

Hydrocarbons a Aromatic
Compounds

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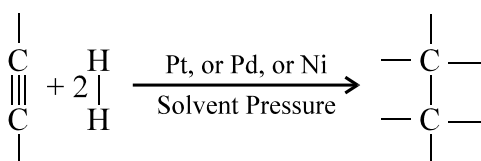
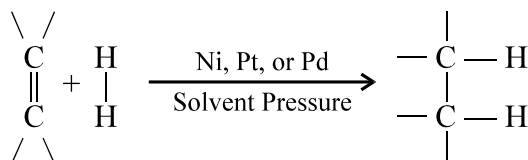
HYDROCARBONS & AROMATIC COMPOUNDS

C1 ALKANES

Methods of Preparation of Alkanes and Cycloalkanes

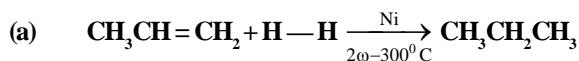
1. Hydrogenation of alkanes and alkynes :

(i) General Reactions :

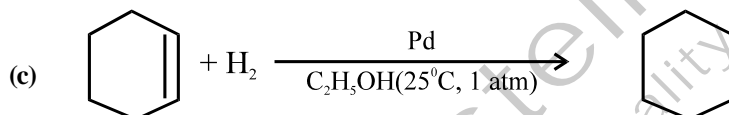
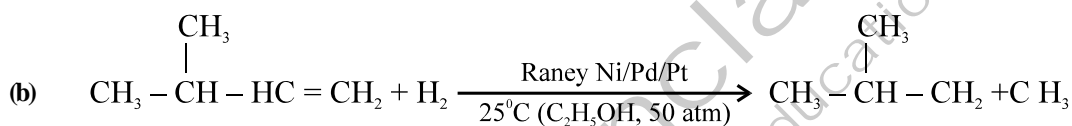


The reaction is usually carried out in the presence of solvent $\text{C}_2\text{H}_5\text{OH}$.

Specified Examples :



[Any reduction that is carried out in this manner is called as Sabatier-Sandereen's reduction]

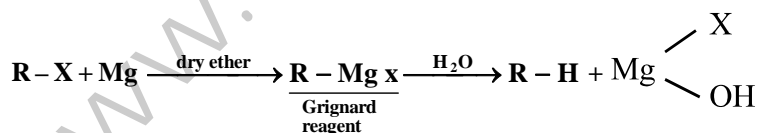


Limitation :

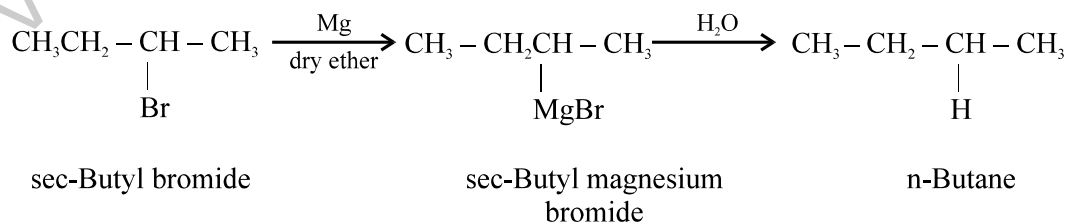
This method can not be used for the preparation of methane.

2. Reduction of Alkyl Halides :

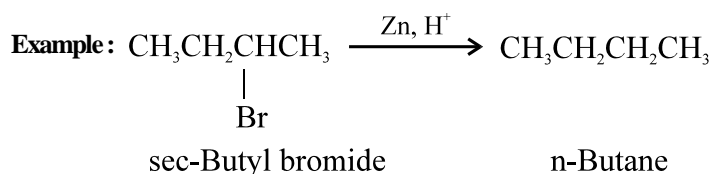
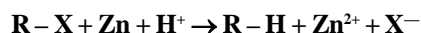
(a) Hydrolysis of Grignard reagent :



Examples :



(b) Reduction by metal and acid

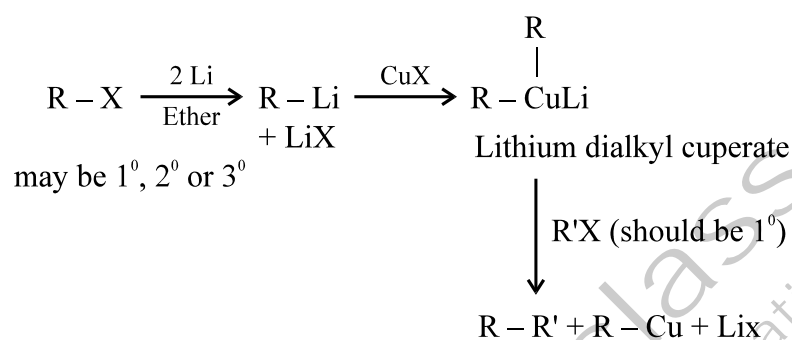
(c) $4R - X + LiAlH_4 \rightarrow 4R - H + LiX + AlX_3$ [X ≠ F]

$LiAlH_4$ can reduce 1° and 2° alkylhalide

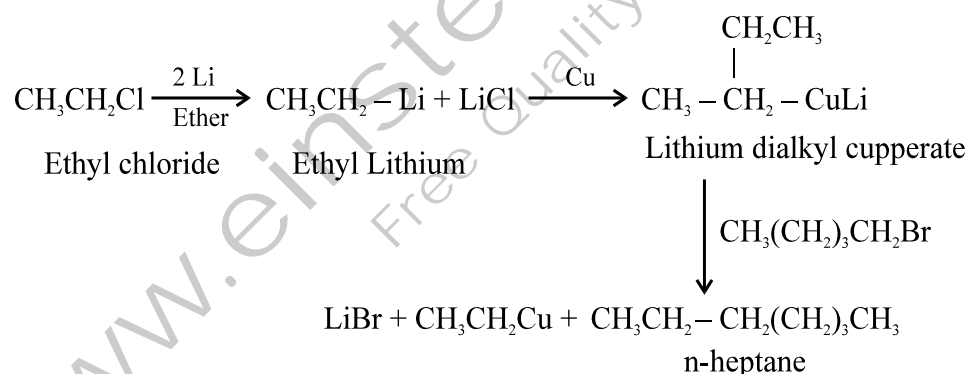
(d) $R - X + n(-C_4H_9)_3SnH \rightarrow RH + (n - C_4H_9)_3SnX$

Tributyl tin hydride

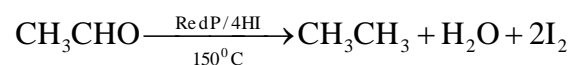
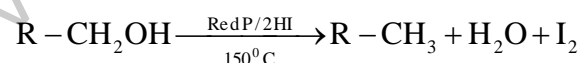
[It can reduce 1° , 2° and 3° alkyl halide].

3. Coupling of alkyl halides with organometallic compounds – (Corey-house alkane synthesis)

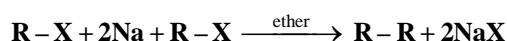
[This method is used to prepare higher alkanes]. This method is particularly suitable for preparation of unsymmetrical alkanes].



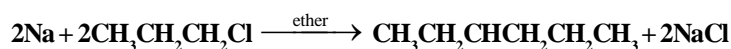
4. By reduction of alcohols, aldehydes, ketones, carboxylic acid



5. By wurtz reaction :

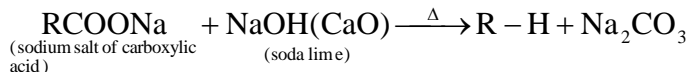


Example :



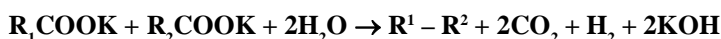
[This method is useful for the preparation of symmetrical alkanes]

6. Decarboxylation (The process of eliminating CO_2 from carboxylic acid is called as decarboxylation)



[The alkane formed in this way always contain one carbon atom less than the carboxylic acid].

7. Kolbe's Electrolytic Method : A concentrated solution of the sodium or potassium salt of carboxylic acid is electrolysed.



[If R_1 and R_2 are different then $\text{R}_1 - \text{R}_1$ and $\text{R}_2 - \text{R}_2$ are also obtained]

other side products are – alkenes, esters, alcohols.

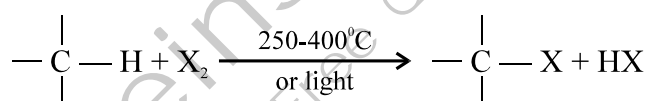
Practice Problems :

- By Wurtz reaction, a mixture of methyl iodide and ethyl iodide gives
 - propane
 - ethane
 - butane
 - a mixture of the above three
- Kolbe's synthesis of sodium salt of butanoic acid gives
 - n-hexane
 - isobutane
 - n-butane
 - propanone
- $(\text{CH}_3)_3\text{C} - \text{MgCl}$ on reaction with D_2O produces
 - $(\text{CH}_3)_3\text{CD}$
 - $(\text{CH}_3)_3\text{OD}$
 - $(\text{CD}_3)_3\text{CD}$
 - $(\text{CD}_3)_3\text{OD}$
- Aq. solution of potassium acetate is electrolysed. Possible organic products are :
 - $\text{CH}_3 - \text{CH}_3$
 - $\text{CH}_3\text{COOCH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 - both (a) and (b) are correct

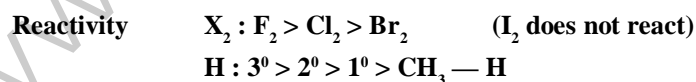
[Answers : (1) d (2) a (3) a (4) d]

C2 General Chemical properties of alkanes :

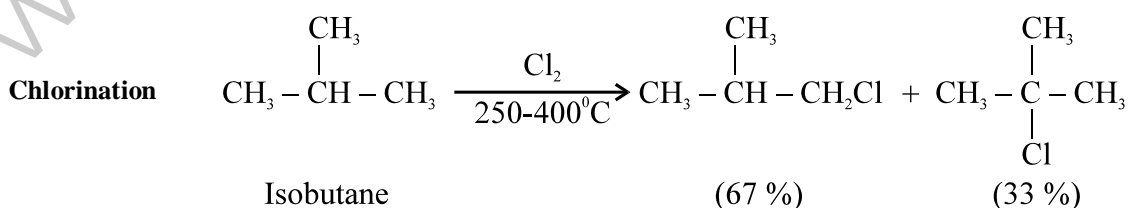
1. Halogenation :



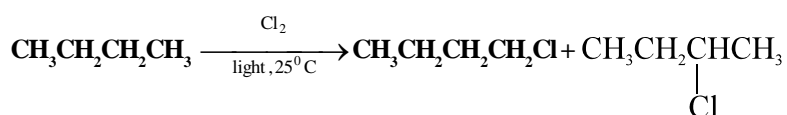
Usually a mixture



Example :



Example :



$$\frac{\text{n-Butyl Chloride}}{\text{sec-Butyl Chloride}} = \frac{\text{no. of } 1^\circ\text{H}}{\text{no. of } 2^\circ\text{H}} \times \frac{\text{reactivity of } 1^\circ\text{H}}{\text{reactivity of } 2^\circ\text{H}}$$

$$= \frac{6}{4} \times \frac{1}{3.8} = \frac{6}{15.2} = \frac{28}{72}\%$$

- The same sequence of reactivity, $3^\circ > 2^\circ > 1^\circ$ is found in Bromination, but with enormously larger reactivity ratios. At 127°C the relative rate per hydrogen atom are $1600 : 82 : 1$. Here, difference in reactivity are so marked so as to outweigh probability factor. Hence bromination is selective product.

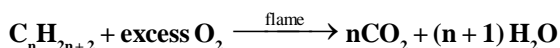
In bromination of isobutane at 127°C

$$\frac{\text{Isobutyl bromide}}{\text{tert-butyl bromide}} = \frac{\text{no. of } 1^\circ\text{H}}{\text{no. of } 3^\circ\text{H}} \times \frac{\text{reactivity of } 1^\circ\text{H}}{\text{reactivity of } 3^\circ\text{H}}$$

$$= \frac{9}{1} \times \frac{1}{1600} = \frac{9}{1600}$$

Hence, tert-butyl bromide happens to be the exclusive product (over 99%)

2. Combustion :

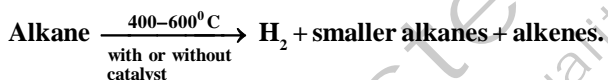


ΔH = enthalpy of combustion

Pyrolysis : (Cracking)

3. Decomposition of a compound by heat alone is known as Pyrolysis

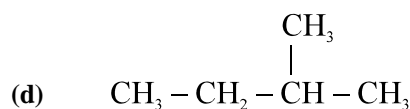
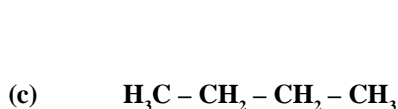
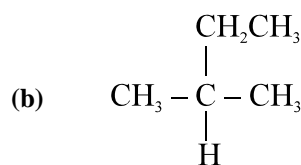
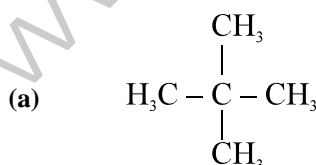
Pyrolysis of alkanes particularly when petroleum is concerned is known as cracking.

