

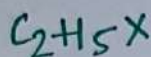
# HALOALKANES AND HALOARENES

(ORGANIC CHAPTER-1)

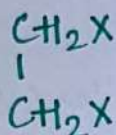
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## Topic-1:- Classification

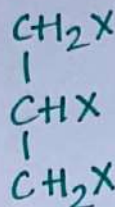
(a) on the basis of number of halogen atom:-



Monohaloalkane



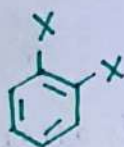
Dihaloalkane



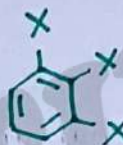
Trihaloalkane



Monohaloarene



Dihaloarene



Trihaloarene

R-X

An alkyl halide

IUPAC-haloalkane

R- Alkyl or substituted alkyl

X - F, Cl, Br, I

Ar-X

An Aryl halide

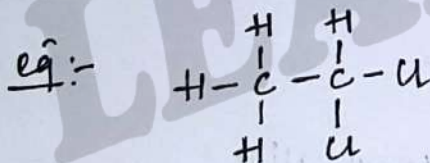
IUPAC-haloarene

Ar- phenyl or substituted phenyl

X - F, Cl, Br, I

The dihalo-compounds having the same type of halogen atom are further classified as:-

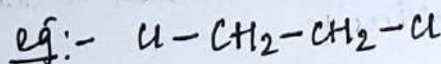
(a) Gem-dihalide:- In these derivative, both the halogen atom are attached to the same carbon atom.



Common name:- Ethylidene chloride

IUPAC name:- 1,1-Dichloroethane

(b) Vic-dihalide:- In these derivative, both the halogen atom are attached to adjacent (vicinal) carbon atom.



Common-name:- Ethylene dichloride

IUPAC name:- 1,2-Dichloroethane  
(1,2-Dichloroethane)

- Gem-dihalide are also known as alkylidene halide
- Vic-dihalide are also known as alkylene halide



(b) compounds containing C-X bond, where carbon is  $sp^3$  hybridised

(i) Alkyl halide or Haloalkane:- The functional group is attached to the carbon, that carbon is directly attached to how many carbon.

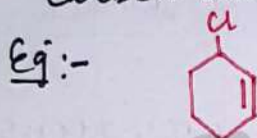
If 0 or 1 -  $1^\circ$   
 2 -  $2^\circ$   
 3 -  $3^\circ$

Eg:-  $CH_3-CH_2-CH_2-Cl$  :- ( $1^\circ$ )

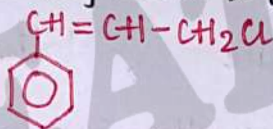
$CH_3-\underset{\substack{| \\ I}}{CH}-CH_3$  :- ( $2^\circ$ )

$CH_3-\underset{\substack{| \\ Br}}{\overset{\substack{CH_3 \\ |}}{C}}-CH_3$  :- ( $3^\circ$ )

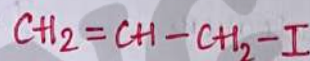
(ii) Allylic Halide:- The halogen atom is attached to the  $sp^3$  hybridised carbon atom which is adjacent to double bond.



3-Chlorocyclohex-1-ene



3-Chloro-1-phenylprop-1-ene

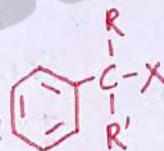


3-Iodoprop-1-ene

(iii) Benzylic Halide:- In these halide, the halogen atom is bonded to a  $sp^3$  hybridised carbon atom which is next to the benzene ring.



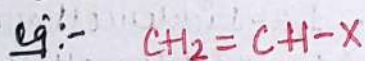
Benzyl Halide



Di-alkylbenzyl halide

(c) Compounds containing C-X bond, where carbon is  $sp^2$  hybridised

(i) Vinyl Halide:- In these halide, the halogen is bonded to carbon-carbon double bond which is  $sp^2$  hybridised.

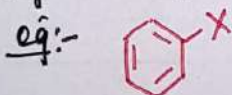


Vinyl halide



1-Halocyclohex-1-ene

(ii) Aryl Halide:- In these halide, the halogen atom is directly attached to  $sp^2$  hybridised carbon atom of the aromatic ring.



Halobenzene

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## Topic-2

### Nomenclature

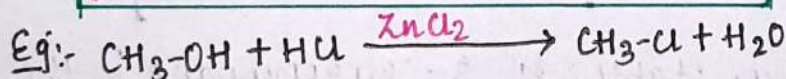
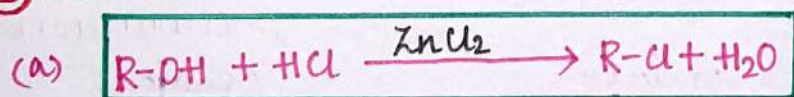
IUPAC names of some halides that were asked in board examination:-

STRUCTURE	IUPAC name	STRUCTURE	IUPAC name
1.	4-Bromo-3-methyl-pent-2-ene	10.	2,4-Dinitrochlorobenzene (2,4-Dinitrochlorobenzene)
2.	2-Bromo-4-chloropentane	11.	1-chloro-2,2-dimethylpropane
3.	4-Chloropent-1-ene	12.	2-chloro-3-methylbutane
4.	2,5-Dichlorotoluene / 1,4-Dichloro-2-methylbenzene	13.	2-Bromo-4-chloropentane
5.	2-Bromo-3-methylbut-2-en-1-ol	14.	3-chloroprop-1-ene
6.	Phenylchloromethane	15.	1,3-Dibromobenzene
7.	1-Bromo-2,2-dimethylpropane	16.	3-Bromotoluene
8.	4-Bromopent-2-ene	17.	Trichloromethane
9.	3-Bromo-2-methylbut-1-ene	18.	2,2-Dibromopropane

## Topic-3

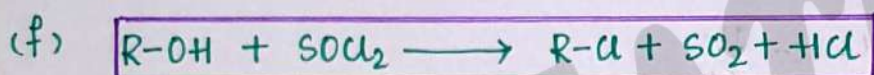
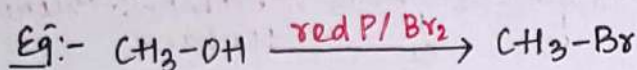
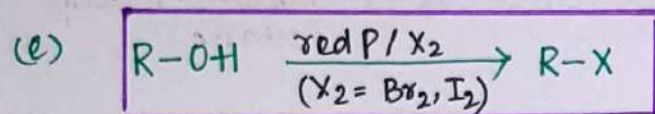
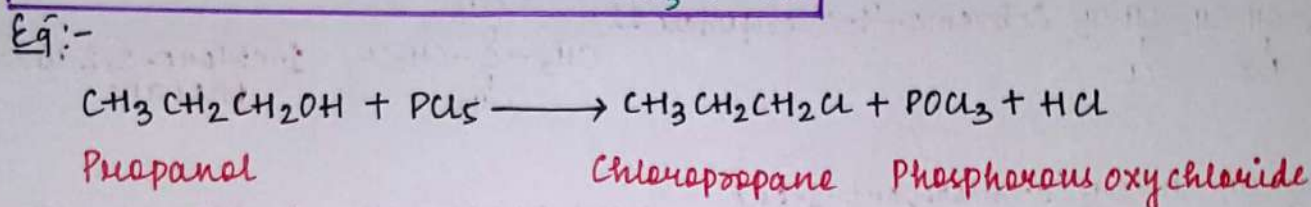
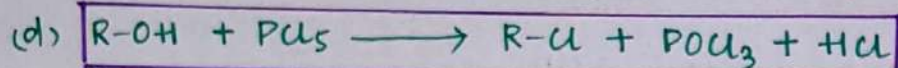
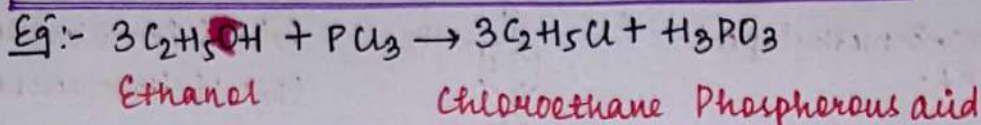
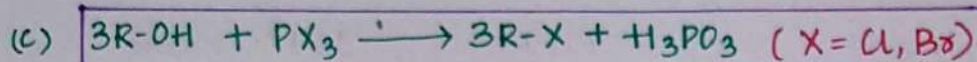
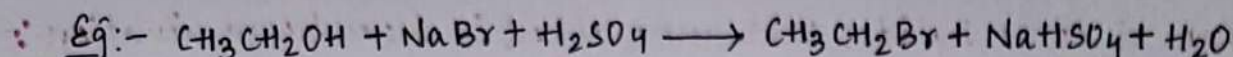
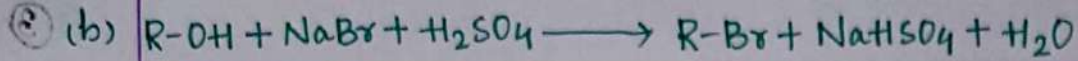
### METHODS OF PREPARATION OF HALOALKANES AND HALOARENES:-

