



**Ranjan Singh**  
Chemistry Classes

JEE (Main & Advanced) • NEET • XI • XII

*Study Package*



**Ranjan Singh**

**M.Sc. Bio-Chemistry(P.U)**

Ex-Faculty : Narayana & Goal

# ORGANIC CHEMISTRY

**HALOALKANE AND  
HALOARENES**



## Director's Message



**Ranjan Singh**  
M.Sc.(Biochemistry), P.U.

Chemistry plays a central and important role in all competitive examinations as well as in day to day life. For last so many years, I have constantly been in touch with students, guiding them in Chemistry and looking into their difficulties for them to succeed in their board as well as competitive examinations (JEE(Mains & Advance) | NEET).

I have felt a need for a good coaching centre to fulfil the requirements of students. Students need a highly experienced and qualified faculty in chemistry, who can guide them well, clear their doubts, provide them the effective & tricky notes, and make them do much needed practice. More importantly they should also be provided Classroom Monitoring, Periodical & Surprise Tests to guide them in the proper direction. I realize that, it is very important to diagnose the basic weaknesses and problems of students not succeeding in JEE(Mains & Advance) | NEET and Board exams. In fact, as question patterns are changing, now they need to have a different approach for these Examinations.

At RANJAN SINGH CHEMISTRY CLASSES, we have our own way to prepare students for Competitive Examinations as well as Board Examination at a time so they can crack the entrance exam like JEE(Mains & Advance) and NEET as well as 12th Board simultaneously. We act as a medium to provide the simplest, easiest and a comfortable way to make students achieve their target. At RANJAN SINGH CHEMISTRY CLASSES(RSCC), we guide our students with the best motivational classes so weak students are also able to believe that, They can do it.

When you join RANJAN SINGH CHEMISTRY CLASSES you become a part of the powerful force which propels you towards your goal and if you get a position among the rankers with my excellent guidance, I will think that our efforts have borne fruits.

**M.Sc(Biochemistry), P.U.**

**Ex-faculty : Narayana IIT Academy**

**& Goal Institute**

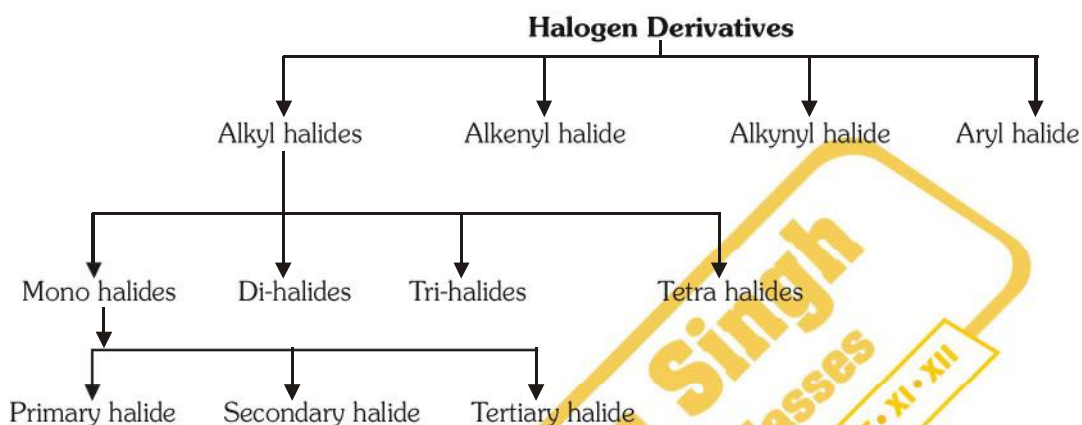
*Ranjan Singh*

## INTRODUCTION :

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as halogen derivatives.

### Classification :

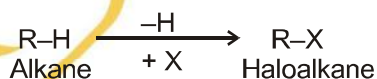
On the basis of nature of hydrocarbon from which they are obtained, hydrocarbon derivatives can be classified as :



- (a) Alkyl halides : Halogen derivative of alkanes.  
 (b) Alkenyl halides : Halogen derivative of alkenes.  
 (c) Alkynyl halides : Halogen derivative of alkynes  
 (d) Aryl halides : Halogen derivative of arenes (aromatic)

## HALOALKANES OR ALKYL HALIDE

- Halogen derivatives of alkanes are formed by substitution of one or more hydrogen atoms of an alkane by halogen (F, Cl, Br or I).

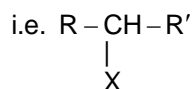


*(Halogen atom is normally represented by X)*

- Halogen derivatives of Alkanes are divided into mono di, tri, etc. Substitution products according to the number of halogen atoms in the molecule.

### MONOHALO ALKANES

- ◆ These are halogen derivatives of alkanes having general formula  $C_nH_{2n+1}X$ . where X = F, Cl, Br and I.
- ◆ Monohalo alkanes are of three types :
  - (a) **Primary alkyl halides** in which halo group is present on primary carbon atom, i.e.  $R - CH_2 - X$
  - (b) **Secondary alkyl halides** in which halo group is present on secondary carbon atom,

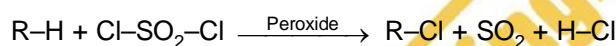
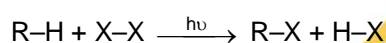


- (c) **Tertiary alkyl halides** in which halo group is present on tertiary carbon atom, i.e.  $\begin{array}{c} \text{X} \\ | \\ \text{R}-\text{C}-\text{R}' \\ | \\ \text{R}'' \end{array}$

### Methods of Preparation of Alkyl Halide :

(a) **By Halogenation of Alkanes**

Halogenation of alkanes takes place by free radical mechanism.



(b) **By Hydrohalogenation of Alkenes**

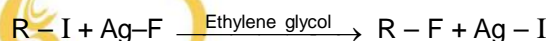
Alkyl halides are formed by addition of hydrogen halide on alkenes according to **Markownikoff's rule**.



(c) **By halogen exchange in alkyl Halides :**

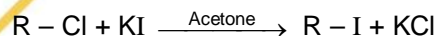
**By Silver Halide :**

This reaction is called **Swart reaction**.



**By Sodium or Potassium Halide :**

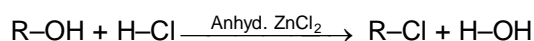
This reaction is called **Finkelstein reaction**.



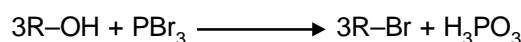
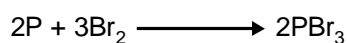
(d) **From Alkanols**

**By Conc. HCl :**

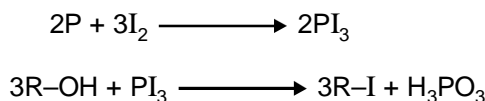
This is called **Grove's method**.



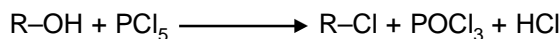
**By Red Phosphorus and Bromine :**



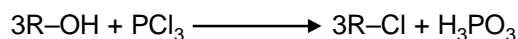
By Red Phosphorus and Iodine :



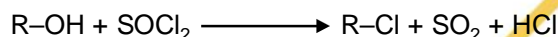
By Phosphorus pentachloride :



By Phosphorus trichloride :

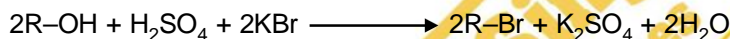


By Thionyl chloride :



The above reaction is performed in the presence of pyridine. Called **Darzens reaction**.