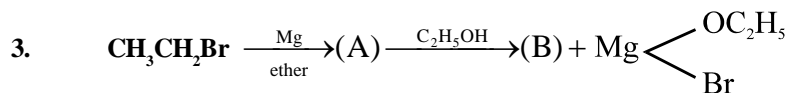


In thermal cracking alkanes are simply passed into a chamber to a high temperature. Large alkanes are converted into smaller alkanes, alkenes and some hydrogen.

Practice Problems :

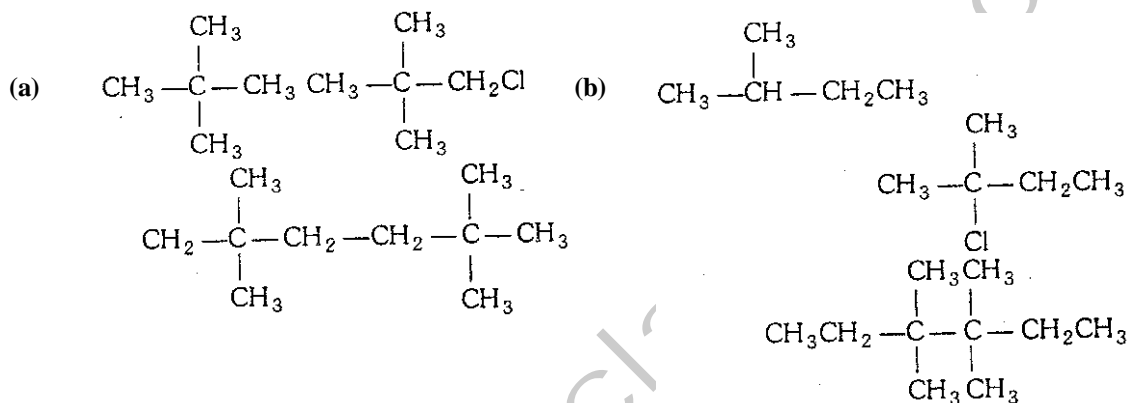
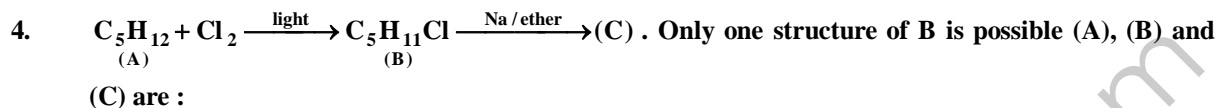
- The number of possible enantiomeric pairs that can be produced during mono chlorination of 2-methyl butane is
 - 2
 - 3
 - 4
 - 1
- An alkane with molecular mass 72 formed only one substitution product. Suggest a structure for the alkane.





Thus A and B in the above reaction sequence are :

- (a) (A) $\text{CH}_3\text{CH}_2\text{MgBr}$ (b) (A) $\text{CH}_3\text{CH}_2\text{MgBr}$
 (B) CH_3CH_3 (B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- (c) (A) CH_3CH_3 (d) (A) CH_3COOH
 (B) $\text{CH}_3\text{CH}_2\text{CH}_3$ (B) CH_3MgBr



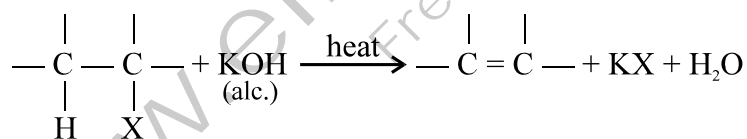
- (c) both correct (d) none is correct

[Answers : (1) a (2) a (3) a (4) a]

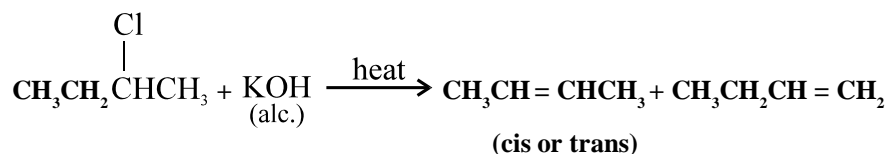
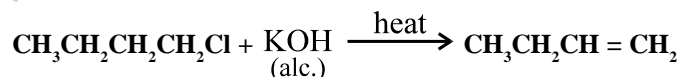
C3 ALKENES

Methods of Preparation of Alkenes :

1. Dehydrohalogenation of Alkyl-Halide : 1,2 - Elimination

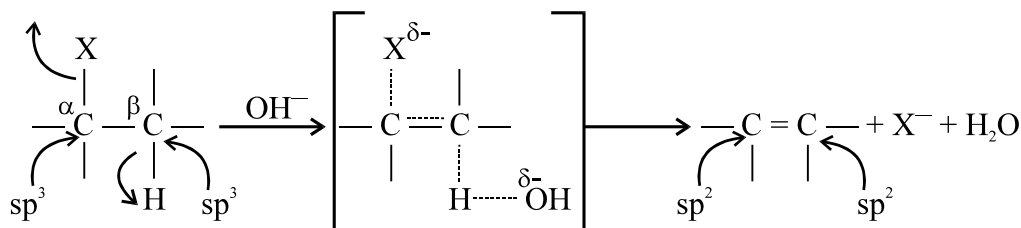


Examples :



Discussion : Dehydrohalogenation means that there is an elimination of one hydrogen atom and one halogen atom. The reagent required is a base, whose function is to remove the hydrogen as a proton.

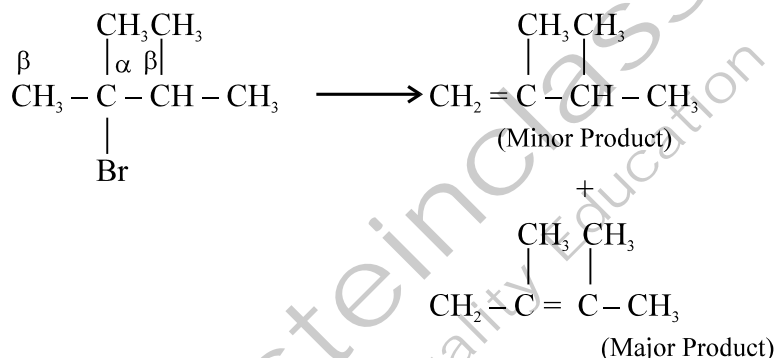
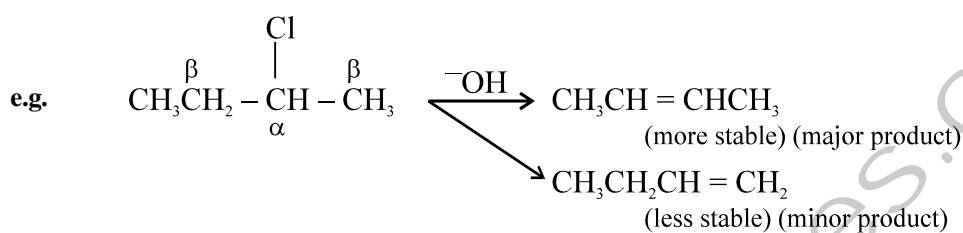
Mechanism - E₂ mechanism :



(-X, and H leaves from opposite side) Partially formed double bond

Now if alkyl halide has more than one β , hydrogen atom then that hydrogen is removed which result in more substituted alkene, this is according to saytzeff's rule.

More substituted alkene means that more no. of Alkyl groups are present around the double bond.



E₂ elimination reactions are characterised by the following :

1. Substrate contains a leaving group; an atom or group that leaves along with electron pair.
2. In position β to the leaving group the substrate contain H-atom that can be abstracted by base.
3. Reaction is brought about by a base.

Typically strong bases like OH^- , RO^- (alkoxide ion) derived from alcohol, $\text{C}_2\text{H}_5\text{O}^-$ ethoxide ion, tert-butoxide ion $(\text{CH}_3)_3\text{CO}^-$ etc.

Heterolytic bond dissociation energy : $\text{RF} > \text{RCl} > \text{RBr} > \text{RI}$

\therefore Reactivity towards E₂ : $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$

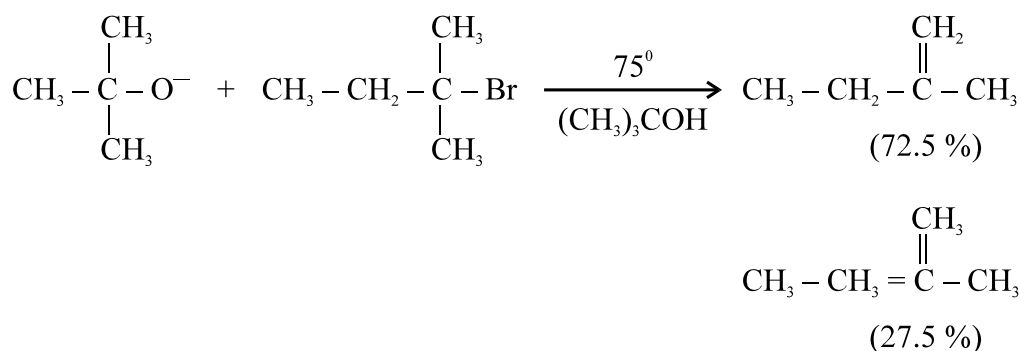
similarly reactivity order of R - X is $3^\circ > 2^\circ > 1^\circ$

as more substituted alkene will form as the branching will increase.

Kinetics of E₂ : Bimolecular.

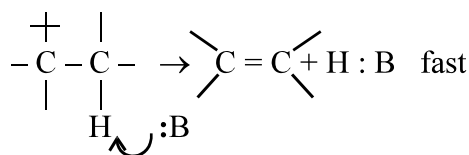
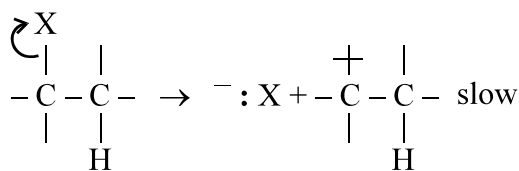
Rate of the reaction $r = k [\text{RX}] [\text{Z}]$
Substrate Base

An exception to saytzeff's rule :



E₁ Mechanism : E₁ involves two steps for same process as it takes place in E₂.

1. The substrate undergo heterolysis slowly to form halide ion and a carbocation.
2. In step (2) the carbocation readily loses a proton to the base and forms the alkene.



Thus a carbocation may

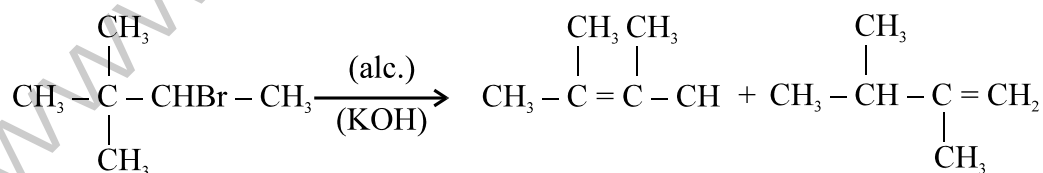
- (a) combine with a nucleophile
- (b) can undergo rearrangement
- (c) eliminate a proton to form the alkene.

Kinetics of E₁ reaction :

$$r = k [\text{R-X}] \quad [\text{Unimolecular reaction}]$$

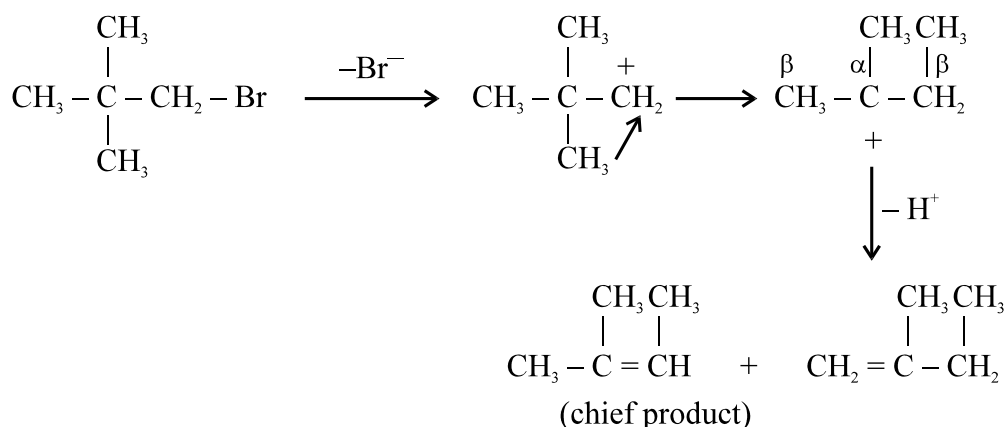
Order of reactivity of R - X for E₁ : 3° > 2° > 1°

Thus because of rearrangement skeleton of carbon chain changes :



Alkene that doesnot contain α-hydrogen in the presence of base can undergo E₁ elimination as follows :

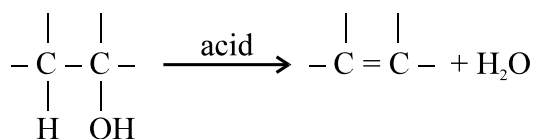
Explanation :