#### ① FROM ALCOHOLS:-



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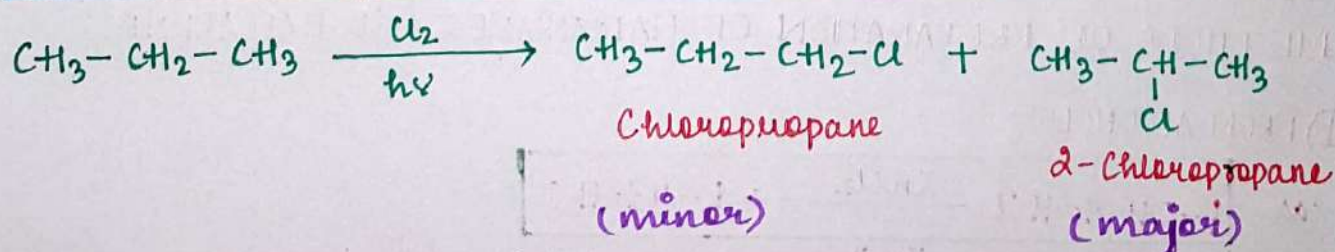


Preparation of chloroalkane from alcohol by using thionyl chloride is the best method because the byproducts are gases which can be easily removed from the reaction mixture leaving behind pure alkyl halide.

Order of reactivity of alcohols with a given haloacid is  $3^\circ > 2^\circ > 1^\circ$

## (2) FROM HYDROCARBONS

### (a) Free radical halogenation / Free radical substitution

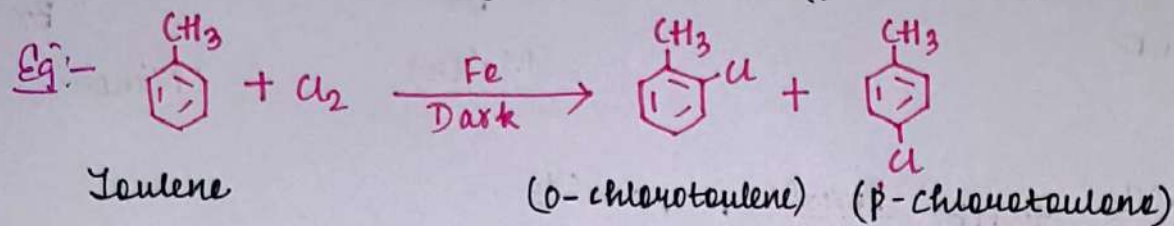
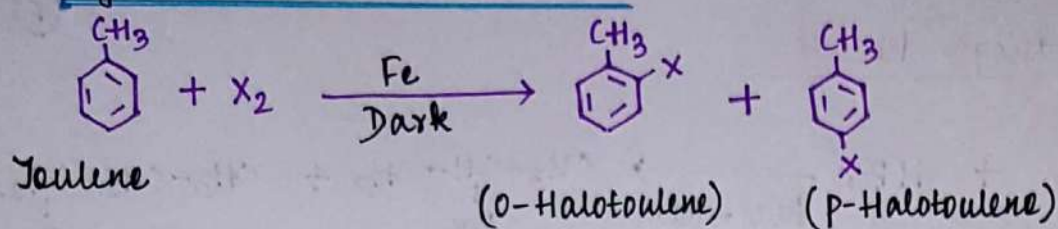


Since,  $2^\circ$  free radical is more stable, so 2-Chloropropane is the major product.

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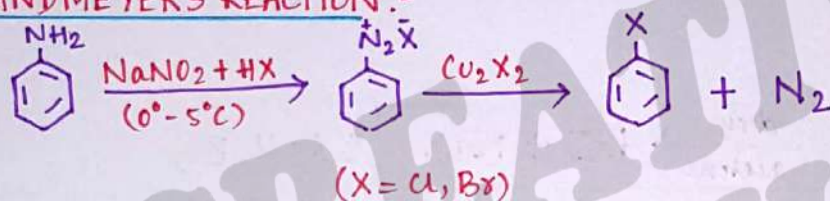


(b) By electrophilic substitution:-

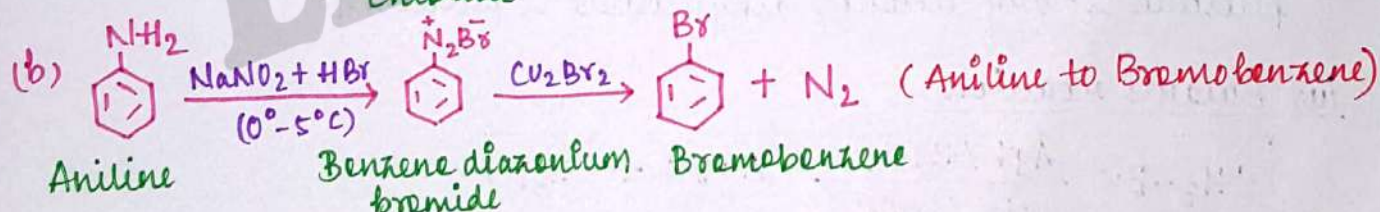
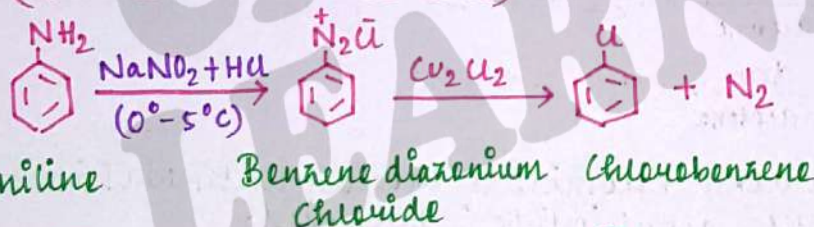


- The ortho and para isomers can easily separated due to their large difference in melting point.
- Iodo-derivative cannot be obtained by direct reaction with iodine as the reaction is reversible.
- Fluoro compounds cannot be prepared by this method due to high reactivity of fluorine.

(c) SANDMEYER'S REACTION:-

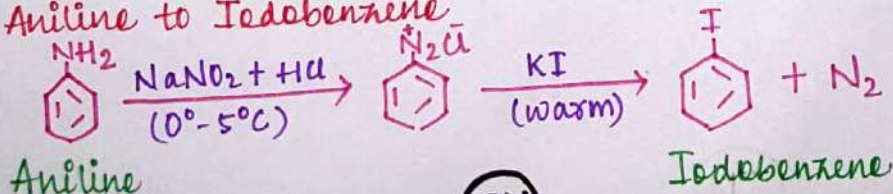


(a) (Aniline to Chlorobenzene)



When aniline is treated with  $\text{NaNO}_2$  and  $\text{HCl}$  at  $(0^\circ-5^\circ\text{C})$  it forms benzene diazonium chloride from which chlorobenzene is prepared by reacting with  $\text{Cu}_2\text{Cl}_2$  and bromobenzene is prepared by reacting with  $\text{Cu}_2\text{Br}_2$ .

