

## Chapter -VII Alkyl and aryl halides

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## Chapter -VII

### Alkyl and aryl halides

**Introduction:** An organic compound formed by the replacement of one hydrogen atom of alkane by one halogen atom, are called as mono halogen derivatives of alkanes.

Similarly, An organic compound formed by the replacement of two or three hydrogen atoms of alkane by two or three halogen atoms, are called as dihalogen derivatives or tri halogen derivatives of alkanes.

General formula of them is  $C_nH_{2n+1}X$  or  $R-X$  they are also called as **alkyl halides**.

Common uses of poly halogen compounds are in agriculture and industrial sectors. They are popularly used for many purposes such as solvents, anesthetics pesticides etc.

#### Classification of alkyl/aryl halides:

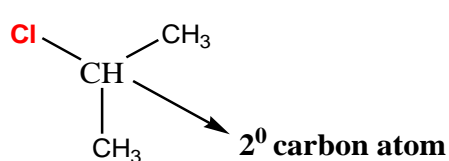
##### 1) On the basis of attached carbon atom:

Alkyl halides fall into different classes depending on how the halogen atom is positioned on the chain of carbon atoms.

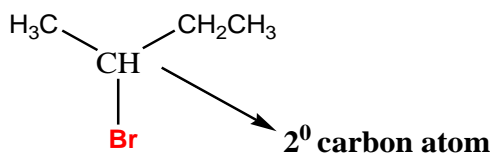
**A) Primary alkyl halide:** In this one, halogen atom is attached to a primary carbon atom. ( $1^0$ )

Examples are 1.  $CH_3-Cl$  2.  $CH_3-CH_2-Br$  3.  $CH_3-CH_2-CH_2-I$  4.  $CH_3-CH_2-F$  etc.

**B) Secondary alkyl halide:** In these derivatives, halogen atom is attached to a secondary carbon atom. ( $2^0$ )

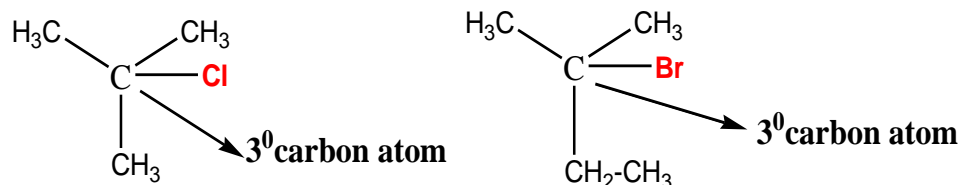


**Sec. Propyl chloride**



**Sec. butyl bromide**

**C) Tertiary alkyl halide:** In these derivatives, halogen atom is attached to a tertiary carbon atom. ( $3^0$ )



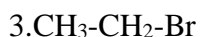
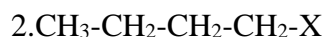
Tertiary butyl chloride

Tertiary pentyl bromide

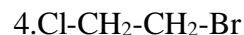
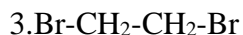
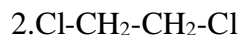
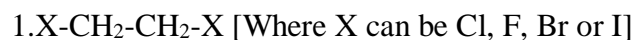
**2) On the basis of no. of attached halogen atom:**

The classification mainly depends on whether they contain one, two, or more halogens.

**A) Mono halogen derivatives:** An alkyl or aryl halide formed by the replacement of one hydrogen atom of alkane by one halogen atom, are called as mono halogen derivatives of alkanes. **Examples:** 1.  $\text{CH}_3\text{-CH}_2\text{-X}$  [Where X can be Cl, F, Br or I]



**B) Dihalogen derivatives:** An alkyl or aryl halide formed by the replacement of two hydrogen atom of alkane by two halogen atom, are called as di halogen derivatives of alkanes. Example:



**C) Dihalogen derivatives:** An alkyl or aryl halide formed by the replacement of three hydrogen atom of alkane by three halogen atom, are called as tri halogen derivatives of alkanes. Example:  $\text{X-CH}_2\text{-CHX-CH}_2\text{-X}$

[Where X can be Cl, F, Br or I]



**D) Tetra halogen /Poly halogen derivatives:** An alkyl or aryl halide formed by the replacement of four hydrogen atom of alkane by four halogen atom, are called as tetra halogen derivatives of alkanes. Examples:  $\text{X-CH}_2\text{-CHX-CHX-CH}_2\text{-X}$



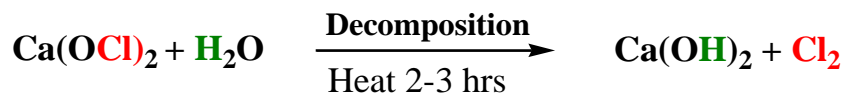
**Chloroform:** Chloroform is an example of tri halogen derivatives of alkanes.

**Methods of preparation:** When bleaching powder in water and ethyl alcohol is heated about 2-3 hours, it is then distilled. Mixture of chloroform and water is obtained as distillate.  $\text{CHCl}_3$  is insoluble in water and heavier than water thus separated by separating funnel and dried over fused  $\text{CaCl}_2$  and purified.

Following reactions are occurs.

