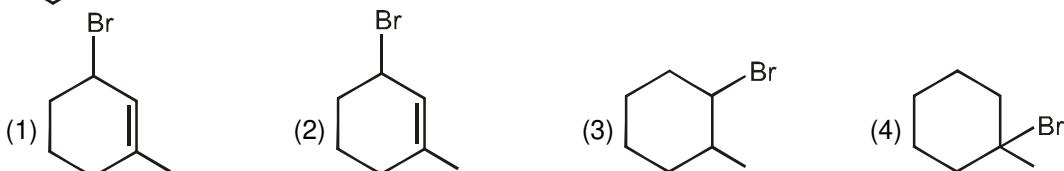
11. To which of the following compounds Br2 adds most readily.

- (1) CH2=CH2      (2) CH3-CH=CH2      (3) CH3-CH=CH-CH3      (4) 

12. CH3-CH2-CH2-CH3 + Cl2 → Major product :

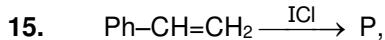


13.  + HBr → Product ; Product is :



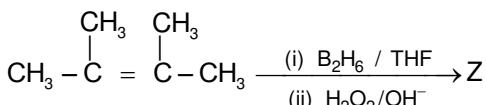
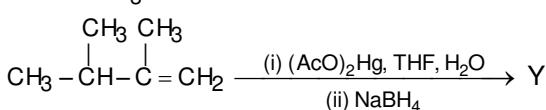
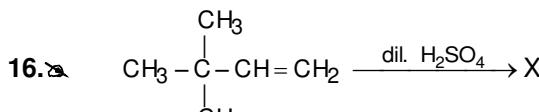
14. Which of the following is the predominant product in the reaction of HOBr with propene ?

- (1) 2-Bromo-1-propanol  
 (2) 3-Bromo-1-propanol  
 (3) 2-Bromo-2-propanol  
 (4) 1-Bromo-2-propanol.



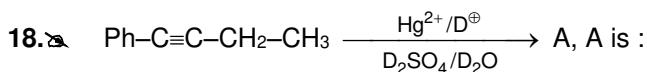
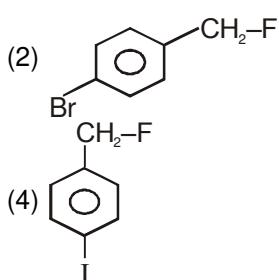
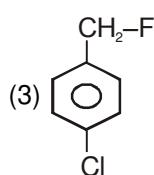
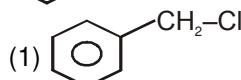
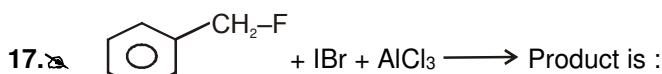
Identify major product 'P' is :

- (1)  $\text{Ph}-\overset{\text{I}}{\underset{\text{I}}{\text{CH}}}-\text{CH}_2-\text{Cl}$       (2)  $\text{Ph}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}}-\text{CH}_2-\text{I}$       (3)  $\text{Ph}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{CH}}}-\text{CH}_2-\text{Cl}$       (4)  $\text{Ph}-\overset{\text{I}}{\underset{\text{I}}{\text{CH}}}-\text{CH}_2-\text{I}$



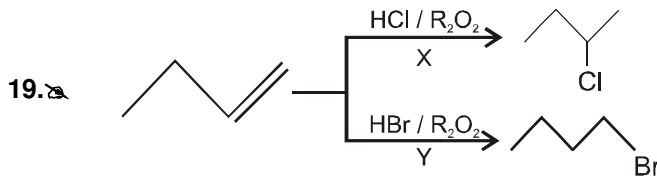
- (1) All three products (X, Y, Z) are different.  
 (3) Y and Z are identical but X is different.

- (2) X and Y are identical but Z is different.  
 (4) All three products (X, Y, Z) are identical.



- (1)  $\text{Ph}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CH}_2-\overset{\text{D}}{\underset{\text{D}}{\text{CH}}}-\text{CH}_3$   
 (3)  $\text{Ph}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CD}_2-\text{CH}_2-\text{CH}_3$

- (2)  $\text{Ph}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\overset{\text{D}}{\underset{\text{D}}{\text{CH}}}-\text{CH}_2-\text{CH}_3$   
 (4)  $\text{Ph}-\overset{\text{O}}{\underset{\text{O}}{\text{C}}}-\text{CD}-\text{CH}_2-\text{CH}_2-\text{CH}_3$



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.

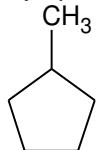
20. Which of the following is the best reagent to convert 1-Methylcyclohexene into 2-methylcyclohexanol ?

- (1) Dil  $\text{H}_2\text{SO}_4$       (2)  $\text{Hg}(\text{OAc})_2 / \text{NaBH}_4, \text{H}_2\text{O}$   
 (3)  $\text{B}_2\text{H}_6/\text{H}_2\text{O}_2, \text{OH}^-$       (4) Conc.  $\text{H}_2\text{SO}_4$

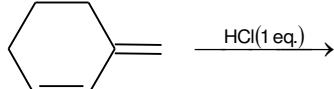
**SECTION-2**

This section contains **5** questions. Each question, when worked out will result in **Numerical Value**.

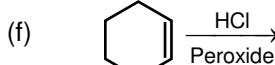
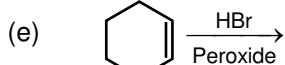
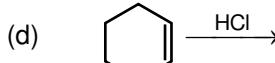
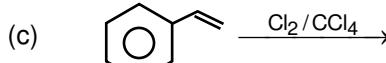
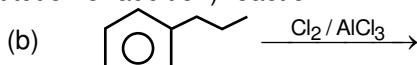
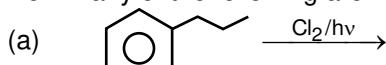
- 21.** How many optically active (all isomers) are obtained on monochlorination of :



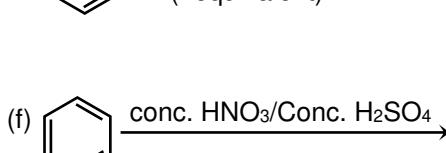
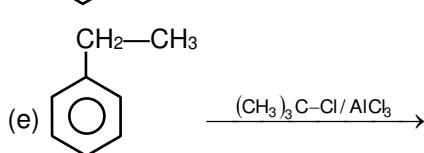
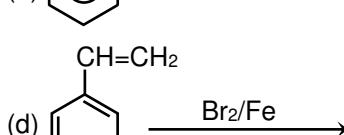
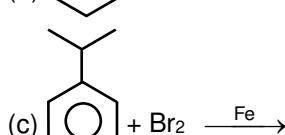
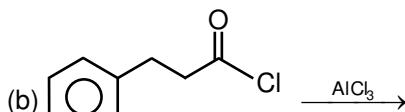
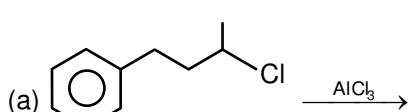
- 22.** The total number of principle products (including stereoisomers) formed in the given reaction will be



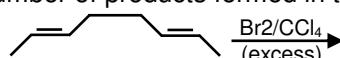
- 23.** How many of the following are free radical (substitution or addition) reaction ?



- 24.** Number of reactions in which electrophile substitution will be observed are



- 25.** Total number of products formed in the following reaction is



**Practice Test-1 (IIT-JEE (Main Pattern))**  
**OBJECTIVE RESPONSE SHEET (ORS)**

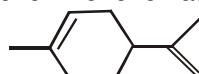
Que.	1	2	3	4	5	6	7	8	9	10	
Ans.											
Que.	11	12	13	14	15	16	17	18	19	20	
Ans.											
Que.	21	22	23	24	25						
Ans.											

**PART - II : JEE (MAIN) / AIEEE OFFLINE PROBLEMS (PREVIOUS YEARS)**

1. What is the product when acetylene reacts with hypochlorous acid ? [AIEEE-2002, 3/225]  
(1)  $\text{CH}_3\text{COCl}$       (2)  $\text{CICH}_2\text{CHO}$       (3)  $\text{Cl}_2\text{CHCHO}$       (4)  $\text{CICH}_2\text{COOH}$ .
2. Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C gives predominantly [AIEEE-2005, 3/225]  
(1) 3-bromobutene under kinetically controlled conditions  
(2) 1-bromo-2-butene under thermodynamically controlled conditions  
(3) 3-bromobutene under thermodynamically controlled conditions.  
(4) 1-bromo-2-butene under kinetically controlled conditions.
3. Acid catalyzed hydration of alkenes except ethene leads to the formation of [AIEEE-2005, 3/225]  
(1) Mixture of secondary and tertiary alcohols      (2) Mixture of primary and secondary alcohols  
(3) Secondary or tertiary alcohol      (4) Primary alcohol
4. 2-Methylbutane on reacting with bromine in the presence of sunlight gives mainly? [AIEEE-2005, 3/225]  
(1) 1-Bromo-3-methylbutane      (2) 1-Bromo-2-methylbutane  
(3) 2-Bromo-3-methylbutane      (4) 2-Bromo-2-methylbutane
5. HBr reacts with  $\text{CH}_2=\text{CH}-\text{OCH}_3$  under anhydrous conditions at room temperature to give [AIEEE-2006, 3/165]  
(1)  $\text{CH}_3\text{CHO}$  and  $\text{CH}_3\text{Br}$       (2)  $\text{BrCH}_2\text{CHO}$  and  $\text{CH}_3\text{Br}$   
(3)  $\text{BrCH}_2-\text{CH}_2-\text{OCH}_3$       (4)  $\text{H}_3\text{C}-\text{CHBr}-\text{OCH}_3$
6. Which of the following reactions will yield 2,2-dibromopropane ? [AIEEE-2007, 3/120]  
(1)  $\text{CH}_3-\text{C}\equiv\text{CH} + 2\text{HBr} \rightarrow$       (2)  $\text{CH}_3\text{CH}=\text{CHBr} + \text{HBr} \rightarrow$   
(3)  $\text{CH}\equiv\text{CH} + 2\text{HBr} \rightarrow$       (4)  $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \rightarrow$
7. How many chiral compounds are possible on monochlorination of 2-methylbutane [AIEEE-2012, 4/120]  
(1) 8      (2) 2      (3) 4      (4) 6
8. The reaction of propene with HOCl ( $\text{Cl}_2 + \text{H}_2\text{O}$ ) proceeds through the intermediate : [JEE(Main) 2016, 4/120]  
(1)  $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{Cl}$       (2)  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}_2^+$   
(3)  $\text{CH}_3-\text{CHCl}-\text{CH}_2^+$       (4)  $\text{CH}_3-\text{CH}^+-\text{CH}_2-\text{OH}$
9. 3-Methyl-pent-2-ene on reaction with HBr in presence of peroxide forms an addition product. The number of possible stereoisomers for the product is : [JEE(Main) 2017, 4/120]  
(1) Zero      (2) Two      (3) Four      (4) Six