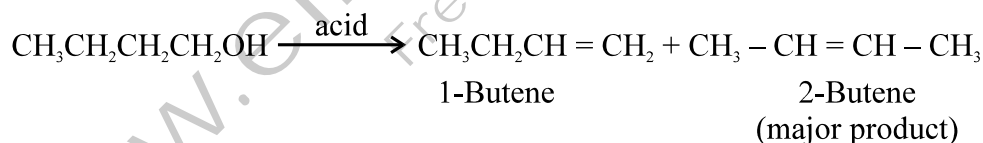
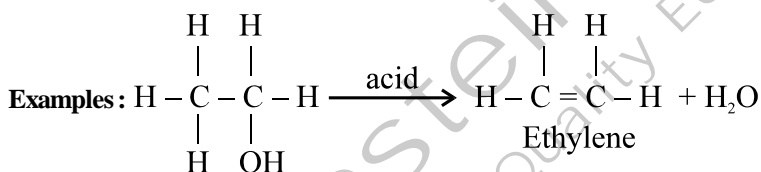
E₂ Vs E₁

- Reactivity of both mechanism increases with as we move from 1^o, 2^o to 3^o substrate.
- But E₂ mechanism depends on concentration of base whereas E₁ mechanism is independent of the concentration of base.
- Stronger the base more E₂ is favoured
- 1^o alkyl halide do not favour to form carbocation so they prefer E₂

2. Dehydration of Alcohols :

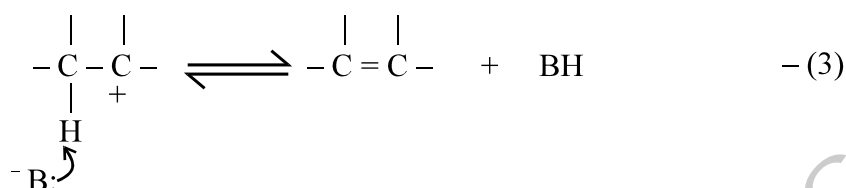
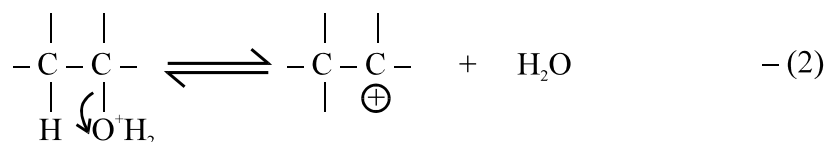
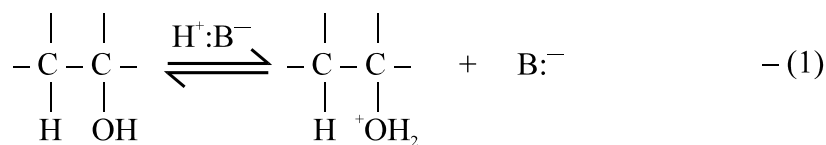


Ease of dehydration of alcohol 3^o > 2^o > 1^o



Ease of dehydration of alcohols : 3^o > 2^o > 1^o

For secondary and tertiary alcohols the following mechanism is accepted :



Dehydration is acid-catalyzed :- Acid transforms the poor leaving group (–OH) into the very good leaving group, –OH₂⁺

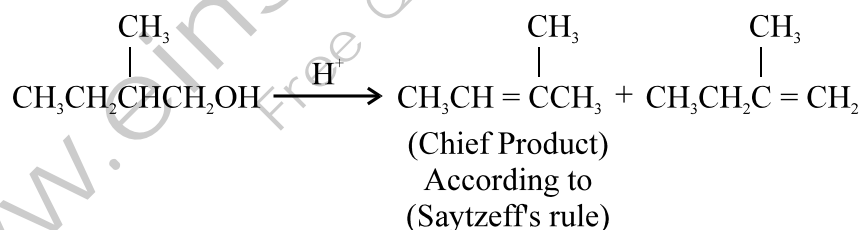
- As dehydration is acid catalysed as acid is not consumed in the reaction. Acid used in step (1) is regenerated in step (3).

Dehydration is reversible :- Unlike base promoted 1, 2-elimination, this elimination is reversible.

- As we shall study later that acid catalysed the hydration of alkenes to give alcohol.
- Thus each step is reversible.
- Under the condition of dehydration, the alkene being quite volatile is generally driven from the reaction mixture and thus equilibrium (3) is shifted in the right side.
- As a consequence the entire reaction is forced toward elimination.

Ease of dehydration of alcohol : 3° > 2° > 1°

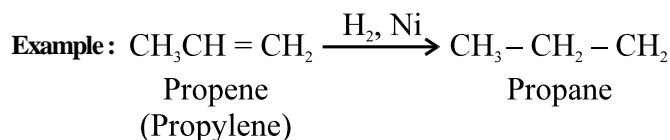
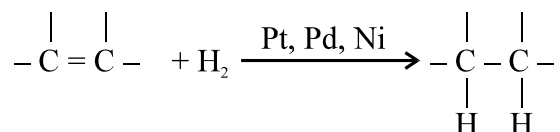
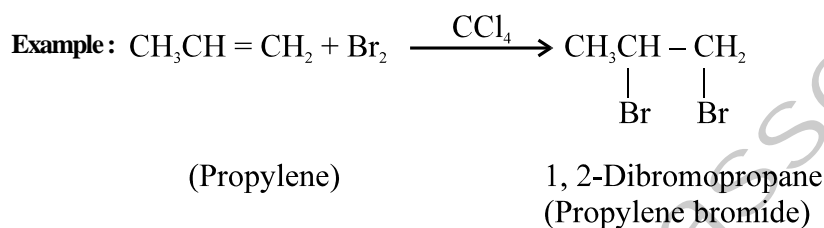
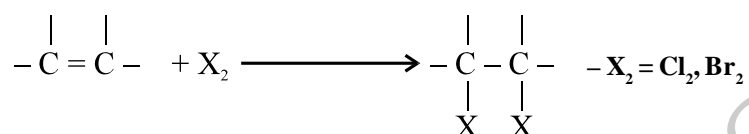
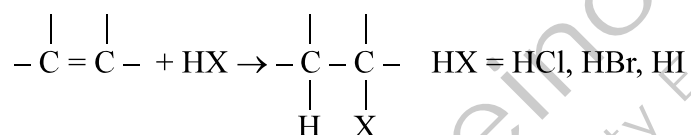
- Rate of dehydration depends on step (2) and step (3) both.
- Where the structure of alkyl group permits the rearrangement of carbocation takes place.



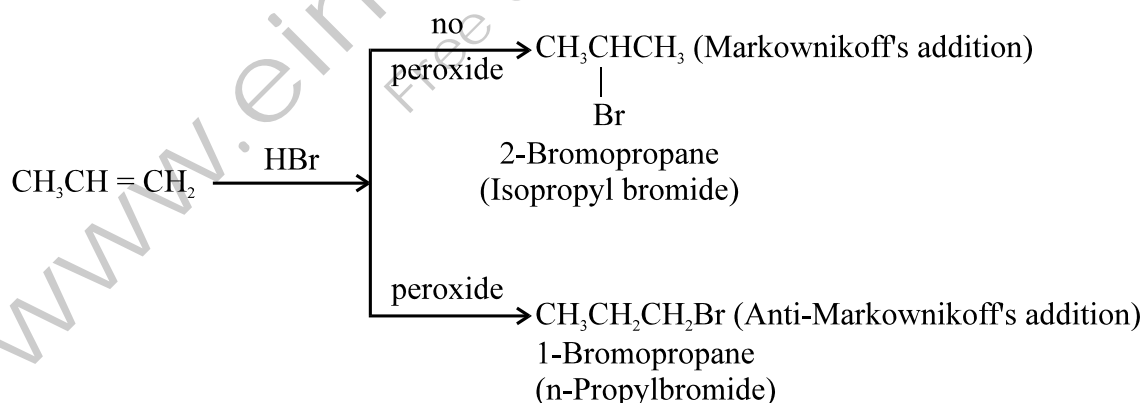
Practice Problems :

1. Identify the possible number of products in the following reaction : $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{Cl})\text{C}_6\text{H}_5 \xrightarrow[\text{heat}]{\text{Alc. KOH}}$
- (a) 1 (b) 2 (c) 3 (d) 4

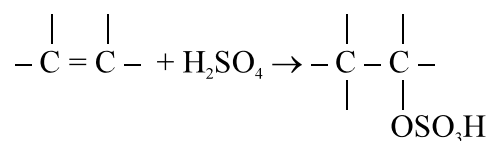
[Answers : (1) b]

C4 Chemical Properties of Alkene :(Addition Reactions)1. **Addition of Hydrogen : Catalytic hydrogenation**2. **Addition of halogens :**3. **Addition of hydrogen halide :**

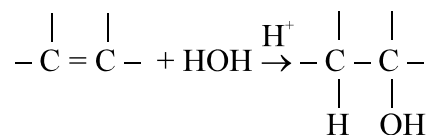
Example:



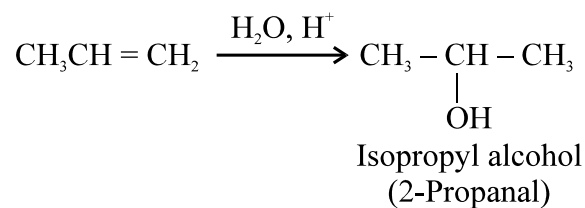
4. Addition of sulfuric acid :



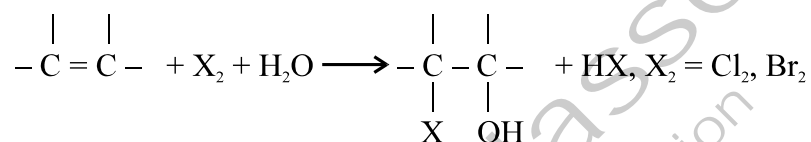
5. Addition of dil-sulfuric acid :



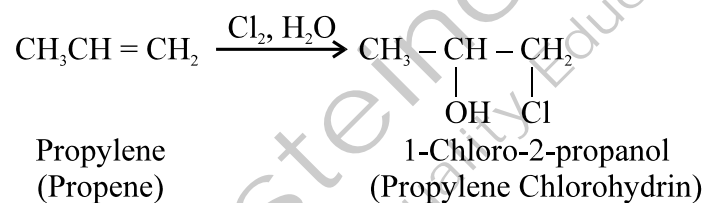
Example :



6. Halohydrin Formation :

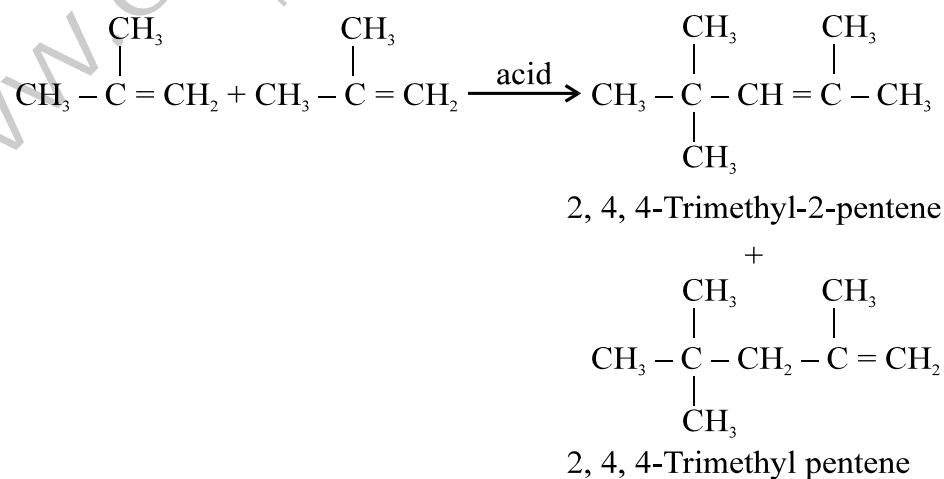


Example :

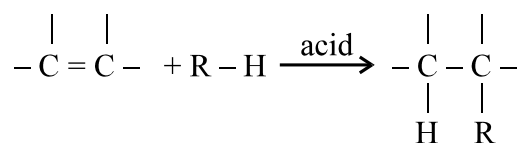


7. Dimerization :

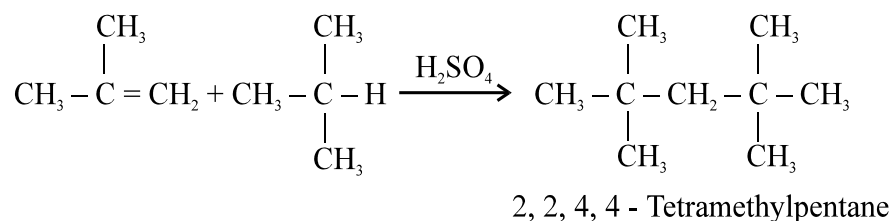
Example :



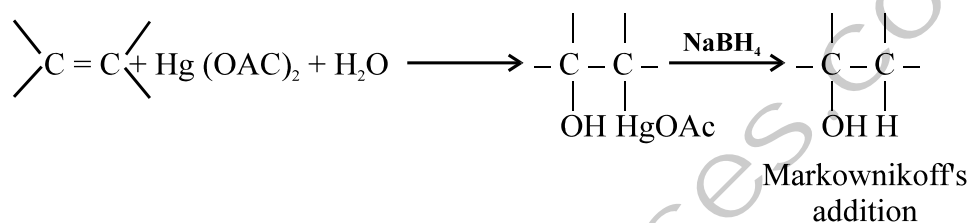
8. Alkylation :



