

Unit 9: Haloalkanes and Haloarenes

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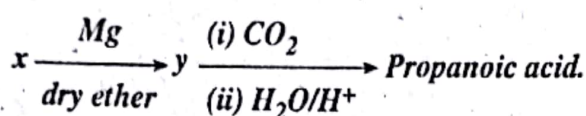
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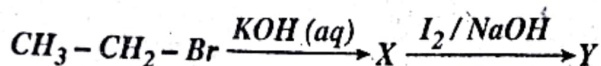
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Or, How can we prepare trichloromethane in laboratory?

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Unit 9: Haloalkanes and Haloarenes

Syllabus

9.1. Haloalkanes:

- ☐ Introduction, classification and isomerism
- ☐ Preparation of monohaloalkanes from alkanes, alkenes and alcohols
- ☐ Physical properties of monohaloalkanes
- ☐ Chemical properties
 - Substitution reactions
 - Elimination reaction (dehydrohalogenation)
 - Grignard's reactions
 - Reduction reactions
 - Wurtz's reaction
- ☐ Polyhaloalkane :
 - Laboratory preparation of trichloromethane from ethanol and propanone
 - Physical properties of trichloromethane
 - Chemical properties : oxidation, reduction, action on Silver Powder, conc. nitric acid, propanone, aqueous alkali, Carbylamine reaction, Remer Tiemann reaction , Iodoform reaction, etc.

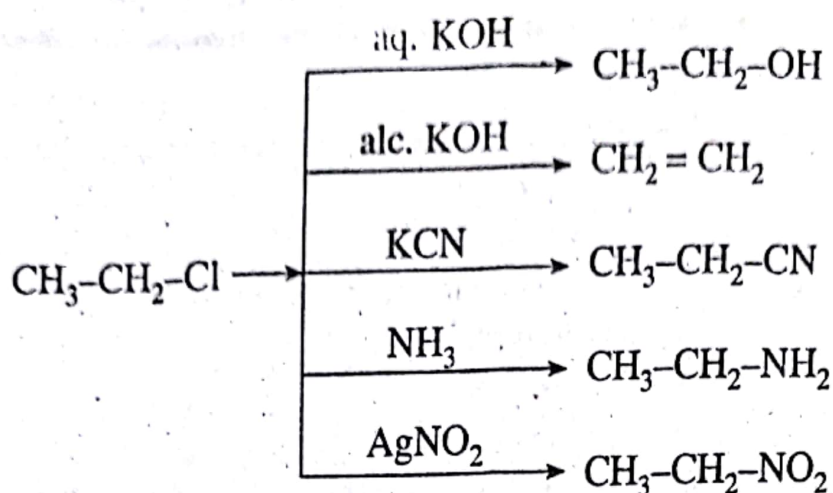
9.2 Haloarenes:

- ☐ Preparation of chlorobenzene from i. benzene ii. benzene diazonium chloride
- ☐ Physical properties
- ☐ Chemical properties
 - Low reactivity of haloarene as compared to haloalkane in term of nucleophilic substitution reaction
 - Reduction of chlorobenzene
 - Electrophilic substitutre reactions
 - Action with Na, Mg and chloral etc.
 - Uses