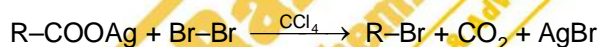
From KBr and Conc.  $H_2SO_4$  :



From KI and  $H_3PO_4$  :



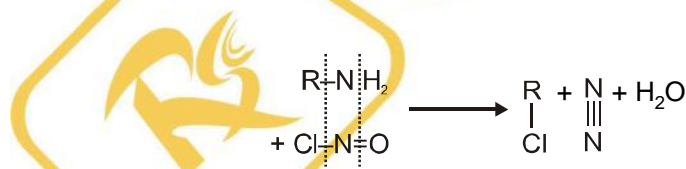
(e) From Alkanoic Acids :



It is called **Hunsdiecker reaction**.

(f) From Alkylamines :

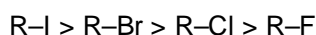
Alkyl chlorides are formed by the reaction of **Tilden's reagent** or **Nitrosyl chloride** (NOCl) on alkylamines.



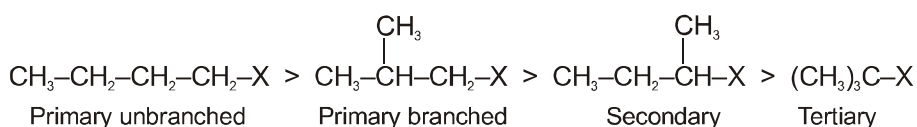
### Physical Properties

- ◆  $CH_3F$ ,  $CH_3Cl$ ,  $CH_3Br$ ,  $C_2H_5F$  and  $C_2H_5Cl$  are found in gaseous state at room temperature.
- ◆ Alkyl halides are normally sweet-smelling gases and liquids, whereas odourless in solid state.
- ◆ All alkyl halides are insoluble in water.
- ◆ Boiling points of alkyl halides change in the following order.

(i) On having same alkyl group



(i) On having same halogen atom

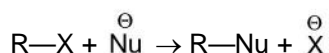
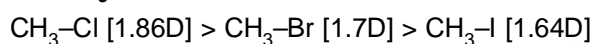


## CHEMICAL PROPERTIES

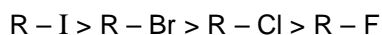
### Nucleophilic substitution reaction [S<sub>N</sub>]:



### Order of dipole moment [CH<sub>3</sub>X]:



In this reaction reactivity order is as follows :



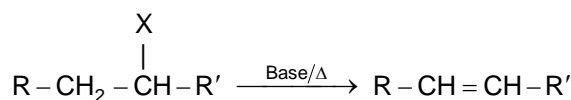
### R—X REACTION

Reagent	Product
Na/dry ether	R-R
KOH (aq.)	ROH
Ag <sub>2</sub> O (moist)	ROH
NaI	RI
NaOR	ROR
R'COOAg	R'COOR
Ag <sub>2</sub> O (dry)	ROR
KCN	RCN
AgCN	RN ≡ C
R'C ≡ CNa	R'C ≡ CR
KNO <sub>2</sub>	RONO
AgNO <sub>2</sub>	RNO <sub>2</sub>
Na <sub>2</sub> SO <sub>3</sub>	RSO <sub>3</sub> Na
NaSR'	RSR'
Na <sub>2</sub> S	R <sub>2</sub> S
KSH	RSH
NH <sub>3</sub>	RNH <sub>2</sub>
RNH <sub>2</sub>	R <sub>2</sub> NH
R <sub>2</sub> NH	R <sub>3</sub> N
R <sub>3</sub> N	R <sub>4</sub> N <sup>+</sup> X <sup>-</sup>

### $\beta$ -Elimination Reaction :

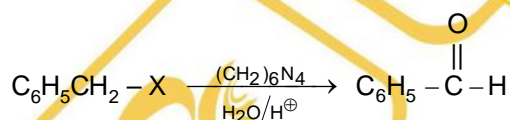
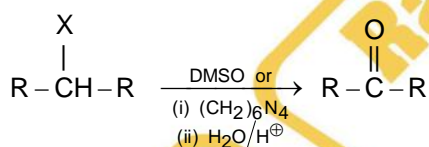
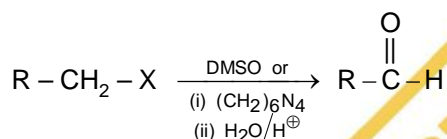
Dehydrohalogenation : Alkyl halides give  $\beta$ -elimination reaction in the presence of strong base such as

alc. KOH/ $\Delta$ , alc. NaOH/ $\Delta$ ,  $\text{RONa}^\ominus/\text{Ethanol}$ , NaH/ $\Delta$ ,  $\text{NaNH}_2/\Delta$



### Oxidation reaction :

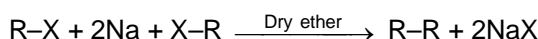
- ◆ Only primary and secondary alkyl halides undergo oxidation. Tertiary alkyl halide does not undergo oxidation.
- ◆ Primary alkyl halides give aldehyde whereas secondary alkyl halides give ketone in this reaction.
- ◆ Oxidising agent is either :
  - (a) Dimethyl sulphoxide or
  - (b) Reaction with  $(\text{CH}_2)_6\text{N}_4$  followed by hydrolysis.
- ◆ Reactivity  $\propto$  number of  $\alpha$ -hydrogens.



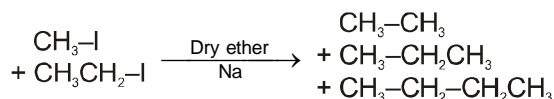
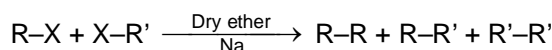
- Note :** (i) Oxidation of Benzyl halides by  $(\text{CH}_2)_6\text{N}_4$  is known as **sommelet aldehyde synthesis**.  
 (ii) Oxidation of alkyl halide with DMSO is known as **swern oxidation**.

### Reaction with Metals

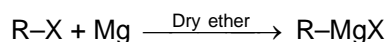
**By Wurtz Reaction :** An alkane having even number of carbon atoms. This is called **Wurtz synthesis** or **Wurtz Reaction**.



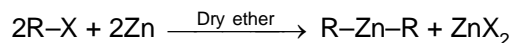
Alkane having odd number of carbon atoms can be obtained by mixed **Wurtz synthesis**.



### Synthesis of Grignard's Reagents



### Synthesis of Frankland's Reagents



### Synthesis of Tetraalkyllead

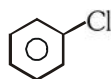


Tetraethyllead and tetramethyllead are high quality antiknock compounds.

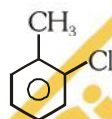
## HALOARENS OR HALOBENZENE OR ARYL HALIDE

If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene.

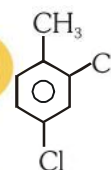
Example :



(Chlorobenzene)



(2-Chlorotoluene)



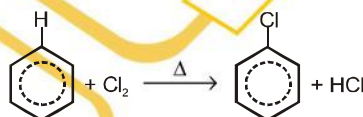
(2,4-Dichlorotoluene)

### Chlorobenzene, C<sub>6</sub>H<sub>5</sub>Cl

#### Methods of Preparation :

#### Chlorination of Benzene :

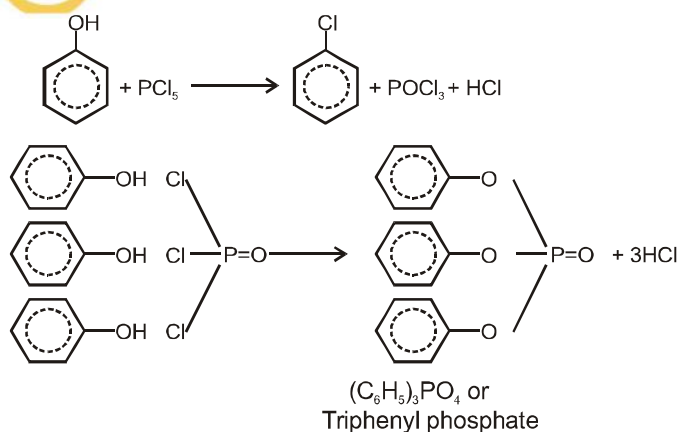
Chlorobenzene is obtained on reacting benzene with chlorine in the presence of a halogen carrier. Lewis acids (AlCl<sub>3</sub>, FeBr<sub>3</sub>, BF<sub>3</sub>, etc) some elements (iron powder, iodine, etc.) or some tertiary amine bases (pyridine) can be used as halogen carriers.