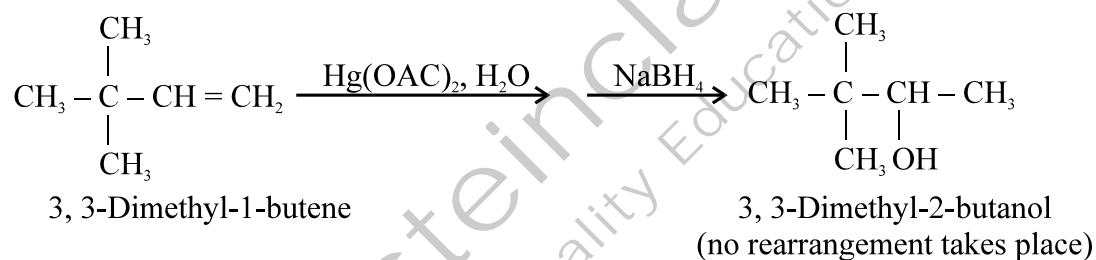
Example :



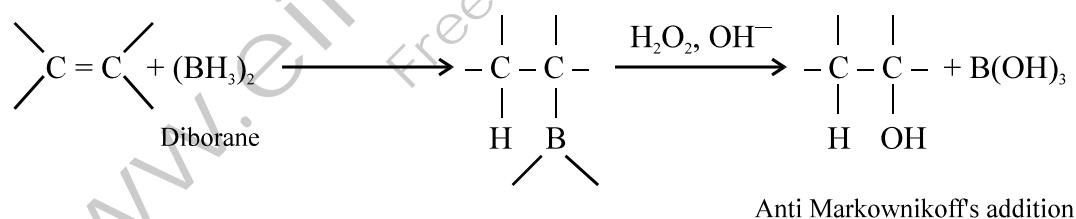
9. Oxymercuration-demercuration :



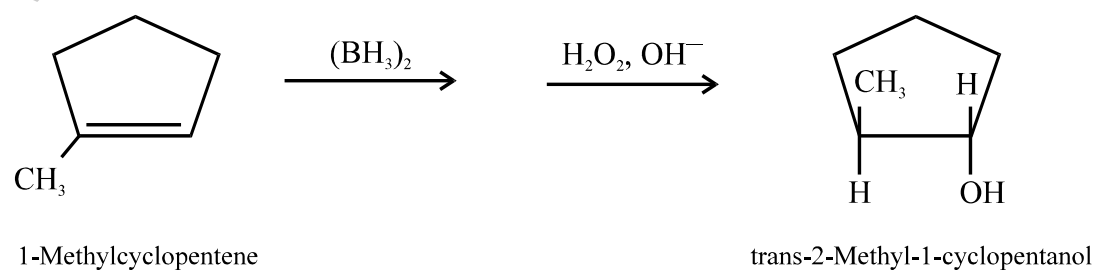
Example :

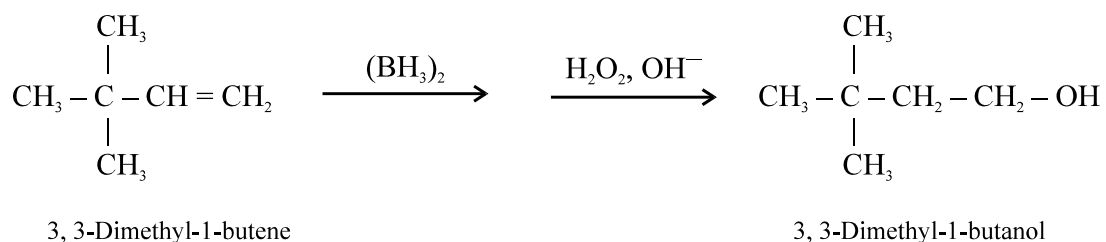


10. Hydroboration-Oxidation

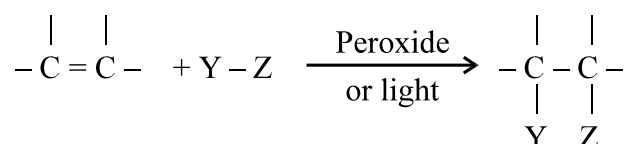


Examples :

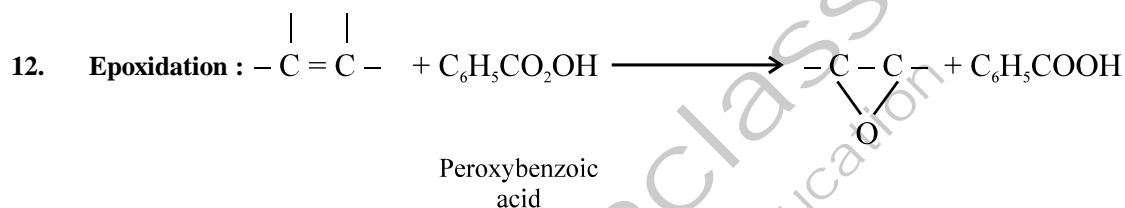
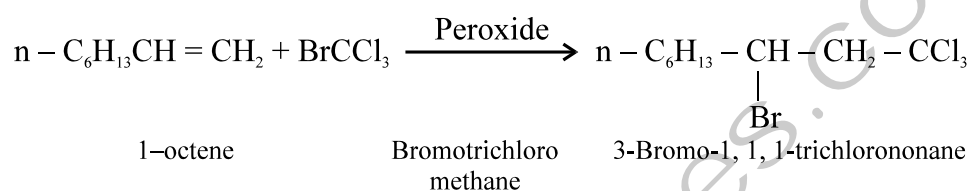




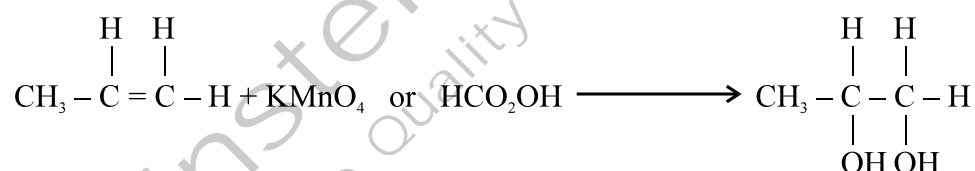
11. Addition of free radicals



Example :

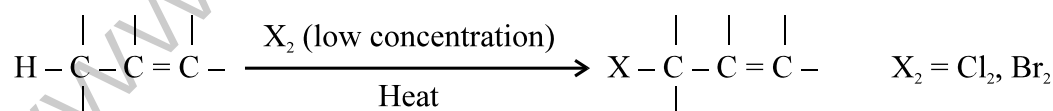


13. Hydroxylation : Glycol formation

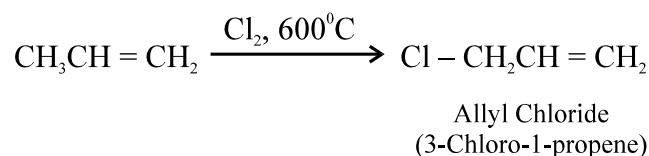


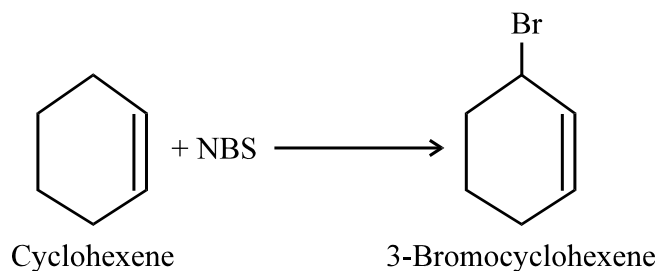
Substitution Reaction :

14. Halogenation : Allylic Substitution



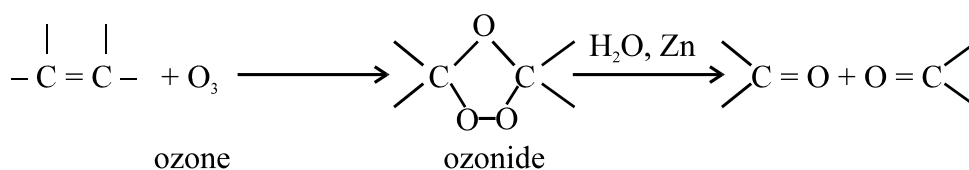
Example :



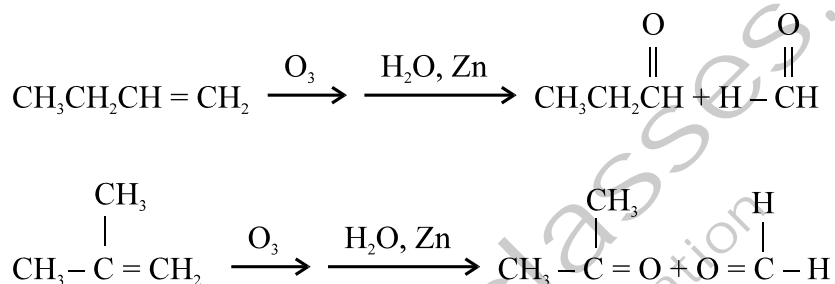


15. **Cleavage Reactions (very important) used to determine structure.**

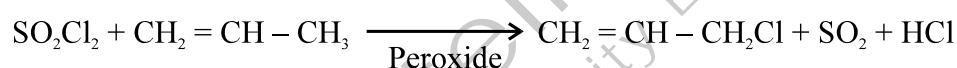
Ozonolysis :



Example :

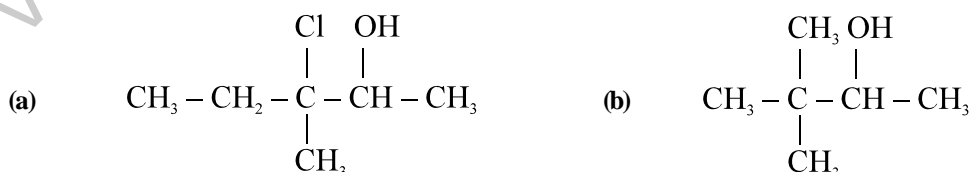


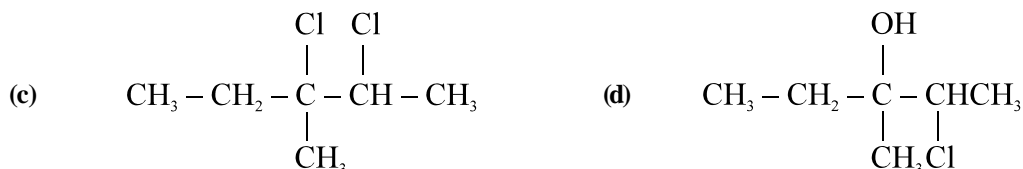
Substitution reactions at allylic positions :



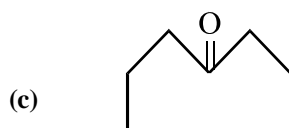
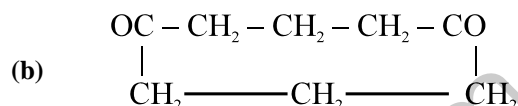
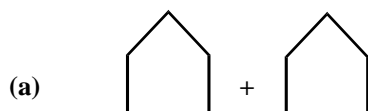
Practice Problems :

- A hydrocarbon containing 2 carbon atoms give Sabatier and Senderen's reaction but does not give precipitate with ammonical silver nitrate solution. The hydrocarbon in question is
 (a) Ethane (b) Acetylene (c) Ethylene (d) none of these
- Which of the following is not correct about the reaction $CH_2=CH_2 + Br_2 \xrightarrow{NaI(aq)}$:
 (a) The products formed are CH_2BrCH_2Br and CH_2BrCH_2I
 (b) The reaction follows polar mechanism
 (c) The reaction occurs readily in solution and is catalysed by inorganic halides
 (d) CH_2ICH_2I is formed only
- 3-methyl-2-pentene on reaction with $HOCl$ gives :



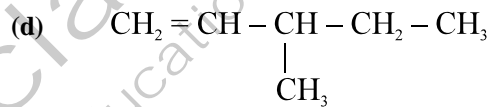
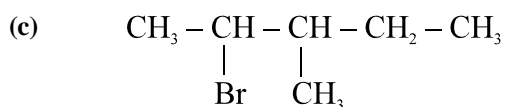
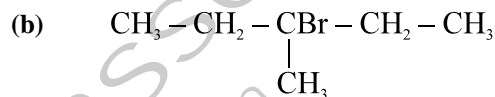
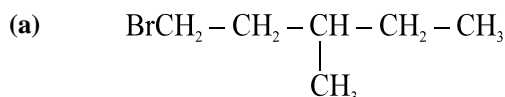


4. Ozonolysis of  will give

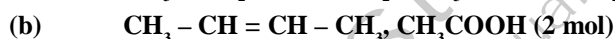
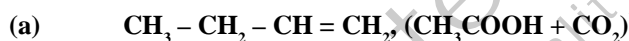