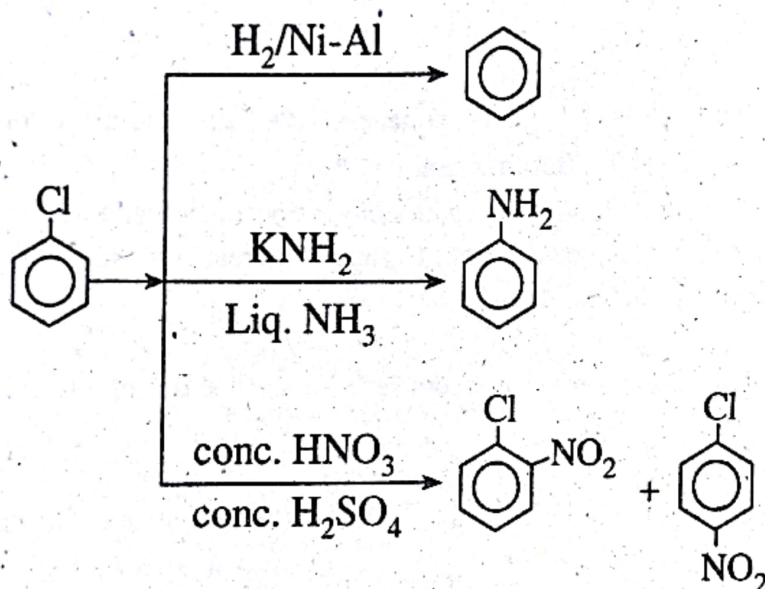
Some important terms, concepts and formulae

1. Alkanes containing halogen are called haloalkane and arene containing halogen are called haloarene.
2. Haloalkane and haloarene are classified as mono-, di-, or polyhalogen compounds. They are polar in nature.
3. Haloalkanes can be prepared by electrophilic addition of halogen acids with alkene.
4. Haloalkanes can also be prepared from alcohols with halogen acids, phosphorous halides and thionyl chloride.
5. Haloarenes can be prepared by electrophilic substitution of arenes with halogens.
6. Haloalkanes are more reactive than haloarenes.

7.



8.



9. Haloalkanes react with Mg in presence of dry ether to give Grignard's reagent.
10. Chloroform is prepared by reaction of ethanol or acetone with bleaching powder.
11. Chloroform changes into deadly poisonous phosgene gas in presence of sunlight and oxygen. So it is placed in air tight dark brown bottle.
12. Chloroform is changed into chloropicrin by reacting with conc. HNO_3 .
13. DDT is insecticide but it is not used nowadays due to its non-biodegradable nature.
14. Chloroform reacts with acetone in presence of a base to give chloroform which is used as a hypnotic.
15. Freons are used as refrigerants but they damage the ozone layer.

Read the above mentioned various definitions, explanations and formulae carefully. Then go through the following solved examples independently. After doing the solved examples, try to solve the other similar questions

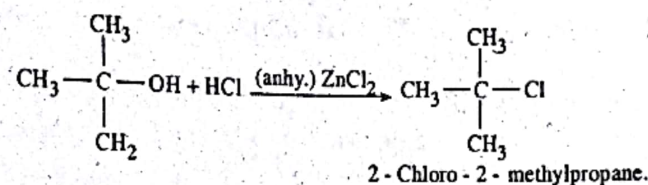
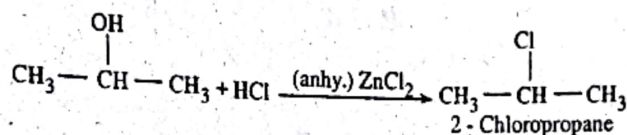
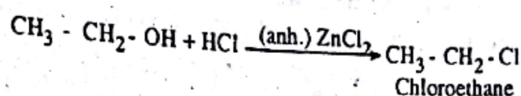
Subject Matter

9.1 Haloalkanes

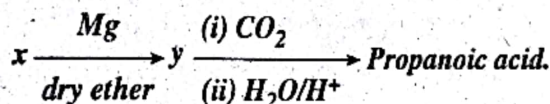
Very Short Questions-Answers

Q.1. How can we get haloalkane by using Lucas reagent?