\* Aniline to Iodobenzene



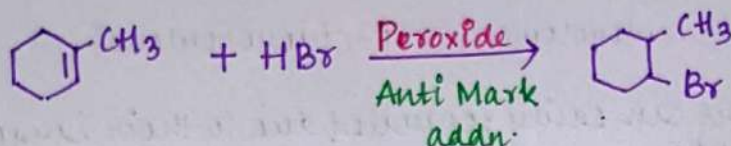
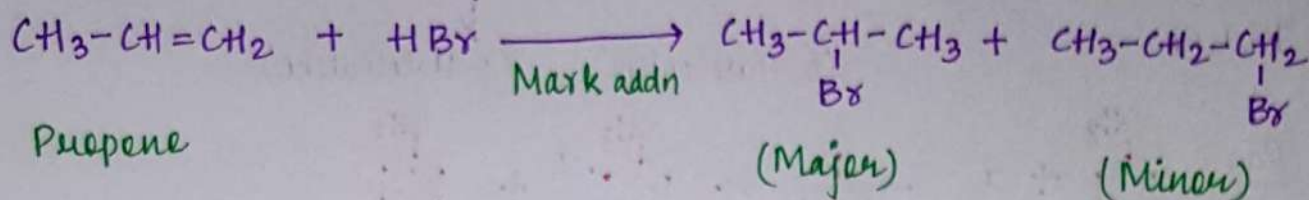
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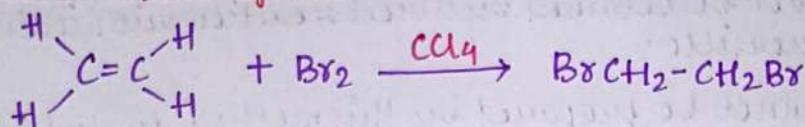
## (d) FROM ALKENES

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### (i) Addition of hydrogen halides:-

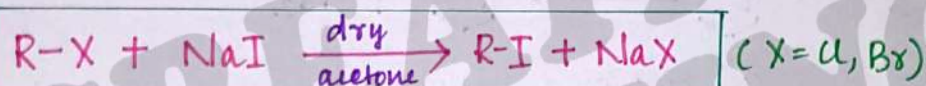


### (ii) Addition of halogens:-

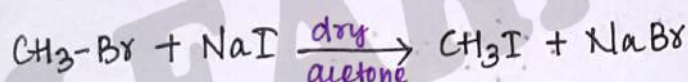
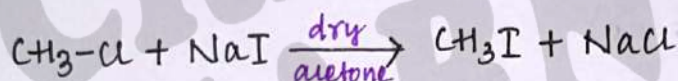
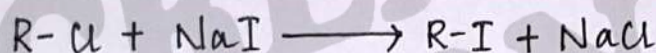


## (e) HALOGEN EXCHANGE

### (i) Finkelstein reaction

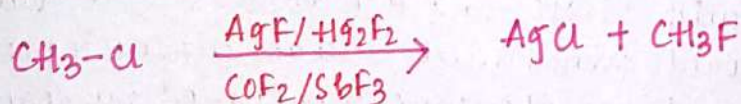
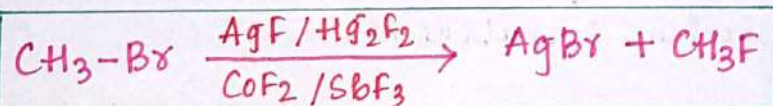


Eg:-



When alkyl chloride or alkyl bromide is treated with NaI in presence of dry acetone, alkyl iodide is prepared.

### (ii) Swarts reaction



Topic-4

## PHYSICAL PROPERTIES

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## 1. SOLUBILITY

Alkyl halides though polar, are immiscible with water because they are not able to form hydrogen bonds with water molecule.

## 2. DENSITY

The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of halogen atom.

## 3. BOILING POINT

• Haloalkanes have higher boiling point as compared to those of corresponding alkanes because this is due to their polarity and strong dipole-dipole interaction between haloalkane molecules.

(i) For the same alkyl group, bp of haloalkanes decreases in the order  $RI > RBr > RI$ . This is because with increase in size and mass of halogen atom, the magnitude of van der Waals force of attraction increases.

Q:- Arrange the compounds in decreasing order of their boiling point  $CH_3I, CH_3Br, CH_3Cl, CH_3F$

Ans:-  $CH_3I > CH_3Br > CH_3Cl > CH_3F$  (bp = boiling point)

(ii) For the same halogen atom, the bp of haloalkanes increase with increase in the size of alkyl group.

Q:- Arrange these  $C_2H_5Cl, C_3H_7Cl, C_4H_9Cl, CH_3Cl$  in increasing order of bp.

Ans:-  $CH_3Cl < C_2H_5Cl < C_3H_7Cl < C_4H_9Cl$

(iii) For isomeric haloalkanes, the bp decrease with branching. i.e.  $1^\circ > 2^\circ > 3^\circ$  because the branching of the chain makes the molecule more compact and therefore decreases the surface area of haloalkanes and so the magnitude of the van der Waals force of attraction decreases.

Q:- Arrange these tert-Butyl bromide, n-Butyl bromide, Isobutyl bromide in decreasing order of their boiling point.

Ans:- n-Butyl bromide > Isobutyl bromide > tert-Butyl bromide.

Q:- Arrange  $CH_3Br, CHBr_3, CH_3Cl, CH_2Br_2$  in increasing order of boiling points.

Ans:-  $CH_3Cl < CH_3Br < CH_2Br_2 < CHBr_3$

Q:- Arrange 1-chloropropane, Isopropyl chloride, 1-chlorobutane in increasing order of boiling points.

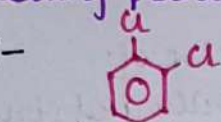
Ans:- Isopropyl chloride < 1-chloropropane < 1-chlorobutane.



- The boiling and melting point of aryl halides are nearly same as that of haloalkanes containing same no. of carbon atoms. The boiling point of monohalogen derivative of benzene are in the order:  
Iodo > Bromo > Chloro > Fluoro.

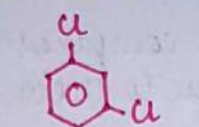
- For the same halogen atom, the boiling and melting points increase as the size of aryl group increases.
- The bp of isomeric dihalobenzenes are nearly the same, but their melting points are quite different.

Eg:-



o-dichlorobenzene

(A)



m-dichlorobenzene

(B)



p-dichlorobenzene

(C)

dec. order of melting point:-  $C > A > B$  (POM)

dec. order of boiling point:-  $A > C > B$  (OPM)

- \* p-dichlorobenzene has the highest melting point because para isomer is more symmetrical and hence its molecules pack closely in the crystal lattice.
- \* o-dichlorobenzene has the highest boiling point due to ortho effect.
- \* m-dichlorobenzene has lowest melting and boiling point because chlorine is a orthopara directing group. So another chlorine atom will attach at ortho and para position but not at meta position. So m-dichlorobenzene is an unstable compound.

## TOPIC-5

### CHEMICAL PROPERTIES

The important reactions of haloalkanes are:-

- (1) Nucleophilic substitution reaction
- (2) Elimination reaction
- (3) Reaction with metals.

Alkyl halide undergo nucleophilic substitution reaction by 2 methods:-

- $S_N^1$  reaction
- $S_N^2$  reaction

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(NT)



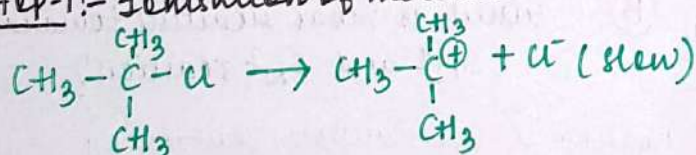
# Difference between $S_N^1$ and $S_N^2$ :-

(9)

$S_N^1$	$S_N^2$
① Nucleophilic substitution unimolecular reaction.	Nucleophilic substitution bimolecular reaction.
② Order-1, Molecularity-2	Order-2, Molecularity-2
③ $R-Cl + Nu^- \rightarrow R-Nu + Cl^-$ Rate = $k[R-Cl]^1[Nu^-]^0$	$R-Cl + Nu^- \rightarrow R-Nu + Cl^-$ Rate = $k[R-Cl]^1[Nu^-]^1$
④ Rate of reaction depends on the conc. of alkyl halide and not on nucleophile. So, unimolecular.	Rate of reaction depends on the conc. of alkyl halide and on nucleophile. So, bimolecular.
⑤ It has 2 step mechanism: 1st:- Ionisation of molecule and formation of carbocation. 2nd:- attack of nucleophile	The approaching of nucleophile and release of $Cl^-$ will occur simultaneously. Hence, it is a single step mechanism.
⑥ Nucleophile will attack both at front side and backside (the front side and back side attack of nucleophile is possible due to $sp^2$ hybridisation and planar structure of carbocation)	Nucleophile will attack only at the backside because in primary alkyl halide, there is less alkyl group and less steric hindrance.
⑦ No transition state complex is found.	Transition state complex is formed.
⑧ Order of reactivity is based on the stability of carbocation. Order is $3^\circ > 2^\circ > 1^\circ$	More bulkier is the group, the backside approach is hindered. Hence, the order of reactivity is $1^\circ > 2^\circ > 3^\circ$
⑨ Due to frontside attack and backside attack retention product and inversion product are obtained. $S_N^1$ is followed by Racemisation.	Due to only backside attack of nucleophile, inversion product is obtained. Inversion of configuration takes place.