Bromobenzene is obtained if bromine is used in place of chlorine in the above reaction.

#### Dehydroxylative Chlorination of Phenol :

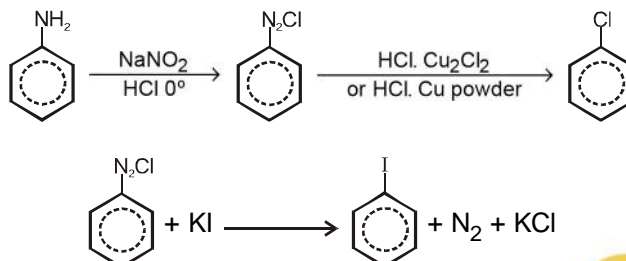
Chlorobenzene is formed on reacting phenol with phosphorus pentachloride. Yields of chlorobenzene are low due to formation of triphenyl phosphate (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>PO<sub>4</sub> as the major product.



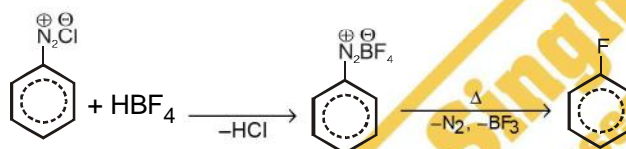


### Sandmeyer's reaction (Deaminative Chlorination of Aniline) :

Chlorobenzene can be obtained by Sandmeyer's reaction (Cuprous chloride, in the presence of  $\text{Cu}_2\text{Cl}_2$ ) or Gattermann reaction (in the presence of copper powder) of the benzenediazonium chloride salt obtained by diazotisation (reaction of aqueous  $\text{NaNO}_2$  and aqueous  $\text{HCl}$  at  $0^\circ\text{C}$ ) of aniline.



For the synthesis of fluorene, benzenediazonium fluoroborate is heated. This is called Balz–Schiemann reaction.



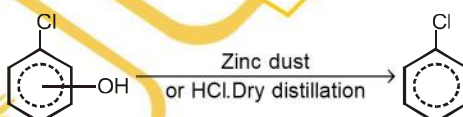
### Decarboxylation of Chlorobenzoic Acids :

Dry distillation of o-, m- or p-chlorobenzoic acid with soda lime gives chlorobenzene by **decarboxylation**.



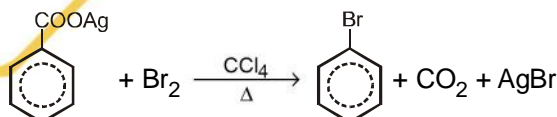
### Dehydroxylation of Chlorophenols :

On dry distillation of o-, m- or p-chlorophenol with zinc dust, chlorobenzene is obtained by **dehydroxylation**.



### Decarboxylative Bromination of Benzoic Acid :

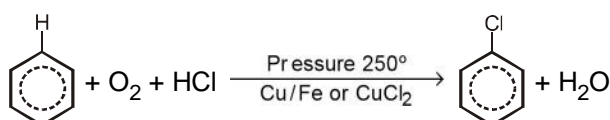
For the preparation of bromobenzene, silver salt of benzoic acid is heated with bromine in  $\text{CCl}_4$  solution. This is called **Borodine–Hunsdiecker reaction**.



Fluorene, chlorobenzene and iodobenzene cannot be prepared by the above method.

### Raschig Process :

Manufacture of chlorobenzene on large scale is carried out by **Raschig process**. In this method, the mixture of benzene vapour,  $\text{HCl}$  gas and the oxygen (air) is passed over heated copper-iron catalyst or  $\text{CuCl}_2$  catalyst with pressure at  $250^\circ\text{C}$ .



### Physical Properties :

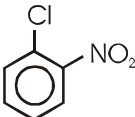
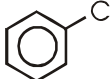
Chlorobenzene is a colourless, volatile, inflammable, liquid (boiling point = 132°C) having faint smell resembling almonds. It is a little bit poisonous (less than benzene), insoluble in water and soluble in organic solvents.

### Reactions :

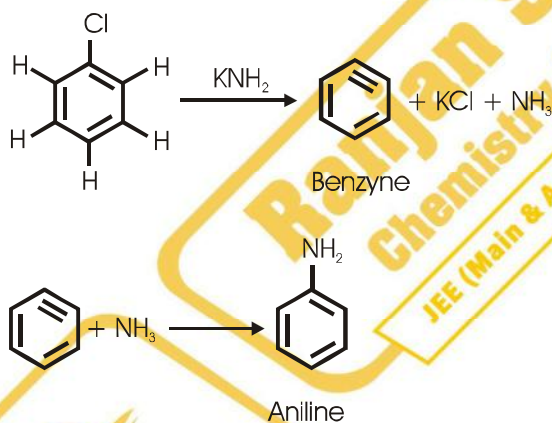
[A] Reactions due to chlorine atom. [B] Reactions due to Benzene ring.

#### Reactions Due to Chlorine Atom :

The reactivity of chlorobenzene increases when – M or – I effect causing groups are bonded at ortho or para positions of chlorobenzene. These groups decrease pi electron density on the ring and then nucleophile can attack easily on chloro benzene.

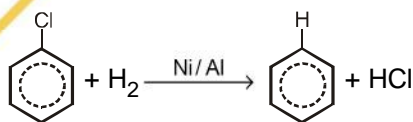
Thus  is more reactive than  towards nucleophilic substitution.

Nucleophilic substitution in chlorobenzene takes place by elimination-addition mechanism. In this reaction **Benzyne** is formed as an intermediate.



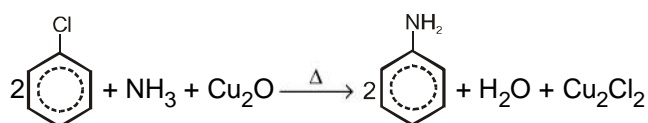
#### Reduction or Dechlorination :

Benzene is formed on reduction of chlorobenzene by nickel-aluminium alloy in the presence of small amounts of a base.



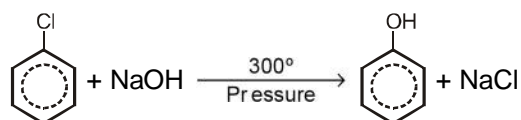
#### Dechlorinative Amination :

On heating with ammonia in the presence of cuprous oxide, aniline is formed.

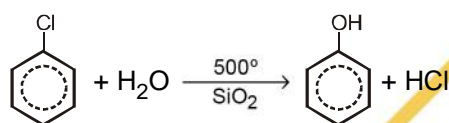


### Dechlorinative Hydroxylation :

[a] **By Dow process** : Phenol is formed on heating chlorobenzene with caustic soda (NaOH) or washing soda ( $\text{Na}_2\text{CO}_3$ ) solution at a high temperature ( $300^\circ\text{C}$ ) under pressure in the presence of a copper salt. This method is used for the manufacture of phenol on large scale and is known as **Dow process**.