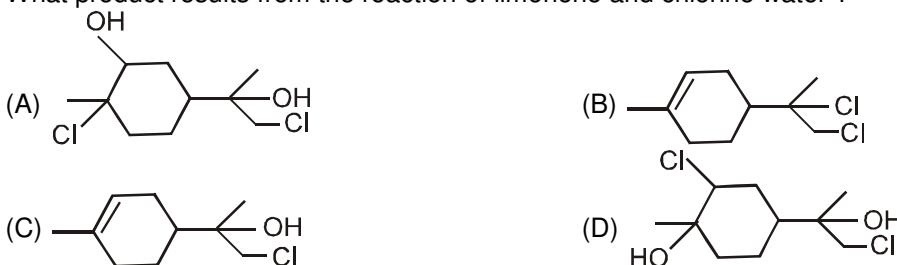
**PART - III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I**

1. The alkene limonene has the following structure,



What product results from the reaction of limonene and chlorine water ?

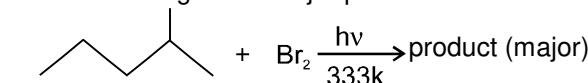
[NSEC-2000]



2. An unknown compound is analyzed to have a molecular mass of 84 and elements has carbon and hydrogen only. When subjected to chlorination in the presence of light, three monochlorinated products are isolated. This compound must be [NSEC-2000]  
(A) methylcyclopentane      (B) cyclohexane  
(C) hexane      (D) 1,3-dimethylcyclobutane



3. Which of the following is the major product of the following reaction ?



[NSEC-2000]

- (A) 3-bromo-2-methylpentane  
(C) 1-bromo-2-methylpentane
- (B) 2-bromo-2-methylpentane  
(D) 4-bromo-2-methylpentane

4. The peroxide effect occurs by :

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

[NSEC-2001]

5. Benzene does not readily undergo  
(A) halogenation (B) nitration

- (C) sulphonation (D) oxidation.

[NSEC-2002]

6. Which compound amongst the following is nitrated with most difficulty ?

- (A) nitrobenzene  
(C) phenol
- (B) m-dinitrobenzene  
(D) quinol.

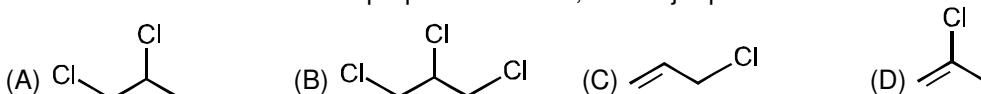
[NSEC-2002]

7. The reaction of toluene with chlorine in the dark and in presence of  $\text{FeCl}_3$  gives predominantly.

[NSEC-2002]

- (A) benzoyl chloride  
(C) m-chlorotoluene
- (B) benzyl chloride  
(D) a mixture of o-and p-chlorotoluenes.

8. In the reaction of chlorine with propene at  $450^\circ\text{C}$ , the major product is



[NSEC-2003]

9. 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  
(C) a base and an acid
- (B) a Bronsted and a Lewis acid  
(D) an acid and an oxidising agent.

10. Select the major product obtained from the addition of HBr to 1-methylcyclohexene.

[NSEC-2005]

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

11. Reaction of benzene with isobutylchloride ( $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$ ) in the presence of anhydrous  $\text{AlCl}_3$  yields

[NSEC-2005]

- (A) tert-butylbenzene  
(C) n-butylbenzene
- (B) iso-butylbenzene  
(D) chlorobenzene.

12. The reagent system for preparing propan-1-ol from propene is

[NSEC-2006]

- (A)  $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$  followed by  $\text{NaBH}_4$   
(C)  $\text{B}_2\text{H}_6$  followed by  $\text{H}_2\text{O}_2$
- (B)  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$   
(D)  $\text{HCO}_2\text{H}/\text{H}_2\text{SO}_4$ .

13. In Friedel - Craft acylation, the amount of  $\text{AlCl}_3$  that must be taken is

[NSEC-2006]

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

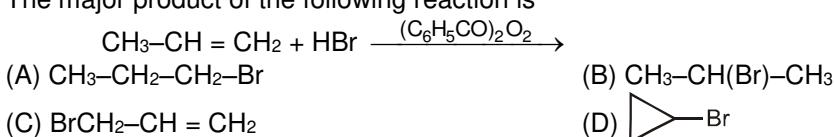
14. For a Friedel-Craft reaction using  $\text{AlCl}_3$ , which compound can be used as solvent, benzene or nitrobenzene?

[NSEC-2006]

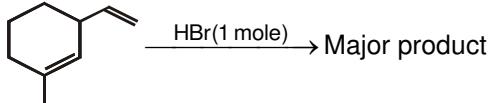
- (A) nitrobenzene but not benzene  
(C) both benzene and nitrobenzene
- (B) benzene but not nitrobenzene  
(D) neither benzene nor nitrobenzene.

15. The major product of the following reaction is

[NSEC-2006]

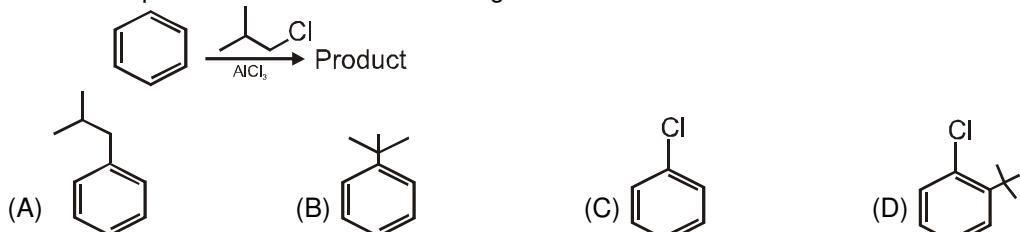


16. The major product formed upon addition of 1 mole of HBr in the following reactions is : [NSEC-2007]

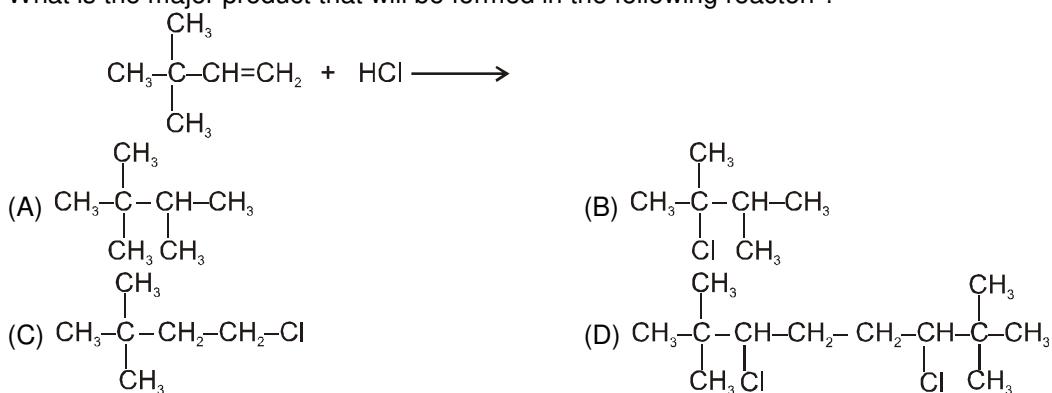


- (A) (B) (C) (D)

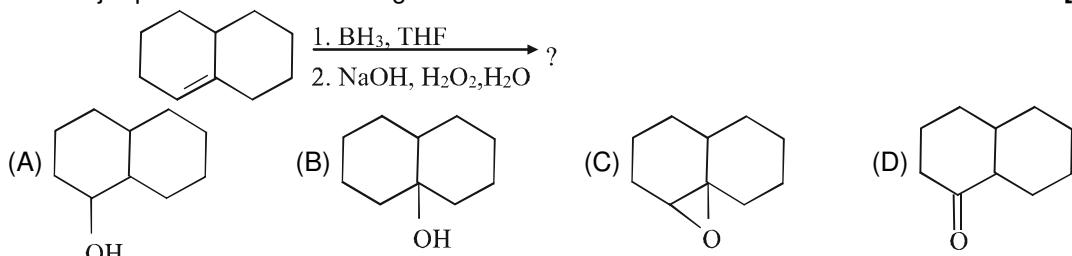
17. Predict the product formed in the following reaction



