

## CHAPTER - 11

# HYDROCARBONS

### SYNOPSIS

Certain organic compounds contain only two elements, hydrogen and carbon and are hence known as hydrocarbons.

The main sources of hydrocarbons are natural gas, petroleum and coal; whereas petroleum is the chief source of aliphatic hydrocarbon, coal is the main source of aromatic hydrocarbons.

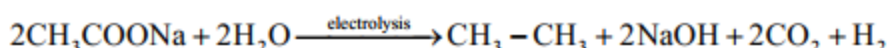
Saturated hydrocarbons are those which contain only single bonds. These are known as alkanes having general formula  $C_nH_{2n+2}$ . Carbon atoms are  $sp^3$  hybridised.

Unsaturated hydrocarbons are those which contain multiple bonds (double or triple). Hydrocarbons containing double bonds are called alkenes ( $sp^2$  hybridised carbon) having general formula  $C_nH_{2n}$  and those containing triple bonds are called alkynes ( $sp$ -hybridised) having general formula  $C_nH_{2n-2}$ .

### ALKANES

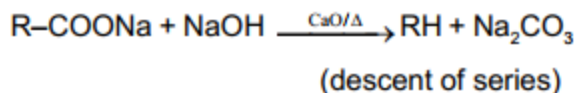
Methods of preparation of alkanes

1. By Kolbe's electrolysis from sodium or potassium salt of fatty acids.

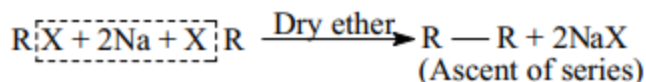


Only alkanes with even number of carbon atoms can be formed.

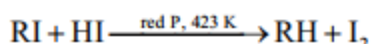
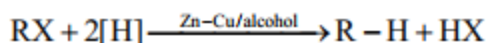
2. By sodalime decarboxylation of sodium or potassium salts of fatty acids.



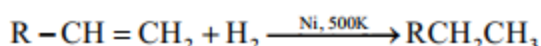
By Wurtz reaction from alkyl halides



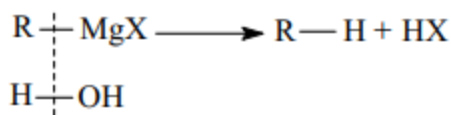
By reduction of alkyl halides



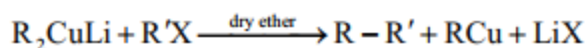
By catalytic hydrogenation of unsaturated hydrocarbons (Sabatier-Senderen's reaction)



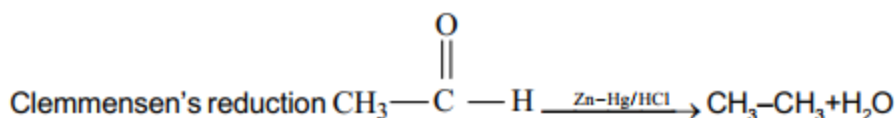
From Grignard reagent



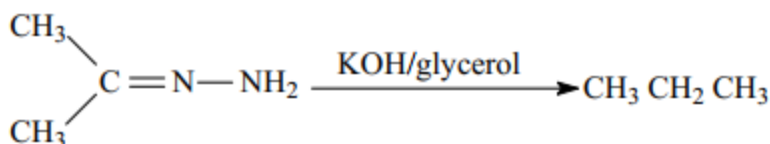
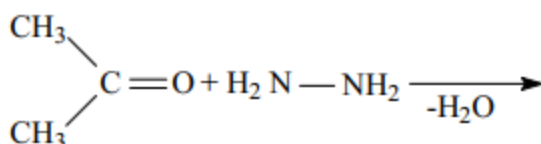
Corey-House synthesis



Frankland reaction  $\text{R} - \boxed{\text{X} + \text{Zn} + \text{X}} - \text{R} \xrightarrow{\text{dry ether}} \text{ZnX}_2 + \text{R} - \text{R}$



Wolf-Kishner reduction



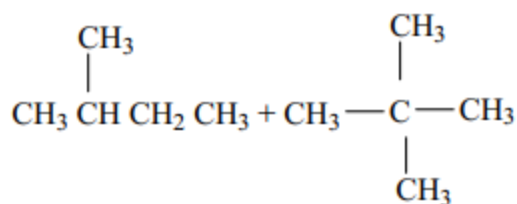
### Physical properties of alkanes

- ❖ The boiling point of straight chain alkanes increases regularly with increase in molecular mass. Boiling point of straight chain isomers are more than branched chain isomers.
- ❖ Alkanes with even number of carbon atoms have higher melting point as compared to next higher or lower alkanes with odd number of carbon atoms. This is called alternation effect or oscillation effect.

### Chemical properties

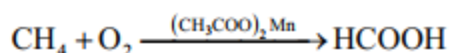
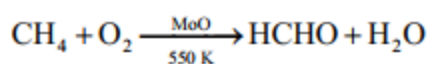
- ❖ Nitration :  $\text{RH} + \text{HONO}_2 \xrightarrow{\Delta} \text{RNO}_2 + \text{H}_2\text{O}$

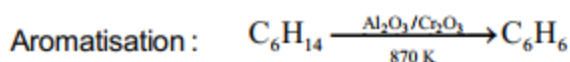
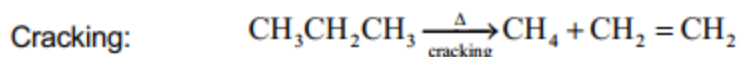
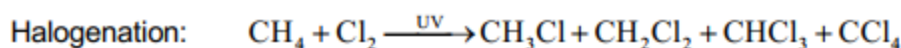
Isomerisation :  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \xrightarrow{\text{anhy. AlCl}_3}$



Sulphonation :  $\text{R} - \text{H} + \text{H}_2\text{SO}_4 \xrightarrow{\Delta} \text{RSO}_3\text{H} + \text{H}_2\text{O}$

Oxidation :  $\text{CH}_4 + \text{O}_2 \xrightarrow{\text{Cu tubes}} \text{CH}_3\text{OH}$



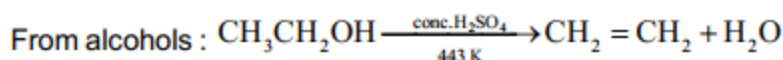


## Alkenes

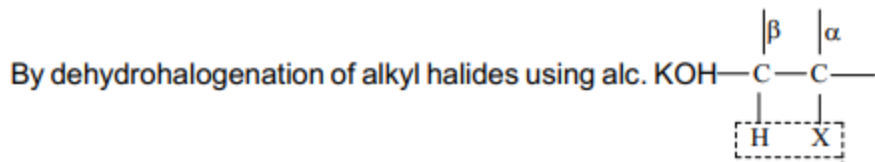
Ethylene is a flat molecule and the carbon-carbon double bond is made up of a strong  $\sigma$ -bond and weak  $\pi$ -bond.

The C—C distance in ethylene molecule is  $1.34 \text{ \AA}$  as compared with the C—C distance of  $1.53 \text{ \AA}$  in ethane.