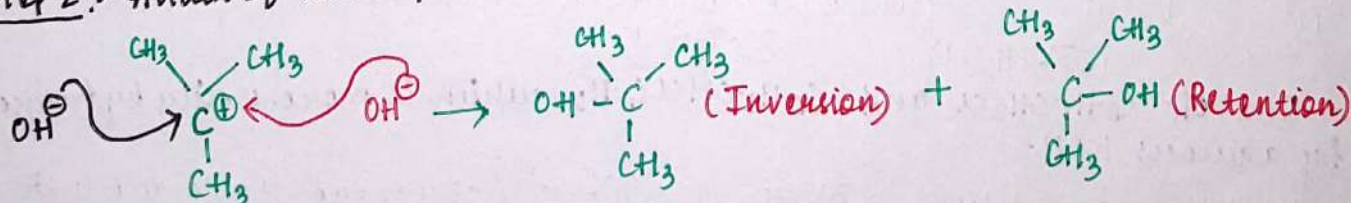
## MECHANISM OF $S_N^1$ :-

Step-1:- Ionisation of molecule.



As slow step is the rate determining step, hence the rate depends on the conc. of alkyl halide and not on nucleophile.

Step-2:- Attack of nucleophile



$S_N^1$  is followed by Racemisation.

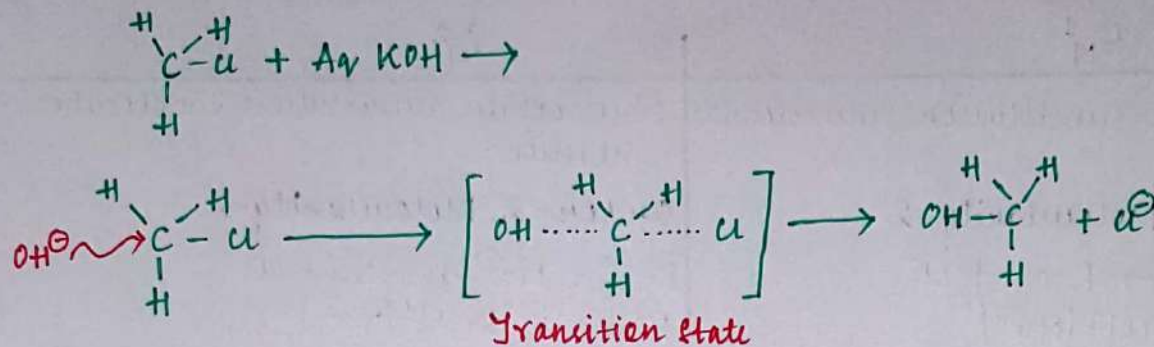
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## MECHANISM OF $S_N2$ :-

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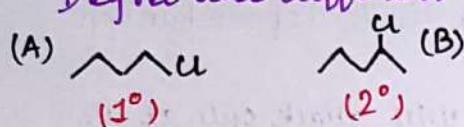
Step-1:- Nucleophile will attack from backside of the leaving group.



The approaching of nucleophile and releasing of  $\text{Cl}^-$  will occur simultaneously. Hence, it is a single step mechanism.

(Q):- TYPE-1

Degree are different



Which is more reactive towards  $S_N1$  and  $S_N2$  reaction? And why?

Ans:-  $S_N2$       A > B (due to steric hindrance)  
 $S_N1$       B > A (2° carbocation is more stable than 1° carbocation)

(Q):- TYPE-2

Degree same but halogen different



Which is more reactive towards  $S_N1$  and  $S_N2$  reaction?

Ans:-  $S_N1$       B > A  
 $S_N2$       B > A (Iodine is a better leaving group as its electronegativity is less than chlorine)

(Q):- TYPE-3

Degree same but position of substituent differ

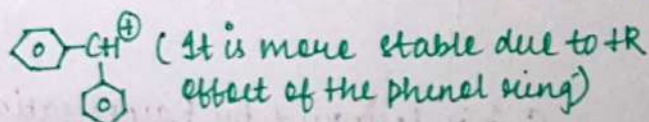
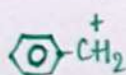


Which is more reactive towards  $S_N1$  and  $S_N2$  reaction?

Ans:-  $S_N1$       A > B  
 $S_N2$       B > A (The substituent nearer to the carbon containing halogen will sterically more hinder the nucleophile from backside attack.  $S_N2$  is slower.)

(Q):- Out of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ , which is more easily hydrolysed by aqueous KOH.

Ans:- under  $S_N1$  conditions



(JM)

So,  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  is more easily hydrolysed.



## AMBIDENT NUCLEOPHILE:-

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The nucleophile which is capable of attacking the molecule through more than one site is called as ambident nucleophile.

eg:- nitrite ion, cyanide ion.

Some important nucleophilic reagents:-

- $\text{NaOH (aq)} \rightarrow \text{OH}^-$  (nucleophile)
- $\text{KOH (aq)} \rightarrow \text{OH}^-$  (nucleophile)
- $\text{KCN (alc)} \rightarrow \text{C}^- \text{N}$  (nucleophile)  
Carbon is the attacking atom.
- $\text{AgCN (alc)} \rightarrow \text{N}^- \text{C}$  (nucleophile)  
Nitrogen is the attacking atom.

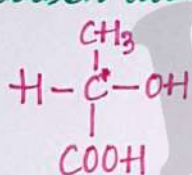
(Q):- Halalkanes react with KCN to form alkyl cyanides as the main product while AgCN forms isocyanides as the chief product. Explain

Ans:- KCN is predominantly ionic. So, both C and N atom are free to donate electron pair. Since, C-C bond is more stable than C-N bond, therefore attack mainly occurs through carbon atom forming alkyl cyanide as the main product.

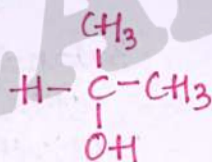
AgCN is mostly covalent in nature. Only N atom is free to donate electron pair and attack mostly occurs through nitrogen atom forming isocyanide as the chief product.

## STERIOCHEMICAL ASPECTS OF NUCLEOPHILIC SUBSTITUTION REACTION:-

① CHIRALITY CENTRE:- A carbon atom which is bonded to four different atoms or groups in the molecule is called chiral carbon or an asymmetric carbon atom.

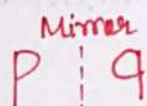


Lactic acid  
(Chiral)  
Optically active



Propan-2-ol  
(Achiral)  
Optically inactive

② CHIRAL OBJECT:- The one that is not superimposable on its mirror image



Chiral  
(non-superimposable)



Achiral  
(superimposable)

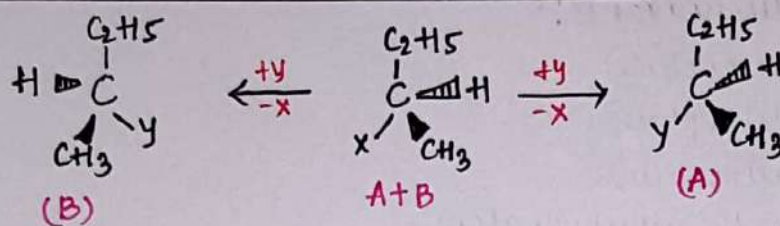
③ ENANTIOMERS:- Compounds which are mirror images of each other and are not superimposable.