18. What is the major product that will be formed in the following reacton ?

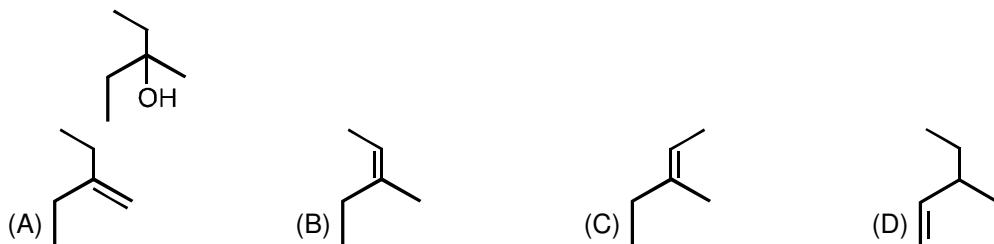


19. The major product in the following reaction is



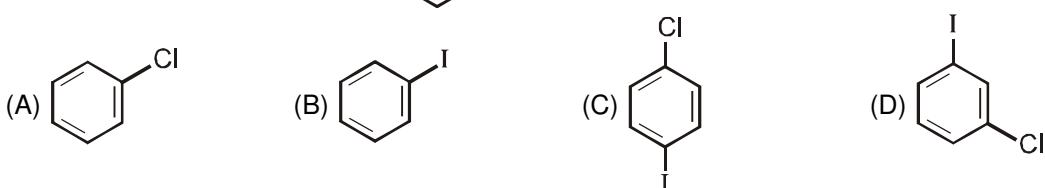
20. Identify the alkene which will not provide the following alcohol upon oxymercuration demercuration.

[NSEC-2008]





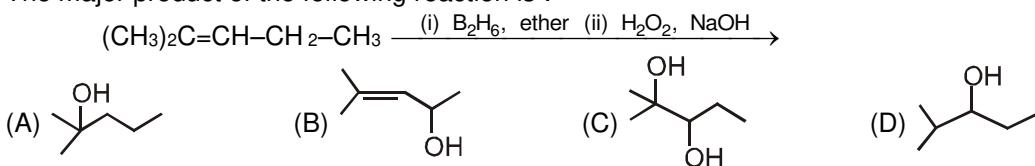
21. The compound X in the reaction, + ICl  $\xrightarrow{\text{anhydrous AlCl}_3}$  X is : [NSEC-2009]



22. 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]

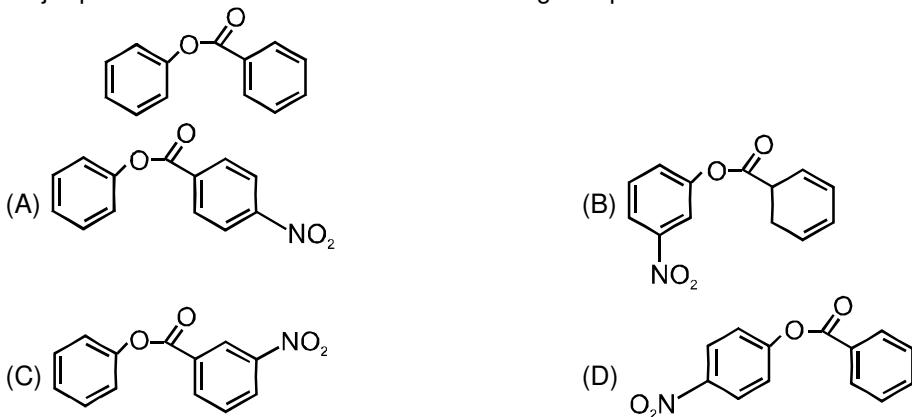
- (A) It is a racemate.  
 (B) It is a product of an addition reaction.  
 (C) It is formed through a cationic intermediate.  
 (D) It is optically active.

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

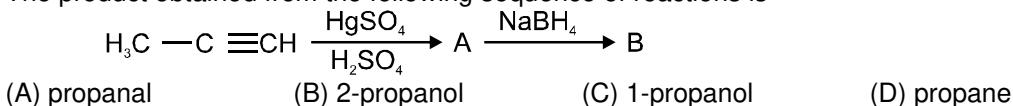


24. The compound which does not react with bromine easily at room temperature is [NSEC-2010]  
 (A) phenol                    (B) 2-butyne                    (C) chlorobenzene                    (D) 1-pentene

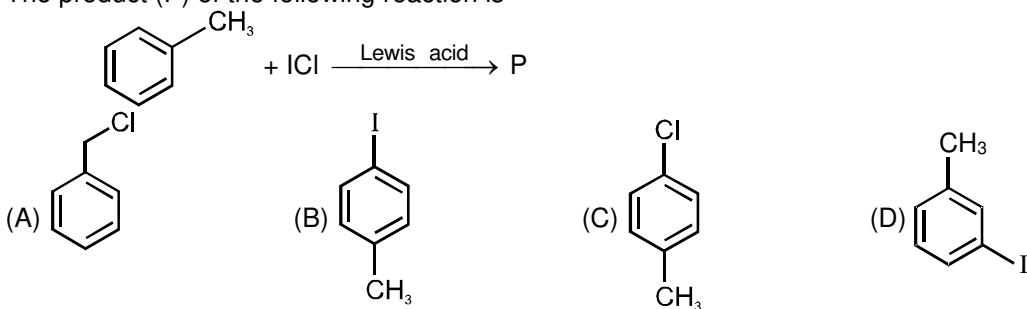
25. Major product of mononitration of the following compound is [NSEC-2011]



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



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





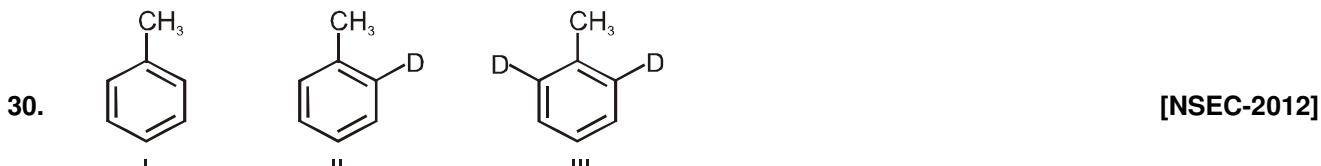
The ‘product’ in the above reaction is :

- (A) 

(B) 

(C) 

(D) This reaction cannot take place



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



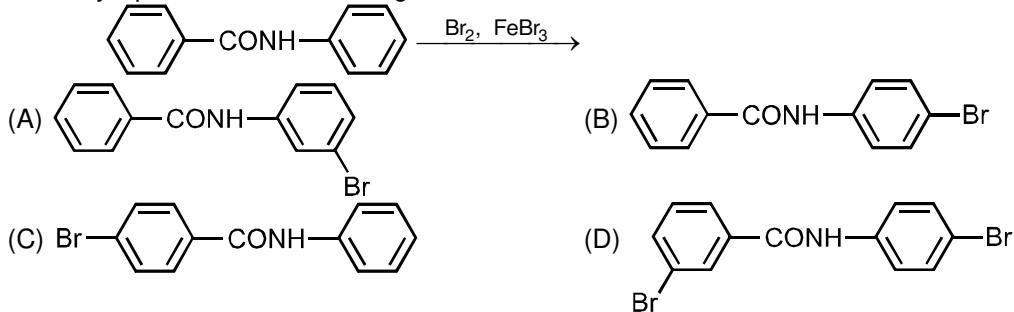
The correct name of the product obtained is

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

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

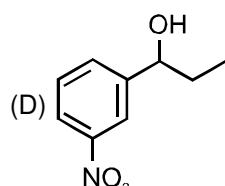
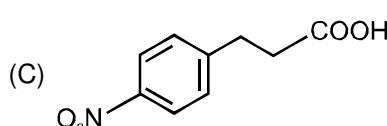
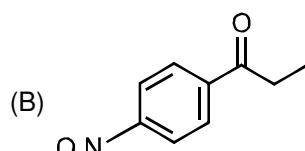
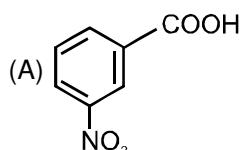
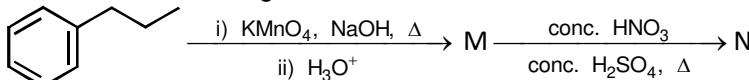
  - (A)  $-\text{NO}_2$  group activates the benzene ring for attack of electrophile at ortho and para position.
  - (B)  $-\text{NH}_2$  group activates the benzene ring for attack of electrophile at ortho and para position.
  - (C) Both  $-\text{NO}_2$  group as well as  $-\text{NH}_2$  group activate the benzene ring for attack of electrophile at ortho and para position.
  - (D) Neither  $-\text{NO}_2$  group nor  $-\text{NH}_2$  group activate the benzene ring for attack of electrophile at ortho and para position.