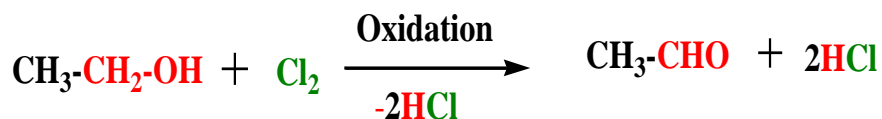
### Step-I Decomposition of bleaching powder:

Reaction of bleaching powder with water (decomposition reaction) to form calcium hydroxide and chlorine gas.



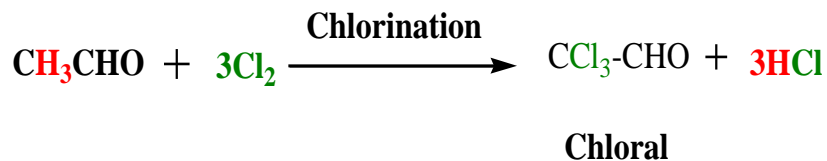
### Step-II Oxidation of ethanol:

In this step prepared chlorine is used for the oxidation of ethyl alcohol (oxidation of  $\text{CH}_2\text{OH}$  to  $-\text{CHO}$  group).



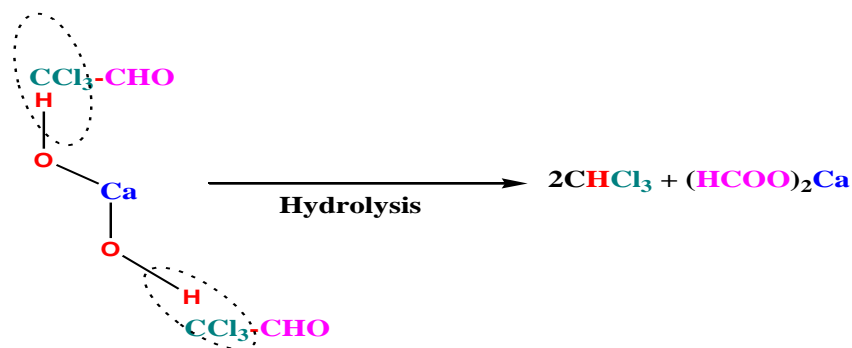
### Step-III Chlorination of acetaldehyde:

It includes chlorination of acetaldehyde (prepared in step-II) by using chlorine as chlorinating agent to form chloral as main product.



- **Step-III Hydrolysis of chloral:**

In this step hydrolysis of synthesized chloral is performed by using calcium hydroxide which is prepared in step-I.



Chloroform is also prepared industrially by the chlorination of methane.

**Physical properties of chloroform:**

1. Chloroform is a colorless volatile liquid (B.P. 61°C) and Freezing point of chloroform is -63°C.
2. It is insoluble in water and heavier than water. **Density** is 1.489 g mL<sup>-1</sup>
3. Inhalation of chloroform vapors for longer time produces unconsciousness.
4. It is non-flammable liquid.
5. Although chloroform is non-poisonous, it forms a poisonous compound (phosgene) in air.

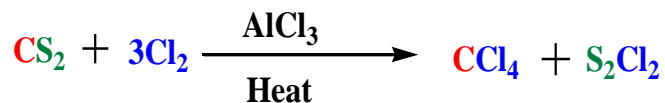
**Carbon tetra chloride (Tetra chloro methane):** Carbon tetrachloride, also known as tetra chloromethane, is an organic compound with the chemical formula CCl<sub>4</sub>. This compound is often classified as a poly halogenated organic compound since it consists of a carbon atom which is attached to more than one halide functional group.

**Carbon Tetrachloride** is used as a solvent for oils and fats, as a refrigerant and as a dry-cleaning agent. Exposure to high concentrations of carbon tetrachloride (including vapor) can affect the central nervous system and degenerate the liver and kidneys. Prolonged exposure can be fatal.

In the past, this compound was widely used in cleaning agents. It was also used in fire extinguishers and was known to serve as a precursor to several refrigerants. However, the use of this compound has been phased out by several governments due to its toxicity.

**Methods of preparation:**

**1. By carbon disulphide and chlorine:** When chlorine and carbon disulphide is reacted in presence of aluminum chloride as catalyst carbon disulphide is formed. Sulphur monochloride

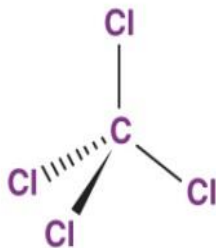
**Sulphur monochloride**

(S<sub>2</sub>Cl<sub>2</sub>) is removed by fractional distillation and CCl<sub>4</sub> is purified by washing with NaOH solution and then re distillation.

**2. By chlorination of methane:** Carbon tetra chloride is also prepared by the chlorination of methane by using chlorine in presence of UV/sunlight. Reaction proceeds through free radical mechanism.



**Structure:**



**Physical properties of carbon tetrachloride:**

1. Colorless liquid having B.P.  $77^{\circ}\text{C}$  with a sickly smell.
2. It is insoluble in water but soluble in ethanol, ether, chloroform, benzene and formic acid.
3. Its vapors are noninflammable.
4. It is used in Industries for synthesis of various fats, oils, resin etc. as a solvent.
5. It is also used as fire extinguisher under the name **Pyrene**.
6. The density of this compound (liquid state) corresponds to 1.5867 grams per cubic cm.
7. Due of symmetric geometry,  $\text{CCl}_4$  is non-polar.