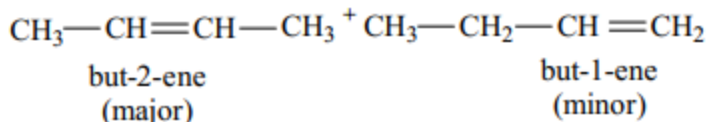
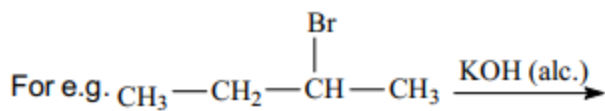
## Methods of preparation of alkenes



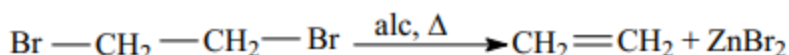
The ease of dehydration of alcohols follows the order  $3^\circ > 2^\circ > 1^\circ$ .



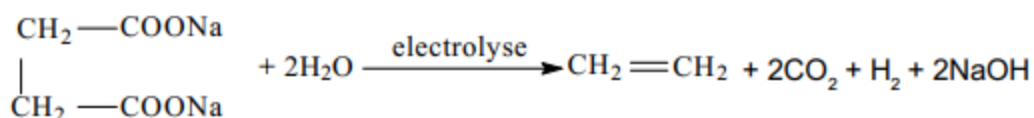
If dehydrohalogenation can occur in two ways, the formation of product is according to Saytzeff's rule.



By dehydrohalogenation of vicinal dihalides

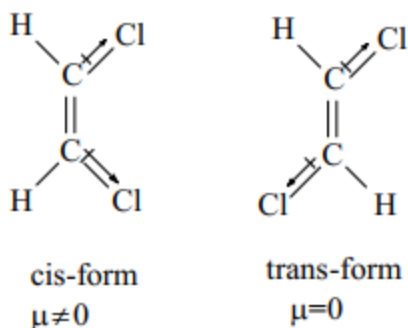


By Kolbe's electrolysis of sodium succinate



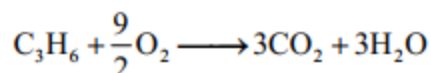
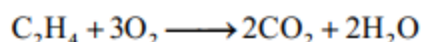
## Physical properties

The boiling points of cis-alkenes are higher whereas melting points of trans-alkenes are more.

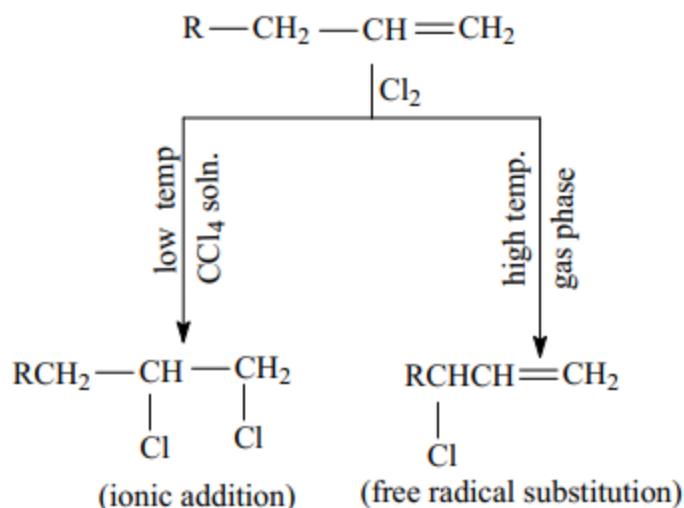


## Chemical properties

Combustion reaction

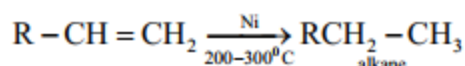


Reaction with halogens:



Addition of halogen is stereoselective (trans).

Hydrogenation:



Reaction with halogen acid  $\text{RCH} = \text{CHR} + \text{HX} \longrightarrow \text{RCH}_2\text{CHXR}$

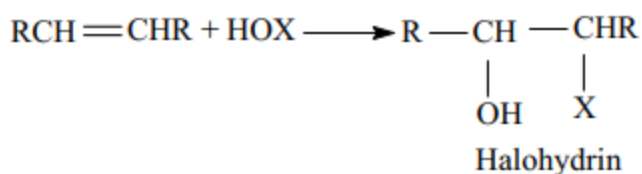
Order of reactivity of the halogen acid is  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

**Markovnikov's rule** : "When addition takes place across the multiple bond of unsymmetrical alkene or alkyne, then the negative part of the addendum goes to that carbon atom, which contains lesser number of hydrogen atom(s)"

**The peroxide effect** : The presence of oxygen or peroxides that are formed when the alkene stands exposed to the air, or added peroxide such as benzoyl peroxide, causes the addition of HBr to take place in the direction opposite to that predicted by Markovnikov's rule. HCl, HI, HF do not exhibit this abnormal reaction.

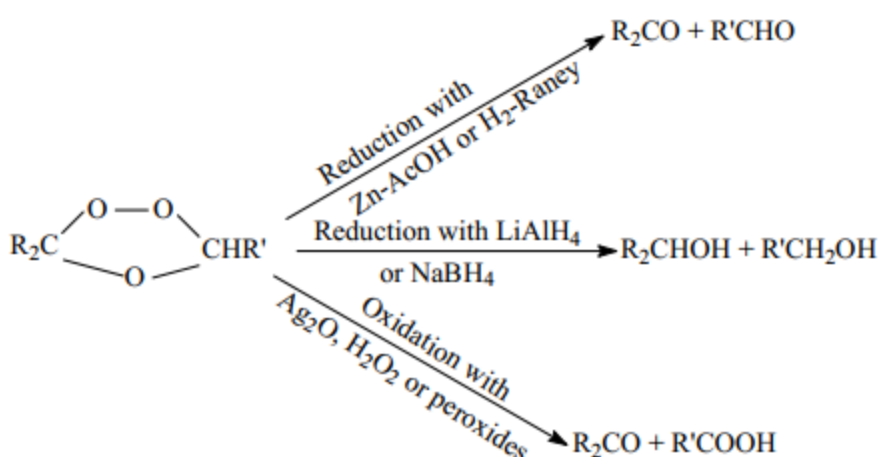
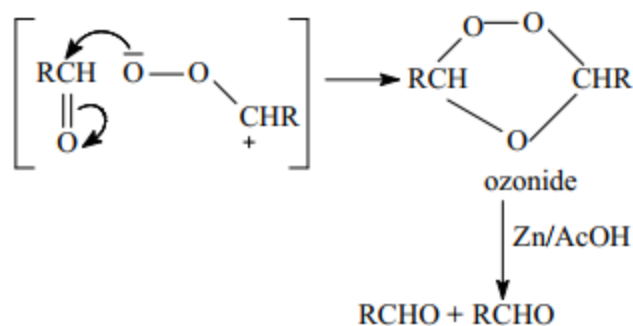
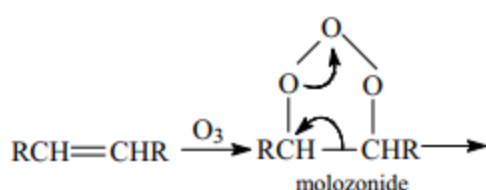
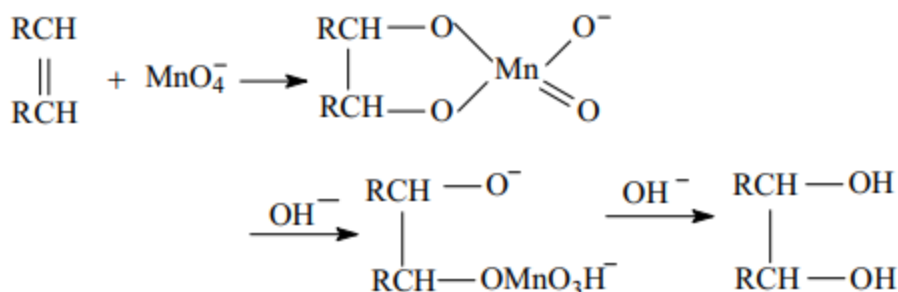
The mechanism of the peroxide effect is a free radical chain reaction