33. The major product of the following reaction is [INSEC-2014]



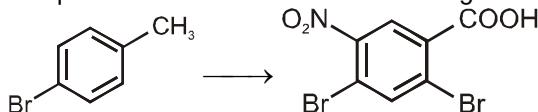
34. The product 'N' of the following reaction is

[NSEC-2014]



35. The best sequence of reactions for the following conversion is

[NSEC-2015]



- (A) (i) 1 mol Br<sub>2</sub> / FeBr<sub>3</sub>    (ii) KMnO<sub>4</sub>, heat    (iii) HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>  
 (B) (i) HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>    (ii) 1 mol Br<sub>2</sub> / FeBr<sub>3</sub>    (iii) KMnO<sub>4</sub>, heat  
 (C) (i) KMnO<sub>4</sub>, heat    (ii) HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>    (iii) 1 mol Br<sub>2</sub> / FeBr<sub>3</sub>  
 (D) (i) 1 mol Br<sub>2</sub> / FeBr<sub>3</sub>    (ii) HNO<sub>3</sub>+H<sub>2</sub>SO<sub>4</sub>    (iii) KMnO<sub>4</sub>, heat

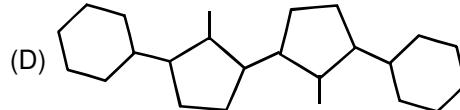
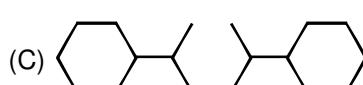
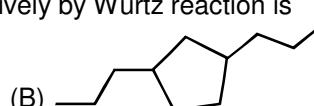
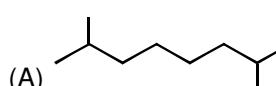
36. 1,3-pentadiene and 1,4-pentadiene are compared with respect to their intrinsic stability and reaction with HI. The correct statement is:

[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

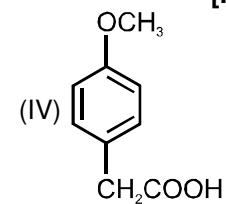
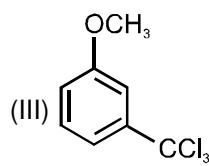
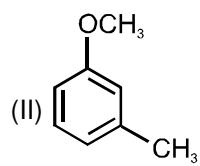
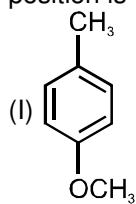
37. The hydrocarbon that cannot be prepared effectively by Wurtz reaction is

[NSEC-2015]



38. The order of reactivity of the following compounds in electrophilic monochlorination the most favorable position is

[NSEC-2015]



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

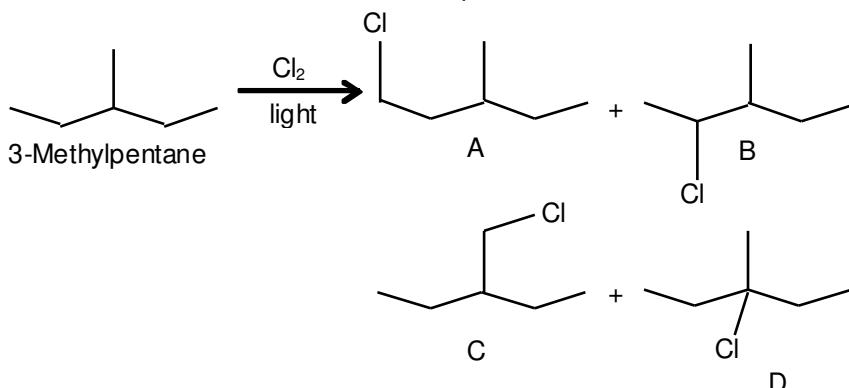
39. The reaction of 1-phenylpropane with limited amount of chlorine in the presence of light gives mainly.

[NSEC-2016]

- (A) 4-chloropropylbenzene    (B) 1-chloro-1-phenylpropane  
 (C) 3-chloro-1-phenylpropane    (D) 2-chloro-1-phenylpropane



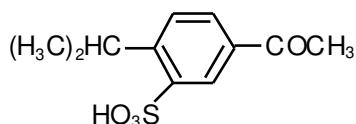
- 40.** 3-Methylpentane on monochlorination gives four possible products. The reaction follows free radical mechanism. The relative reactivities for replacement of  $-H$  are  $3^\circ : 2^\circ : 1^\circ = 6 : 4 : 1$ . [NSEC-2016]



Relative amounts of A, B, C and D formed are



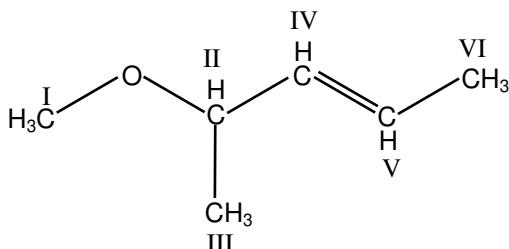
41. The best sequence of reactions for preparation of the following compound from benzene is



[NSEC-2016]

- (A) (i)  $\text{CH}_3\text{COCl}/\text{AlCl}_3$  (ii) Oleum (iii)  $(\text{CH}_3)_2\text{CH}-\text{Cl}$  (1 mole)/ $\text{AlCl}_3$   
(B) (i)  $(\text{CH}_3)_2\text{CH}-\text{Cl}$  (1 mole)/ $\text{AlCl}_3$  (ii)  $\text{CH}_3\text{COCl}/\text{AlCl}_3$  (iii) Oleum  
(C) (i) Oleum (ii)  $\text{CH}_3\text{COCl}/\text{AlCl}_3$  (iii)  $(\text{CH}_3)_2\text{CH}-\text{Cl}$  (1 mole)/ $\text{AlCl}_3$   
(D) (i)  $(\text{CH}_3)_2\text{CH}-\text{Cl}$  (1 mole)/ $\text{AlCl}_3$  (ii) Oleum (iii)  $\text{CH}_3\text{COCl}/\text{AlCl}_3$

- 42.** In the given compound the order of ease with which hydrogen atom can be abstracted from carbons I to VI is : [NSEC-2017]

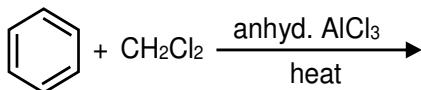


- (A) I > VI > IV = V > I > III      (B) II > I > VI > III > IV = V  
 (C) II > I > III > VI > IV = V      (D) IV > II > I > III > IV = V

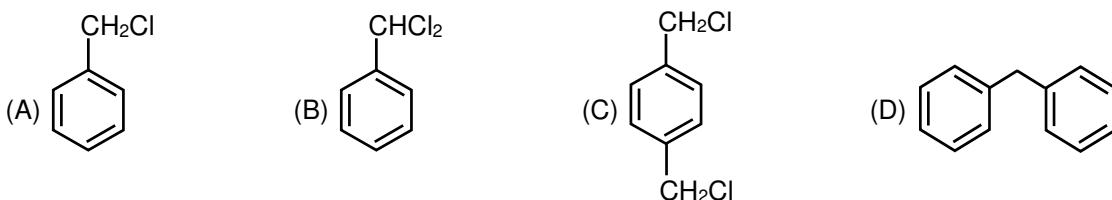
43. Addition of bromine to cis-3-hexene gives  
(A) racemic dibromide  
(B) a mixture of diastereomeric dibromide  
(C) optically active dibromide  
(D) meso dibromide

[NSEC-2017]

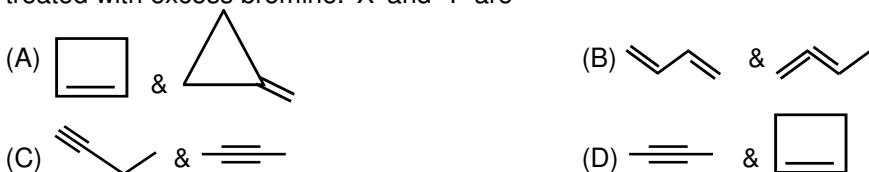
45. The major product of the following reaction is



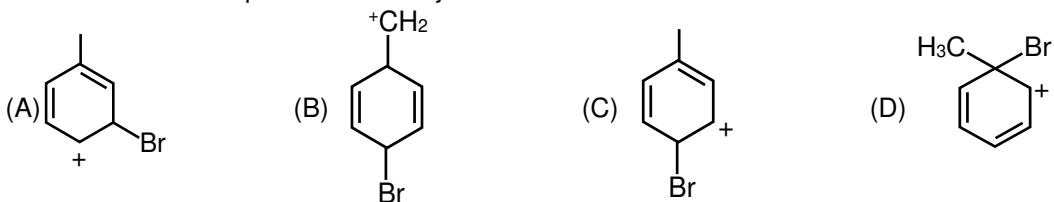
Excess



46. Two isomeric hydrocarbons 'X' and 'Y' ( $\text{C}_4\text{H}_6$ ), give the same product ( $\text{C}_4\text{H}_8\text{O}$ ) on catalytic hydration with dilute acid. However, they form different products but with same molecular formula ( $\text{C}_4\text{H}_6\text{Br}_4$ ) when treated with excess bromine. 'X' and 'Y' are [NSEC-2019]



47. The structure that represents the major intermediate formed in bromination of toluene is [NSEC-2019]



## PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.

Max. Marks : 66

### Important Instructions

#### A. General :

- The test is of 1 hour duration.
- The Test Booklet consists of 22 questions. The maximum marks are 66.

#### B. Question Paper Format

- Each part consists of five sections.
- Section-1 contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
- Section-2 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
- Section-3 contains 5 questions. The answer to each of the questions is a numerical value, ranging from 0 to 9 (both inclusive).
- Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 2 questions relate to paragraph. Each question pertaining to a particular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
- Section-5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

#### C. Marking Scheme :

- For each question in Section-1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (- 1) mark will be awarded.