**Did you know? :** In the past, this compound was widely used in cleaning agents. It was also used in fire extinguishers and was known to serve as a precursor to several refrigerants. It is also used as a cleaning agent. However, the health hazards associated with this compound and the serious environmental damage caused by chlorofluorocarbons, the use of this compound has been phased out by the governments of several countries.

**Aryl halides:** Aryl halides are aromatic halogen compounds in which one or more halogen atom is directly attached to the carbon atom of benzene ring or aromatic ring.

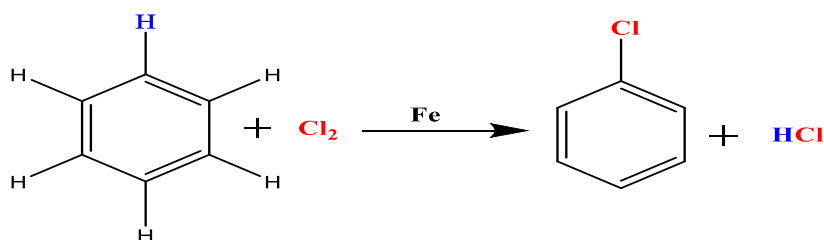
An aryl halide also known as haloarene or halogeno arene.

Aryl halides are represented by the formula.  $\text{Ar-X}$  (Where  $\text{X} = \text{F}, \text{Cl}, \text{Br}$  and  $\text{I}$ )

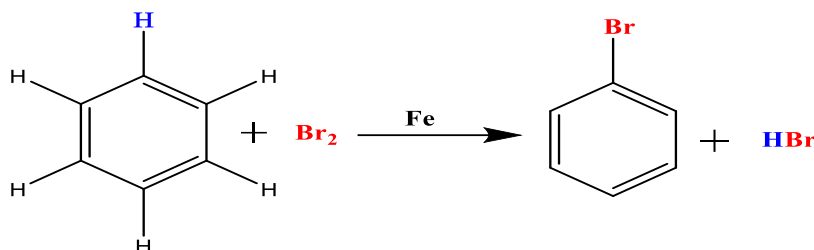
**Methods of formation of aryl halides:**

**1. Direct halogenations:** Chlorobenzene and bromobenzene can be prepared by direct chlorination and bromination of benzene with one molecule of  $\text{Cl}_2$  or  $\text{Br}_2$  respectively in presence of Iron or aluminum amalgam at room temperature.

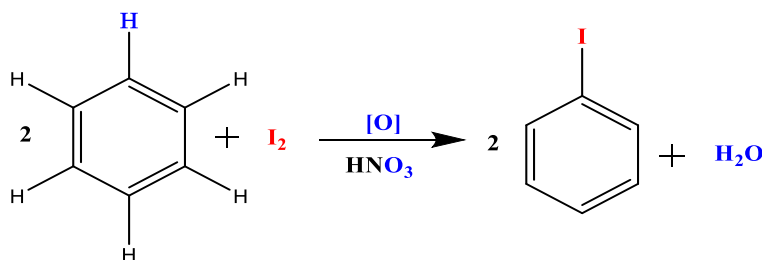
Chlorination:



Bromination:

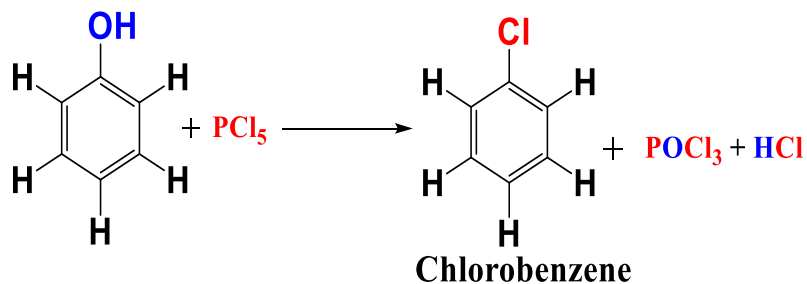


Iodination of benzene is done in the presence of an oxidizing agent like nitric acid.