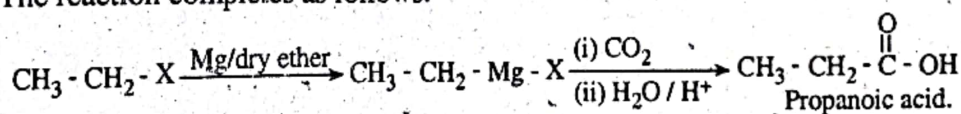
Ans: Lucas reagent is a mixture of concentrated hydrochloric acid and anhydrous zinc chloride. When alcohol is dissolved in Lucas reagent corresponding haloalkanes are obtained as:



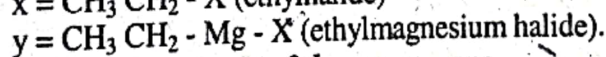
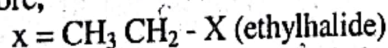
Q.2. Identify *x* and *y* in the following reaction:



Ans: The reaction completes as follows:

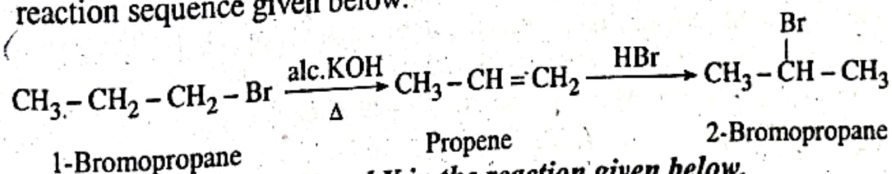


Therefore,

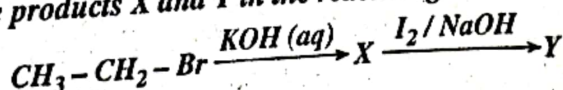


Q.3. Convert 1-bromopropane to 2-bromopropane.

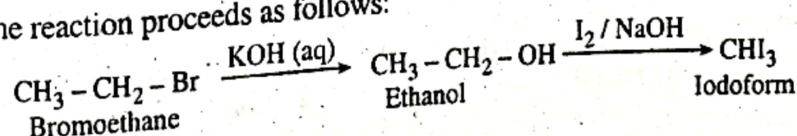
Ans: 1-Bromopropane can be converted into 2-bromopropane as shown in the reaction sequence given below:



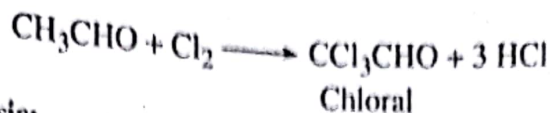
Q.4. Identify the products *X* and *Y* in the reaction given below.



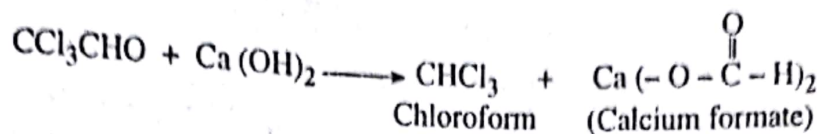
Ans: The reaction proceeds as follows:



(ii) Chlorination:

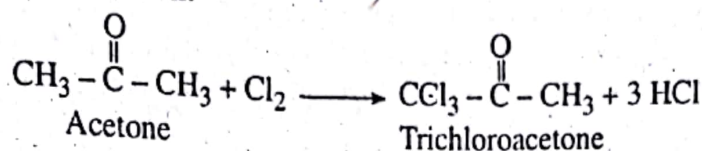


(iii) Hydrolysis:

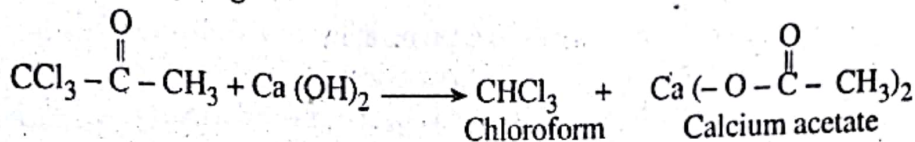


From acetone

(i) Chlorination:



(ii) Hydrolyzing:



Instrumentation:

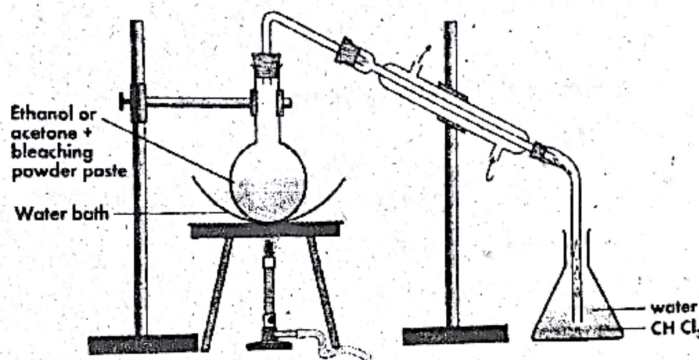


Fig: Laboratory Preparation of Chloroform.