## Reaction with hypohalous acid

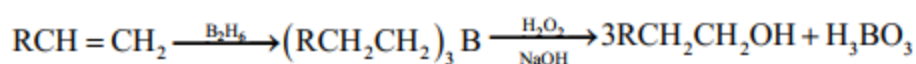


### Hydroxylation

Alkaline  $\text{KMnO}_4$  oxidises alkene to glycol and pink colour fades. This is a test for unsaturation, called Baeyer test and alkaline  $\text{KMnO}_4$ ,  $(\text{MnO}_4^- + \text{OH}^-)$  is called Baeyer's reagent.

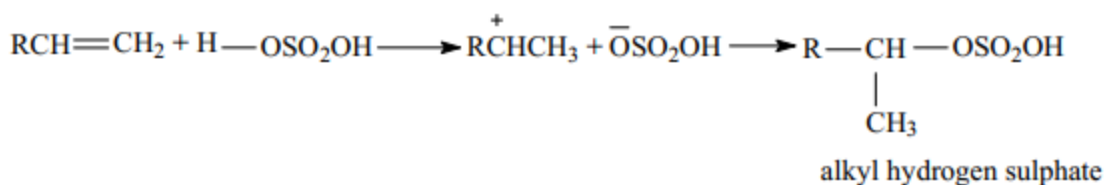


### Hydroboration

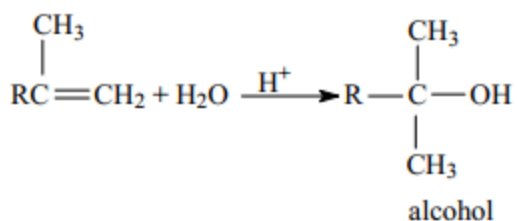


The addition is syn-addition.

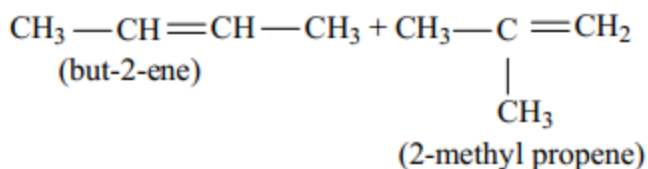
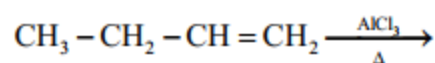
Reaction with conc.  $\text{H}_2\text{SO}_4$



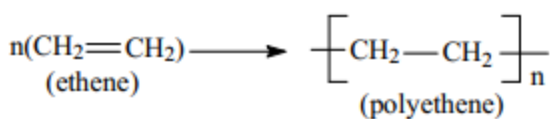
### Hydration



### Isomerisation

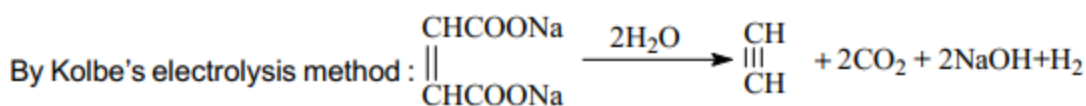
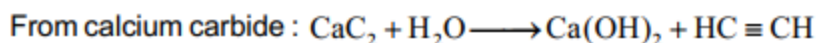


Polymerisation

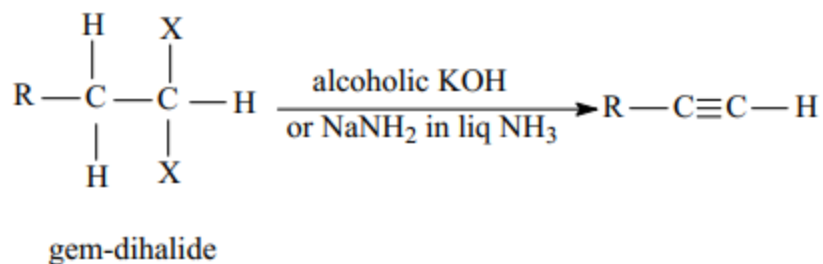
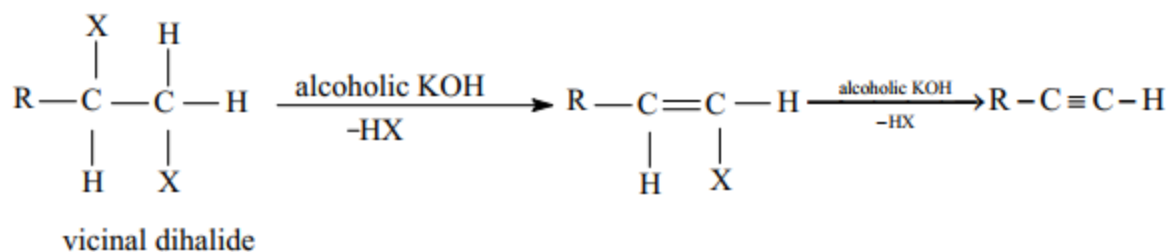


## Alkynes

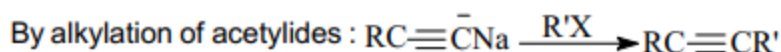
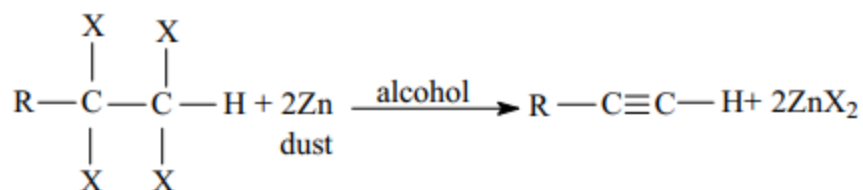
### Methods of preparation of alkynes



By dehydrohalogenatio of vicinal and gem-dihalides



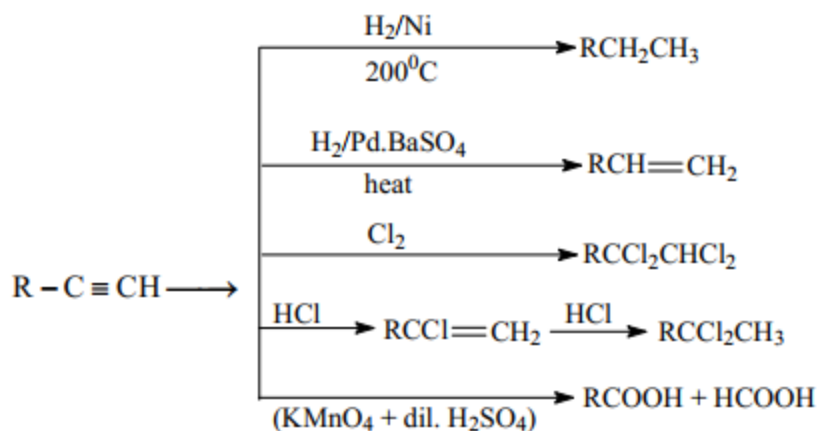
By dehalogenation of tetrahalide or trihalide