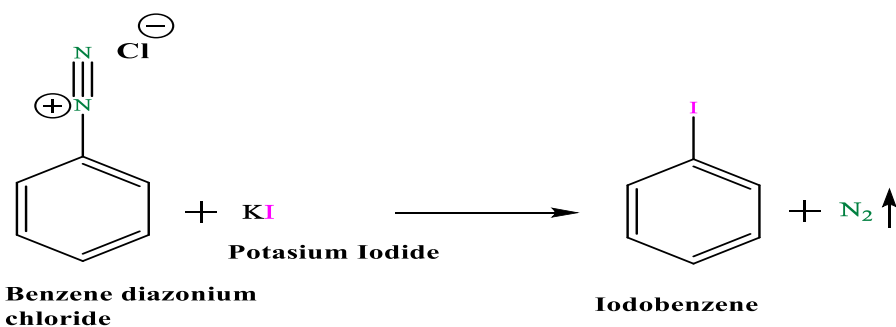
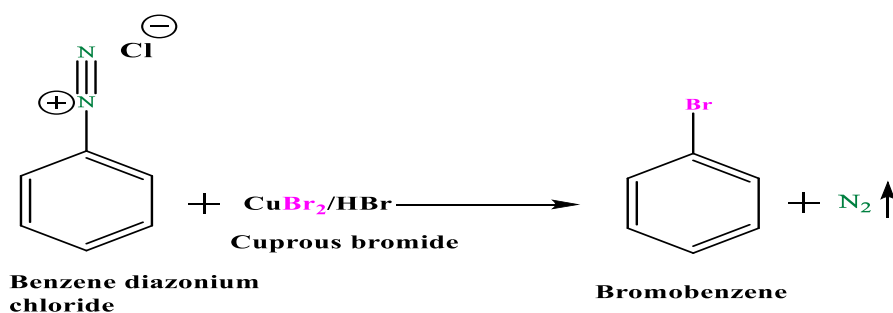
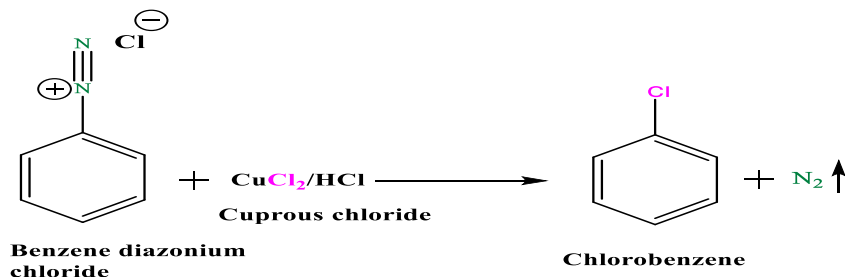


**2. From Phenol:** Phenol on heating with Phosphorus pentachloride ( $\text{PCl}_5$ ) gives chlorobenzene.

In this case Phosphorus pentachloride acts as chlorinating agent to benzene and gives monochloro derivative.



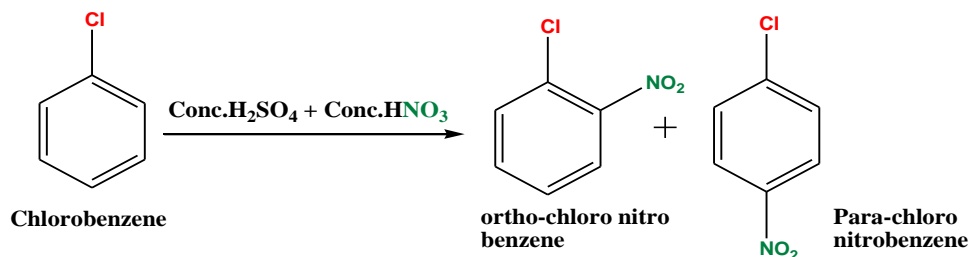
**3. By Sandmeyer's reaction:** Benzene diazonium chloride solution on treatment with cuprous chloride ( $\text{CuCl}_2$ ), cuprous bromide ( $\text{CuBr}_2$ ) and KI solution gives chloro benzene and Iodo benzene respectively.



**Nuclear reactions of aryl halide:**

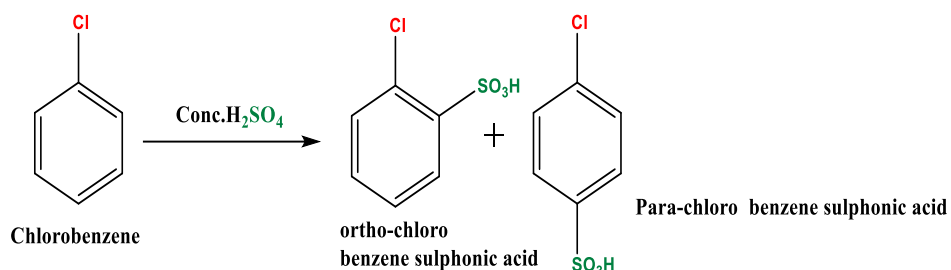
**A) Nuclear reactions:**

**1) Nitration Reaction:** Chloro benzene on heating with nitrating mixture gives a mixture of ortho and para chloro benzene.

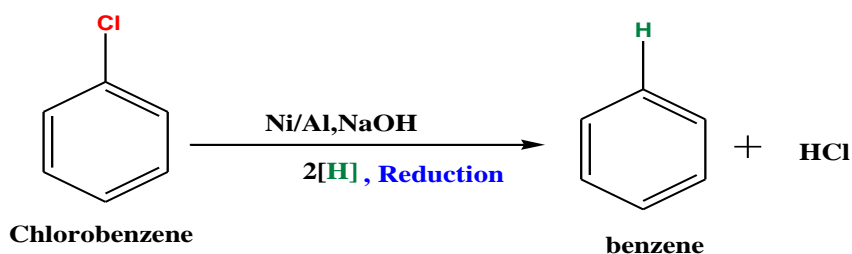




2) **Sulphonation reaction:** Chlorobenzene on heating with conc.  $\text{H}_2\text{SO}_4$  forms a mixture of ortho and para chloro benzene sulphonic acid.