(4) RACEMIC MIXTURE:- The process of conversion of one enantiomer or optically active compound into a racemic mixture is called racemization. An equimolar mixture of a pair of enantiomers is called racemic mixture.

(5) INVERSION, RETENTION, RACEMIZATION:-



- If (A) is the only compound obtained, the process is called Retention.
- If (B) is the only compound obtained, the process is called Inversion.
- If a 50:50 (equal) mixture of A and B is obtained, the process is Racemization.

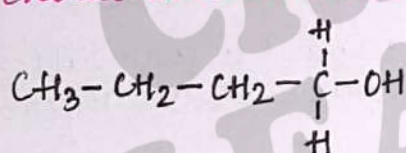
(Q):- Give Reasons:-

(i) Racemic mixture is optically inactive.

Ans:- A racemic mixture is optically inactive as it is a mixture containing two enantiomers in equal proportion and have zero optical rotation.

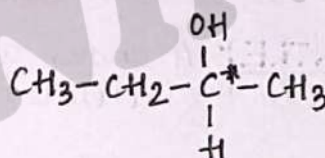
(ii) Why is butan-1-ol optically inactive but butan-2-ol is optically active?

Ans:- butan-1-ol is optically inactive due to the absence of chiral carbon atom. butan-2-ol is optically active due to the presence of chiral carbon atom.



(Butan-1-ol)

Achiral  
(Optically inactive)



(Butan-2-ol)

Chiral  
(Optically active)

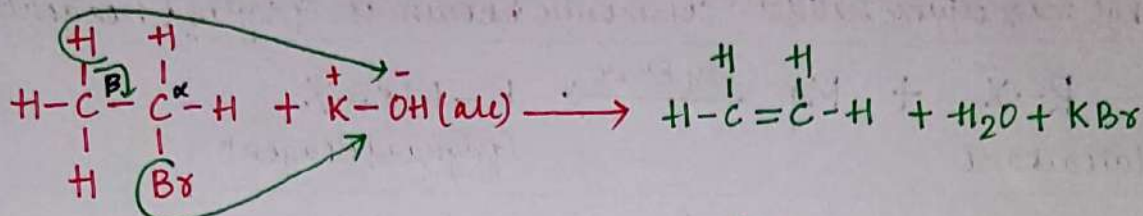
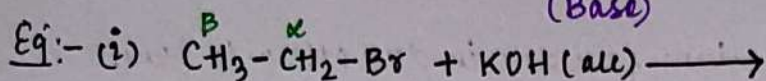
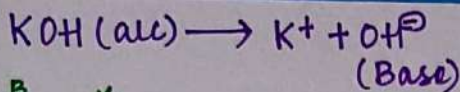
(iii) (±) 2-Butanol is optically inactive

Ans:- (±) 2-Butanol is a racemic mixture. i.e., there are two enantiomers in equal proportions. The rotation by one enantiomer will be cancelled by the rotation due to other isomer, making the mixture optically inactive.

## (2) ELIMINATION REACTION

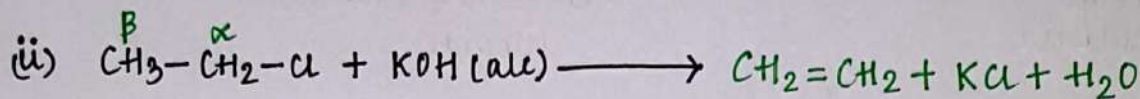
When a haloalkane having at least one β-hydrogen atom is treated with (alc) KOH, then there is elimination of hydrogen from the β-carbon atom and halogen from the α-carbon atom. As a result, we get alkene as the product. Since, β-hydrogen atom is involved in elimination, it is also called as β-elimination.





Bromoethane

Ethene



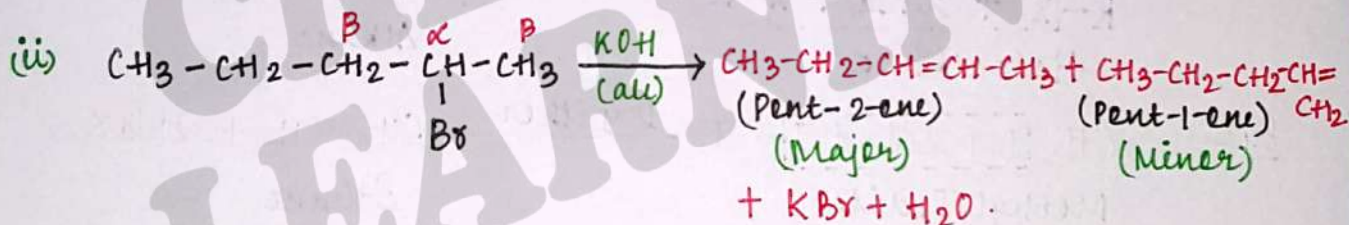
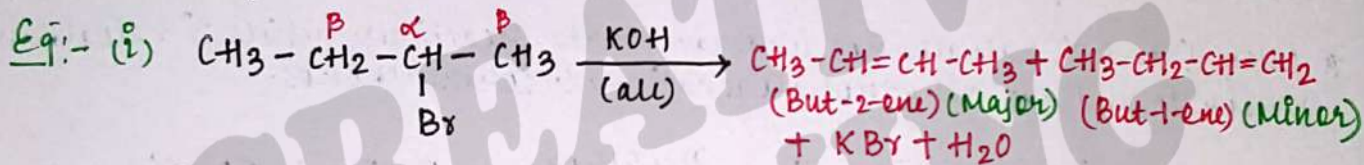
Chloroethane

Ethene

In the dehydrohalogenation of 2° and 3° haloalkanes, when there is a possibility of formation of 2 alkene (one major and one minor), there we apply Saytzeff's rule or Zeffsayt's rule.

### SAYTZEFF'S RULE OR ZEFFSAYT'S RULE:-

If there is a possibility of formation of 2 alkene then the more substituted alkene is more stable.



(Q):- The treatment of alkyl chlorides with aqueous KOH leads to formation of alcohols but in presence of alcoholic KOH, alkenes are the major products. Explain.

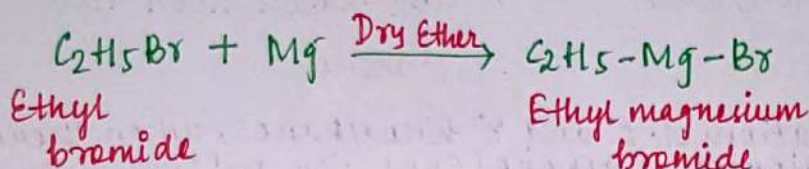
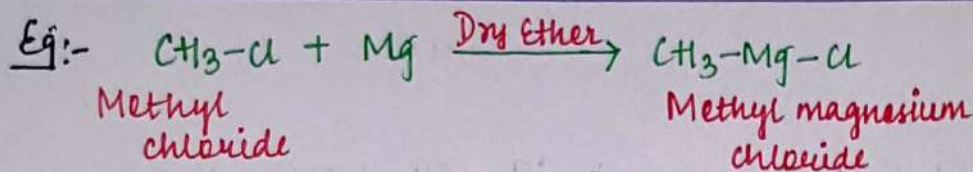
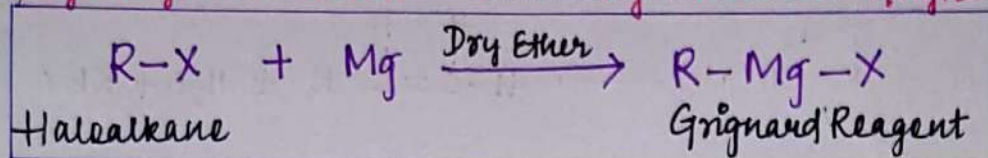
Ans:- In aqueous solution, KOH is almost completely ionized to give OH<sup>-</sup> ions. These being strong nucleophiles result into substitution reaction on alkyl halide to form alcohols. At the same time in aqueous solution, the OH<sup>-</sup> ions are highly hydrated. This hydration reduces the basic character of OH<sup>-</sup> ions which, therefore, fails to abstract a proton (H<sup>+</sup>) from the β-carbon atom of alkyl chloride to form an alkene.