Procedure: First of all, bleaching powder paste is prepared by mixing 100 g of bleaching powder into 200 mL of water in a round bottom flask, and 25 mL of ethanol or acetone is added to it. The flask is then heated gently on water bath until a mixture of chloroform and water distill over. The mixture from the receiver is transferred into a separating funnel and the lower layer of chloroform is poured into a conical flask.

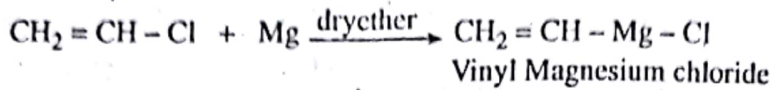
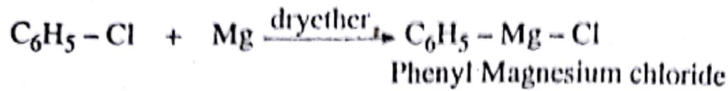
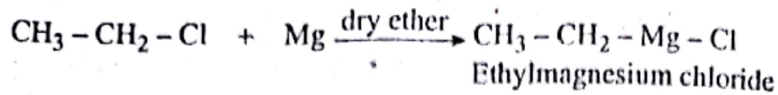
The impure chloroform is washed with dilute caustic soda and then with water successively in a separating funnel. It is then dried over anhydrous calcium chloride and redistilled between 60-65°C to obtain pure chloroform.

Long Questions-Answers

Q.10. How is Grignard's reagent prepared? What precautions should be taken for preparation of Grignard's reagent? How does $\text{CH}_3\text{CH}_2\text{MgBr}$ reacts with

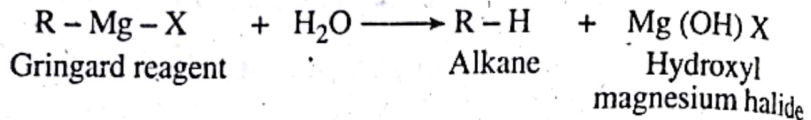
(a) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$ (b) H_2O (c) $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ (d) CO_2 show the final product after aqueous work-up?

Ans: Grignard's reagent is aryl/alkylmagnesiumhalide ($\text{R}-\text{Mg}-\text{X}$). It falls under the category of organometallic compound. It can be prepared in laboratory by heating either alkylhalide, arylhalide or vinylhalide with Mg-metal in the presence of a non-aqueous solvent, dry ether. The reactions involved are:



Precautions:

- (i) Grignard's reagent is very sensitive to water molecule. When it comes in contact with water, it gets decomposed to alkane as follows:



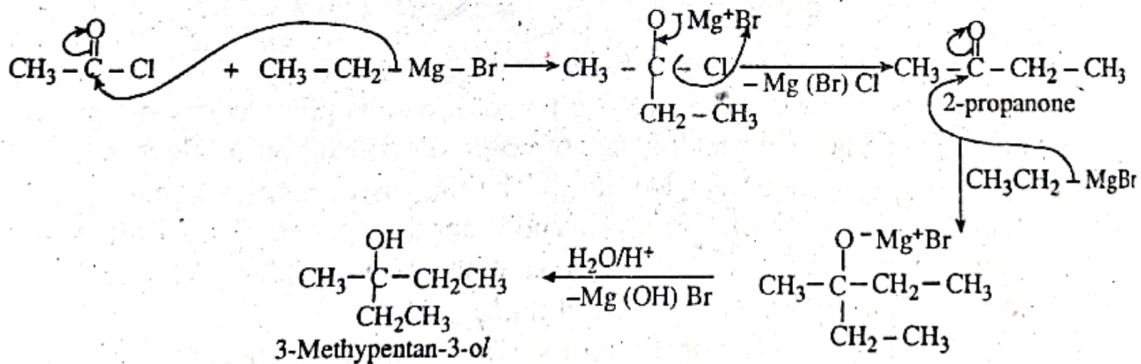
Therefore, during the preparation of Grignard's reagent there should not be the presence of any traces of water molecule i.e. all the reagents should be anhydrous and apparatus over dried.