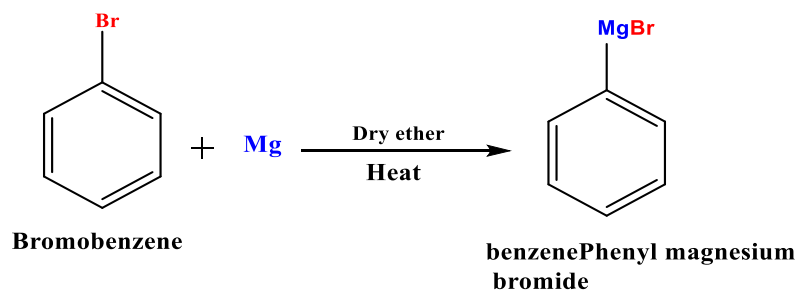


3) **Reduction reaction:** Chloro benzene on reduction with nickel alloy in the presence of alkali yields benzene.

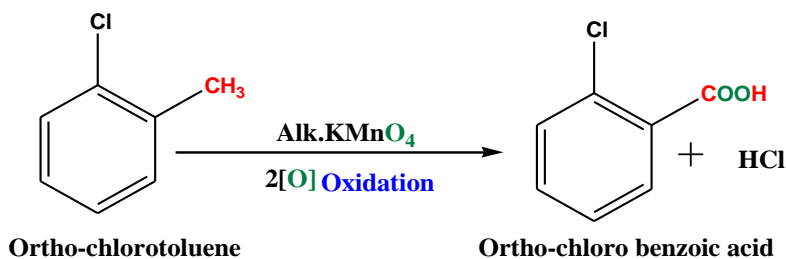


#### Side chain reactions of aryl halide:

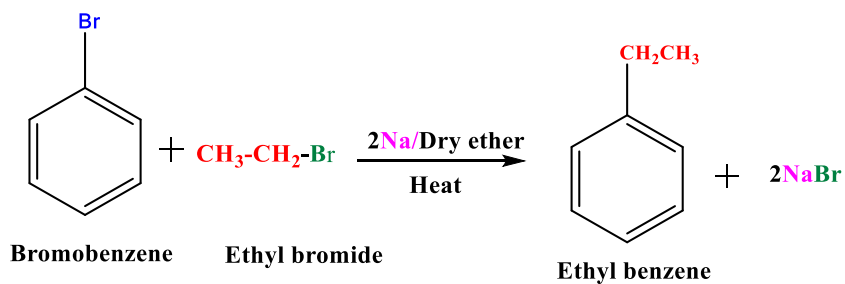
1. **Reaction with Mg:** Bromo benzene in presence of magnesium metal to form phenyl magnesium bromide.



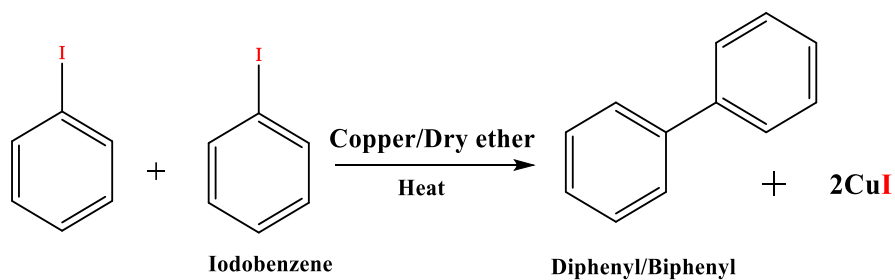
2. **Oxidation with alkaline  $\text{KMnO}_4$ :** ortho-chloro toluene on oxidation with alkaline  $\text{KMnO}_4$  solution gives ortho-chloro benzoic acid.



3. **Wurtz-Fitting reaction:** A mixture of bromo benzene and ethyl bromide in the presence of dry ether reacts with sodium metal to form ethyl benzene.



4. **Ullmann synthesis:** Iodobenzene on heating in a sealed tube with copper powder forms diphenyl.





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DEPARTMENT OF CHEMISTRY

**Question Bank**

Class: B.Sc. Semester -I

**Name of Paper:** Organic Chemistry (Paper –II) CHE-102

**Title of Chapter:** Alkyl and aryl halide.

**Questions:**

1. What are alkyl halides? How
2. Give any two methods for the preparation of
  - A) Chloroform from ethanol
  - B) Carbon tetrachloride from carbon disulfide.
3. What are aryl halides? How will you prepare chloro benzene from
  - A) Phenol
  - B) By Sandmeyer's reaction.
4. How will you prepare Bromobenzene and Iodobenzene from
  - A) Benzene
  - B) by Sandmeyer's reaction
5. Give the nitration reaction of chlorobenzene?
6. Describe the sulphonation reaction of chlorobenzene?
7. Give Wurtz-Fittig reaction of bromobenzene?
8. Describe Ullmann reaction of Iodobenzene?
9. How will you prepare orthochloro benzoic acid from ortho toluene by oxidation reaction?
10. Explain physical properties of
  - A) Chloroform
  - B) Carbon tetrachloride
11. Explain classification of alkyl or aryl halide on the basis of no. of attached halogen atom?