In contrast, an alcoholic solution of KOH contains alkoxide (RO<sup>-</sup>) ions which being a stronger base than OH<sup>-</sup> ions preferentially eliminates a molecule of HCl from an alkyl chloride to form an alkene.



### ③ REACTION WITH METALS:-

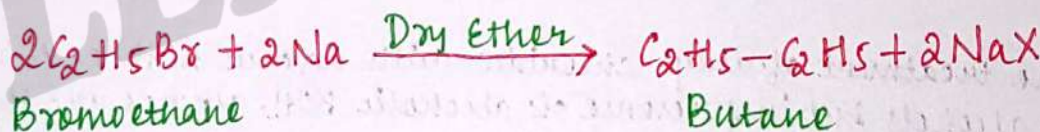
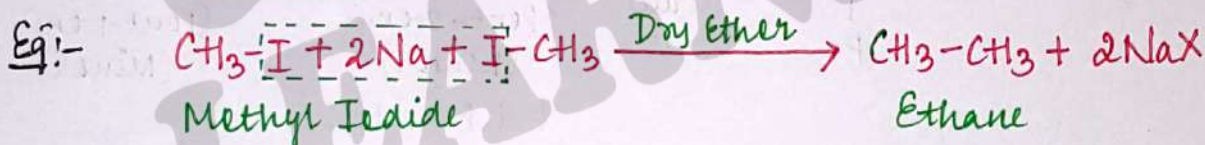
Haloalkanes react with dry magnesium powder in dry ether to form alkyl magnesium halides commonly known as Grignard reagent.



### WURTZ REACTION:-

When 2 same alkyl halide react with metallic Na in presence of dry ether we get higher alkanes containing double the number of carbon atoms present in the haloalkane.

\* Only 1° and 2° haloalkanes undergo Wurtz reaction while 3° haloalkanes prefer to undergo dehydrohalogenation to form alkenes.



### TOPIC-6

### REACTION OF HALOARENES:-

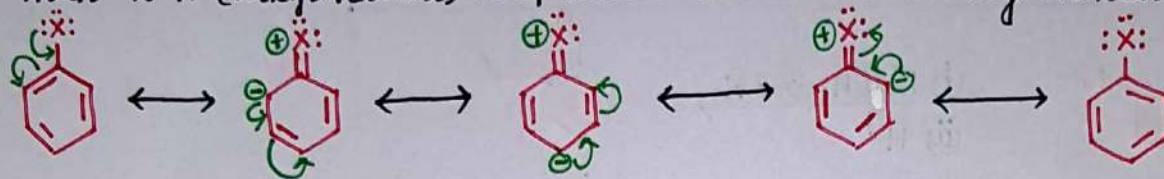
- ① NUCLEOPHILIC SUBSTITUTION
- ② ELECTROPHILIC SUBSTITUTION
- ③ REACTION WITH METALS



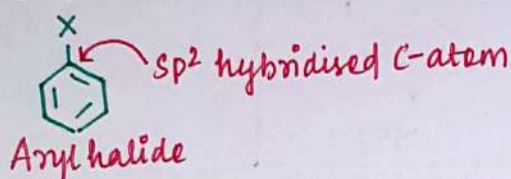
### ① NUCLEOPHILIC SUBSTITUTION REACTION:-

Haloarenes are less reactive towards nucleophilic substitution reactions because:-

- ① **RESONANCE EFFECT:-** In haloarenes, the electron pair on halogen atom are in conjugation with the  $\pi$ -electron of the benzene ring. So C-X bond acquires partial double bond character due to resonance. So C-X bond is much stronger than R-X (alkyl halide) and hence cannot be easily broken.



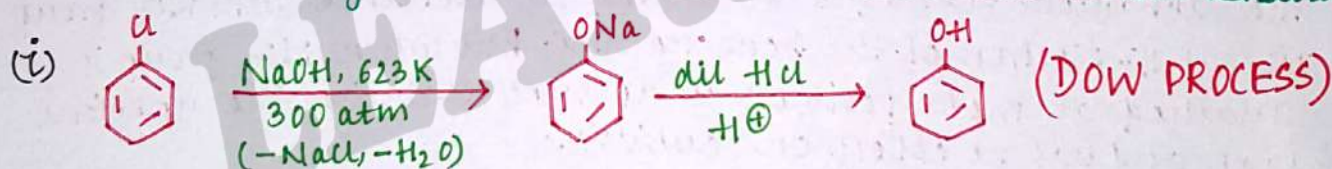
- ② **DIFFERENCE IN HYBRIDISATION:-** In aryl halides, the halogen atom is attached to  $sp^2$  hybridised carbon atom. So C-X bond is shorter due to compact size of  $sp^2$  hybrid orbitals as compared to C-X bond in alkyl halides where halogen atom is attached to  $sp^3$  hybridised carbon atom. Since, it is difficult to break a shorter bond than a longer bond.



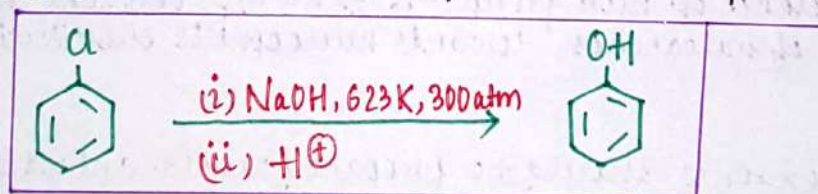
- ③ **INSTABILITY OF PHENYL CATION:-** In haloarenes, the phenyl cation formed as a result of self ionisation is not stabilised by resonance.

- ④ Due to possible repulsion between nucleophile and electron rich benzene ring.

Haloarenes undergo substitution reaction under some drastic condition:-



Chlorobenzene                      Sodiumphenoxide                      phenol



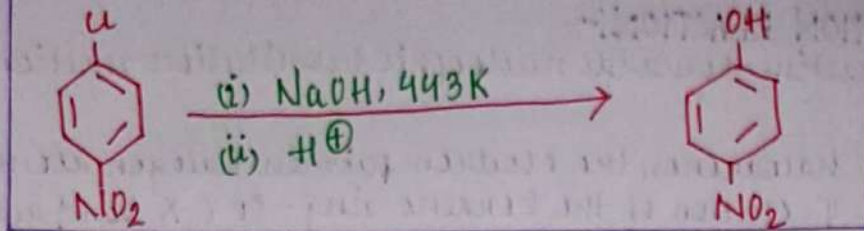
Chlorobenzene

Phenol

If electron withdrawing group ( $-NO_2$ , CN) is attached at o & p positions then it increases the reactivity towards nucleophilic substitution reaction. As the no of electron withdrawing group increases, hence the reactivity increases.



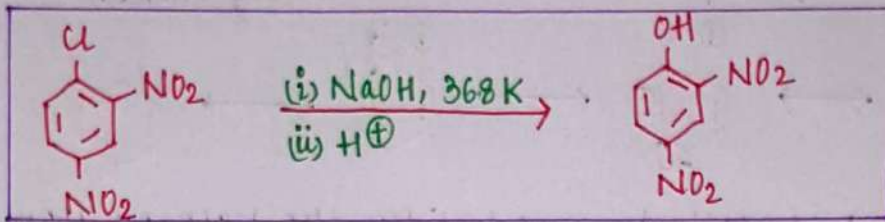
(ii)



p-Chloronitro benzene

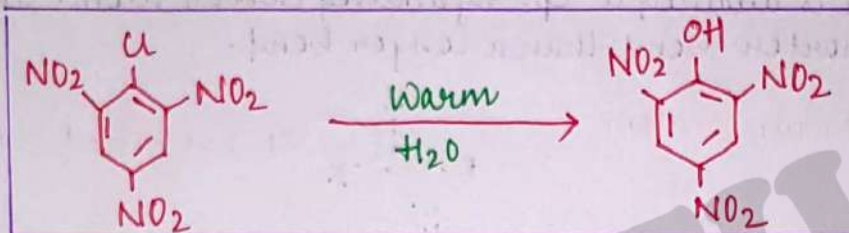
p-Nitrophenol

(iii)

2,4-Dinitro  
chlorobenzene

2,4-Dinitrophenol

(iii)

2,4,6-Trinitro  
chlorobenzene  
(Picryl chloride)2,4,6-Trinitrophenol  
(Picric Acid)

(Q):- Why does  $\text{NO}_2$  group show its effect only at ortho and para positions but not at meta position?