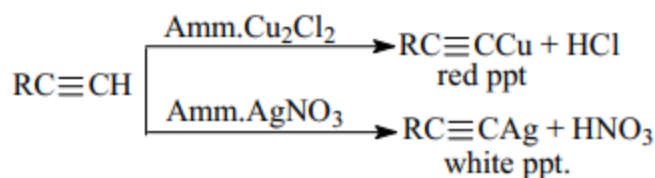
R'X should be 1° alkyl halide since higher 2° and 3° halides give mainly alkenes when they react with sodium salt of alkyne.

### Chemical properties

Addition reactions:

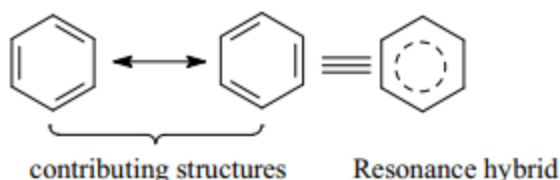


Substitution reactions :



## BENZENE

Structure of benzene : The orbital structure of benzene is explained on the basis of hybridisation. All the carbon atoms in the molecule are  $sp^2$  hybridised which means that the three orbitals in the valence shell of each carbon atom are hybridised to form three equivalent hybrid orbitals.



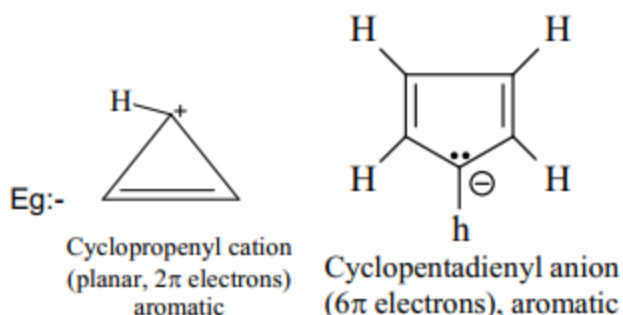
## Aromaticity (Huckel rule)

The main essentials for aromaticity are

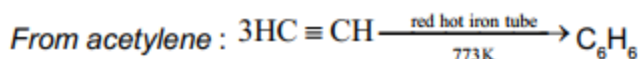
The molecule should contain a cyclic cloud of delocalised  $\pi$ -electrons above and below the molecular plane.

For molecule to be aromatic, the ring must be planar.

For aromaticity, there must be a total of  $(4n + 2)\pi$  electrons. This is known as Huckel's rule.



## Methods of preparation of benzene



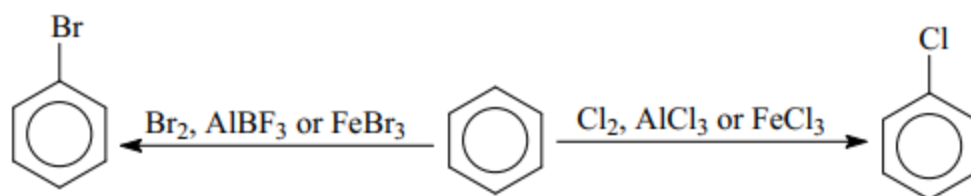
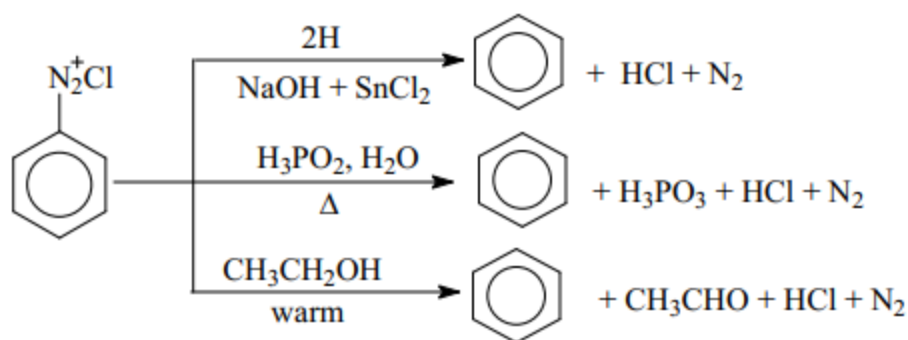


From sodium benzoate (lab method) :  $\text{C}_6\text{H}_5\text{COONa} + \text{NaOH} \xrightarrow{\text{CaO}} \text{C}_6\text{H}_6 + \text{Na}_2\text{CO}_3$

From phenol :  $\text{C}_6\text{H}_5\text{OH} \xrightarrow[\text{distillation}]{\text{Zn-dust}} \text{C}_6\text{H}_6 + \text{ZnO}$

From chlorobenzene by reduction :  $\text{C}_6\text{H}_5\text{Cl} + 2[\text{H}] \xrightarrow[\text{NaOH}]{\text{Na-Al alloy}} \text{HCl} + \text{C}_6\text{H}_6$

From reduction of diazonium compounds:

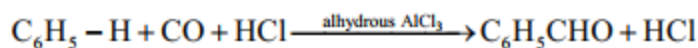


Direct iodination is reversible and hence is carried out in the presence of  $\text{HIO}_3$  or  $\text{HNO}_3$  which makes this reaction irreversible.

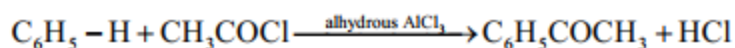
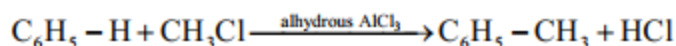
Nitration :  $\text{C}_6\text{H}_6 + \text{HNO}_3 \xrightarrow[330\text{ K}]{\text{H}_2\text{SO}_4} \text{C}_6\text{H}_5 - \text{NO}_2 + \text{H}_2\text{O}$

Sulphonation :  $\text{C}_6\text{H}_6 + \text{H}_2\text{SO}_4 \xrightarrow[330\text{ K}]{\text{SO}_3} \text{C}_6\text{H}_5 - \text{SO}_3\text{H}$

Gattermann-Koch aldehyde synthesis :



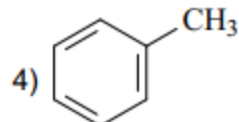
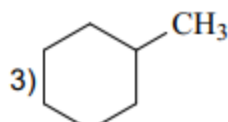
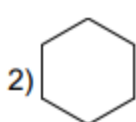
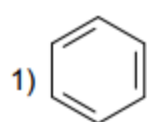
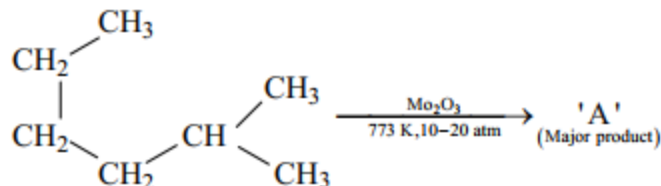
Alkylation and acylation (Friedel-Crafts reactions):