**Multiple choice questions:**

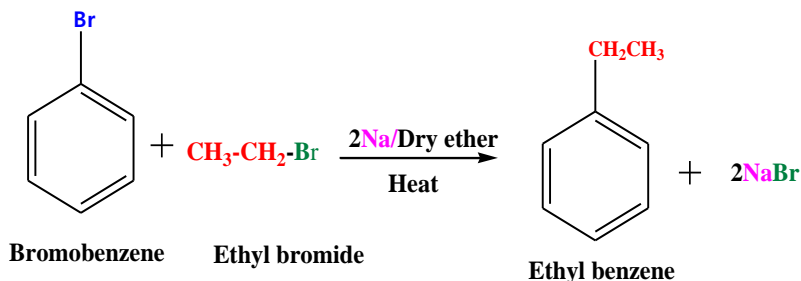
- If alkyl halide is tertiary then the halogen attached to carbon will be.  
a) Secondary      b) Primary      c) Tertiary      d) Quaternary
- Organic compounds formed by the replacement of one hydrogen atom of alkane by one halogen atom are called as..... derivative of alkanes.  
a) Dihalogen      b) Monohalogen      c) Trihalogen      d) None of these
- Which of the following is general formula for alkyl halide....  
a)  $C_nH_{2n+1}X$       b)  $C_{n-1}H_{2n+1}X$       c)  $C_nH_{2n-2+1}X$       d)  $C_nH_{n+1}X$
- Which of the following is aldehyde is formed during the synthesis of chloroform..  
a) Acetal      b) Formaldehyde      c) Butanal      d) Pentanal
- Which of the following is correct formula for bleaching powder...  
a)  $Ca(OCl)_2$       b)  $Ca_2(OCl)_2$       c)  $K_2(OHCl)_2$       d)  $Ca_2(O_2Cl)_2$
- Which of the following is used as an oxidizing agent in synthesis of chloroform...  
a)  $Cl_2$       b)  $Br_2$       c)  $I_2$       d)  $ICl_2$
- In the final step of synthesis (Hydrolysis step) which of the provided reagent is used..  
a) Sodium hydroxide      b) Potassium hydroxide      c) Calcium hydroxide      d) Water
- Choose the correct statement for Chloroform.  
a) Chloroform is a colored volatile liquid with dirty smell.  
b) Chloroform is insoluble in water and heavier than water.  
c) Inhalation of chloroform vapors produces blood coagulation.  
d) Chloroform is monohalogen derivative of alkane.
- Which of the following is the method of synthesis for carbon tetrachloride?  
a) Action of bromine with carbon disulphide in presence of  $AlCl_3$ .  
b) Action of chlorine with methylene dichloride in presence of  $FeBr_3$ .  
c) Action of bleaching powder with acetyl chloride in presence of  $ZnCl_2$ .  
d) Action of chlorine with carbon disulphide in presence of  $AlCl_3$ .
- Correct general formula for the aryl halide...  
a)  $Ar-X$       b)  $R-X$       c)  $CH_3-X$       d)  $C_5H_{10}-X$

11. Which of the following is suitable catalyst for chlorination and bromination of benzene...
- a) Fe            b) Na            c) K            d) Cs
12. Phenol on heating with..... gives chlorobenzene.
- a)  $\text{PCl}_5$             b)  $\text{Cl}_2$             c)  $\text{POCl}_3$             d)  $\text{P}_2\text{O}_5$
13. What will be the product if Benzene diazonium salt reacted with cuprous bromide in presence of hydrobromic acid....
- a) Bromobenzene    b) Chlorobenzene    c) Iodobenzene    d) *p*-nitrobenzene
14. What happens when Benzene diazonium salt reacted with potassium iodide....
- a) *p*-nitrobenzene    b) *p*-chlorobenzene    c) Iodobenzene    d) *p*-nitro phenol
15. What happens when Benzene diazonium salt reacted with cuprous chloride in presence of HCl..
- a) Bromobenzene    b) Chlorobenzene    c) Iodobenzene    d) *p*-nitrobenzene
16. When chlorobenzene undergoes nitration reaction gives.....
- a) ortho and para chloronitro benzene  
b) para and meta chloronitro benzene  
c) para and ortho bromonitro benzene  
d) only parachloronitro benzene.
17. What will be the probable product when chlorobenzene undergoes reaction with Conc.  $\text{H}_2\text{SO}_4$
- a) ortho and para chloro benzene sulphonic acid.  
b) para and meta benzene sulphonic acid.  
c) para and ortho benzene sulphonic acid  
d) only parachloro benzene sulphonic acid
18. Chlorobenzene undergoes reduction with nickel alloy in presence of alkali...
- a) *p*-diclorobenzene    b) Benzene    c) Toluene    d) *p*-hydroxybenzene
19. How will you prepare phenyl magnesium bromide (Grignard reagent) from magnesium..
- a) Bromobenzene reacts with magnesium metal in the presence of dry ether.  
b) Chlorobenzene reacts with sodium metal in the presence of dry toluene.  
c) Biphenyl reacts with magnesium metal in the presence of DMF.  
d) Phenol reacts with Iron metal in the presence of acetic acid.

20. *o*-chlorotoluene on oxidation with alkaline  $\text{KMnO}_4$  gives....