[b] **By steam** : On passing a mixture of chlorobenzene and steam through heated silica at  $500^\circ\text{C}$ , phenol is formed.



### Reaction with Metals

**Fitting Reaction :**



**Wurtz-Fitting Reaction :**



**With Magnesium Metal :**

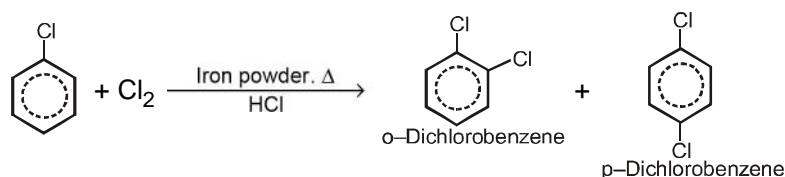
In order to obtain high yields of phenylmagnesium halide, iodobenzene (or bromobenzene) is reacted with magnesium in dry and pure ether. Fluorobenzene and chlorobenzene react very slowly. Therefore, they are practically not suitable for preparing a Grignard's reagent.



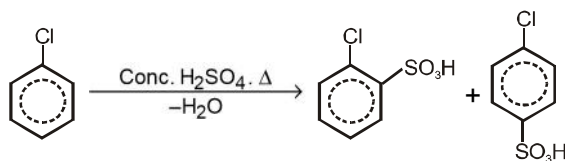
**Reactions Due to Benzene Ring :**

[i] **Electrophilic Substitution or  $\text{S}_\text{E}$  Reactions :**

**Halogenation :**

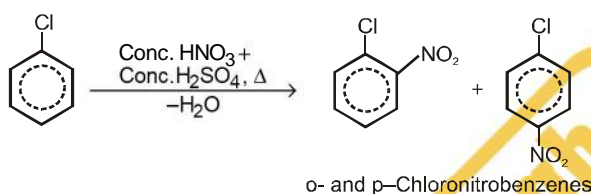


**Sulphonation :**



o- and p-chlorobenzenesulphonic acids

**Nitration :**

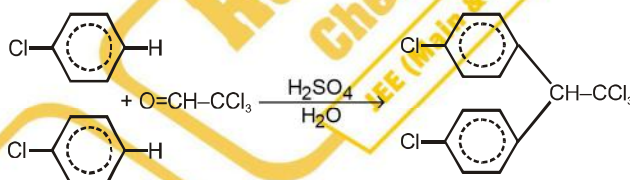


o- and p-Chloronitrobenzenes

**[iii] Condensation Reaction :**

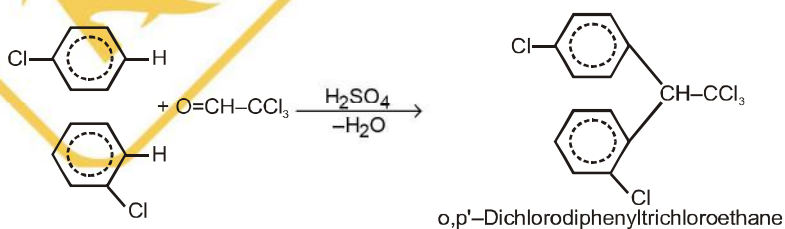
**Bimolecular Condensation with Chloral :**

On heating mixture of chlorobenzene and chloral hydrate in the presence of small amount of concentrated sulphuric acid, p, p'-dichlorodiphenyltrichloroethane, whose abbreviated name is **D.D.T.** It is a strong germicide and its IUPAC name is 1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane.



D.D.T

In the above reaction o, p'-dichloro isomer is also formed in minor amount (about 25%) as a by-product.



o,p'-Dichlorodiphenyltrichloroethane

**Uses :**

- [1] In the manufacture of strong germicide, D.D.T.
- [2] In the manufacture of many medicines and compounds (phenol, aniline, alkylbenzenes, dichlorobenzenes, phenylmagnesium halides, etc.) and as intermediate in several reactions.
- [3] As a solvent.

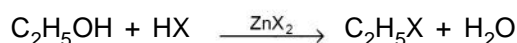
## TOPIC WISE MCQS

### Methods of preparation of alkyl halide

- The formation of an alkyl halide by reaction of hydrogen halide on an unsymmetrical alkene is an example of -  
(A) A nucleophilic addition reaction  
(B) An electrophilic addition reaction  
(C) A free radical reaction  
(D) An elimination reaction

- When propylene reacts with HBr in presence of peroxide, the product formed is -  
(A) n-Propyl alcohol  
(B) Propylene peroxide  
(C) n-Propyl bromide  
(D) 1,3 Dibromo propene

- In reaction



the order of reactivity of HX is -

- (A) HBr > HI > HCl  
(B) HI > HCl > HBr  
(C) HCl > HBr > HI  
(D) HI > HBr > HCl
- Which of the following leads to the formation of an alkyl halide -



(D) All

- Which halide/ halides not prepared by Darzen reaction -

- (A) R- Cl                      (B) RBr  
(C) R I                        (D) (B) & (C) both

- Which reaction is termed as Darzen's Reaction-

- (A) ROH + HCl              (B) ROH + PCl<sub>5</sub>  
(C) ROH + SOCl<sub>2</sub>        (D) ROH + PCl<sub>3</sub>

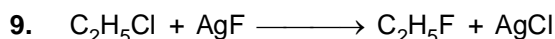
- The reaction of silver carboxylates with bromine dissolved in carbon tetrachloride is called -

- (A) Hofmann reaction  
(B) Borodine reaction

(C) Borodine - Hunsdiecker reaction

(D) Hypobromide reaction

- In the Hunsdiecker reaction -  
(A) Number of carbon atoms decrease  
(B) Number of carbon atoms increase  
(C) Number of carbon atoms remain same  
(D) None of the above



The above reaction is called -

- (A) Hunsdiecker              (B) Swart  
(C) Strecker                  (D) Wurtz

### Physical properties of alkyl halide

- Which of the following statement is correct -

(A) Decreasing order of density of alkyl halides is RI > RBr > RCl > RF

(B) The stability order of alkyl halides is RF > RCl > RBr > RI

(C) Among isomeric alkyl halides the decrease in boiling point 1° > 2° > 3°

(D) All are correct

- Which statement is not correct -

(A) Polyhalides are lighter than water

(B) Halo alkanes have higher boiling points as compared to those of corresponding alkanes

(C) Halides are soluble in organic solvents

(D) None

- An alkyl halide is insoluble in water because-

(A) Alkyl halide is non polar & H<sub>2</sub>O is polar

(B) Both are polar

(C) Alkyl halide does not form hydrogen bond with water

(D) Alkyl halide has halogen atom in it.