(d) None

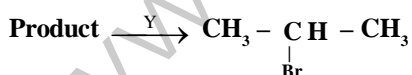
5. Sample of 2, 3-dibromo-3-methyl pentane is heated with zinc dust. The resulting product is isolated and heated with HBr. Indicate which is the structure that represents the final organic product in the reaction



6.
$$\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \xrightarrow[\text{1equiv.}]{\text{H}_2/\text{Pt}} \text{A} \xrightarrow{\text{O}_3/\text{H}_2\text{O}} \text{A and B are}$$



7. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformations



(a) X = dilute aqueous NaOH, 20°C;
Y = HBr/acetic acid, 20°C

(b) X = concentrated alcoholic NaOH, 80°C,
Y = HBr / acetic acid, 20°C

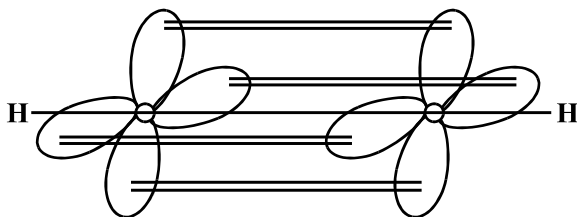
(c) X = dilute aqueous NaOH, 20°C,
Y = Br₂ / CHCl₃ / 0°C

(d) X = concentrated alcoholic NaOH, 80°C ;
Y = Br₂ / CHCl₃ . 0°C

[Answers : (1) c (2) d (3) d (4) b (5) b (6) b (7) b]

C5 ALKYNES:Electronic Structure of Triple Bond :

- Acetylene is known to have a linear structure.
- $\text{C} \equiv \text{C}$ – distance of 1.20 Å is the shortest carbon – carbon bond length known.
- The carbon-hydrogen bond length of 1.06 Å is shorter than that in ethylene or in ethane. Thus it is stronger than either.
- The $\text{sp}^2 - \text{s}$ σ -bonds are shorter than $\text{sp}^3 - \text{s}$ σ -bonds. The trend also holds for the $\text{sp} - \text{s}$ bonds in acetylene.
- Superimposed on the σ -electrons are two orthogonal π -electron system.

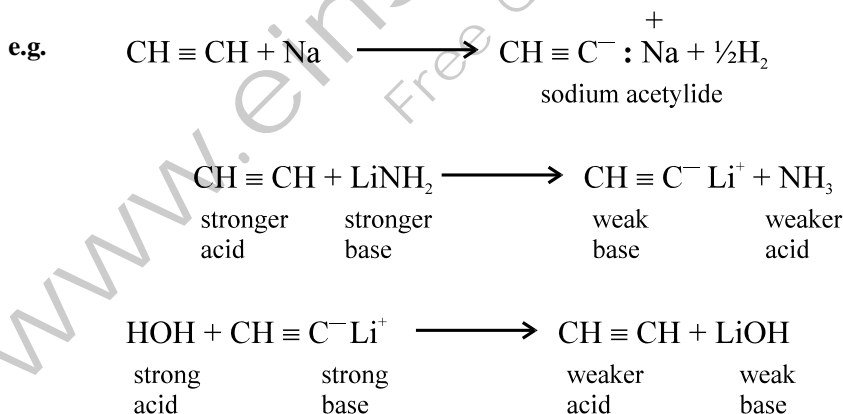


Overlap of the p-orbitals on one carbon with the p-orbitals on the other carbon permits pairing of electrons. Two s-bonds are formed, which together make a single cylindrical sheath about the line joining the nuclei.

- Thus carbon-carbon "triple bond" is thus made up of one strong σ -bond and two weaker π -bonds. It has total strength of 198 kCal. It is stronger than the carbon-carbon double bond of ethylene and carbon-carbon single bond of ethane and is shorter than either.

2. Acidity of Alkynes : Very weak acids :

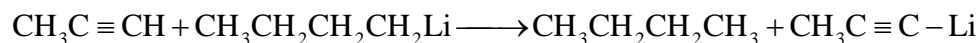
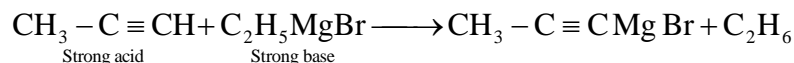
- In our earlier consideration of acids we took acidity to be a measure of the tendency of a compound to lose the hydrogen ion.
- Appreciable acidity is shown by those compounds in which hydrogen is attached to rather electronegative atom like ($\text{F} > \text{O} > \text{N} > \text{C}$). The bond holding the hydrogen is polar, thus relatively positive hydrogen can separate as positive ion, and more electronegative atom can hold the negative charge effectively.
- In view of the electronegativity series $\text{F} > \text{O} > \text{N} > \text{C}$ it is not surprising that $\text{HF} > \text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$.
- In organic chemistry we are frequently concerned with the acidities of compounds do not turn litmus red or neutralize aqueous bases. Yet they have tendency to lose proton H^+ to small extent.
- A triply bonded carbon behaved as it is more electronegative than carbon which is singly or double bonded. As a result the hydrogen bonded to terminal alkyne shows the hydrogen bonded to terminal alkyne shows appreciable acidity.



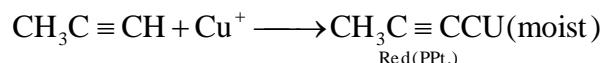
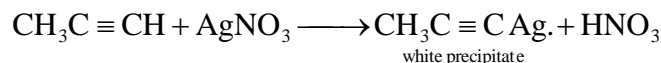
Relative Acidities : $\text{H}_2\text{O} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{NH}_3 > \text{RH}$

Relative Basicities : $\text{OH}^- < \text{OR}^- < \text{CH} \equiv \text{C}^- < \text{NH}_2^- < \text{R}^-$

If a terminal alkyne is treated with an alkyl magnesium halide or an alkyl lithium the alkane is displaced from its salt and the metal acetylide is obtained.



only terminal alkynes give these reaction :



C6. Method of Preparation of Alkynes :

Industrial method of preparation :

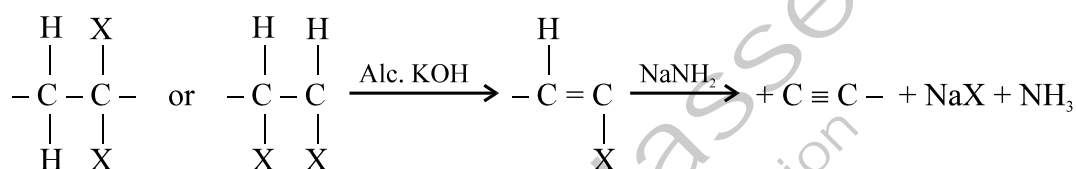
1. Acetylene is formed from the reaction of inorganic compound calcium carbide with water



2. $2\text{CH}_4 \xrightarrow{1500^\circ\text{C}} \text{CH} \equiv \text{CH} + 3\text{H}_2$

3. Laboratory methods of preparation :

Dehydrohalogenation of gem or vicinal dihalide :



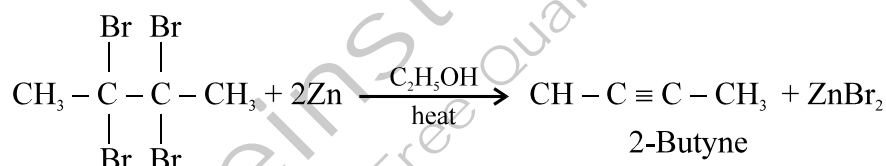
gem-dihalid

vic-dihalide

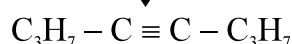
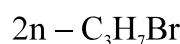
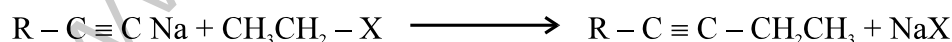
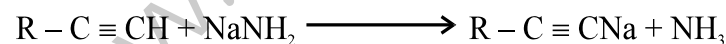
vinyl halide

vinyl halide requires the stronger base sodamide NaNH_2 .

4. Dehalogenation of vic-tetrahalogen compounds :



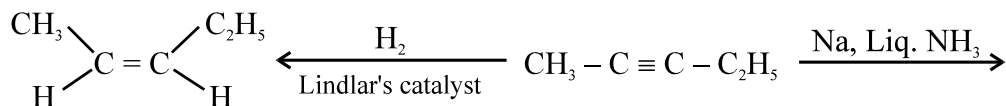
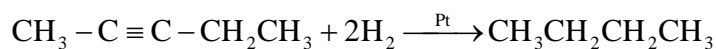
5. Alkyl substitution in acetylene (Method of preparation of higher alkynes) :



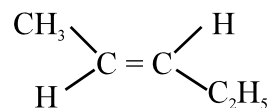
This method is good for synthesis of alkynes when applied to primary halides that do not have branches close to reaction centre. With secondary halide and even with primary halides that have branches closer to the reaction centre, elimination is usually the major reaction.

C7 Chemical Properties of Alkyne :

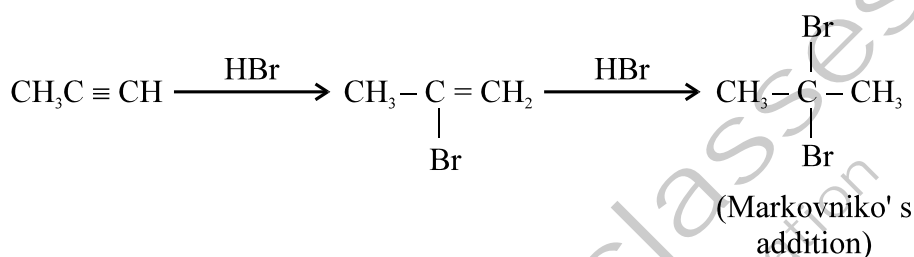
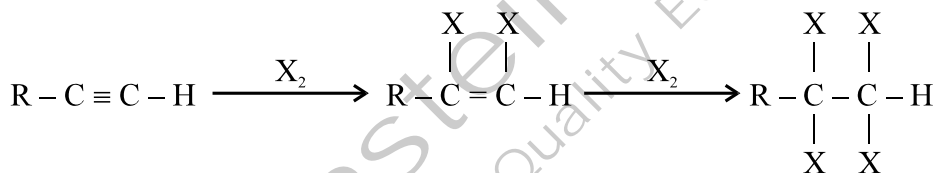
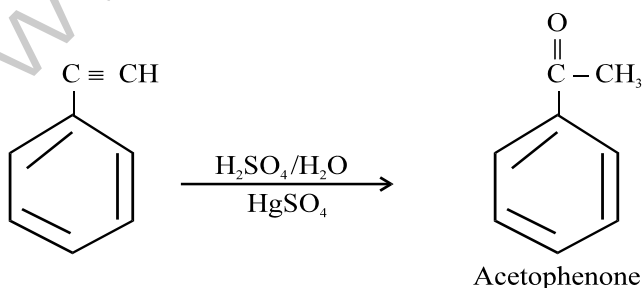
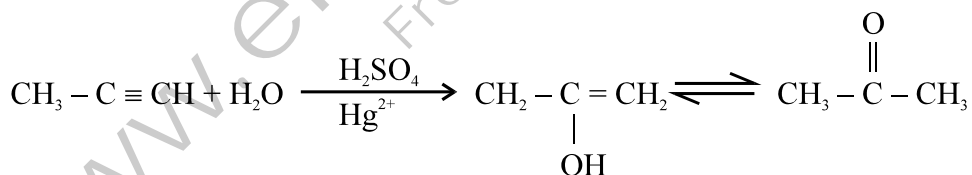
Addition reaction at the triple bond : π -electrons of alkyne add electrophiles in reactions similar to additions to alkenes. Alkynes can add two moles of reagent but are less reactive than alkenes.

1. Hydrogenation

(cis)



(trans)

2. HX (HCl, HBr, HI)3. Halogen (Br₂, Cl₂)4. Addition of water

4. $\text{CH} \equiv \text{CH} \xrightarrow{\text{HgSO}_4/\text{H}_2\text{SO}_4} \text{B} \xleftarrow{\text{reaction R}} \text{A}$. A, B and reaction R are :

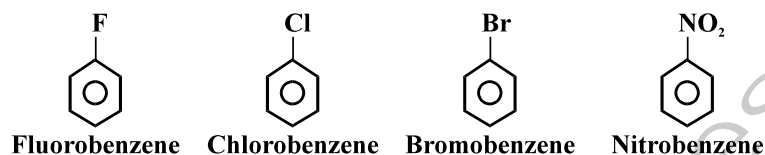
- (a) $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} - \text{Cl}$, CH_3CHO , (b) CH_3CN , CH_3CHO ,
 Rosenmund (Pd/BaSO₄, H₂) Stephen
 (SnCl₂/HCl)
 (c) $\text{CH} \equiv \text{CH}$, CH_3CHO , (d) all of above
 hydroboration oxidation
 [Answers : (1) c (2) b (3) a (4) d]

Aromatic Compounds :

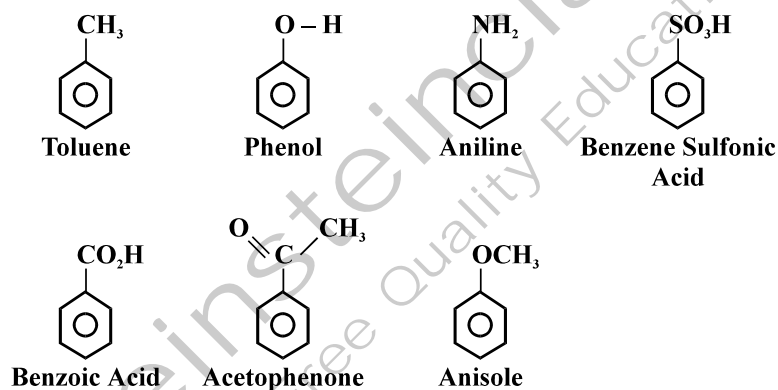
C8 Nomenclature of Benzene Derivatives :

Two systems are used in naming monosubstituted benzenes.