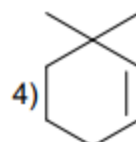
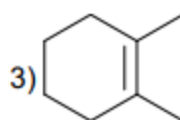
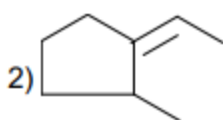
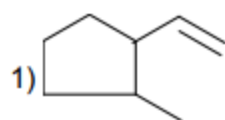
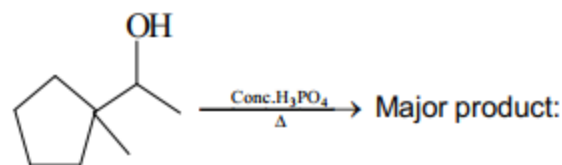
**PART-I (JEE MAIN)**

**SECTION-I- Straight objective type questions**

- CH<sub>4</sub> is formed when
  - 1) Sodium acetate is heated with soda lime
  - 2) Chloromethane is treated with sodium in dry ether
  - 3) Aqueous solution of sodium acetate is electrolysed
  - 4) All of the above
- Photochemical chlorination of alkane is initiated by a process of:
  - 1) pyrolysis
  - 2) substitution
  - 3) homolysis
  - 4) peroxidation
- n-pentane and isopentane can be distinguished by
  - 1) Br<sub>2</sub>
  - 2) O<sub>3</sub>
  - 3) conc. H<sub>2</sub>SO<sub>4</sub>
  - 4) KMnO<sub>4</sub>
- n-pentane is converted to isopentane on treatment with
  - 1) LiAlH<sub>4</sub>
  - 2) H<sub>2</sub>/Ni
  - 3) AlCl<sub>3</sub>/HCl
  - 4) Zn/HCl
- Identify 'A' in the given chemical reaction



- Identify the major product in the following chemical reaction



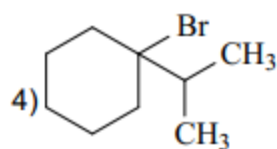
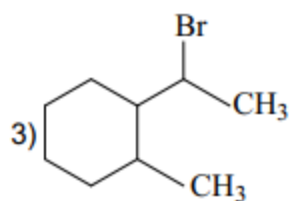
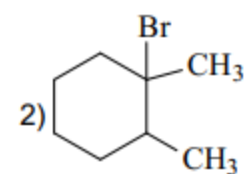
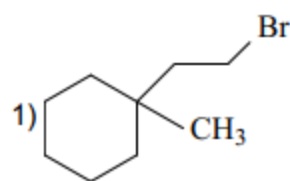
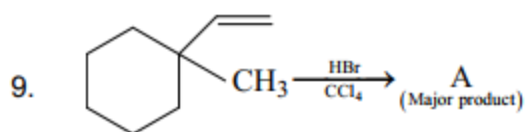
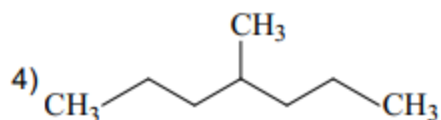
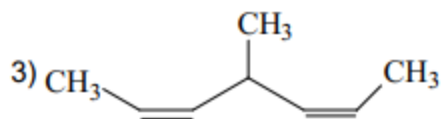
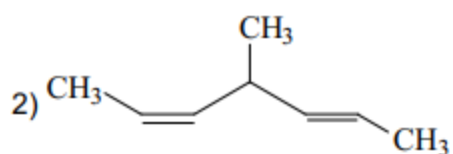
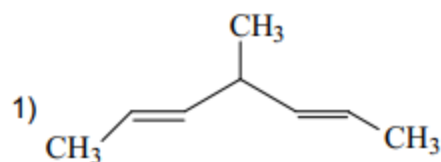
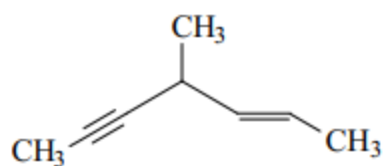
7. Statement 1 : Addition of  $\text{Br}_2$  to 1-butene gives 1,2-dibromobutane

Statement 2 : The product contains one asymmetric carbon

Choose the correct option

- 1) Both statement 1 and statement 2 are correct
- 2) Both statement 1 and statement 2 are incorrect
- 3) Statement 1 is correct but statement 2 is incorrect
- 4) Statement 1 is incorrect but statement 2 is correct

8. Hydrogenation of the following compound in the presence of Lindlar's catalyst gives

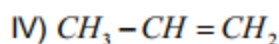
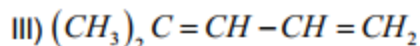
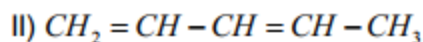
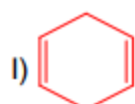


10. But-2-ene on reaction with alkaline  $\text{KMnO}_4$  at elevated temperature followed by acidification will give:

- 1) one molecule of  $\text{CH}_3\text{CHO}$  and one molecule of  $\text{CH}_3\text{COOH}$
- 2) one molecule of  $\text{CH}_3-\text{CH}(\text{OH})-\text{CH}(\text{OH})-\text{CH}_3$
- 3) two molecules of  $\text{CH}_3\text{COOH}$
- 4) two molecules of  $\text{CH}_3\text{CHO}$

11. Match each of the compounds in Column-I with the product of reductive ozonolysis ( $\text{O}_3 + \text{Zn}/\text{H}_2\text{O}$ ) in Column-II

**Column-I**



**Column-II**

P) Formaldehyde

Q) Glyoxal

R) Propane-1,3-dial

S) Acetone

T) Acetaldehyde

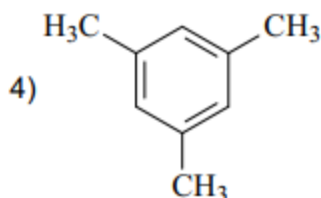
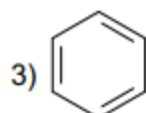
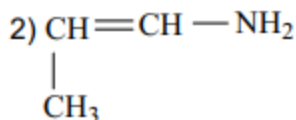
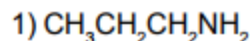
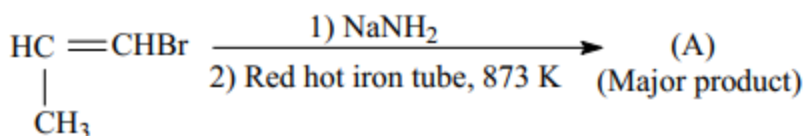
A) I  $\rightarrow$  R; II  $\rightarrow$  PQ; III  $\rightarrow$  PQS; IV  $\rightarrow$  PT

B) I  $\rightarrow$  Q; II  $\rightarrow$  PQ; III  $\rightarrow$  PQT; IV  $\rightarrow$  T

C) I  $\rightarrow$  Q; II  $\rightarrow$  PQ; III  $\rightarrow$  PQS; IV  $\rightarrow$  PT