- The correct order of polarity of alkyl halides is :

(A) RI > RBr < RCl > RF

(B) RF > RCl > RBr > RI

(C) RCl > RF > RBr > RI

(D) None

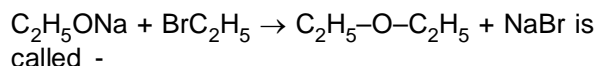
- Which chloride is the most reactive towards aqueous NaOH in -

(A) Methyl chloride        (B) Chlorobenzene

(C) Vinyl chloride          (D) Benzyl chloride

15. The  $S_N^2$  reactivity order for halides :-  
 (A)  $R - F > R - Cl > R - Br > R - I$   
 (B)  $R - I > R - Br > R - Cl > R - F$   
 (C)  $R - Br > R - I > R - Cl > R - F$   
 (D)  $R - Cl > R - Br > R - F > R - I$
16. In  $S_N^1$  reaction, the first step involves the formation of :-  
 (A) Free radical (B) Carbanion  
 (C) Carbocation (D) Final product
17. The rate law for the reaction,  $RCl + Na(aq.) \rightarrow ROH + NaCl$  is given by,  $rate = K_1 [RCl]$ . The rate of the reaction will be :-  
 (A) Doubled on doubling the concentration of sodium hydroxide  
 (B) Halved on reducing the concentration of alkyl halide to half  
 (C) Decreased on increasing the temperature of the reaction  
 (D) Unaffected by increasing the temperature of the reaction
18. Chlorobenzene is -  
 (A) More reactive than ethyl bromide  
 (B) More reactive than isopropyl chloride  
 (C) As reactive as methyl chloride  
 (D) Less reactive than benzyl chloride
19. When an alkyl halide reacts with an alkoxide, the product is -  
 (A) Ether (B) Ester  
 (C) Hydrocarbon (D) Alcohol
20.  $CH_3 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{Br}}{\text{CH}} - CH_3 \xrightarrow[\text{williamson}]{SN^1, C_2H_5ONa} \text{Ether}$   
 Ether is -  
 (A)  $CH_3 - \overset{\text{OC}_2\text{H}_5}{\text{C}} - CH_2 - CH_3$   
 (B)  $CH_3 - \underset{\text{CH}_3}{\text{CH}} - \underset{\text{OC}_2\text{H}_5}{\text{CH}} - CH_3$   
 (C) Both correct  
 (D) None is correct
21. 2-Bromobutane on heating with alcoholic alkali forms -  
 (A)  $\alpha$  - Butylene only  
 (B)  $\beta$  - Butylene only  
 (C) 20% of  $\beta$ -Butylene+ 80% of  $\alpha$ -Butylene  
 (D) 80%  $\beta$ -Butylene + 20%  $\alpha$ -Butylene
22. An organic compound on treatment with alcoholic KOH gives a hydrocarbon of a molecular formula  $C_4H_8$ . Oxidation of the hydrocarbon gives propionic acid and  $CO_2$ . The organic compound should be -  
 (A)  $C_2H_5 - CH_2 - CH_2Cl$   
 (B)  $CH_3 - CH_2 - \underset{\text{Cl}}{\text{CH}} - CH_3$   
 (C)  $CH_3 - CH - \underset{\text{Cl}}{\text{CH}} - CH_3$   
 (D)  $CH_3 - CH - \underset{\text{Cl}}{\text{CH}} - CH_2Cl$
23. (A)  $\xrightarrow{Cl_2}$  (B)  $\xrightarrow{aq. KOH}$  (C)  $\xrightarrow{O}$   $CH_3CHO$ , Identify A, B & C -  
 (A) Ethylalcohol Ethyl chloride & Ethane  
 (B) Ethane, Ethylchloride &  $CH_3-CH_2-OH$   
 (C) Propane, Propylchloride &  $CH_3-CH_2-CH_2-OH$   
 (D) All the above
24. An alkyl halide reacted with a metal cyanide to give an alkanenitrile. The metal cyanide is -  
 (A)  $AgCN$  (B)  $KCN$   
 (C)  $Cu_2(CN)_2$  (D)  $Ba(CN)_2$
25. Ethylthioalcohol can be obtained when  $C_2H_5Br$  reacts with -  
 (A)  $KSH$  (B)  $NaOH$   
 (C)  $K_2S$  (D)  $Na_2S$
26. Which one of the following reaction is known as strecker;s reaction -  
 (A)  $R - X + NaI \rightarrow R - I + NaX$   
 (B)  $R - X + Na_2SO_3 \rightarrow R - SO_3Na + NaX$   
 (C)  $RCOOAg + Br_2 \rightarrow R - Br + AgBr + CO_2$   
 (D) None of the above

27. The reaction



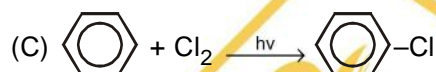
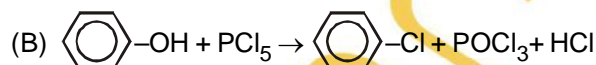
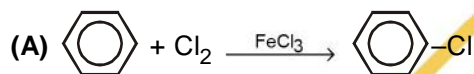
- (A) Frankland reaction  
(B) Wurtz reaction  
(C) Williamson's synthesis  
(D) Cannizzaro reaction

### Methods of Preparation of Aryl Halide

28. Which of the following reactions can be used to obtain chlorobenzene from benzenediazonium chloride ?

- (a) Sandmeyer reaction  
(b) Balz-Schmann reaction  
(c) Rashing process  
(d) Gattermann reaction
- (A) a and b                      (B) a, b and c  
(C) a, c and d                (D) c and d

29. The best method for the preparation of chlorobenzene is :



30. Highest yield of chlorobenzene is obtained in the reaction :

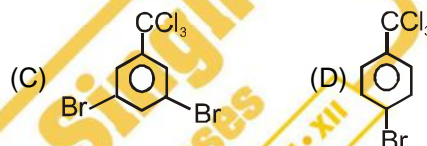
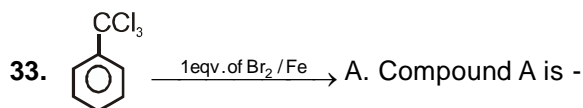


31. C<sub>6</sub>H<sub>5</sub>Cl prepared by aniline with :

- (A) HCl  
(B) Cu<sub>2</sub>Cl<sub>2</sub>  
(C) Cl<sub>2</sub> in presence of anhydrous AlCl<sub>3</sub>  
(D) HNO<sub>2</sub> and then heated with Cu<sub>2</sub>Cl<sub>2</sub>

32. The chlorobenzene is generally obtained from a corresponding diazonium salt by reacting it with:

- (A) Cu<sub>2</sub>Cl<sub>2</sub>                      (B) CuSO<sub>4</sub>  
(C) Cu                              (D) Cu(NH<sub>3</sub>)<sub>4</sub><sup>2+</sup>



### Properties of Aryl Halide

34. An important insecticide is obtained by the action of chloral on chlorobenzene. It is :

- (A) BHC                              (B) Gammexene  
(C) DDT                              (D) Lindane

35. C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Cl + KCN (aq.)  $\rightarrow$  X + Y

Compounds X and Y are :

- (A) C<sub>6</sub>H<sub>6</sub> + KCl                      (B) C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>CN + KCl  
(C) C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub> + KCl                (D) None of these

36. Chlorobenzene is :

- (A) Less reactive than benzyl chloride  
(B) More reactive than ethyl bromide  
(C) Nearly as reactive as methyl chloride  
(D) More reactive than isopropyl chloride

37. What is the decreasing order of reactivity amongst the following compounds towards aromatic electrophilic substitution :

- I. Chlorobenzene                      II. Benzene  
III. Anilinium chloride                IV. Toluene
- (A) I > II > III > IV                (B) IV > II > I > III  
(C) II > I > III > IV                (D) III > I > II > IV

38. The commercial uses of DDT and benzene hexachloride are :

- (A) DDT is a herbicide, benzene hexachloride is a fungicide  
 (B) Both are insecticides  
 (C) Both are herbicides  
 (D) DDT is a fungicide and benzene hexachloride is a herbicide

39. Following equation illustrates :  $C_6H_5Cl + 2NaOH \xrightarrow[200 \text{ atm}]{200-250^\circ C} C_6H_5ONa + NaCl + H_2O$

- (A) Dow's process (B) Kolbe's process  
 (C) Carbylamine test (D) Haloform reaction