Ans:- When  $\text{NO}_2$  group is attached at ortho and para position, then the carbanion formed is stabilised by resonance with  $\text{NO}_2$  group as well as  $\pi$ -electron of the benzene ring. But when  $\text{NO}_2$  group is attached at meta position it does not stabilise the negative charge and has no effect on reactivity.

OR

Give Reason: The presence of nitro group ( $-\text{NO}_2$ ) at o/p-positions increases the reactivity of haloarenes towards nucleophilic substitution reaction.

(Q):- Give Reason:-

- (i) Grignard's reagents should be prepared under anhydrous conditions.
- (ii) The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.
- (iii) C-X bond length in haloarene is smaller than C-X bond length in  $\text{CH}_3\text{-X}$ .

Ans:- (i) Grignard's reagents are very reactive. In the presence of moisture, they react to give alkanes. So they should be prepared under anhydrous conditions.

JM



(ii) [You can answer this in both ways. First is on the basis of hybridisation and second is on the basis of resonance]

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① In chlorobenzene, the Cl atom is attached to  $sp^2$  hybridised C atom whereas in cyclohexyl chloride, the Cl atom is attached to  $sp^3$  hybridised C atom. Due to greater s-character,  $sp^2$  hybrid carbon atom is more electronegative than  $sp^3$  hybrid carbon atom. So the C-Cl bond in chlorobenzene has less tendency to release electrons to Cl than C-Cl bond in cyclohexyl chloride. Hence, C-Cl bond of cyclohexyl chloride is more polar and has higher dipole moment.

② The C-Cl bond in chlorobenzene acquires a partial double bond character due to resonance. Whereas, in cyclohexyl chloride C-Cl bond is pure single bond. Hence, C-Cl bond in chlorobenzene is shorter than C-Cl bond in cyclohexyl chloride. Therefore the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(iii) Due to delocalisation of lone pair of electron on X atom over the benzene ring, C-X bond in halobenzene acquires a partial double bond character while in  $CH_3-X$ , C-X bond is purely a single bond. Therefore C-X bond in halobenzene is shorter than  $CH_3X$ .

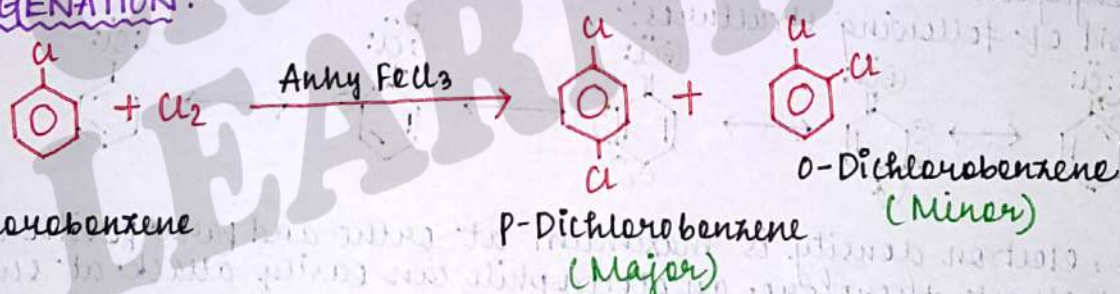
OR

You can explain on the basis of hybridisation.

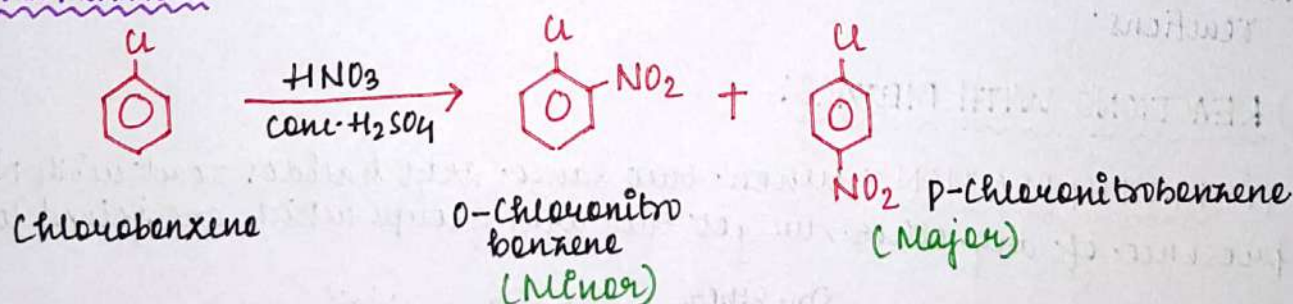
## ② ELECTROPHILIC SUBSTITUTION:-

Electrophilic substitution occurs at o & p positions. However, p-product usually predominates over the o-product due to steric hindrance.

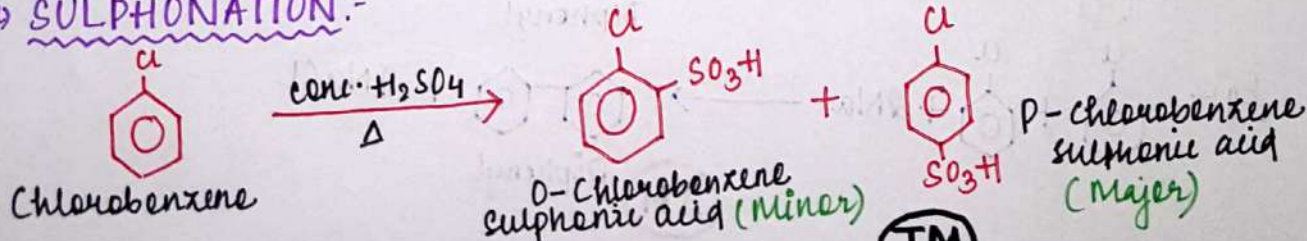
### (i) HALOGENATION:-



### (ii) NITRATION:-



### (iii) SULPHONATION:-

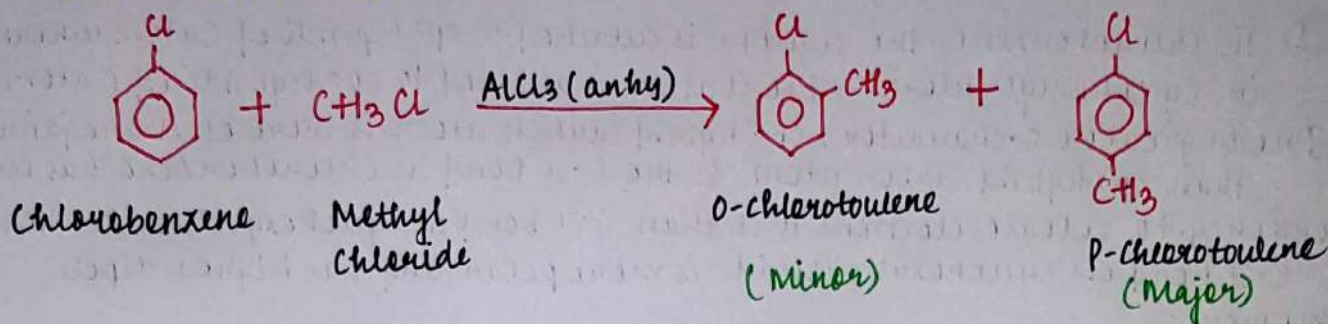


(JM)