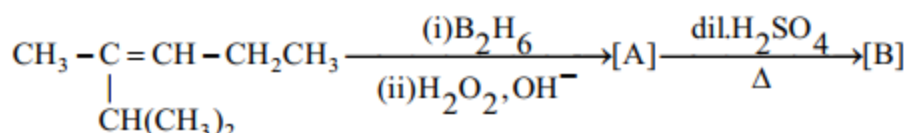
D) I  $\rightarrow$  R; II  $\rightarrow$  PQT; III  $\rightarrow$  PQS; IV  $\rightarrow$  PT

12. The major product(A) in the following reaction is

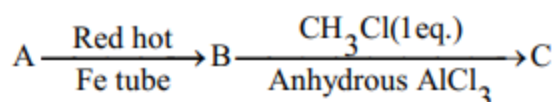


**SECTION-II - Numerical Type Questions**

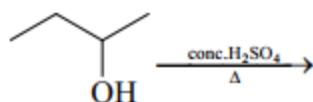
13. How many of the following compounds will form acetic acid on reaction with acidic  $\text{KMnO}_4$ ?  
Prop-1-ene, 2-Methylbut-2-ene, 2-Methylpropene, But-2-ene, Cyclohexene
14. How many  $\text{sp}^3$  hybridized carbon atom(s) is/are present in the major product (B) of the following reaction sequence?



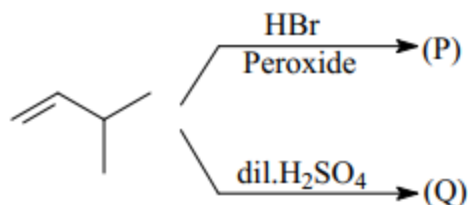
15. In the following sequence of reactions, the maximum number of atoms present in molecule 'C' in one plane is ..... (A is the lowest molecular weight alkyne)



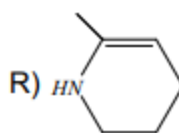
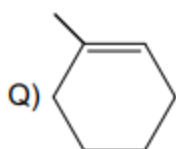
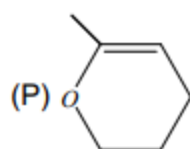
16. The total number of organic product (including stereoisomers) obtained in the following reaction is .....



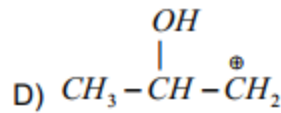
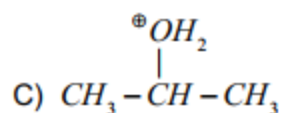
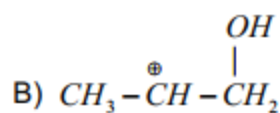
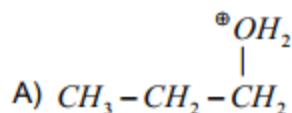
17. The total number of asymmetric carbon atom(s) present in the major products (P) and (Q) of the following reactions is .....

**PART-II (JEE ADVANCED)****Section-III - Only one option correct type**

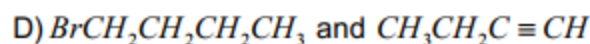
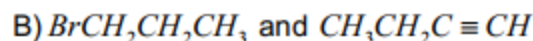
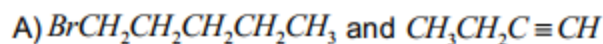
18. Rank the following in the increasing order of rate of reaction with HBr.

A)  $\text{R} > \text{P} > \text{Q}$ B)  $\text{R} > \text{Q} > \text{P}$ C)  $\text{Q} > \text{R} > \text{P}$ D)  $\text{P} > \text{Q} > \text{R}$

19. The reaction of propene with  $\text{dil. H}_2\text{SO}_4$  will proceed through which one of the following intermediates?



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



21. In the presence of a peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markovnikov addition to alkenes because

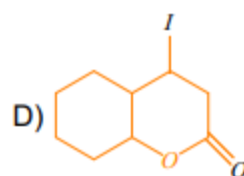
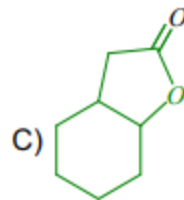
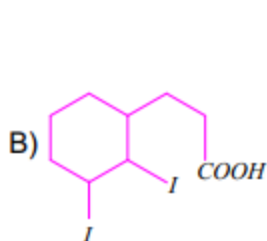
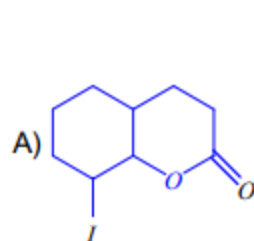
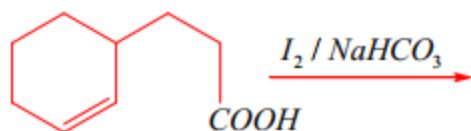
A) both are highly ionic

B) one is oxidising and the other is reducing

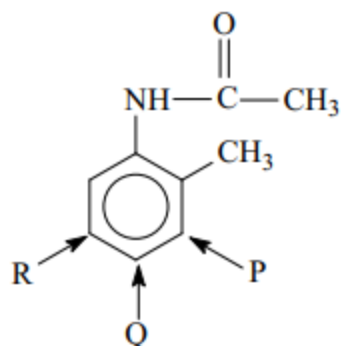
C) one of the steps is endothermic in both the cases

D) all steps are endothermic in both the cases

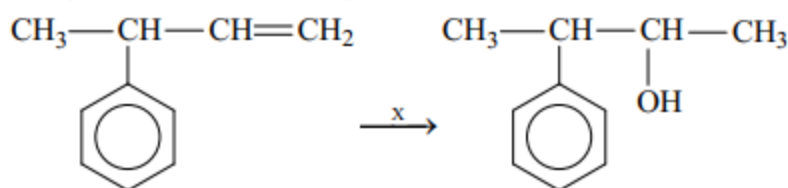
22. The major product in the following reaction is



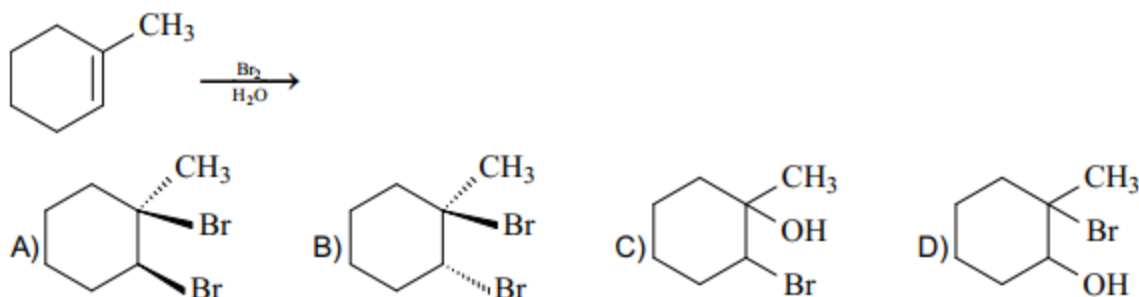
23. Identify the position where electrophilic aromatic substitution is most favourable in the following compound



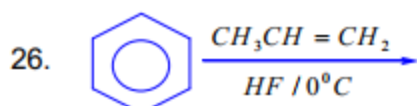
24. Reagent 'X' in the following reaction is