40. Replacement of Cl of chlorobenzene to give phenol requires drastic condition but chlorine of 2,4-dinitrochlorobenzene is readily replaced because :

- (A)  $NO_2$  make ring electron rich at ortho and para  
 (B)  $NO_2$  withdraw  $e^-$  from meta position  
 (C)  $NO_2$  donates  $e^-$  at meta position  
 (D)  $NO_2$  withdraws  $e^-$  from ortho/para position

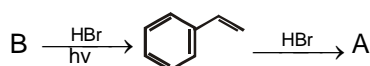
41. Aryl halide is less reactive than alkyl halide towards nucleophilic substitution because :

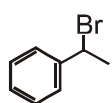
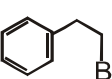
- (A) Less stable carbonium ion  
 (B) Due to large C-Cl bond energy  
 (C) Inductive effect  
 (D) Resonance stabilization and  $sp^2$  hybridisation of C attached to halide

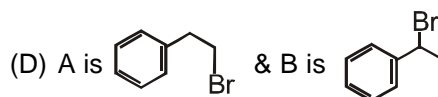
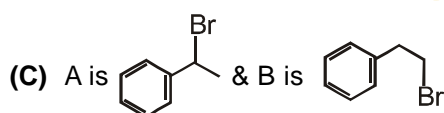
42. When phenyl magnesium bromide reacts with t-butanol, the product would be -

- (A) Benzene (B) Phenol  
 (C) t-butyl benzene (D) t-butyl phenyl ether

43. Analyse the following reaction and identify the nature of A and B



- (A) Both A and B are   
 (B) Both A and B are 



44. Which of the following catalysts is used in the preparation of chlorobenzene by Gattermann reaction ?

- (A)  $CuSO_4$  (B)  $CuCl_2$   
 (C)  $Cu_2Cl_2$  (D) Cu

45. Which of the following catalysts is used in the preparation of chlorobenzene by Sandmeyer's reaction ?

- (A)  $CuCl_2$  (B)  $Cu_2Cl_2$   
 (C)  $CuSO_4$  (D) Cu

46. Which of the following compounds is obtained by Borodine-Hunsdiecker reaction of silver benzoate ?

- (A) Fluorobenzene (B) Chlorobenzene  
 (C) Bromobenzene (D) Iodobenzene

47. Which of the following reagents is used for obtaining chlorobenzene from p-chlorophenol ?

- (A) Zinc dust (B) Soda lime  
 (C) Sodamide (D) Copper powder

48. All of the following properties are exhibited by chlorobenzene, except :

- (A) Almond-like faint smell (B) Volatility  
 (C) Inflammability  
 (D) Nonpoisonous nature

49. In Dow process, chlorobenzene is reacted with which of the following reagents ?

- [A]  $O_2 + HCl$  [B] NaOH  
 [C]  $H_2O$  [D]  $Na_2CO_3$   
 (A) A and C (B) A and D  
 (C) B and C (D) B and D

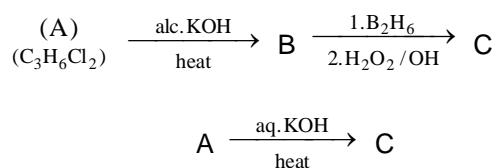
50. Condensation of chlorobenzene and chloral hydrate is carried out in the presence of concentrated sulphuric acid for obtaining ?

- (A) D.D.T. (B) Chloropicrin  
 (C) B.H.C  
 (D) Dichlorodiphenylethane



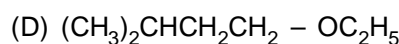
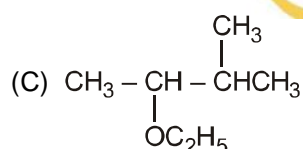
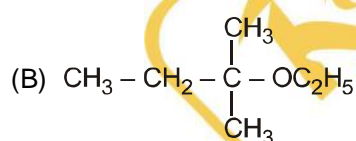
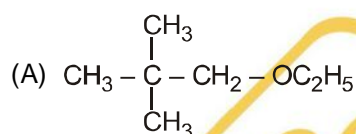
## MISCELLANEOUS QUESTIONS

1. Consider the following sequence of reactions.

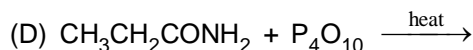
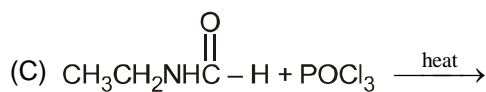
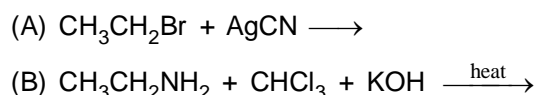


The compound (A) is -

- (A)  $\text{CH}_3\text{CH}_2\text{CHCl}_2$  (B)  $\text{CH}_3\text{CCl}_2\text{CH}_3$   
 (C)  $\text{CH}_3\text{CHClCH}_2\text{Cl}$  (D)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$
2. A compound (X),  $\text{C}_4\text{H}_8\text{Cl}_2$ , on hydrolysis with aqueous KOH gives a product (Y) which on heating with  $\text{I}_2$  and dilute NaOH gives a yellow precipitate of iodoform. The compound (X) is -
- (A)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCl}_2$   
 (B)  $\text{CH}_3\text{CH}_2\text{CHClCH}_2\text{Cl}$   
 (C)  $\text{CH}_3\text{CH}_2\text{CCl}_2\text{CH}_3$   
 (D)  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$
3. Neopentyl bromide is allowed to react with sodium ethoxide in ethanol. The major substitution product formed in the reaction is -



4. Which of the following reactions will not give an isocyanide -



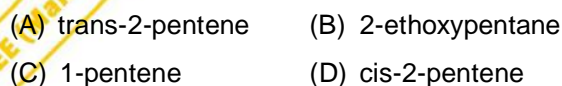
5. Which of the following processes does not occur during the formation of  $\text{CHCl}_3$  from  $\text{C}_2\text{H}_5\text{OH}$  and bleaching powder -



6. Which of the following reactions is not expected to give a satisfactory yield of alkyl iodide -



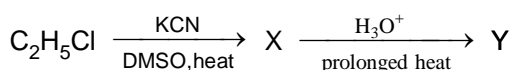
7. 2-Bromopentane is heated with potassium ethoxide in ethanol. The major product is -



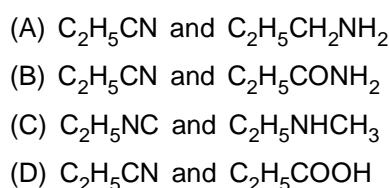
8. An aromatic primary amine (A) is heated with another compound (B) in the presence of alcoholic KOH to give a bad-smelling compound having the formula  $\text{C}_6\text{H}_5\text{NC}$ . The compound (B) can be prepared by heating another compound (C) with chlorine and slaked lime. The compound (C) is -