- (ii) The anhydrous solvent, dry ether, used during the preparation of Grignard's reagent is highly inflammable so there should be no naked flames anywhere near the apparatus.

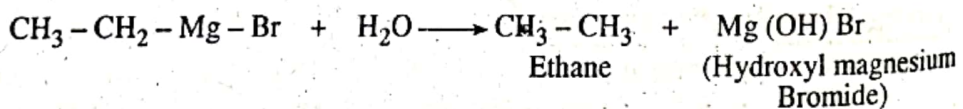
Reaction of $\text{CH}_3\text{CH}_2\text{MgBr}$ with

- (a) $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$: $\text{CH}_3\text{CH}_3\text{MgBr}$ reacts with $\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl}$

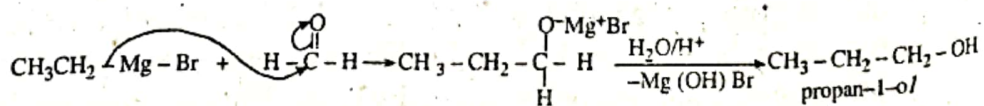
give a ketone first which further reacts with another molecule of the Grignard's reagent to give tertiary (3°) alcohol.



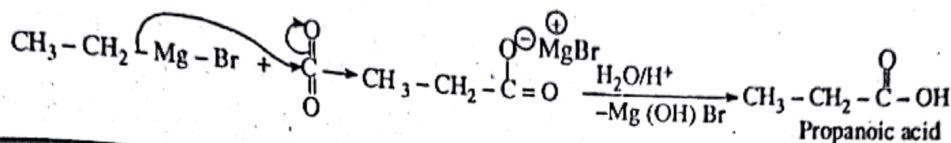
- (b) H_2O : $\text{CH}_3\text{CH}_2\text{MgBr}$ reacts with water molecule to give ethane



- (c) $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$: $\text{CH}_3\text{CH}_3-\text{MgBr}$ reacts with $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{H}$ to give primary alcohol.



- (d) CO_2 : $\text{CH}_3\text{CH}_2\text{MgBr}$ reacts with CO_2 to give a carboxylic acid. The carboxylic acid formed has one carbon atom more than the parent alkyl group in grignard's reagent.

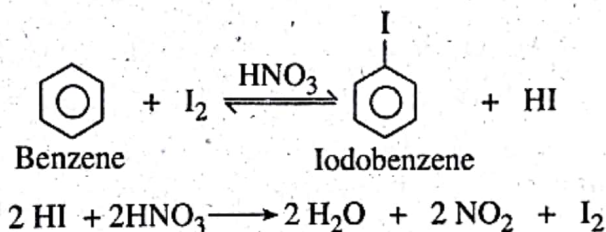


9.2. Haloarenes

Very Short Questions-Answers

- Q.1. Iodination of Benzene is carried out in the presence of oxidizing agent like HNO_3 . Why?

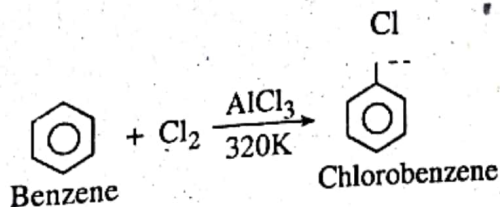
Ans: The iodination of benzene with iodine is a reversible process so, some oxidizing agent such as HNO_3 should be used, which will oxidize the side product such as HI otherwise the reaction takes place in the backward direction too.