25. The major product in the following reactions is



#### Section IV - One or more option correct type



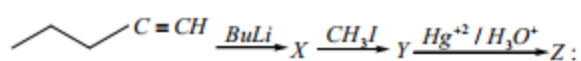
In the above reaction :

- A) The attacking electrophile is  $\text{CH}_3\overset{\oplus}{\text{C}}\text{HCH}_3$  B) The major product is
- C) HF is a catalyst D) The major product is

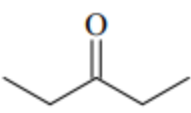
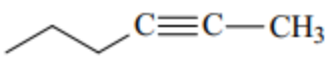
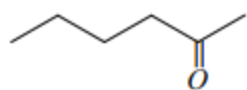
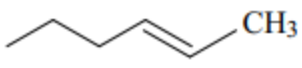
27. Addition of one equivalent of HBr on (P)  $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{CH} = \text{CH}_2$  and (Q)  $\text{CH} \equiv \text{C} - \text{CH} = \text{CH}_2$  separately gives

- A)  $\text{CH} \equiv \text{C} - \text{CH}_2 - \text{CHBr} - \text{CH}_3$  in case of P
- B)  $\text{CH}_2 = \text{CBr} - \text{CH} = \text{CH}_2$  in case of Q
- C)  $\text{CH}_2 = \text{CBr} - \text{CH}_2 - \text{CH} = \text{CH}_2$  in case of P
- D)  $\text{CH} \equiv \text{C} - \text{CHBr} - \text{CH}_3$  in case of Q

28. Consider the reaction



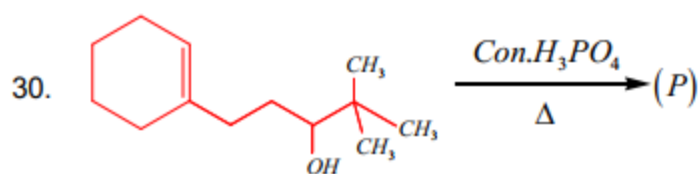
Choose the correct option(s)

- A) Z is 
- B) Y is 
- C) Z is 
- D) Y is 

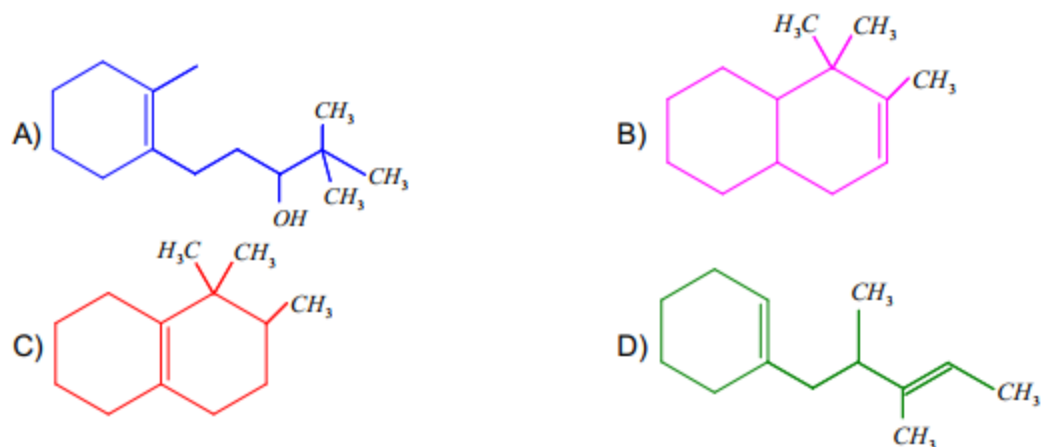
29. The addition of  $\text{Br}_2$  to trans-2-butene produces

- A) (+)-2,3-dibromobutane
- B) (-)-2,3-dibromobutane
- C) Optically inactive 2,3-dibromobutane
- D) meso-2,3-dibromobutane



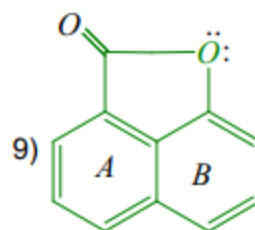
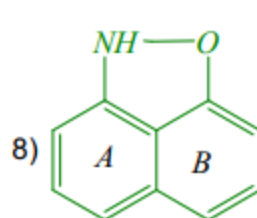
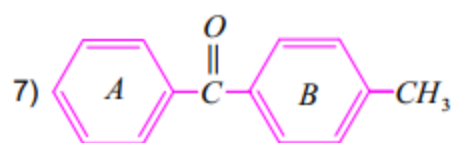
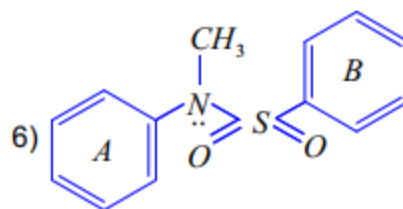
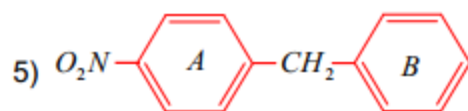
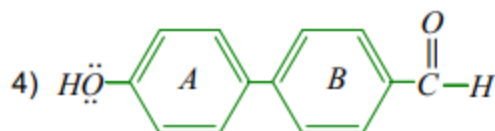
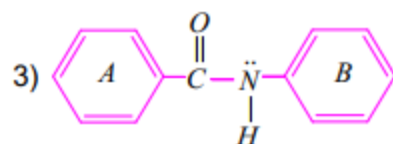
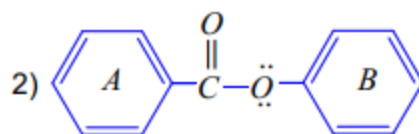
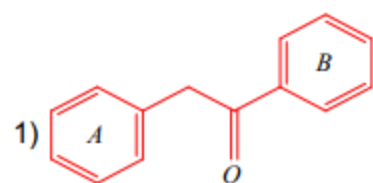