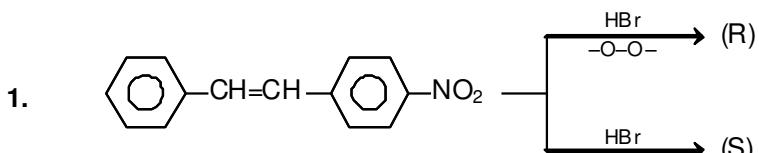


10. For each question in Section-2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be awarded for incorrect answer in this section.

11. For each question in Section-3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

**SECTION-1 : (Only One option correct Type)**

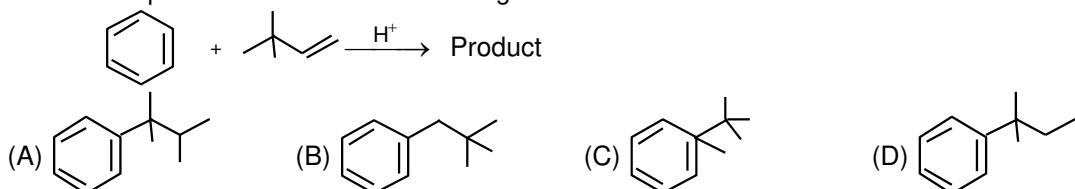
This section contains 8 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.



P & Q are :

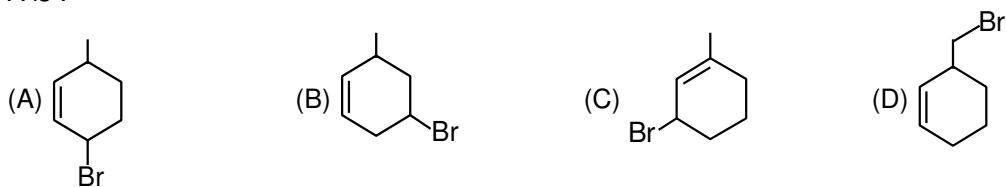


- 2.** What is the product formed in the following reaction.



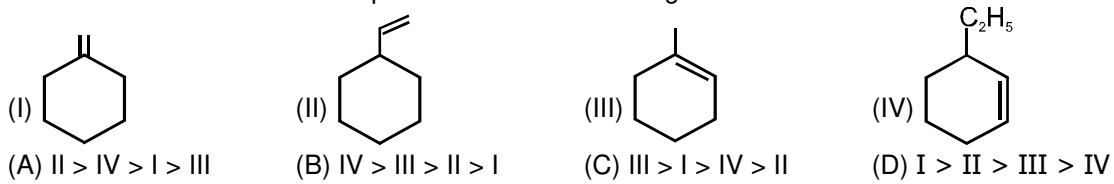
3.  Major product (A)

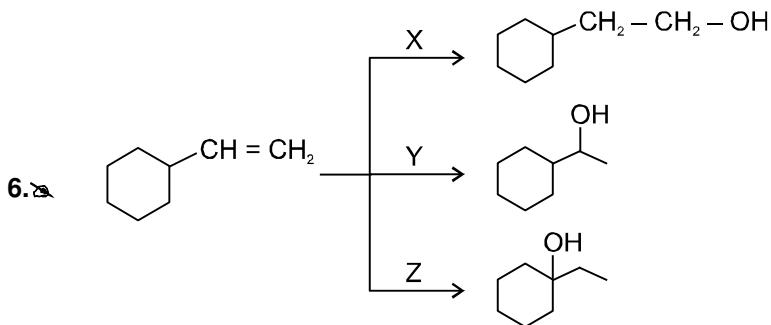
A is :



4. The reaction of toluene with  $\text{Cl}_2$  in presence of  $\text{FeCl}_3$  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

5. What is correct order of electrophilic addition of following alkene ?

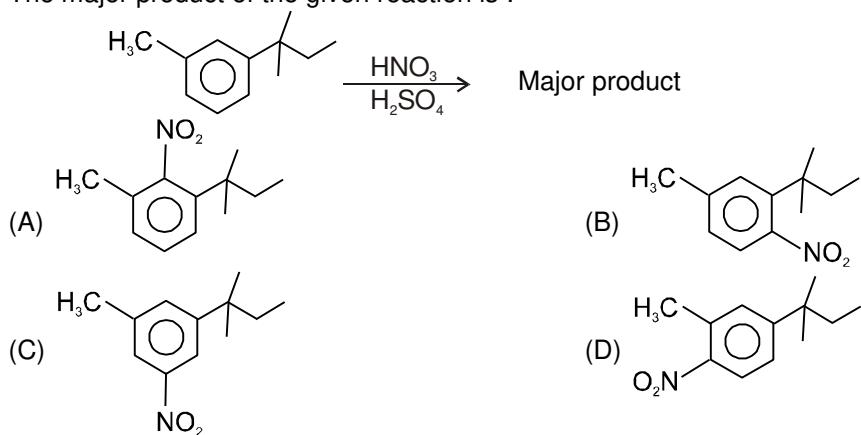




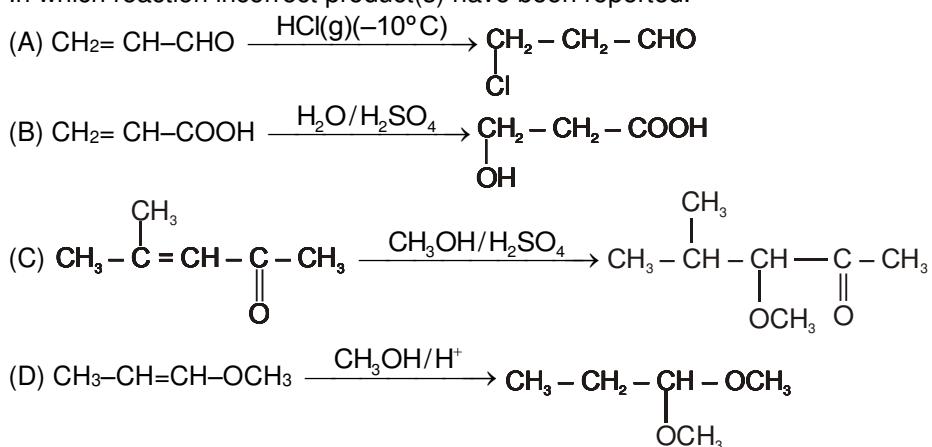
X, Y, Z reaction are :

- (A) Simple hydration reaction  
(B) Hydroboration oxidation, hydration and oxymercuration demercuration  
(C) Hydroboration oxidation, oxymercuration demercuration and hydration  
(D) Oxymercuration demercuration, hydroboration oxidation and hydration

7. The major product of the given reaction is :



**8.** In which reaction incorrect product(s) have been reported.



**Section-2 : (One or More than one options correct Type)**

This section contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

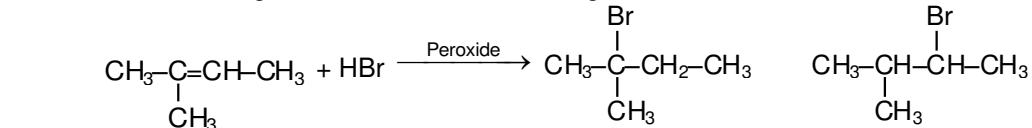
9. In the chlorination of Methane which of the following reaction involve in the chain termination step.



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

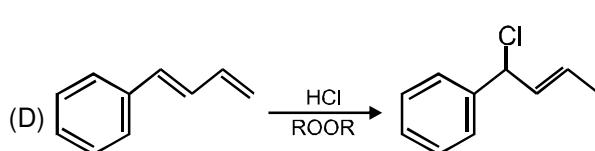
- (A)  $(\text{CH}_3)_3\text{CH} + \text{Br}_2 \xrightarrow{\text{h}\nu} (\text{CH}_3)_3\text{CBr} + \text{HBr}$       (B)  $(\text{CH}_3)_3\text{C}=\text{CH}_2 + \text{Br}_2 \longrightarrow \begin{array}{c} \text{Br} \\ | \\ \text{CH}_3-\text{C}-\text{CH}_2 \\ | \\ \text{CH}_3 \end{array}$
- (C)  $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{Cl}_2 \xrightarrow{\text{h}\nu} \begin{array}{c} \text{CH}_2-\text{CH}=\text{CH}_2 \\ | \\ \text{Cl} \end{array}$       (D)  $\text{Ph}-\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow[\text{h}\nu]{\text{R}_2\text{O}_2} \text{Ph}-\text{CH}_2-\begin{array}{c} \text{Br} \\ | \\ \text{CH}_2 \end{array}$

11. Which of the following statements are correct for give reaction.



- (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.