9. Consider the following sequence of reactions.



The products (X) and (Y) are, respectively -



10. The order of decreasing  $S_N1$  reactivities of the halides  
 (I)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$       (II)  $\text{CH}_2 = \text{CHCHClCH}_3$   
 (III)  $\text{CH}_3\text{CH}_2\text{CHClCH}_3$   
 is -  
 (A) I > II > III      (B) II > I > III  
 (C) II > III > I      (D) III > II > I
11.  $\text{C}_2\text{H}_5\text{Br}$  can be obtained in the laboratory by the action of ethyl alcohol with :  
 (A) KBr      (B)  $\text{NH}_4\text{Br}$   
 (C)  $\text{Br}_2$       (D) KBr and conc.  $\text{H}_2\text{SO}_4$
12. Which one is an organometallic compound ?  
 (A)  $\text{C}_2\text{H}_5\text{ONa}$       (B)  $\text{C}_2\text{H}_5\text{SNa}$   
 (C)  $\text{C}_2\text{H}_5\text{MgI}$       (D) All of these
13. A grignard reagent is prepared by the action of magnesium in dry ether on :  
 (A)  $\text{C}_2\text{H}_5\text{OH}$       (B)  $\text{C}_2\text{H}_6$   
 (C)  $\text{C}_2\text{H}_5\text{Cl}$       (D)  $\text{C}_2\text{H}_5\text{CN}$
14. Which is the correct formula of bleaching powder ?  
 (A)  $\text{Ca}(\text{OCl})\text{Cl}$       (B)  $\text{CaO}(\text{OCl})$   
 (C)  $\text{Ca}(\text{OCl})_2$       (D)  $\text{Ca}(\text{OCl})_2\text{Cl}$
15. When the reaction between methyl iodide and sodium ethoxide occurs, we get :  
 (A) methyl acetate      (B) ethyl methyl ketone  
 (C) ethyl acetate      (D) ethyl methyl ether
16. Heating together of sodium ethoxide and ethyl iodide will give :  
 (A) ethyl alcohol      (B) acetaldehyde  
 (C) diethyl ether      (D) acetic acid
17.  $\text{CH}_3\text{OH} \xrightarrow{\text{PI}_3} (\text{A}) \xrightarrow{\text{KCN}} (\text{B}) \xrightarrow{\text{Hydrolysis}} (\text{C})$   
 The compound (C) is :  
 (A)  $\text{CH}_3\text{OH}$       (B)  $\text{HCOOH}$   
 (C)  $\text{CH}_3\text{CHO}$       (D)  $\text{CH}_3\text{COOH}$
18.  $\text{C}_2\text{H}_5\text{Br} \xrightarrow{\text{KCN}} (\text{A}) \xrightarrow[\text{HCl}]{\text{Hydrolysis}} (\text{B})$  The compound B (in above reaction) is :  
 (A) ethylene chloride      (B) acetic acid  
 (C) propionic acid      (D) ethyl cyanide
19. When iodoform is heated with Ag powder it forms :  
 (A) acetylene      (B) ethylene  
 (C) methane      (D) ethane
20. When  $\text{CCl}_4$  is boiled with hot ethanolic KOH, the product formed is KCl and :  
 (A) formic acid      (B) methyl alcohol  
 (C) formaldehyde      (D) potassium carbonate
21. The reaction,  $\text{R}-\text{Br} + \text{NaCN} \longrightarrow \text{R}-\text{C} + \text{NaBr}$ , is an example of :  
 (A) elimination reaction  
 (B) nucleophilic substitution  
 (C) electrophilic substitution  
 (D) oxidation reduction
22. Which alkyl halide has maximum reactivity ?  
 (A)  $\text{CH}_3\text{CH}_2\text{Br}$       (B)  $\text{CH}_3\text{Br}$   
 (C)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$       (D)  $\text{H}_3\text{CCH}_2\text{CH}_2\text{CH}_2\text{Br}$
23. Decreasing order of reactivity of alkyl halide is :  
 (A)  $\text{RI} > \text{RCI} > \text{RBr}$       (B)  $\text{RBr} > \text{RCI} > \text{RI}$   
 (C)  $\text{RI} > \text{RBr} > \text{RCI}$       (D)  $\text{RCI} > \text{RBr} > \text{RI}$
24. Butanenitrile may be prepared by heating :  
 (A) propyl alcohol with KCN  
 (B) butyl alcohol with KCN  
 (C) butyl chloride with KCN  
 (D) propyl chloride with KCN
25. Grignard reagent adds to :  
 (A)  $>\text{C}=\text{O}$       (B)  $-\text{C}\equiv\text{N}$   
 (C)  $>\text{C}=\text{S}$       (D) all of these
26. For the reaction,  

$$\text{C}_2\text{H}_5\text{OH} + \text{HX} \xrightarrow{\text{ZnX}_2} \text{C}_2\text{H}_5\text{X}$$
 The decreasing order of reactivity of halogen acids is :  
 (A)  $\text{HI} > \text{HCl} > \text{HBr}$       (B)  $\text{HI} > \text{HBr} > \text{HCl}$   
 (C)  $\text{HCl} > \text{HBr} > \text{HI}$       (D)  $\text{HBr} > \text{HI} > \text{HCl}$
27. Which of the following alkyl halide is hydrolysed by  $S_N1$  mechanism ?  
 (A)  $(\text{CH}_3)_2\text{CHX}$       (B)  $\text{CH}_3\text{CH}_2\text{X}$   
 (C)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{X}$       (D)  $(\text{CH}_3)_3\text{CX}$
28.  $S_N1$  reaction is favoured by :  
 (A) non-polar solvents  
 (B) bulky groups on the carbon atom attached to halogen atom  
 (C) small groups on the carbon atom attached to halogen atom  
 (D) none of the above

29. An organic halide with formula  $C_6H_{13}Br$  on heating with alc. KOH gives two isomeric alkenes (A) and (B) with formula  $C_6H_{12}$ . On reductive ozonolysis of mixture (A) and (B), the following compounds are obtained :  
 $CH_3COCH_3$ ,  $CH_3CHO$ ,  $CH_3CH_2CHO$  and  $(CH_3)_2CHCHO$  The organic halide is :  
 (A) 2-bromohexane  
 (B) 3-bromo-2-methylpentane  
 (C) 2,2-bromo-2-methylpentane  
 (D) none of the above
30.  $(CH_3)_2CHCl + NaI \longrightarrow (CH_3)_2CHI + NaCl$  The above reaction is known as :  
 (A) Finkelstein reaction (B) Stephen's reaction  
 (C) Kolbe's reaction (D) Wurtz reaction
31. In elimination reactions, the reactivity of alkyl halides is in decreasing order :  
 (A)  $T > S > P$  (B)  $P > S > T$   
 (C)  $S > P > T$  (D) none of these
32. What happens when  $CCl_4$  is treated with  $AgNO_3$  solution ?  
 (A)  $NO_2$  will be evolved  
 (B) A white ppt. will be formed  
 (C)  $CCl_4$  will dissolve in  $AgNO_3$  solution  
 (D) No reaction takes place
33. Terminal dihalides on heating with zinc and methanol, we get :  
 (A) alkenes (B) cycloalkanes  
 (C) alkynes (D) alkanes
34. Tert. butyl chloride preferably undergoes hydrolysis by :  
 (A)  $S_N1$  mechanism (B)  $S_N2$  mechanism  
 (C) any of (a) and (b) (D) none of these
35. The reaction conditions leading to the best yield of  $C_2H_5Cl$  are :  
 (A)  $C_2H_6(\text{excess}) + Cl_2 \xrightarrow{UV \text{ light}}$   
 (B)  $C_2H_6 + Cl_2 \xrightarrow{\text{Dark, Room temp.}}$   
 (C)  $C_2H_6 + Cl_2(\text{excess}) \xrightarrow{UV \text{ light}}$   
 (D)  $C_2H_6 + Cl_2 \xrightarrow{UV \text{ light}}$
36. Arrange the following in order of their decreasing acid strength :  
 (A)  $HClO > HClO_2 > HClO_3 > HClO_4$   
 (B)  $HClO_4 > HClO_3 > HClO_2 > HClO$   
 (C)  $HClO > HClO_4 > HClO_3 > HClO_2$   
 (D)  $HClO_4 > HClO > HClO_2 > HClO_3$
37. The order of reactivity of alkyl halides depends upon :  
 (A) nature of alkyl group  
 (B) nature of halogen atom  
 (C) nature of both alkyl group and halogen atoms  
 (D) none of the above
38. Compound  $C_4H_8Cl_2$  (A) on hydrolysis gives a compound  $C_4H_8O$  (B) which reacts with hydroxylamine and does not give any test with Tollens' reagent. What are (A) and (B) ?  
 (A) 1,1-Dichlorobutane and butanal  
 (B) 2,2-Dichlorobutane and butanal  
 (C) 1,1-Dichlorobutane and butan-2-one  
 (D) 2,2-Dichlorobutane and butan-2-one
39. Which one of the following compounds is stable ?  
 (A)  $CH_3CH(OH)_2$  (B)  $(CH_3)_2CH(OH)_2$   
 (C)  $CCl_3CH(OH)_2$  (D) None of these
40. Isobutyl magnesium bromide with dry ether and absolute alcohol gives :  
 (A)  $(CH_3)_2CHCH_2OH$  and  $CH_3CH_2MgBr$   
 (B)  $(CH_3)_2CHCH_2CH_2CH_3$  and  $Mg(OH)Br$   
 (C)  $(CH_3)_3CH$  and  $CH_3CH_2OMgBr$   
 (D)  $(CH_3)_3CH$ ,  $H_2C = CH_2$  and  $Mg(OH)Br$
41. Isopropyl chloride undergoes hydrolysis by :  
 (A)  $S_N1$  mechanism  
 (B)  $S_N2$  mechanism  
 (C)  $S_N1$  and  $S_N2$  mechanism  
 (D) Neither  $S_N1$  nor  $S_N2$  mechanism
42. Which one of the following is most reactive towards nucleophilic substitution ?  
 (A)  $H_2C = CH - Cl$  (B)  $C_6H_5Cl$   
 (C)  $CH_3 - CH = CH - Cl$  (D)  $ClCH_2 - CH = CH_2$