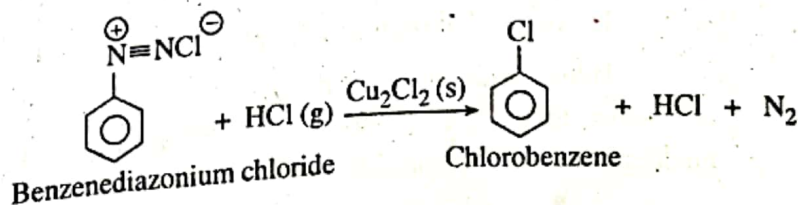
- Q.2. How can you prepare chlorobenzene from benzene and benzene diazonium chloride?

Ans: Chlorobenzene can be prepared by the following two methods:

- (i) **From benzene:** When benzene is reacted with chlorine in the presence of anhydrous AlCl_3 , Chlorobenzene is obtained.

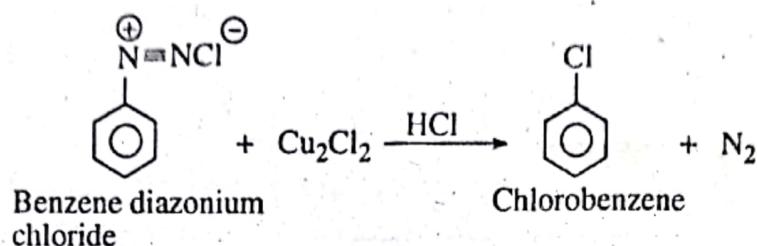


- (ii) **From benzene diazonium chloride:** Chlorobenzene is obtained from benzene diazonium chloride by reacting it with HCl gas in the presence of Cu_2Cl_2 (s).



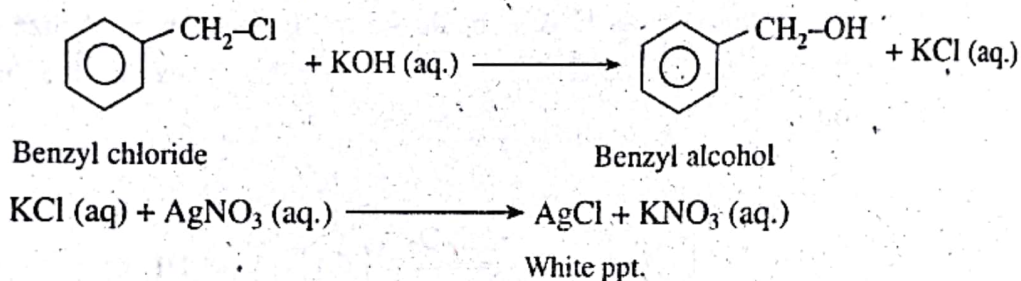
Q.3. What is Sandmeyer's reaction? Give an example of it.

Ans: The reaction of benzenediazonium chloride with Cu_2Cl_2 in the presence of anhydrous HCl to give chlorobenzene is a good example of sandmeyer's reaction.



Q.4. How can you distinguish between benzylchloride and chlorobenzene?

Ans: Benzylchloride is easily hydrolyzed with aqueous KOH to form water soluble KCl which gives white precipitate of AgCl on treating with an aqueous solution of silver nitrate. i.e.

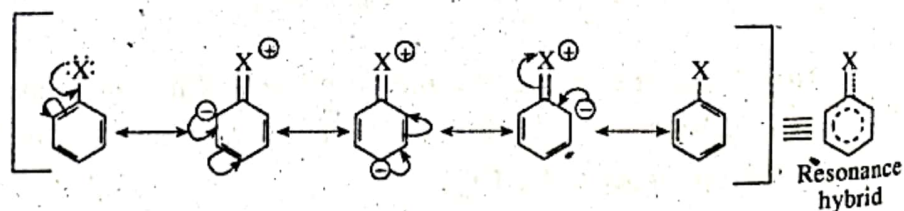


Chlorobenzene, on the otherhand, is less reactive towards nucleophilic substitution reactions. Hence it is not easily hydrolyzed by alkali. Therefore, it does not respond to the above test.