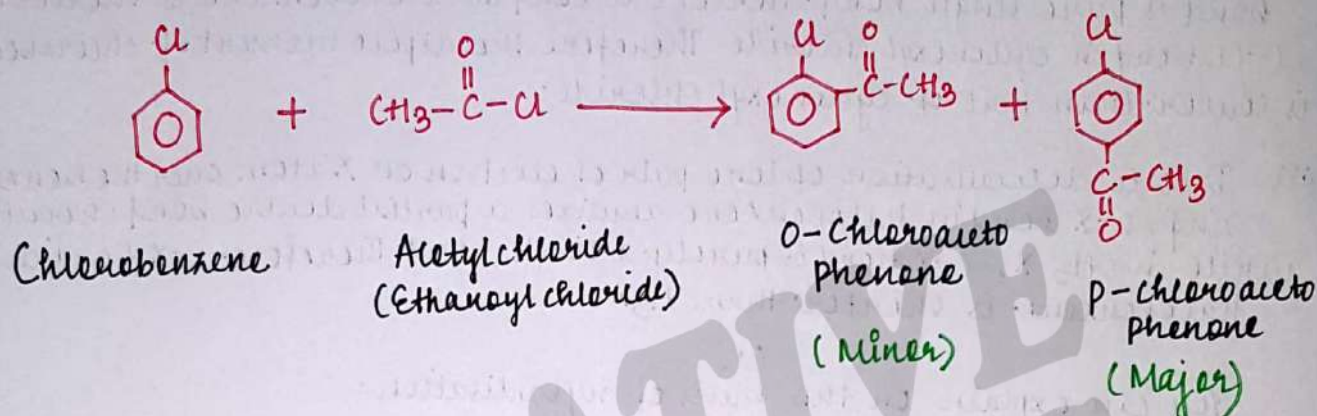


## (iv) FRIEDEL-CRAFTS ALKYLATION:-

(18)

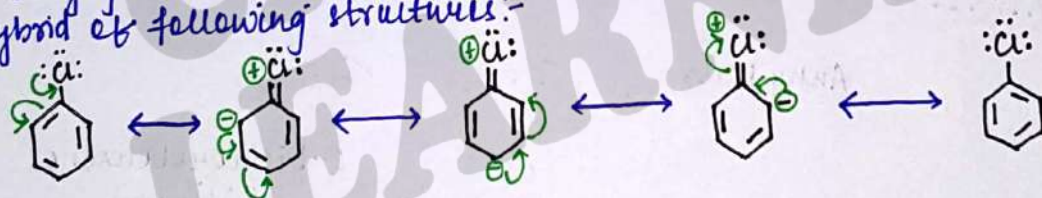


## (v) FRIEDEL-CRAFTS ACYLATION:-



(Q):- Although chlorine is an electron withdrawing group, yet it is ortho-para directing in nucleophilic substitution reaction. Why?

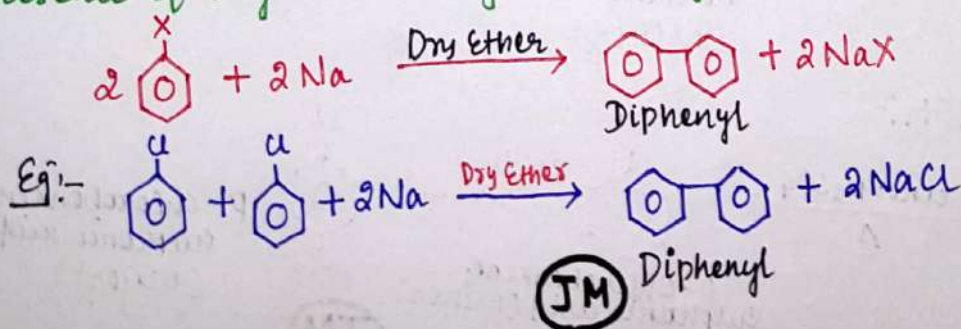
Ans:- In chlorobenzene, one of the lone pair of electron of chlorine atom conjugates with the  $\pi$ -electron of the benzene ring. It is the resonance hybrid of following structures:-



Since, electron density is maximum at ortho and para positions due to +R effect, therefore an electrophile can easily attack at such positions. Hence, chlorobenzene is o,p-directing in electrophilic aromatic substitution reactions.

## (3) REACTIONS WITH METALS:-

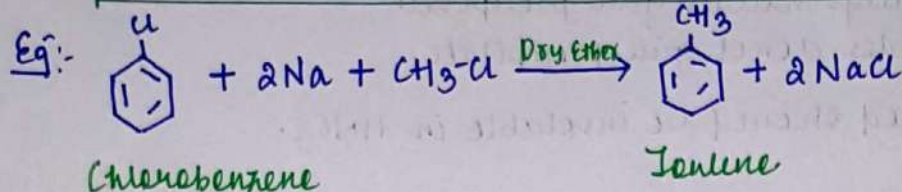
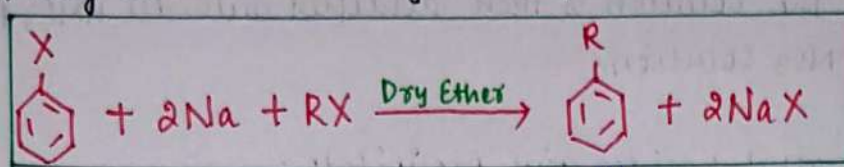
(i) FITTIG REACTION:- When two same aryl halides react with Na in presence of dry ether, we get two aryl groups which are joined together.





## (ii) WURTZ-FITTING REACTION:-

When alkyl halide reacts with aryl halide in presence of sodium and dry ether, then we get alkyl benzene



## (Q):- DEFINE INVERSION AND RETENTION.

Ans:- Inversion:- If the product formed in a reaction has a stereochemistry opposite to that of reactant, it leads to inversion of configuration.

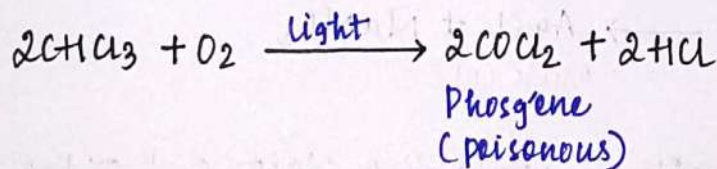
Retention:- If the product formed in a reaction has same stereochemistry as that of reactant, this process is called retention of configuration.

## TOPIC-7

### POLYHALOGEN COMPOUNDS:-

- (i) Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) is used as propellant in aerosols, as paint remover. Exposure to higher levels causes nausea, dizziness.
- (ii) The trihalogen derivatives of methane are called haloforms.  
eg:-  $\text{CHCl}_3$  (chloroform),  $\text{CHI}_3$  (Iodoform, used as an antiseptic)
- \* (iii) Chloroform is stored in dark coloured bottles as in presence of light, it gets converted into highly poisonous substance, phosgene ( $\text{COCl}_2$ )

Preparation of phosgene:-



(iv) DDT is 1,1,1-trichloro-2,2-bis ethane (4-chlorophenyl) and is used as a powerful insecticide.

(v)  $\text{CCl}_4$  is used as a fire extinguisher under the name pyrene.

(vi) Freon-12 ( $\text{CF}_2\text{Cl}_2$ ) is used as a refrigerant.



## Distinctions between Pairs of organic compounds containing halogen:-

**Silver nitrate test:-** In this test, the halide is warmed with aqueous or alcoholic KOH. The solution is then acidified with dil  $\text{HNO}_3$  followed by addition of  $\text{AgNO}_3$  solution.

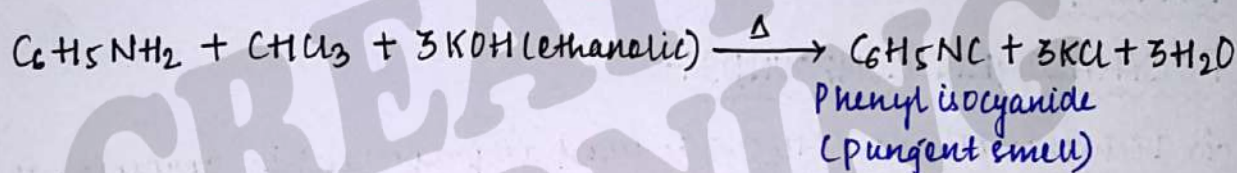
- Alkyl, benzyl and allyl halides give precipitate.
  - Aryl and vinyl halides do not give precipitate.
- \* The precipitate formed should be insoluble in  $\text{HNO}_3$ .

**(Q):-** How will you distinguish between the following pairs of compounds:-

(i) Chloroform and carbon tetrachloride

(ii) Benzyl chloride and chlorobenzene

**Ans:-** (i) On heating chloroform with aniline and ethanolic KOH, it forms a pungent smelling isocyanide whereas carbon tetrachloride does not give this test.



(ii) On adding sodium hydroxide and silver nitrate to both the compounds, benzyl chloride forms white precipitate but chlorobenzene does not form white precipitate.



[In exam, you can either write the statement or the reaction]