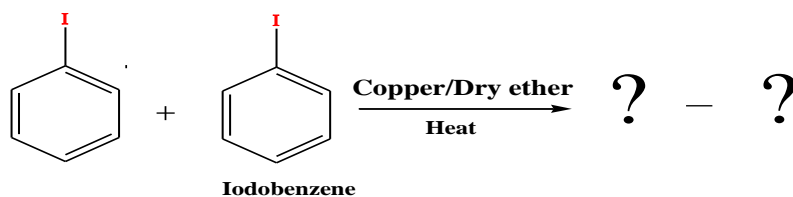
- a) *p*-chloro benzoic acid                      b) *o*-chloro benzoic acid  
c) *m*-chloro benzoic acid                      d) *p*-chloro benzoic acid

21. The name of the following reaction is...



- a) Clemmenson reduction reaction              b) Aldol condensation reaction  
c) Sandmeyer's reaction                          d) wurtz-Fitting reaction

22. What will be the product(s) of following reaction..



- a) Biphenyl and Cuprous iodide                      b) benzophenone and cuprous iodide  
c) Acetophenone and cuprous bromide              d) Naphthalene and cuprous iodide

23. Which C-X bond has the highest bond energy per mole?

- a) C-Br                      b) C-Cl                      c) C-F                      d) C-I

**Explanation:** Bond energies depend on many factors: electron affinities, sizes of atoms involved in the bond, differences in their electronegativity, and the overall structure of the molecule.

There is a general trend in that the shorter the bond length, the higher the bond energy.

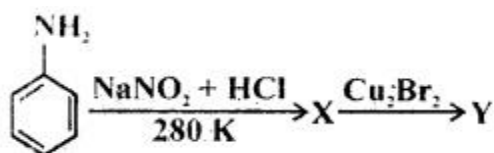
24. Alkyl halides are immiscible in water though they are polar because

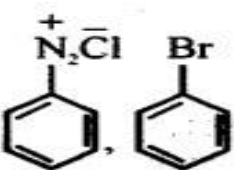
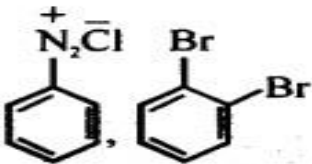
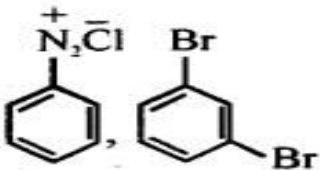
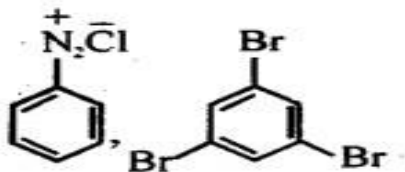
- (a) they react with water to give alcohols  
**(b) they cannot form hydrogen bonds with water**  
(c) C -X bond cannot be broken easily  
(d) they are stable compounds and are not reactive

25. Which of the following compounds has the highest boiling point?

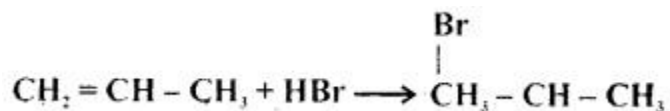
- (a)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$   
 (b)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$   
 (c)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$   
 (d)  $(\text{CH}_3)_3\text{CCl}$

26. 'X' and 'Y' in the following reaction are...



- (a) 
- (b) 
- (c) 
- (d) 

27. The following reaction is an example of..



- (a) Nucleophilic addition  
 (b) Free radical addition  
 (c) Electrophilic addition  
 (d) Electrophilic substitution

28. Which alkyl halide has the highest reactivity for a particular alkyl group?

- a) R-F                      b) R-Cl                      c) **R-I**                      d) R-Br

29. When ethyl chloride reacts with nascent hydrogen, what is the formed product?

- a) Methane                      b) Propane                      c) Butane                      **d) Ethane**

30. When two moles of ethyl chloride react with two moles of sodium in the presence of ether what will be formed?

- a) 2 moles of ethane    b) 1 moles of ethane    c) 2 moles of butane    d) 1 moles of butane

**Explanation:** Wurtz reaction is method of preparation of higher alkanes from lower alkyl halides. This is coupling reaction. In this reaction alkyl halides are reacted with sodium metal in presence of dry ether and higher alkanes with even number of carbon atoms only are formed, by this method.

31. In primary alkyl halides, carbon attached to the halogen atom is further attached to how many carbon atoms?

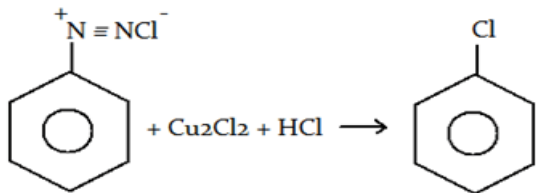
- a) 1                      b) 2                      c) 3                      d) 4

32. Which one of the following possess highest melting point?

- a) Chlorobenzene    b) o-dichlorobenzene    c) m-dichlorobenzene    **d) p-dichlorobenzene**

**Explanation:** p-dichlorobenzene molecule has symmetrical structure. It can fit well in its crystal lattice. The intermolecular forces of attraction are strong. Hence, it possesses highest melting point.