Q.5. Why is nucleophilic substitution reaction in chlorobenzene difficult as compared to chloroethane?

Ans: The chlorine in chlorobenzene is bonded to sp^2 -hybridized carbon atom whereas the chlorine in chloroethane is bonded to sp^3 -hybridized C-atom. The sp^3 -hybridized C-atom is less electronegative than sp^2 -hybridized C-atom. So, the C-Cl bond in Chlorobenzene is less polar than C-Cl bond in Chloroethane.

The C-Cl bond in chlorobenzene has partial double bond character due to the resonating structures generated by the delocalization of the lone pair on halogen into the ring. This is shown below:



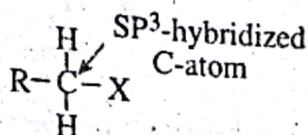
In contrast no such resonance is possible in chloroethane.

Hence, due to less polar nature as well as partial double bond characteristic of C-Cl bond in chlorobenzene, it is less reactive towards nucleophilic substitution than chloroethane.

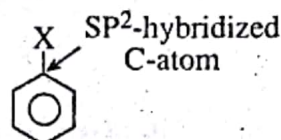
Q.6. *Haloalkanes are more easily hydrolyzed than haloarene why?*

Ans: Haloalkanes undergo hydrolysis more easily than haloarenes due to the following reasons:

- (i) Halogen atom in haloalkane is linked to sp^3 -hybridized carbon atom by single covalent bond while halogen atom in haloarenes is linked with sp^2 -hybridized C-atom. The sp^3 -hybridized carbon atom is less electronegative than sp^2 -hybridized carbon atom. Thus, C-X bond in haloalkane is more polar than in haloarene. So, halogen atom in haloalkane is easily displaced by a nucleophile.

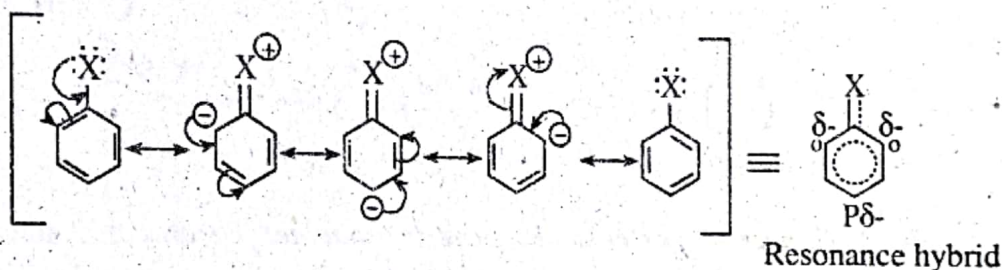


Haloalkane (More polar)



Haloarene (Less polar)

- (ii) Haloarenes are stabilized by resonance. The lone pair of electrons present on the halogen atom is delocalized into the benzene nucleus to give different resonating structures shown below:

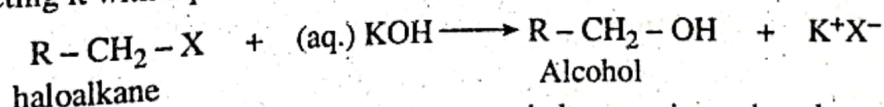


Such resonance is impossible in haloalkanes. So, we can say that haloarenes are more stabilized due to resonance than the haloalkanes. Therefore, haloalkanes undergo hydrolysis more easily than haloarenes.