Product (P) may not be

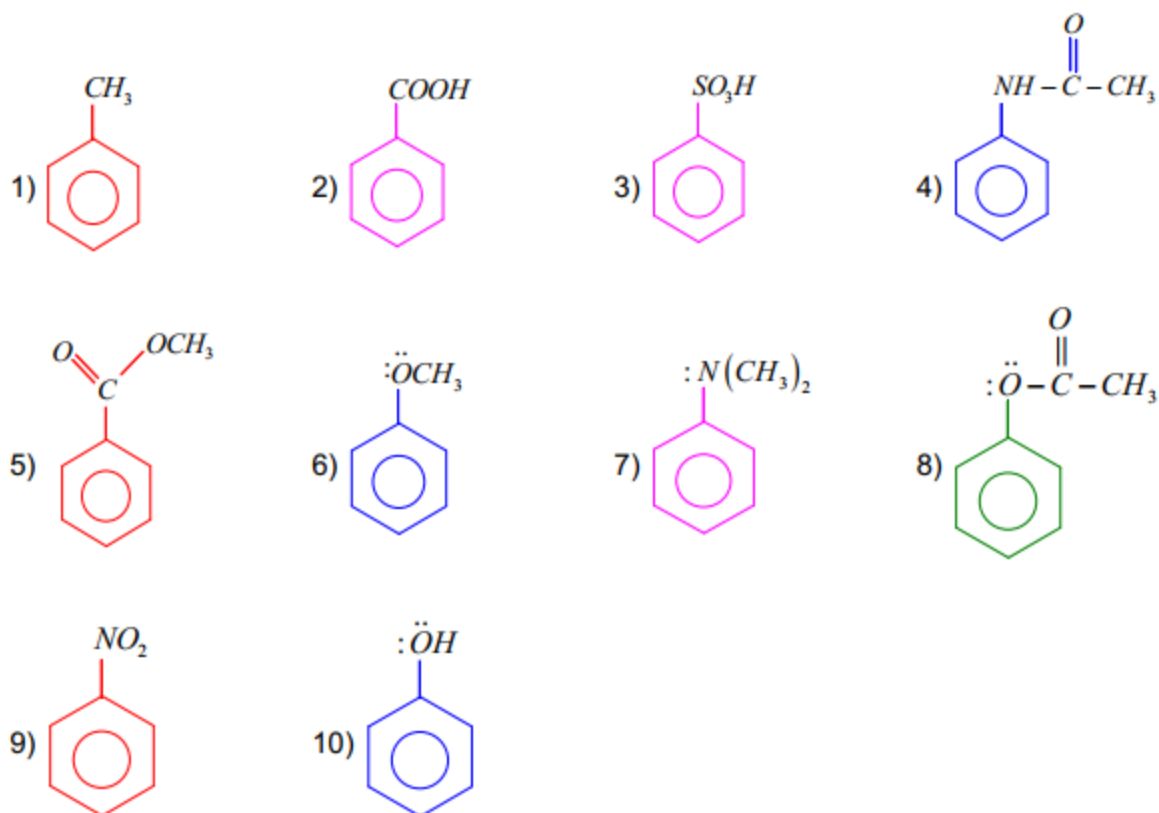


### Section V - Numerical type questions

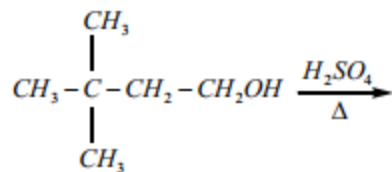
31. Each of the compounds shown below has two aromatic rings labelled as 'A' and 'B'. Identify the total number of compound(s) in which ring 'B' is more reactive than ring 'A' for electrophilic aromatic substitution reaction.



32. Examine the structural formulas shown below and find out the total number of compound(s) that can undergo electrophilic nitration more rapidly than fluorobenzene.



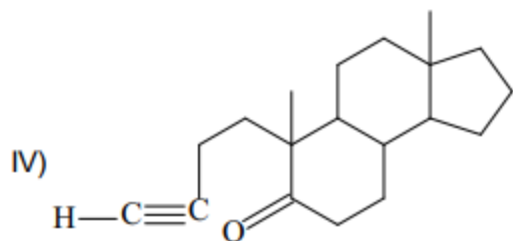
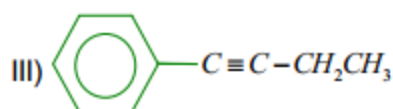
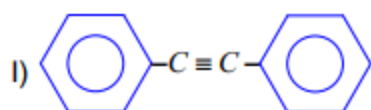
33. The total number of alkenes (including stereoisomers) obtained by dehydrobromination of 3-bromo-3-cyclopentylhexane using alcoholic KOH is .....
34. In bromination of propyne with bromine, 1,1,2,2-tetrabromopropane is obtained in 27% yield. The amount of 1,1,2,2-tetrabromopropane obtained from 1 g of bromine in this reaction is .....  $\times 10^{-1}$  g. (Molar mass: Bromine = 80 g/mol)
35. The number of alpha-hydrogen atoms present in the most stable carbocation intermediate involved in the following reaction is .....



**Section-VI - Matrix match type**

36. Match the following

**Column-I (Compounds)**



**Column-II (Characteristic reaction)**

P) Reacts with  $H_2 - Pd / CaCO_3$

Q) Forms trans alkene when reacted with  $Na/Liq.NH_3$

R) Reacts with ammoniacal  $AgNO_3$

S) Forms  $CO_2$  on oxidative ozonolysis

A) I → PQ; B → PRS; C → PQ; D → PRS

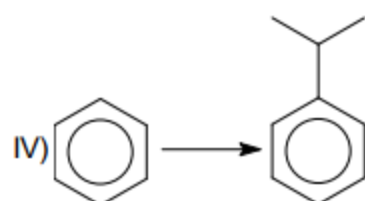
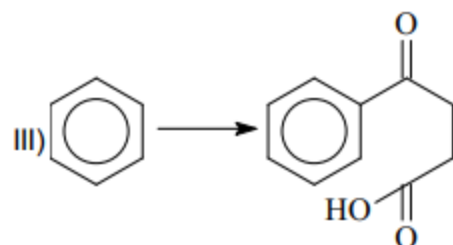
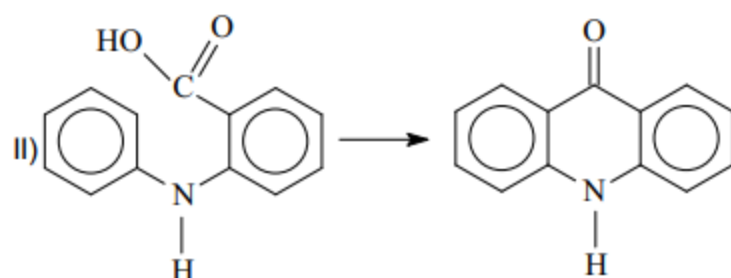
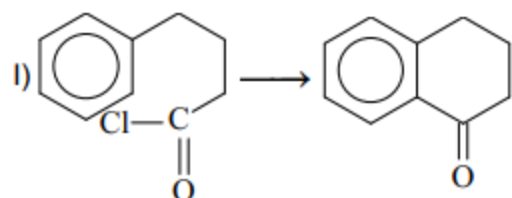
B) I → PQ; B → PQRS; C → PQ; D → PQRS

C) I → PQS; B → PRS; C → PQS; D → PRS

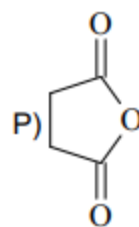
D) I → PQS; B → PQRS; C → PQS; D → PQRS

37. Match the following

**Column-I (Conversion)**



**Column-II (Reagent)**



Q)  $AlCl_3$

R)  $H_3PO_4$

S) n-propyl chloride

A) I  $\rightarrow$  Q; II  $\rightarrow$  Q; III  $\rightarrow$  PR; IV  $\rightarrow$  QS

B) I  $\rightarrow$  R; II  $\rightarrow$  Q; III  $\rightarrow$  PQ; IV  $\rightarrow$  RS

C) I  $\rightarrow$  R; II  $\rightarrow$  R; III  $\rightarrow$  PR; IV  $\rightarrow$  RS

D) I  $\rightarrow$  Q; II  $\rightarrow$  R; III  $\rightarrow$  PQ; IV  $\rightarrow$  QS