43. The order of reactivities of the following alkyl halides for a  $S_N2$  reaction is :
- (A)  $RF > RCl > RBr > RI$  (B)  $RF > RBr > RCl > RI$   
(C)  $RCl > RBr > RF > RI$  (D)  $RI > RBr > RCl > RF$
44. The reactivity order of halides for dehydrohalogenation is :
- (A)  $R-F > R-Cl > R-Br > R-I$   
(B)  $R-I > R-Br > R-Cl > R-F$   
(C)  $R-I > R-Cl > R-Br > R-F$   
(D)  $R-F > R-I > R-Br > R-Cl$
45. Identify the set of reagent and reaction conditions 'X' and 'Y' in the following set of transformations,
- $$CH_3 - CH_2 - CH_2Br \xrightarrow{X} \text{Product} \xrightarrow{Y} CH_3 - \underset{\text{Br}}{\text{CH}} - CH_3$$
- (A) X = Dilute aqueous NaOH,  $20^\circ\text{C}$   
Y = HBr/acetic acid,  $20^\circ\text{C}$   
(B) X = Concentrated alcoholic NaOH,  $80^\circ\text{C}$   
Y = HBr/acetic acid,  $20^\circ\text{C}$   
(C) X = Dilute aqueous NaOH,  $20^\circ\text{C}$   
Y =  $Br_2/CHCl_3$ ,  $0^\circ\text{C}$   
(D) X = Concentrated alcoholic NaOH,  $80^\circ\text{C}$   
Y =  $Br_2/CHCl_3$ ,  $0^\circ\text{C}$
46. When an alkyl halide is heated with dry  $Ag_2O$ , it produces :
- (A) ester (B) ether  
(C) ketone (D) alcohol
47. Among the following the most reactive towards alcoholic KOH is :
- (A)  $CH_3CH_2Br$  (B)  $(CH_3)_2CHBr$   
(C)  $CH_3CH_2CH_2Br$  (D)  $CH_3COCH_2CH_2Br$
48. The major product obtained on treatment  $CH_3CH_2CH(F)CH_3$  with  $CH_3O^-/CH_3OH$  is :
- (A)  $CH_3CH_2CH(OCH_3)CH_3$   
(B)  $CH_3CH = CHCH_3$   
(C)  $CH_3CH_2CH = CH_2$   
(D)  $CH_3CH_2CH_2CH_2OCH_3$
49. A compound (A)  $C_5H_{10}Cl_2$  on hydrolysis gives  $C_5H_{10}O$  which reacts with  $NH_2OH$ , forms iodoform but does not give Fehling test. (A) is :
- (A)  $CH_3 - \underset{\text{Cl}}{\overset{\text{Cl}}{\text{C}}} - CH_2CH_2CH_3$   
(B)  $CH_3CH_2 - \underset{\text{Cl}}{\overset{\text{Cl}}{\text{C}}} - CH_2CH_3$   
(C)  $CH_3CH_2CH_2\underset{\text{Cl}}{\text{CH}}\underset{\text{Cl}}{\text{CH}_3}$   
(D)  $CH_3\underset{\text{Cl}}{\text{CH}} - \underset{\text{Cl}}{\text{CH}} - CH_2CH_3$
50. The major product formed in the following reaction,
- $$CH_3 - \underset{\text{H}}{\overset{\text{CH}_3}{\text{C}}} - CH_2Br \xrightarrow[CH_3OH]{CH_3O^-} \text{is :}$$
- (A)  $CH_3 - \underset{\text{H}}{\overset{\text{CH}_3}{\text{C}}} - CH_2OCH_3$  (B)  $CH_3 - \underset{\text{OCH}_3}{\text{CH}} - CH_2CH_3$   
(C)  $CH_3 - \underset{\text{CH}_3}{\text{C}} = CH_2$  (D)  $CH_3 - \underset{\text{OCH}_3}{\overset{\text{CH}_3}{\text{C}}} = CH_2$





## ANSWER KEY

### TOPIC WISE MCQS

Ques.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	B	C	D	D	D	C	C	A	B	D	A	C	B	D	B	C	B	D	A	C
Ques.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	D	A	B	B	A	B	C	C	A	A	D	A	A	C	B	A	B	D	A	D
Ques.	41	42	43	44	45	46	47	48	49	50										
Ans.	D	A	C	D	B	C	A	D	D	A										

### MISCELLANEOUS QUESTIONS

Ques.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Ans.	A	C	A	D	C	D	A	B	D	C	D	C	C	A	D	C	D	C	A	D
Ques.	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Ans.	B	B	C	D	D	B	D	B	B	A	A	D	B	A	A	B	C	D	C	C
Ques.	41	42	43	44	45	46	47	48	49	50										
Ans.	C	D	D	B	B	B	D	B	A	D										



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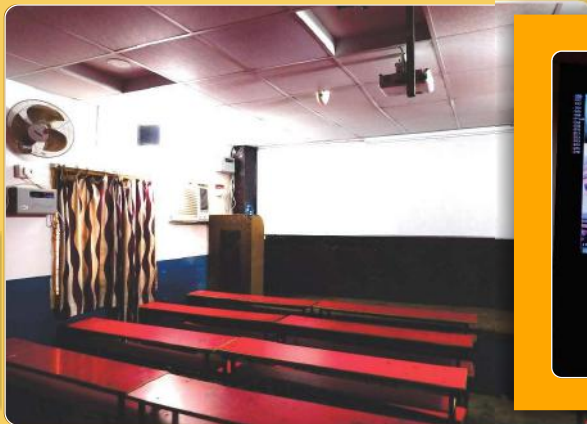
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