33. What is the name of the following reaction?



- a) Chlorination    b) Sandmeyer's reaction    c) Perkin reaction    d) Substitution reaction

34. Benzene reacts with chlorine to form benzene hexachloride in presence of which of the following reactant?

- a) Nickel                      b) AlCl<sub>3</sub>                      c) **Bright sunlight**                      d) Zinc



35. The increasing order of nucleophilicity would be?

- a)  $\text{Cl}^- < \text{Br}^- < \text{I}^-$       b)  $\text{I}^- < \text{Cl}^- < \text{Br}^-$       c)  $\text{Br}^- < \text{Cl}^- < \text{F}^-$       d)  $\text{I}^- < \text{Br}^- < \text{Cl}^-$

36. Alkyl halides are considered to be very reactive compounds towards nucleophile because..

- a) They have an electrophilic carbon  
**b) They have an electrophilic carbon and good leaving group**  
 c) They have an electrophilic carbon and bad leaving group  
 d) They have an Nucleophilic carbon and good leaving group

37. Alkyl halides undergo a type of reaction

- a) Nucleophilic addition      b) Nucleophilic addition      c) Elimination      d) both 'a' and 'c'

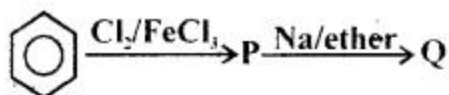
38. Which of the following molecules has highest dipole moment?

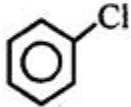
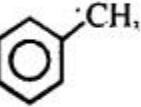

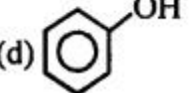
- (a)  $\text{CH}_3\text{Cl}$       (b)  $\text{CH}_2\text{Cl}_2$       (c)  $\text{CHCl}_3$       (d)  $\text{CCl}_4$

39. Arrange the following compounds in-decreasing order of their boiling points

- (i)  $\text{CH}_3\text{Br}$       (ii)  $\text{CH}_3\text{CH}_2\text{Br}$       (iii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$       (iv)  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$   
 (a) (i) > (ii) > (iii) > (iv)      (b) (iv) > (iii) > (ii) > (i)  
 (c) (i) > (iii) > (ii) > (iv)      (d) (iii) > (iv) > (i) > (ii)

40. The end product (Q) is in the following sequence of reaction



- (a)       (b)   
 (c)       (d) 

41. Which of these can be used as moth repellent?

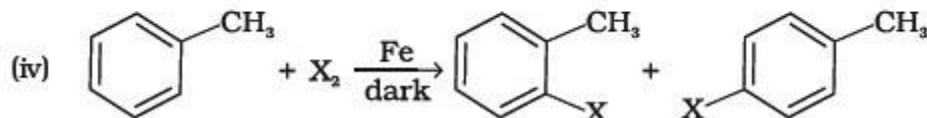
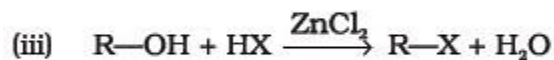
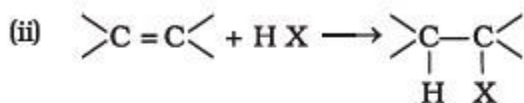
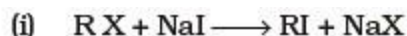
- a) Benzene hexachloride      b) Benzal chloride      c) Hexachloroethane      d) Tetrachloroethane

**Explanation:** Hexachloroethane can be used as moth repellent. It has also been used as a plasticizer for cellulose esters in place of camphor, a polymer additive, a component of fungicidal and insecticidal formulations, in the formulation of extreme pressure lubricants, and in the manufacture of fire extinguishing fluids.

42. Haloalkanes are...

- a) Monohaloalkanes      b) dihaloalkanes      c) Trihaloalkanes      d) All

43. Which of the following is halogen exchange reaction?



44. Trihaloalkanes have number of halogen atom (s):

- a) Two                      b) Three                      c) One                      d) Four

45. p-dichlorobenzene has higher melting point than its o- and m- isomers because

(a) p-dichlorobenzene is more polar than o- and m- isomer.

**(b) p-isomer has a symmetrical crystalline structure.**

(c) boiling point of p-isomer is more than o- and m-isomer.

(d) All of these are correct reasons.

46. Fittig reaction can be used to prepare

- (a) Toluene                      (b) Acetophenone                      (c) Diphenyl                      (d) Chlorobenzene

47. The ether used in Wurtz synthesis is

- a) . Acidic                      b) . Basic                      c) . Aqueous                      d) . Dry

48. In primary alkyl halides, the halogen atom is attached to a carbon which is further attached to how many carbon atoms

- a) Two                      b) Three                      c) One                      d) Four

49. The best method of preparation of alkyl halides is a reaction of the alcohol with

- a) Zn / HCl                      b)  $\text{SOCl}_2$  / Pyridine                      c)  $\text{PCl}_3$                       d)  $\text{PCl}_5$

50. In Fittig reaction, aryl halides when treated with \_\_\_\_\_ in dry ether give an analogous compound in which two aryl groups are joined together.

- a) K                      b) Mg                      c) Na                      d) Ca

51. Of the options give, the one statement about trichloromethane (Chloroform) that is correct is

a) It should be stored in a well ventilated place, exposed to sunlight

b) A lower level of its presence in the air can lead to slightly impaired hearing and vision.

c) A high level of its presence in air causes dizziness, nausea and numbness in fingers and toes.

d) It is used in the production of Freon refrigerant R-22

52. Tetrachloromethane is also known as \_\_\_\_ .

a) Chloroform      b) carbontetrachloride      c) DDT      d) Freon

53. Which of the following is not an Electrophilic substitution reaction of haloarenes?

a) Sulphonation      b) Nitration      c) Halogenations      d) Wurtz-Fittig reaction