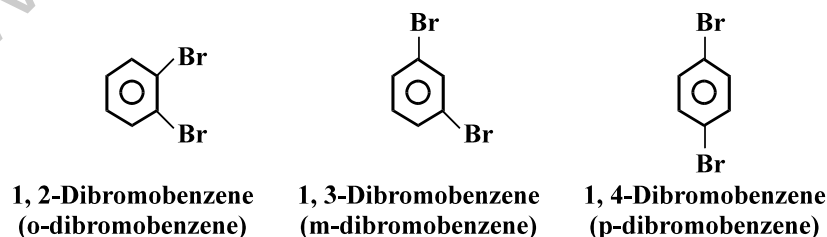
In certain compound benzene is the parent name and the substituent is simply indicated by prefix we have for example



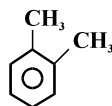
For other compound, the substituent and the benzene ring taken together may form a new parent name. Methylbenzene is usually called toluene, hydroxybenzene is almost always called phenol, and aminobenzene is almost always called aniline. These and other examples are indicated here.



When two substituents are present their relative positions are indicated by the prefixes ortho, meta and para (abbreviated as o-, m- and p-) or by the use of numbers. For the dibromobenzene we have



The dimethylbenzenes are often called xylenes

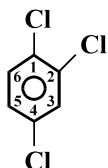


1,2-Dimethylbenzene
(o-xylene)

IMPORTANT:

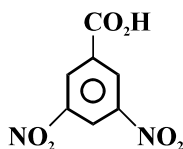
Numbers can be used for two or more substituents but ortho, meta, para must not be used for more than two substituents.

If more than two groups are present on the benzene ring, their positions must be indicated by numbers e.g.

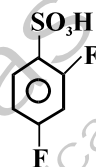


1, 2, 4 - Trichlorobenzene

We notice that the benzene ring is numbered so as to give minimum possible numbers to the substituents. When more than two substituents are present and the substituents are different they are listed in alphabetical order. When the substituent is one that when taken together with the benzene ring gives a new base name, that substituent is assumed to be position 1 and the new parent name is used



3, 5 - Dinitrobenzoic acid

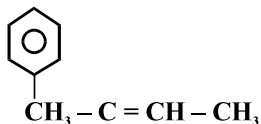


2, 4 - Difluorobenzene
Sulfonic acid

When C_6H_5 - group is named as a substituent it is called phenyl group. A hydrocarbon composed of one saturated chain and one benzene ring is usually named as a derivative of the Larger Structural Unit.

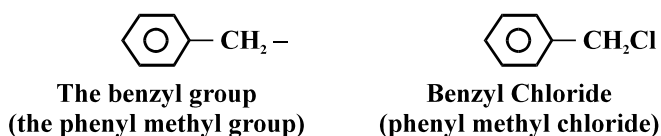
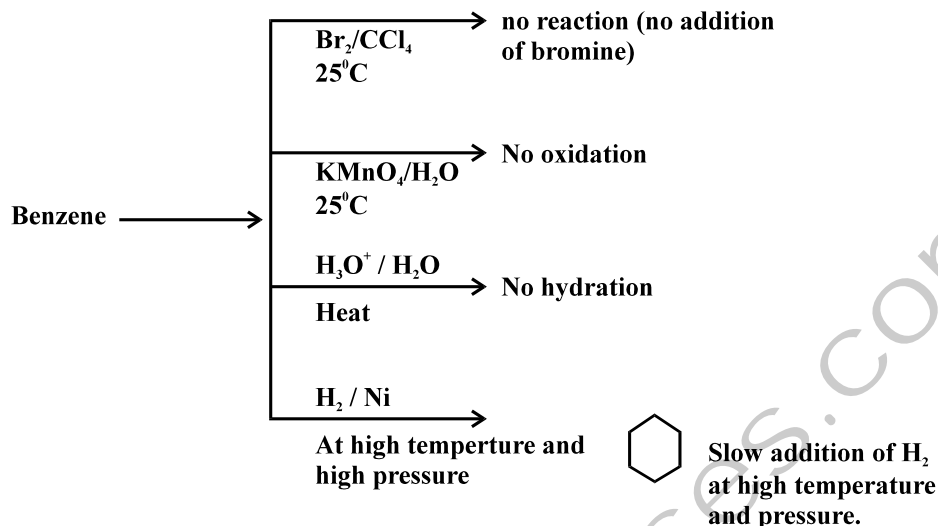


If the side chain is unsaturated, the compound may be named as a derivative of that chain, regardless of the ring size e.g.

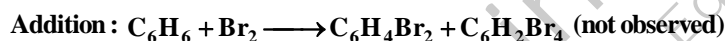
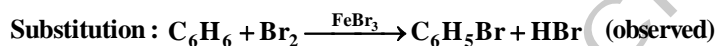


2-Phenyl-2-butene

The phenyl group is abbreviated as C_6H_5 - or Ph-. The name benzyl is the alternative name of the phenylmethyl group. It is sometimes abbreviated as BZ.

**C9A Properties of Benzene :**

C9B Benzene does react with the Br₂ but only in the presence of Lewis acid catalyst such as ferric bromide FeBr₃.



When benzene reacts with bromine only one monobromo benzene is observed or formed.

Kekule Structure for benzene :**C9C Huckle Rule (4n + 2)π Electron Rule :**

Huckle's rule is concerned with the compounds containing one planar ring in which each atom has a p-orbital as in benzene ring. His calculations shows that planar monocyclic ring containing (4n + 2) π electrons where n = 0, 1, 2, 3... (i.e. rings containing 2, 6, 10, 14 etc.....π electrons) have closed shells of delocalized electrons should be aromatic with substantial resonance energies.

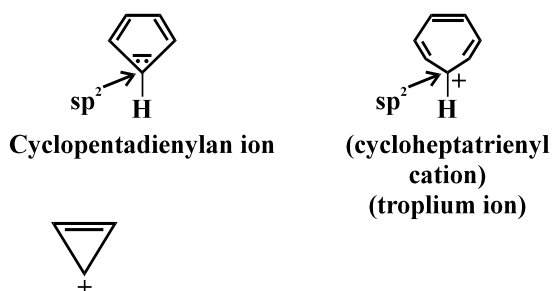


Benzene has 6 π electrons so it is a Huckle number & is aromatic.



8 π electrons, not a Huckle number so it is not aromatic although it contain alternate single & double bonds.

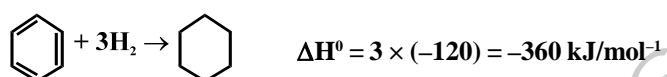
Aromatic Ions : (Also known as non-benzoic aromatic ions)



Aromatic Compounds : are defined as those in which π -electrons are delocalized over the entire ring and that is stabilized by delocalization of the π -electron.

The stability of benzene : Benzene shows unusual behaviour by undergoing substitution reaction then addition reaction. On the basis of Kekule Structure we should expect it to undergo addition reaction. But it is more stable than the Kekule Structure suggests. How ?

Resonance Energy : Heat of hydrogenation of benzene using Kekule structure suggests that,



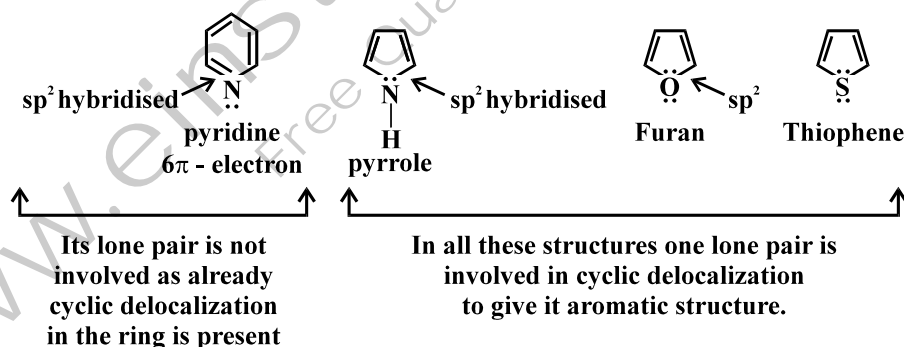
[If one mole of H_2 adds to double bond then -120kJ/mol of energy is released as here 3 mol of H_2 are added so energy released is $3 \times (-120)$]. But actual amount of heat released is -208 kJ/mol . So the difference in actual heat released and that calculated from Kekule structure is 152 kJ/mol . This energy is called as **Resonance Energy**.

Resonance Explanation of Benzene : It is found that carbon-carbon bond length in benzene is same. They

have a bond order between single and double bond



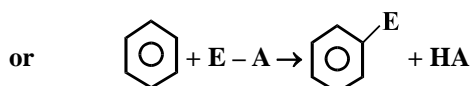
Heterocyclic Aromatic Compounds :



C10A Electrophilic Aromatic Substitution Reaction :

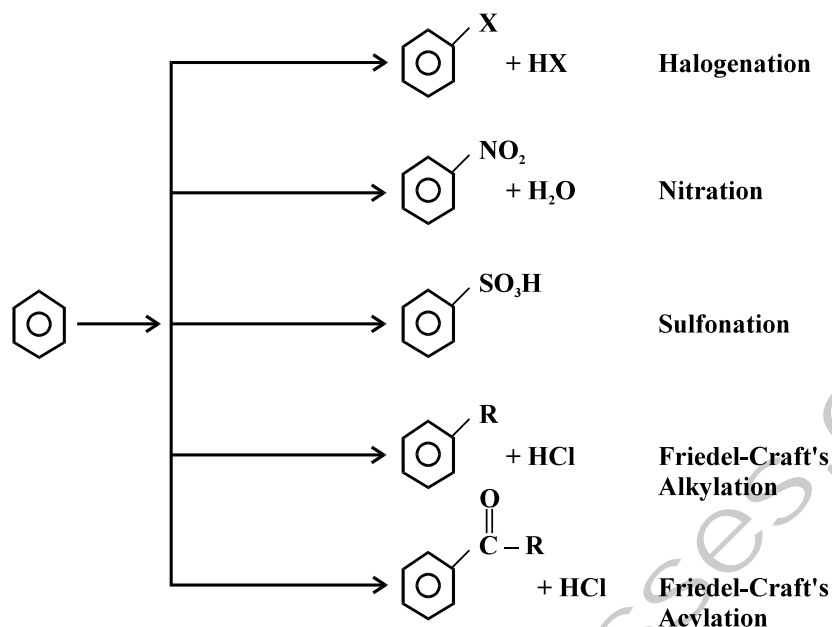
General Reaction :

Aromatic hydrocarbons are known as arenes. Arenes are designated as Ar-H just as Alkanes.



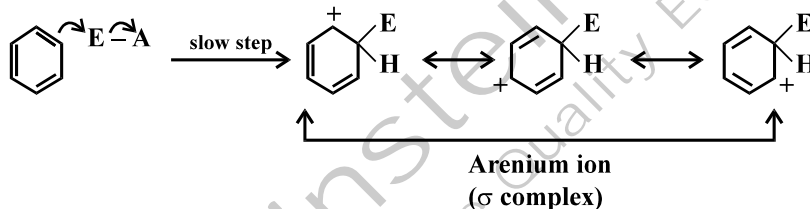
The most characteristic reaction of benzoid arenes are substitution reaction that occur when they react with electrophilic reagents. The reactions are of general type as shown above.

Electrophilic aromatic substitutions allow the direct introduction of wide variety of groups onto an aromatic ring. They are listed as follows :

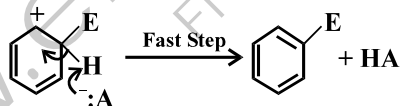


General mechanism of Electrophilic Aromatic Substitution :

Step – 1 (Rate determining step)



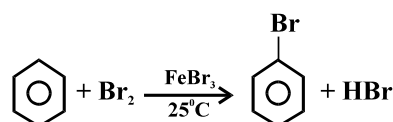
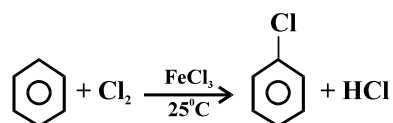
Step – 2



(The proton is removed by any of the base present e.g. by the anion derived from the electrophile)

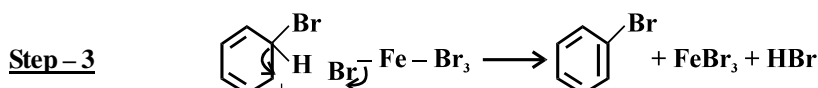
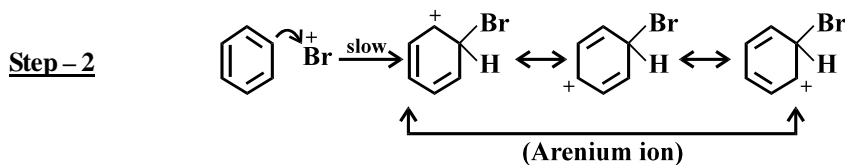
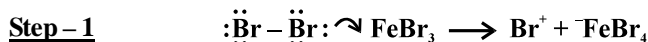
1. Halogenation of Benzene :

Benzene does not react with the bromine or chlorine unless a lewis acid is present in the mixture.