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

- (A)  $\text{F}_3\text{C}-\text{CH}=\text{CH}_2 + \text{HCl} \longrightarrow \text{F}_3\text{C}-\underset{\text{Cl}}{\text{CH}}-\text{CH}_3$
- (B)  $\text{CH}_3-\text{CH}=\text{CH}-\overset{\text{O}}{\text{C}}-\text{OCH}_3 + \text{ICl} \longrightarrow \begin{array}{c} \text{CH}_3-\underset{\text{Cl}}{\text{CH}}-\text{CH}-\overset{\text{O}}{\text{C}}-\text{OCH}_3 \\ | \\ \text{I} \end{array}$
- (C)  $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_3 + \text{HBr} \xrightarrow{\text{ROOR}} \text{C}_6\text{H}_5\text{CH}_2-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$
- (D) 

13. Which statement is /are correct.

- (A) No primary kinetic isotope effect is observed during nitration of benzene  
 (B)  $K_H/K_D = 1$  for halogenation of benzene  
 (C)  $K_H/K_D = 1$  for sulphonation of benzene  
 (D)  $K_H/K_D$  is  $> 1$  for alkylation of benzene

14. Which of the following statements is/are incorrect ?

- (A) Nitrobenzene will give meta-nitrotoluene on reaction with  $\text{CH}_3\text{Cl}/\text{AlCl}_3$ .  
 (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  $\text{CH}_3\text{Cl}/\text{AlCl}_3$ .

### Section-3 : (Numerical Value Correct Type.)

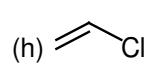
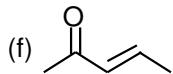
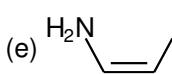
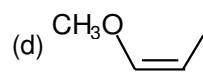
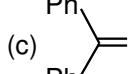
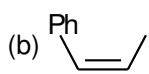
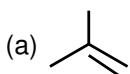
This section contains 5 questions. Each question, when worked out will result in a numerical value from 0 to 9 (both inclusive)

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

- |   |  |   |  |
|---|--|---|--|
| (a) $-\text{NH}_2$                                    | (b) $-\text{NR}_2$                                     | (c) $-\text{NO}_2$                            | (d) $-\text{NH}_3^+$                         |
| $(e) -\text{O}-\overset{\text{O}}{\text{C}}-\text{R}$ | $(f) -\text{NH}-\overset{\text{O}}{\text{C}}-\text{R}$ | $(g) -\overset{\text{O}}{\text{C}}-\text{Cl}$ | $(h) -\overset{\text{O}}{\text{C}}-\text{H}$ |
| $(i) -\text{SO}_3\text{H}$                            | $(j) -\text{CH}_3$                                     | $(k) -\text{CH}=\text{CR}_2$                  |  |

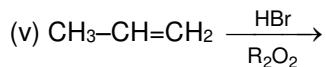
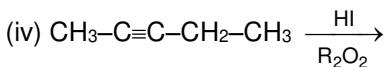
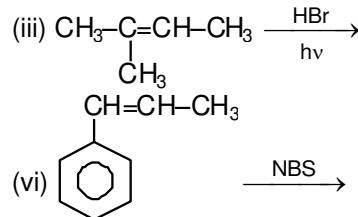
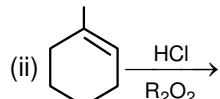
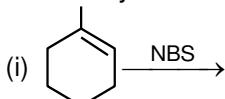


16. How many alkenes react faster than propene with dil.  $\text{H}_2\text{SO}_4$ ?

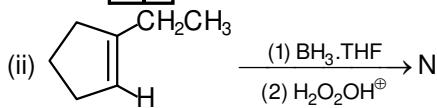
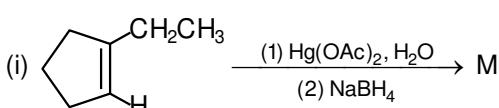


17. When addition of  $\text{Br}_2$  was carried out in presence of aq.  $\text{NaCl}$  on ethene then total number of possible product are –

18. How many reactions will proceed through free radical addition mechanism ?



19. In the given reactions M is the number of major products obtained in I<sup>st</sup> reaction and N number of major products obtained in II<sup>nd</sup> reaction. Report your answer as **[M] [N]**.



#### SECTION-4 : Comprehension Type (Only One options correct)

This section contains 1 paragraphs, each describing theory, experiments, data etc. 2 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D).

#### Paragraph for Question Nos. 20 to 21

Consider experimental data shown in this table :

Alkene	Relative rate	Alkene	Relative rate
$\text{CH}_2=\text{CH}_2$	1	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	5,400
$\text{CH}_2=\text{CH}-\text{CH}_3$	61	$(\text{CH}_3)_2\text{C}=\text{CHCH}_3$	130,000
	1700	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	1,800,000
	2600		

20. Rate of electrophilic addition on isobutylene is significantly higher than cis or trans-2-Butene chiefly due to –

(A) Lesser stability of (isobutylene) in comparison to or .

(B) Higher dipole moment of in comparison to cis or trans-2-Butene.

(C) Better stabilization of positive charge acquired during formation of bromonium ion intermediate by Me-groups

(D) High angle strain in the molecule

21. Which of the following would be expected to have highest rate of electrophilic addition of  $\text{Br}_2$  ?
- (A)  $\text{Ph}-\text{CH}=\text{CH}_2$
- (B)  $\begin{array}{c} \text{Ph} \\ | \\ \text{H}_3\text{C}-\text{C}=\text{CH}_2 \end{array}$
- (C)  $\text{Ph}-\text{CH}=\text{CH}-\text{CH}_3$
- (D) All react with the same rate, since the rate depends only on  $[\text{Br}_2]$  and not on the substrate.

**SECTION-5 : Matching List Type (Only One options correct)**

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct.

22. Match List I (Compounds) with List II (% meta electrophilic substitution product) and select the correct answer using the code given below the lists :

	<b>List I</b>		<b>List II</b>
(P)	$\text{Ar}-\text{CH}_3$	(1)	64.6
(Q)	$\text{ArCH}_2\text{Cl}$	(2)	34
(R)	$\text{ArCHCl}_2$	(3)	4.5
(S)	$\text{ArCCl}_3$	(4)	15

Codes:

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

**Practice Test-2 (IIT-JEE (ADVANCED Pattern))**  
**OBJECTIVE RESPONSE SHEET (ORS)**

<b>Que.</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
<b>Ans.</b>										
<b>Que.</b>	<b>11</b>	<b>12</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>	<b>18</b>	<b>19</b>	<b>20</b>
<b>Ans.</b>										
<b>Que.</b>	<b>21</b>	<b>22</b>								
<b>Ans.</b>										

**APSP Answers****PART – I**

- |            |     |            |     |            |     |            |     |            |     |
|------------|-----|------------|-----|------------|-----|------------|-----|------------|-----|
| <b>1.</b>  | (4) | <b>2.</b>  | (3) | <b>3.</b>  | (1) | <b>4.</b>  | (2) | <b>5.</b>  | (4) |
| <b>6.</b>  | (1) | <b>7.</b>  | (1) | <b>8.</b>  | (3) | <b>9.</b>  | (3) | <b>10.</b> | (2) |
| <b>11.</b> | (4) | <b>12.</b> | (2) | <b>13.</b> | (3) | <b>14.</b> | (4) | <b>15.</b> | (2) |
| <b>16.</b> | (4) | <b>17.</b> | (4) | <b>18.</b> | (3) | <b>19.</b> | (1) | <b>20.</b> | (3) |
| <b>21.</b> | 4   | <b>22.</b> | 4   | <b>23.</b> | 2   | <b>24.</b> | 5   | <b>25.</b> | 3   |

**PART – II**

- |           |     |           |     |           |     |           |     |           |     |
|-----------|-----|-----------|-----|-----------|-----|-----------|-----|-----------|-----|
| <b>1.</b> | (3) | <b>2.</b> | (2) | <b>3.</b> | (3) | <b>4.</b> | (4) | <b>5.</b> | (4) |
| <b>6.</b> | (1) | <b>7.</b> | (3) | <b>8.</b> | (1) | <b>9.</b> | (3) |           |     |

**PART – III**

- |            |     |            |     |            |     |            |     |            |     |
|------------|-----|------------|-----|------------|-----|------------|-----|------------|-----|
| <b>1.</b>  | (D) | <b>2.</b>  | (D) | <b>3.</b>  | (B) | <b>4.</b>  | (D) | <b>5.</b>  | (D) |
| <b>6.</b>  | (B) | <b>7.</b>  | (D) | <b>8.</b>  | (C) | <b>9.</b>  | (C) | <b>10.</b> | (D) |
| <b>11.</b> | (A) | <b>12.</b> | (C) | <b>13.</b> | (C) | <b>14.</b> | (A) | <b>15.</b> | (A) |
| <b>16.</b> | (B) | <b>17.</b> | (B) | <b>18.</b> | (B) | <b>19.</b> | (A) | <b>20.</b> | (D) |
| <b>21.</b> | (B) | <b>22.</b> | (A) | <b>23.</b> | (D) | <b>24.</b> | (C) | <b>25.</b> | (D) |
| <b>26.</b> | (B) | <b>27.</b> | (B) | <b>28.</b> | (B) | <b>29.</b> | (B) | <b>30.</b> | (D) |
| <b>31.</b> | (C) | <b>32.</b> | (B) | <b>33.</b> | (B) | <b>34.</b> | (A) | <b>35.</b> | (A) |
| <b>36.</b> | (A) | <b>37.</b> | (B) | <b>38.</b> | (B) | <b>39.</b> | (B) | <b>40.</b> | (C) |
| <b>41.</b> | (B) | <b>42.</b> | (B) | <b>43.</b> | (A) | <b>44.</b> | (B) | <b>45.</b> | (D) |
| <b>46.</b> | (C) | <b>47.</b> | (C) |            |     |            |     |            |     |