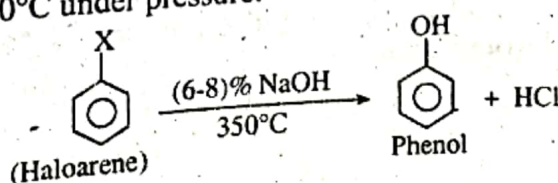
- (iii) From the different resonating structures and the resonance hybrid, we find that there exists a partial double bond characteristic in between the haloarene carbon and halogen atom. But in haloalkane, there is distinct single bond between the carbon and halogen. As a double bond is shorter and more stronger than a single bond, the haloalkanes undergo hydrolysis more easily than haloarenes.

This is also proved by the following chemical reactions given below:

A haloalkanes can be easily converted into alcohol by simply reacting it with aqueous KOH as:



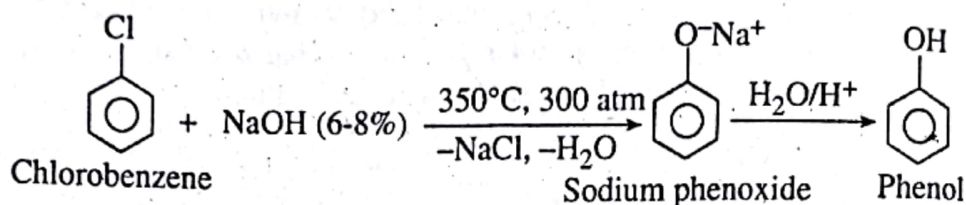
However, If we want to convert haloarene into phenol, we need to react it with (6-8)% of NaOH at a very high temperature of around 350°C under pressure.



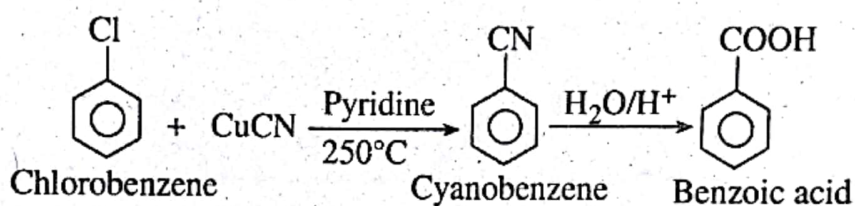
Q.7. How do you convert chlorobenzene to

(i) Phenol (ii) Benzoic acid (iii) Toluene (iv) Aniline

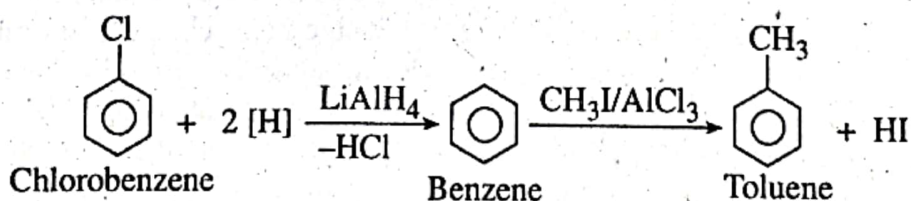
Ans: (i) **Conversion of Chlorobenzene to phenol:** Chlorobenzene can be converted into phenol by reacting it with (6-8)% solution of NaOH at around 350°C under a pressure of around 300 atm followed by acid hydrolysis.



(ii) **Conversion of chlorobenzene to benzoic acid:** For this, the chlorobenzene is first converted into cyanobenzene by reacting it with CuCN at 250°C in the presence of pyridine. The product thus obtained is then hydrolysed in acidic medium to get benzoic acid.



(iii) **Conversion of chlorobenzene to Toluene:** To obtain Toluene from chlorobenzene, chlorobenzene is first reduced to benzene by reducing it in the presence of LiAlH₄. The product, benzene, is then reacted with Methyl iodide (CH₃I) in the presence of anhydrous AlCl₃ to get Toluene.



(iv) **Conversion of chlorobenzene to aniline:** Chlorobenzene can be converted into Aniline by reacting it with ammonia (NH₃) in the presence of Cu₂O at a temperature of around 250°C and 50 atm. pressure.