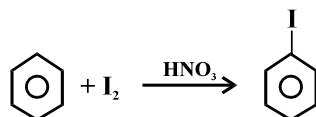


Anhydrous AlCl_3 can also be used as Lewis acid along with FeCl_3 , FeBr_3 , FeCl_3 or FeBr_3 are generated in the mixture by adding iron to it. The iron then react with halogen to produce the ferric halide.

Mechanism

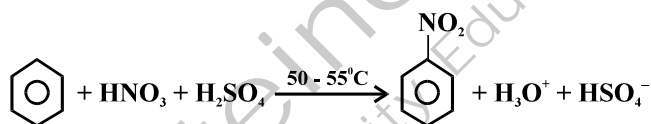


Chlorination of benzene can be done in presence of FeCl_3 in the same way as shown above. Fluorination of benzene requires special condition as it react so rapidly with benzene. Iodination also requires special technique as iodine is so unreactive, the reaction has to be carried out in the presence of the strong oxidizing agent like nitric acid HNO_3 .



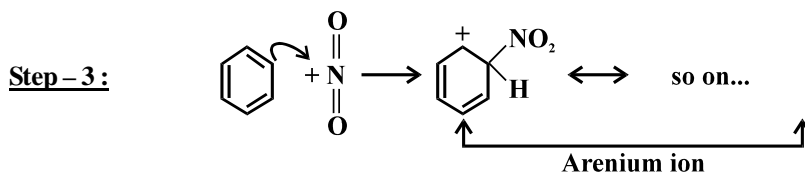
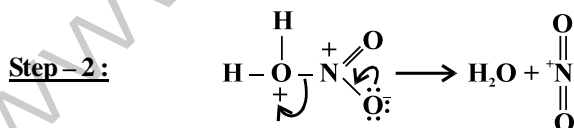
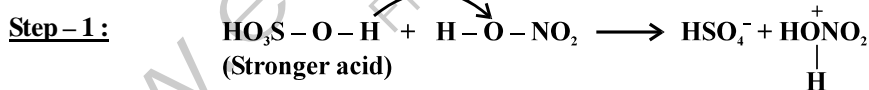
2. Nitration of Benzene :

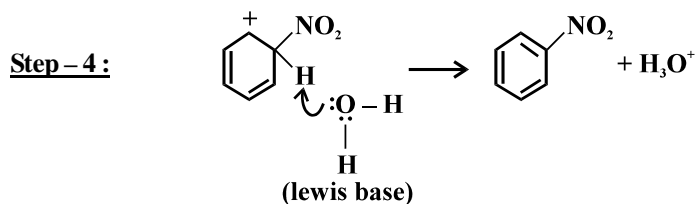
Benzene reacts slowly with hot concentrated nitric acid to yield nitrobenzene. The reaction is much faster if it reacts with mixture of nitric acid and sulfuric acid concentrated.



Concentrated sulfuric acid increases the rate by increasing the concentration of electrophile i.e, NO_2^+ (nitronium ion)

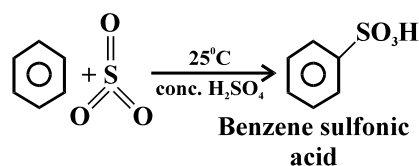
Mechanism :





3. Sulphonations of Benzene :

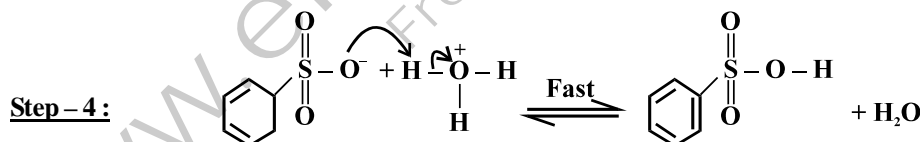
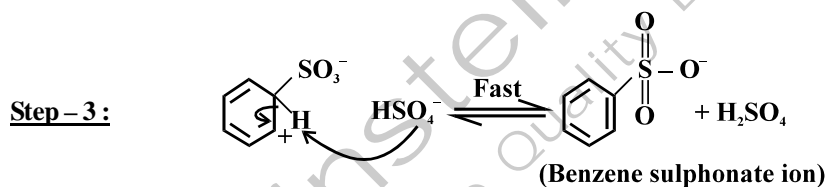
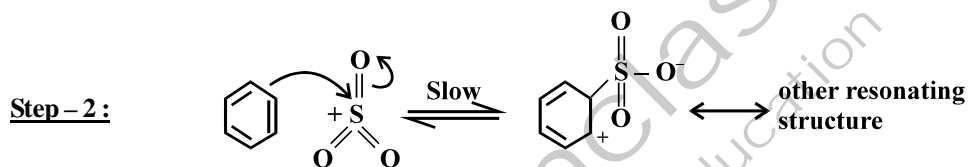
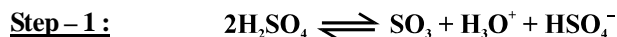
Benzene reacts with fuming sulfuric acid at room temperature to produce benzene sulfonic acid. Fuming sulfuric acid is the sulfuric acid that contains added SO_3 . Sulfonation can also take place with concentrated sulfuric acid alone but that takes place slowly.



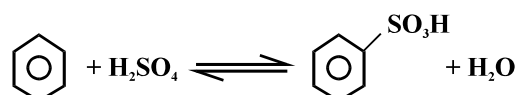
In either reaction electrophile appears to be sulfur trioxide SO_3 .

Mechanism :

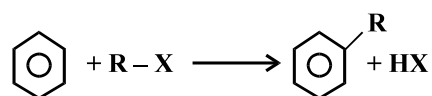
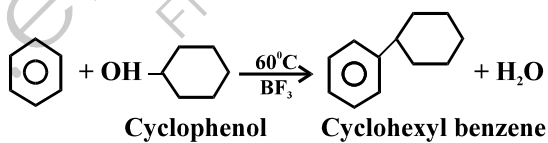
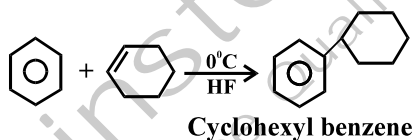
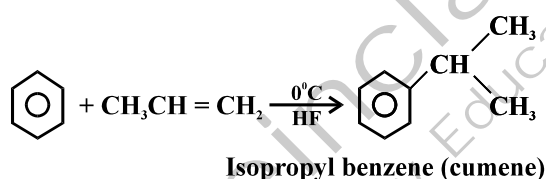
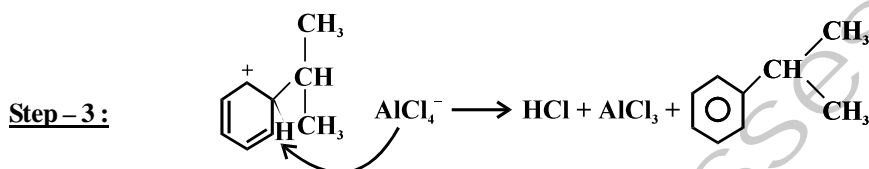
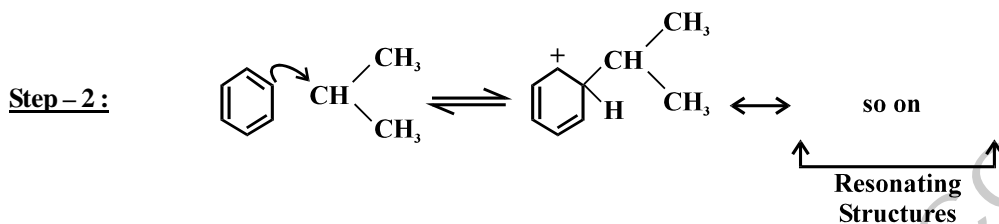
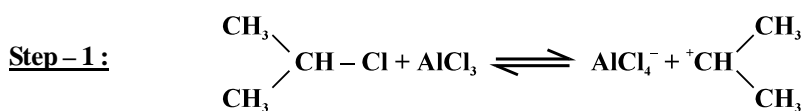
Sulphonation of Benzene :



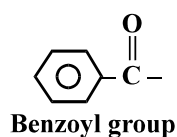
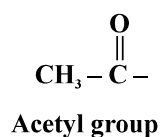
As all the steps are in equilibrium so overall reaction is also in equilibrium.

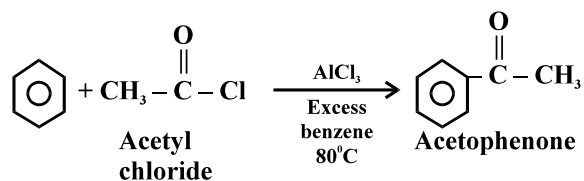


The position of equilibria can be influenced by using concentrated sulfuric acid or fuming sulfuric acid. Under these conditions equilibrium positions lies more towards to the right.

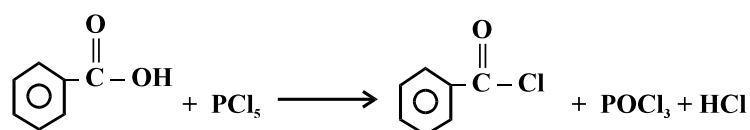
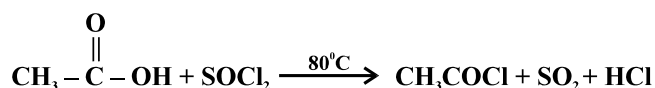
4. Friedel-Crafts Alkylation :Mechanism :

5. Friedel Craft Acylation : The $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-$ group is called acyl group. Two common acyl groups are the acetyl group and Benzoyl group.

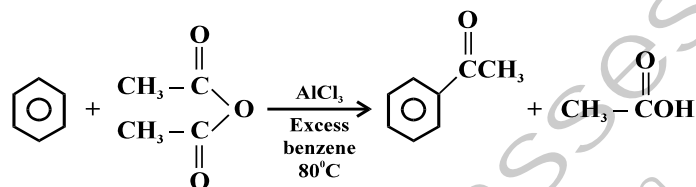




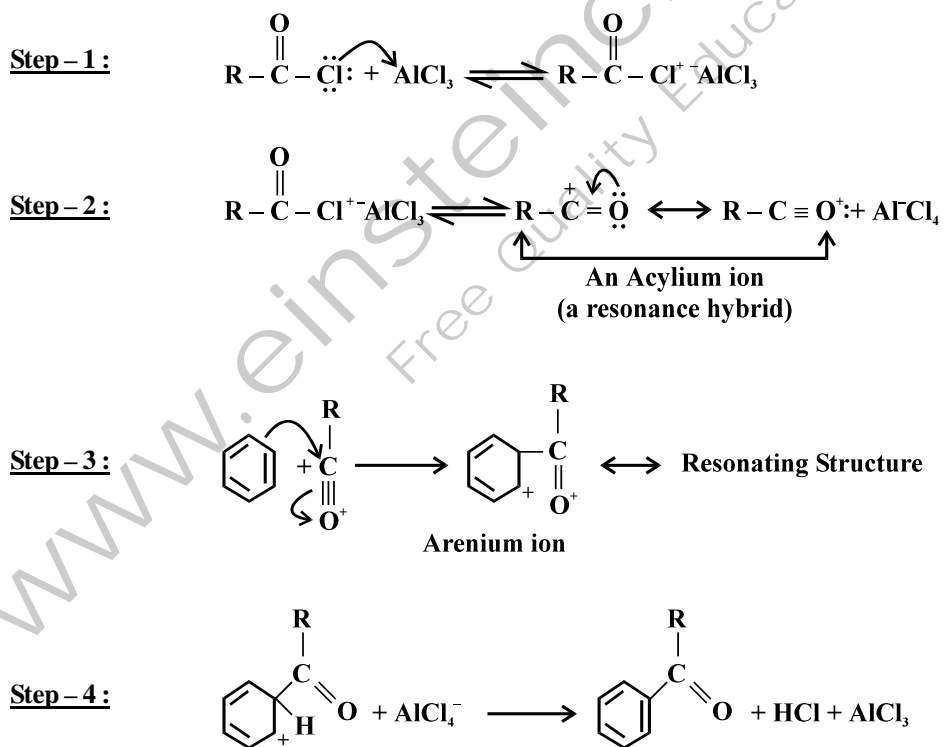
Acyl chloride are also obtained from by treating carboxylic acids with thionyl chloride (SOCl₂) or phosphorous pentachloride (PCl₅)

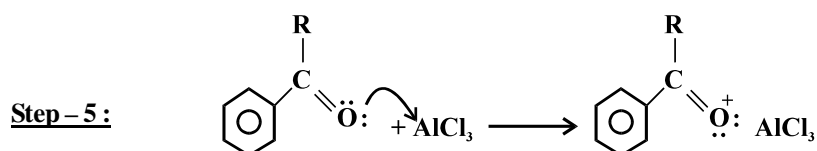


Friedal craft acylation can also be done in the presence of acetic anhydride e.g.