**PART – IV**

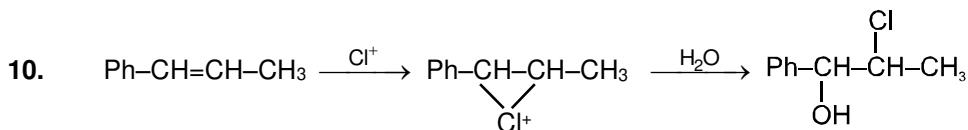
- |            |                          |            |       |            |                      |            |       |            |       |
|------------|--------------------------|------------|-------|------------|----------------------|------------|-------|------------|-------|
| <b>1.</b>  | (A)                      | <b>2.</b>  | (A)   | <b>3.</b>  | (C)                  | <b>4.</b>  | (D)   | <b>5.</b>  | (C)   |
| <b>6.</b>  | (C)                      | <b>7.</b>  | (D)   | <b>8.</b>  | (C)                  | <b>9.</b>  | (BC)  | <b>10.</b> | (ACD) |
| <b>11.</b> | (AD)                     | <b>12.</b> | (BCD) | <b>13.</b> | (AB)                 | <b>14.</b> | (ABC) |            |       |
| <b>15.</b> | 6 (a , b , e, f , j , k) |            |       | <b>16.</b> | 6 (a, b, c, d, e, g) |            |       | <b>17.</b> | 3     |
| <b>18.</b> | 2                        | <b>19.</b> | 12    | <b>20.</b> | (C)                  | <b>21.</b> | (B)   | <b>22.</b> | (B)   |



## APSP Solutions

### PART – I

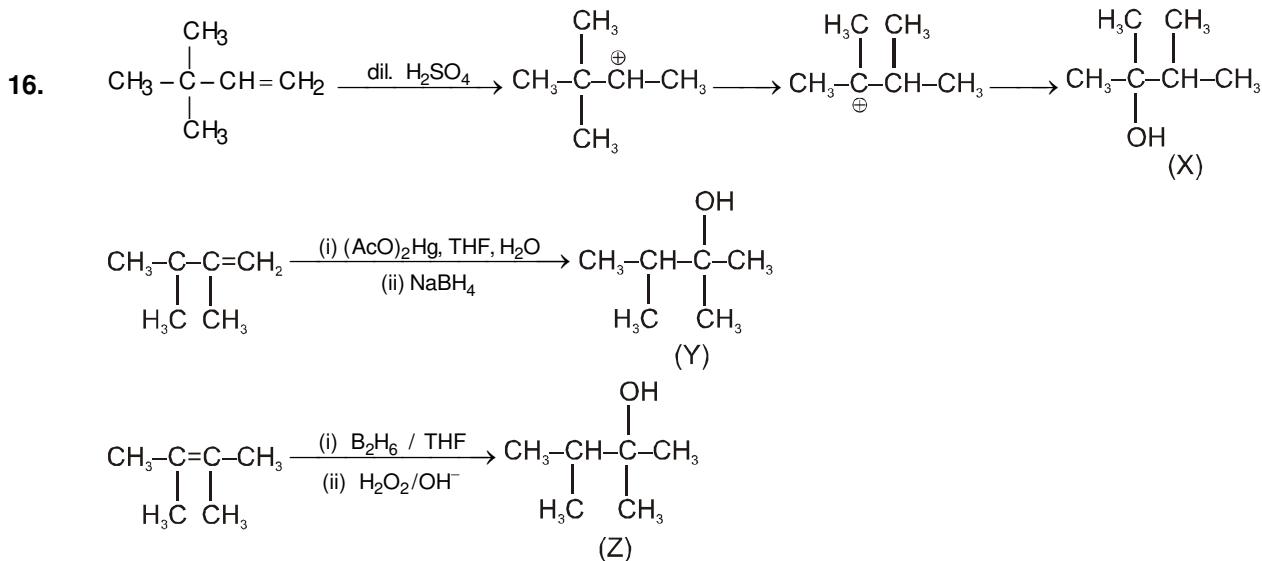
1. It is allylic substitution reaction.
2. Reaction A is free radical addition reaction and all are electrophilic addition reactions.
3. In this reaction  $\text{HNO}_3$  accepts  $\text{H}^+$  from  $\text{H}_2\text{SO}_4$  in the mechanism. Hence it is a base.
4. It is a free radical substitution reaction.
5. In presence of  $+M$  effect rate of mononitration increase and in presence of  $-M$  effect rate will decreases.
6. Chlorination of methane is a free radical reaction which occurs by the following mechanism  
 Initiation  $\text{Cl}\ddot{\text{C}}\text{l} \xrightarrow{\text{Homolytic Fission}} 2\text{Cl}\cdot$
7. Free radical substitution takes place at the highest degree carbon.



11. The rate of electrophilic addition reaction is proportional to stability of carbocation.

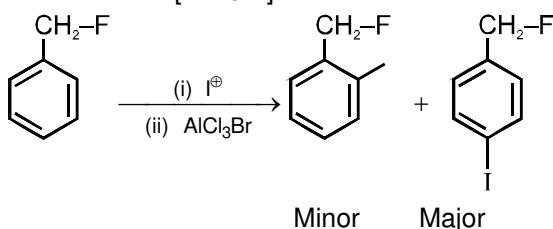
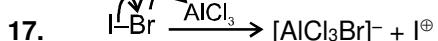
12. Relative yield of product = relative reactivity  $\times$  probability factor  
 For 1° relative yield =  $1 \times 6 = 6$   
 For 2° relative yield =  $3.8 \times 4 = 27.2$

13. It is an anti Markovnikov addition.



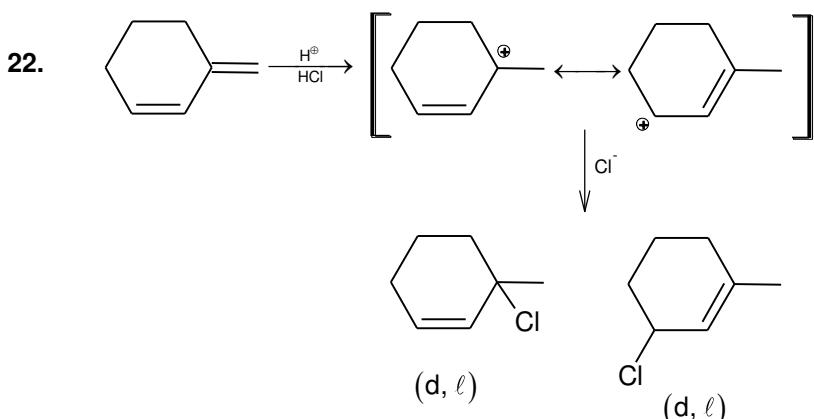
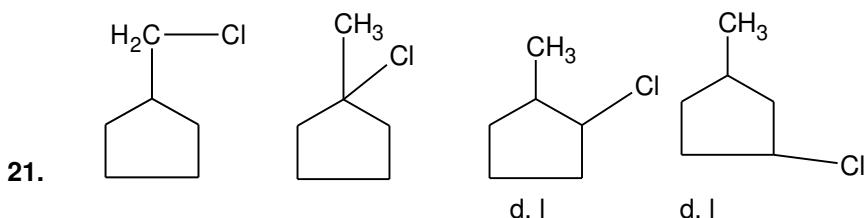
All products are identical.

Hydrocarbon



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

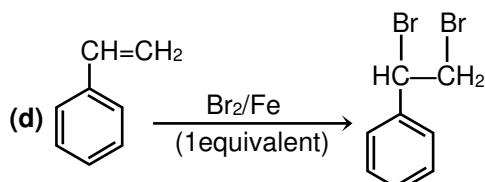
20. The product can be achieved by anti-Markovnikov addition of water.



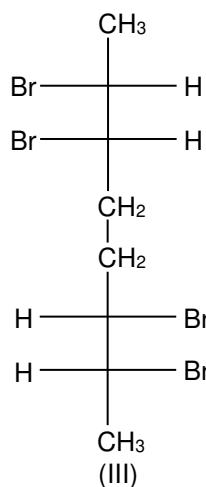
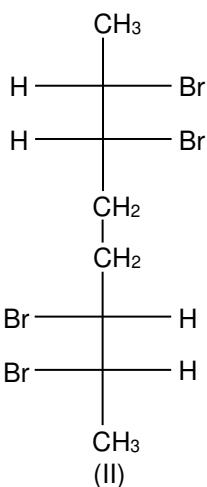
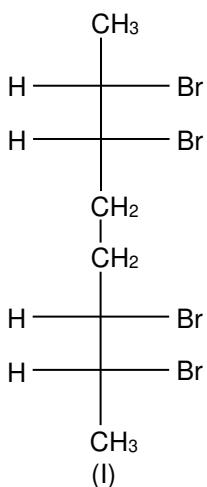
23. 2 (a, e)

- (a) is free radical substitution reaction
- (b) is electrophilic substitution reaction
- (c, d, f) are electrophilic addition reaction
- (e) is free radical addition reaction

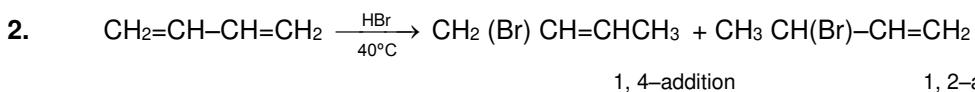
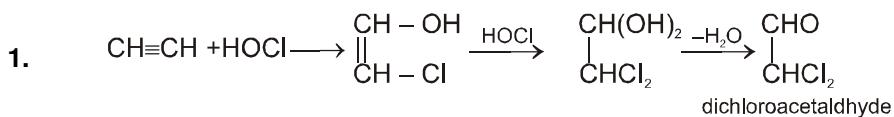
24. (a, b, c, e, f)