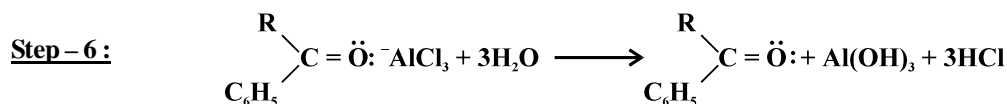


Mechanism:



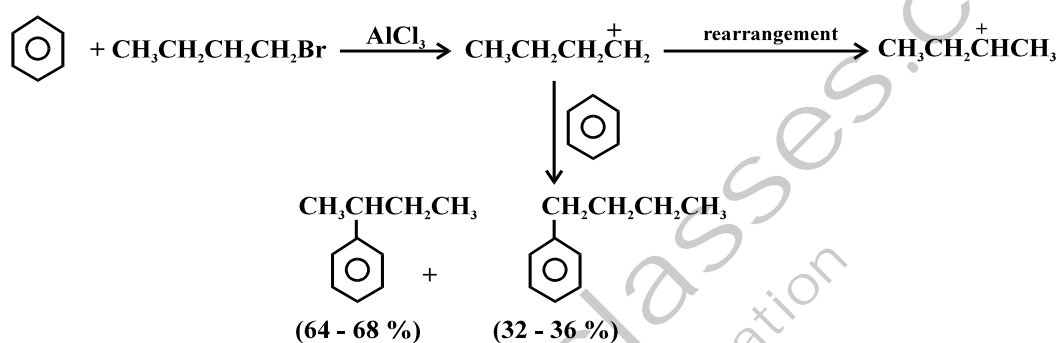


Treating this complex with water liberates the ketone

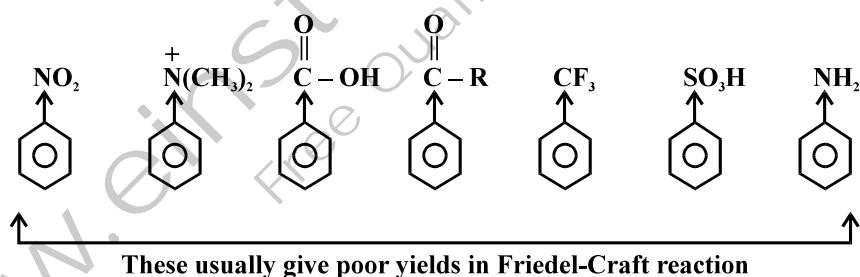


Limitations of Friedel-Craft's Reactions :

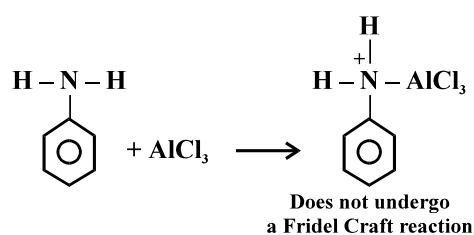
1. When the carbocation formed from an alkyl halide, alkene or alcohol can rearrange to more stable carbocation, thus major product obtained from the reaction is usually the one from the more stable carbocation. When benzene is alkylated with butyl bromide then sec-butyl benzene is the major product as 1^o-carbocation undergoes rearrangement.



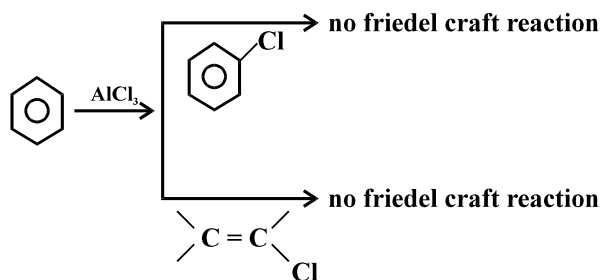
2. Friedel-Craft's reaction usually give poor yields when powerful electron-withdrawing groups are present on the aromatic ring or when the ring bears an $-\text{NH}_2$, $-\text{NHR}$ or $-\text{NR}_2$ group. This applies to both alkylation and acylation.



3. The amino groups $-\text{NH}_2$, $-\text{NHR}$ and $-\text{NR}_2$ are changed into powerful electron withdrawing groups by Lewis acid used to catalyze Friedel-Craft's reaction.

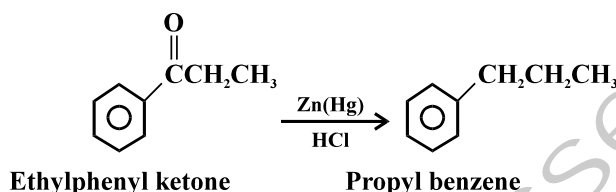


4. Aryl and vinyl halides cannot be used as the halide component because they do not form carbocations readily



6. Clemmensen Reduction :

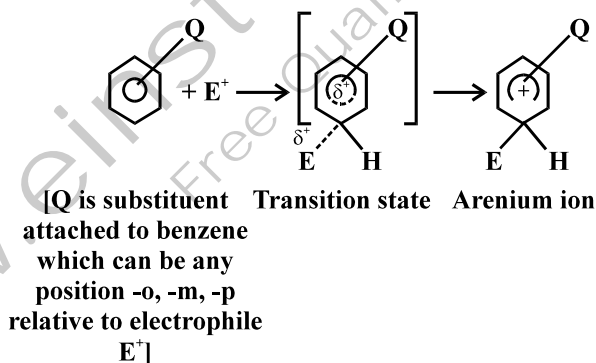
Rearrangements of the carbon chain do not occur in Friedel-Craft's acylation. The acylium ion is more stabilized by resonance is more stable than any other carbocation. Thus there is no driving force for rearrangement. Thus there is possible of formation of n-alkyl benzene. The ketone group can be reduced to $-\text{CH}_2-$ group in the presence of HCl & Zn(Hg) .



7. The effect of Electron-Releasing and Electron - withdrawing groups :

Groups which activate the benzene ring towards the electrophilic substitution, whereas other groups deactivate the ring. Group which activate the ring means that the group increases the relative rate of reaction. We mean that aromatic compound with an activating group reacts faster in electrophilic substitution than benzene.

The General mechanism is shown as follows :

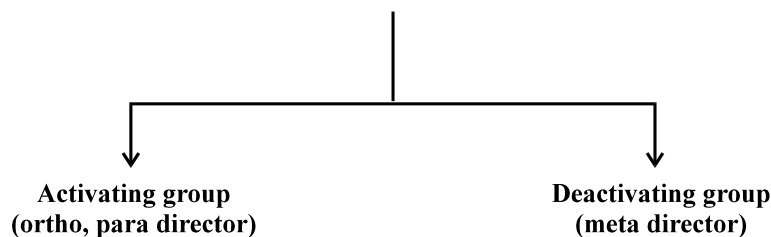


If $\text{Q} \rightarrow$ is electron withdrawing it destabilises the transition state so is the arenium ion so reaction is slower.

If $\text{Q} \rightarrow$ is electron releasing it stabilizes the transition state so the reaction is faster.

8. Effect of substituents on Reactivity and Orientation :

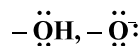
Substituent groups can be divided into two classes according to their influence on the reactivity of the ring.



Activating group increase the reactivity towards the electrophile than benzene. Deactivating group decreases the reactivity than benzene.

Effect of substituent on Electrophilic Aromatic Substitution :

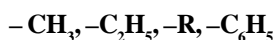
Ortho-Para director Strongly Activating



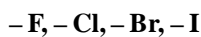
Moderately Activating :



Weakly Activating :

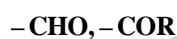
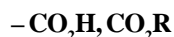


Weakly Deactivating

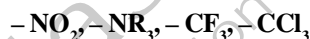


Meta director

Moderately Deactivating :



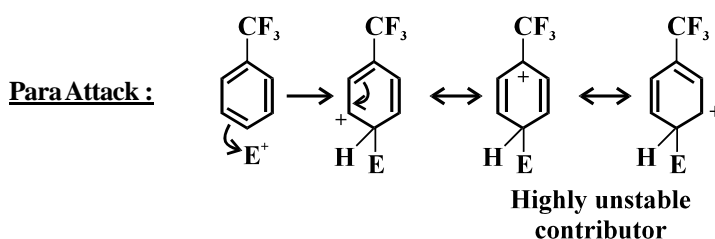
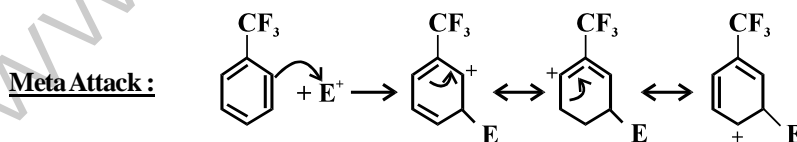
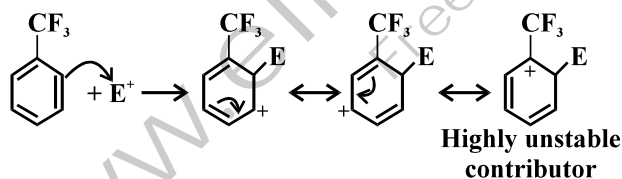
Strongly Deactivating



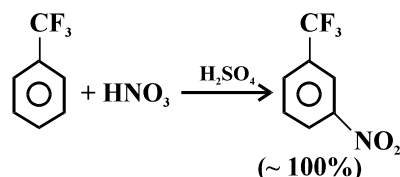
9. Meta-directing group : All meta directing groups are having either a full positive charge or partial positive charge. As a typical example let us consider the trifluoromethyl groups.

We can understand how the trifluoromethyl group affects the orientation in electrophilic aromatic substitution if we examine the resonance structures of the arenium ion that would be formed when the electrophile attacks at the ortho, meta and para positions of the trifluoromethyl benzene.

OrthoAttack :

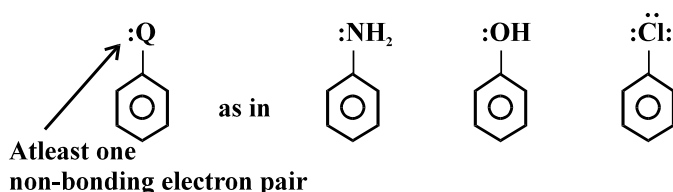


As we see from the resonance structures for the arenium ion arising from the ortho and para attack that one contributing structure is highly unstable relative to all others because the positive charge is located on the ring carbon that bears the electron withdrawing group. We see no such resonance structure in arenium ion arising from meta attack. This means that arenium ion formed by meta attack should be most stable of the three.

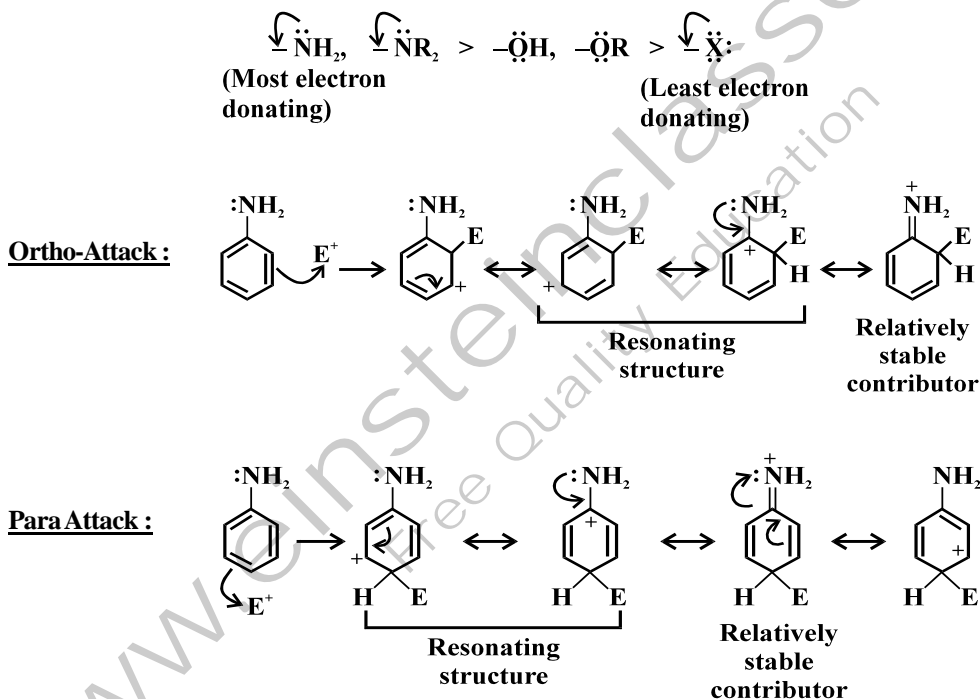


10. Ortho-Para Directing Groups :

Except for the alkyl and phenyl substituents, all of the ortho-para directing groups are of following general type :



The electron donating resonance effect applies with decreasing strength in the following order :



In meta attack the relative stable contributor resonating structure does not form.