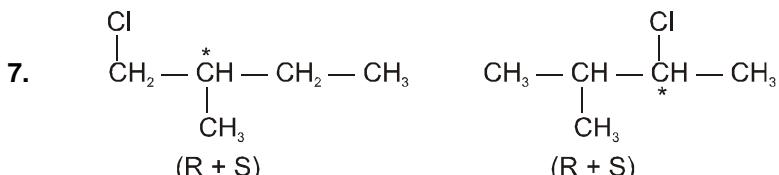
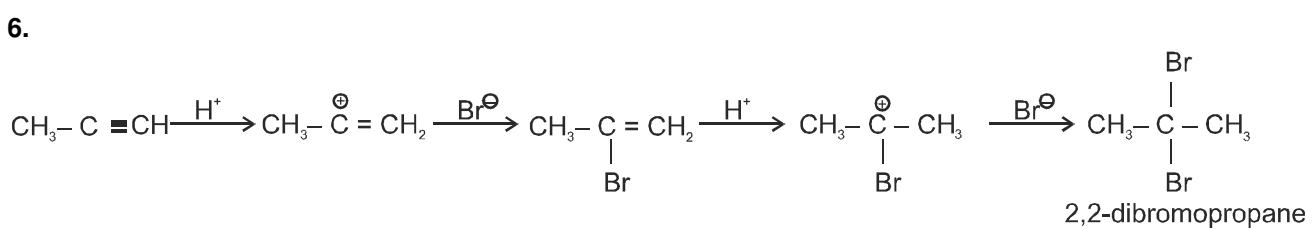
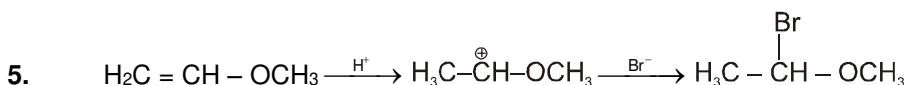
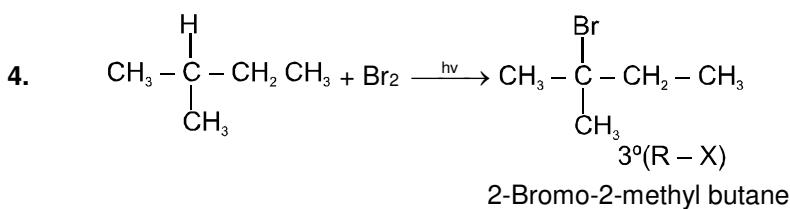
25.



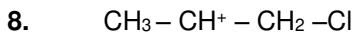
## PART - II



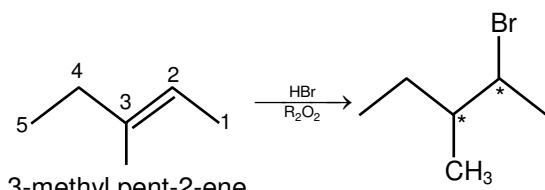
Therefore, 1-bromo-2-butene will be the main product under thermodynamically controlled conditions.



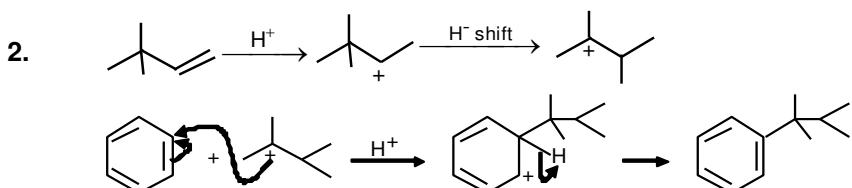
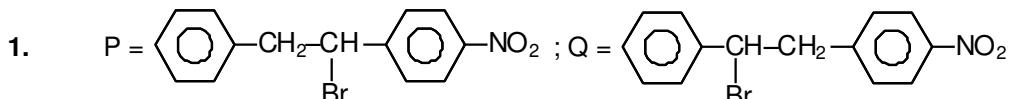
Four monochloro derivatives are chiral.



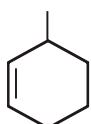
9.



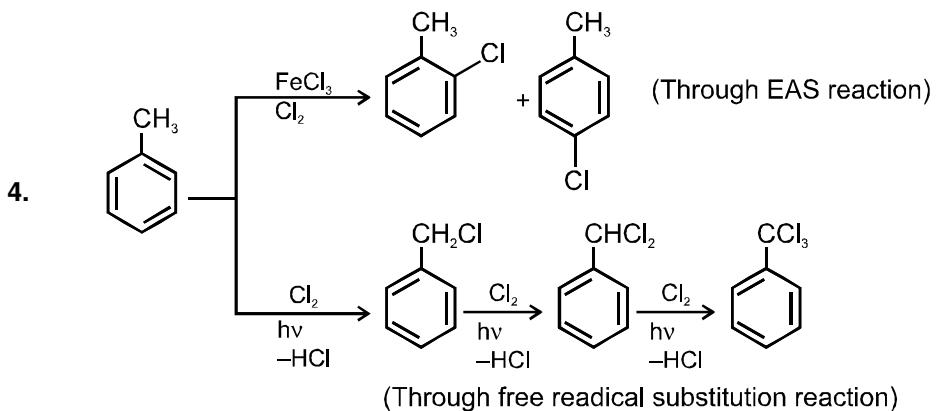
Total stereo centers = 2, Total stereo isomers = 4

**PART – IV**

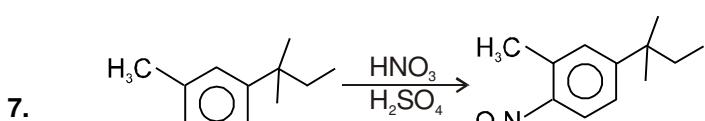
3. The given reaction occur via free radical substitution mechanism. Major product will depend on the stability of free radical.



Most stable free radical

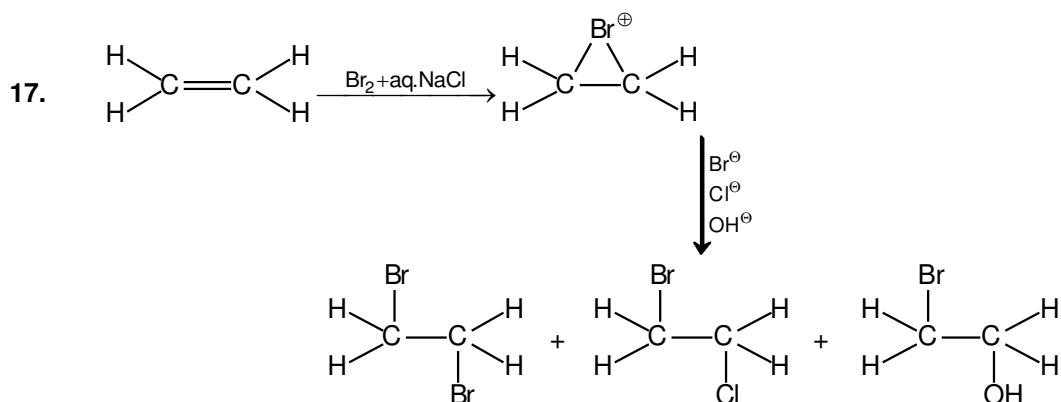


5. Electron releasing group and stability of carbocation/halonium ion will decide rate of reaction in electrophilic addition reaction.
6. X = Hydroboration oxidation, Y = oxymercuration & demercuration, Z = Simple hydration reaction



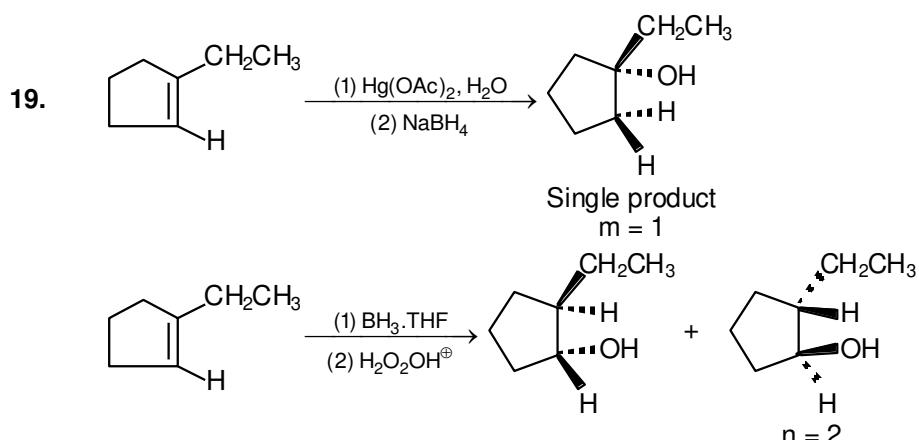
$-\text{C}_6\text{H}_4\text{CH}_3$  group is more ring activity than  $\text{CH}_3\text{CH}_2\text{CH}_3$ , para position wrt  $-\text{CH}_3$  group is more crowded than ortho.

8. The more stable carbocation of alkene gives the major product in electrophilic addition reactions.
9. Option 'D' is chain propagating step.
14. (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.
16. Rate of  $E^\oplus$  addition  $\propto$  stable cation



Formation of these three products clearly indicates about formation of cyclic Bromonium ion.

18. Only (iii) & (v).



22. EWG groups are meta directing.



## NOTES



## NOTES