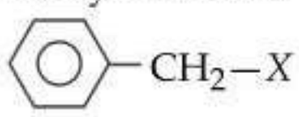
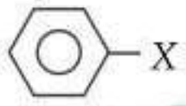

# Haloalkanes and Haloarenes

- Halogen derivatives are derived from hydrocarbons by the replacement of one or more hydrogen atoms with halogens.
- **Classification :**

**Halogenated hydrocarbons**

- **Aliphatic**
  - **Monohalides** (on the basis of nature of C – X bond)
    - C is $sp^3$ hybridised
      - (i) Alkyl halides $R - X$
      - (ii) Allylic halides $R-CH=CH-CH_2X$
      - (iii) Benzylic halides 
    - C is $sp^2$ hybridised
      - (i) Aryl halides 
      - (ii) Vinyl halides ($C=C-X$)
    - C is $sp$ hybridised
      - Alkynyl halides $-C\equiv C-X$
  - **Dihalides**
    - Gem dihalide (both $X$ on same C)
    - Vic-dihalide ($X$ on adjacent C)
    - α-ω (On terminal C)
  - **Trihalides**
  - **Tetrahalides**
- **Aromatic**

## Aliphatic Halogen Derivatives

- **Methods of preparation :**

$RCH_2OH + HX \xrightarrow[-H_2O]{ZnCl_2}$

$RCH_2OH + PX_5 \xrightarrow[-H_2O]{-POX_3}$

$RCH_2OH + SOX_2 \xrightarrow{pyridine}$

$RCH_2COOAg + X_2 \xrightarrow[\Delta]{CCl_4}$ (Hunsdiecker reaction)

$RCH_2Cl + NaX \xrightarrow{Acetone}$ (Finkelstein reaction)

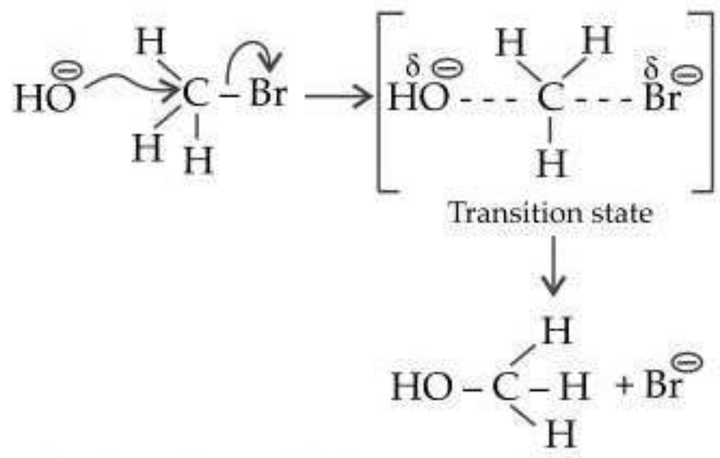
$R - CH_3 + X_2 \xrightarrow{Acetone}$

$\longrightarrow RCH_2X$

- **Mechanism of substitution reaction :** The alkyl halides undergo nucleophilic substitution reactions. The order of reactivity is

  $R - F < R - Cl < R - Br < R - I$

  - **$S_N2$ reaction :** The mechanism is a one step concerted mechanism in which attack of nucleophile and the displacement of the halide ions take place simultaneously.




  - **Order of reactivity towards $S_N2$ :**

    $CH_3 - X > CH_3CH_2 - X > (CH_3)_2CH - X > (CH_3)_3C - X$

    Rate of $S_N2$ reaction depends upon the concentration of halide and nucleophile both so it is called bimolecular nucleophilic substitution. $S_N2$ reaction proceeds through inversion of configuration.

- **$S_N1$ reaction :** Mechanism is of two steps :

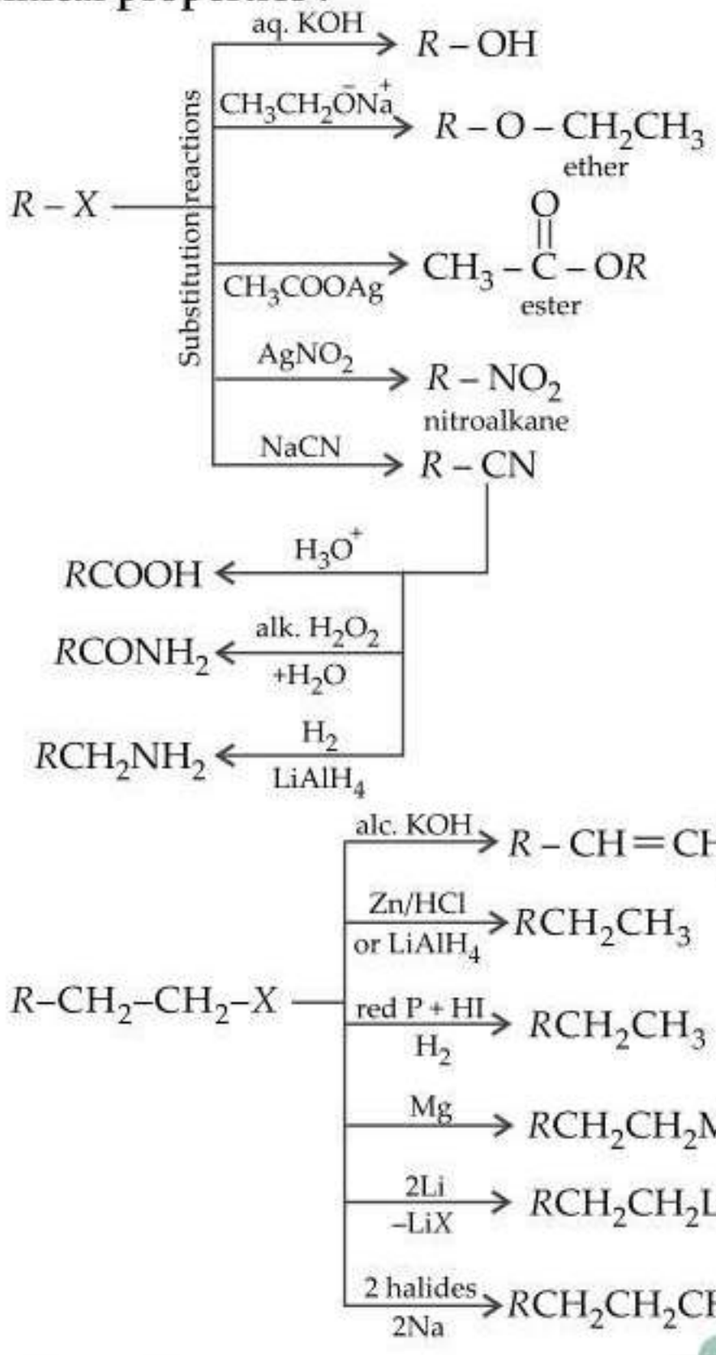
  First step : $R_3C - X \xrightarrow[\text{R.D. Step}]{slow} R_3C^{\oplus} + X^{\ominus}$

  Second step : $R_3C^{\oplus} + :Nu^{\ominus} \xrightarrow{fast} R_3C - Nu$

  So rate depends only upon the concentration of halide because it is only participating in slow or rate determining step.

– **Reactivity order :** $(CH_3)_3C - X > (CH_3)_2CHX > CH_3CH_2X > CH_3 - X$

- **Chemical properties :**



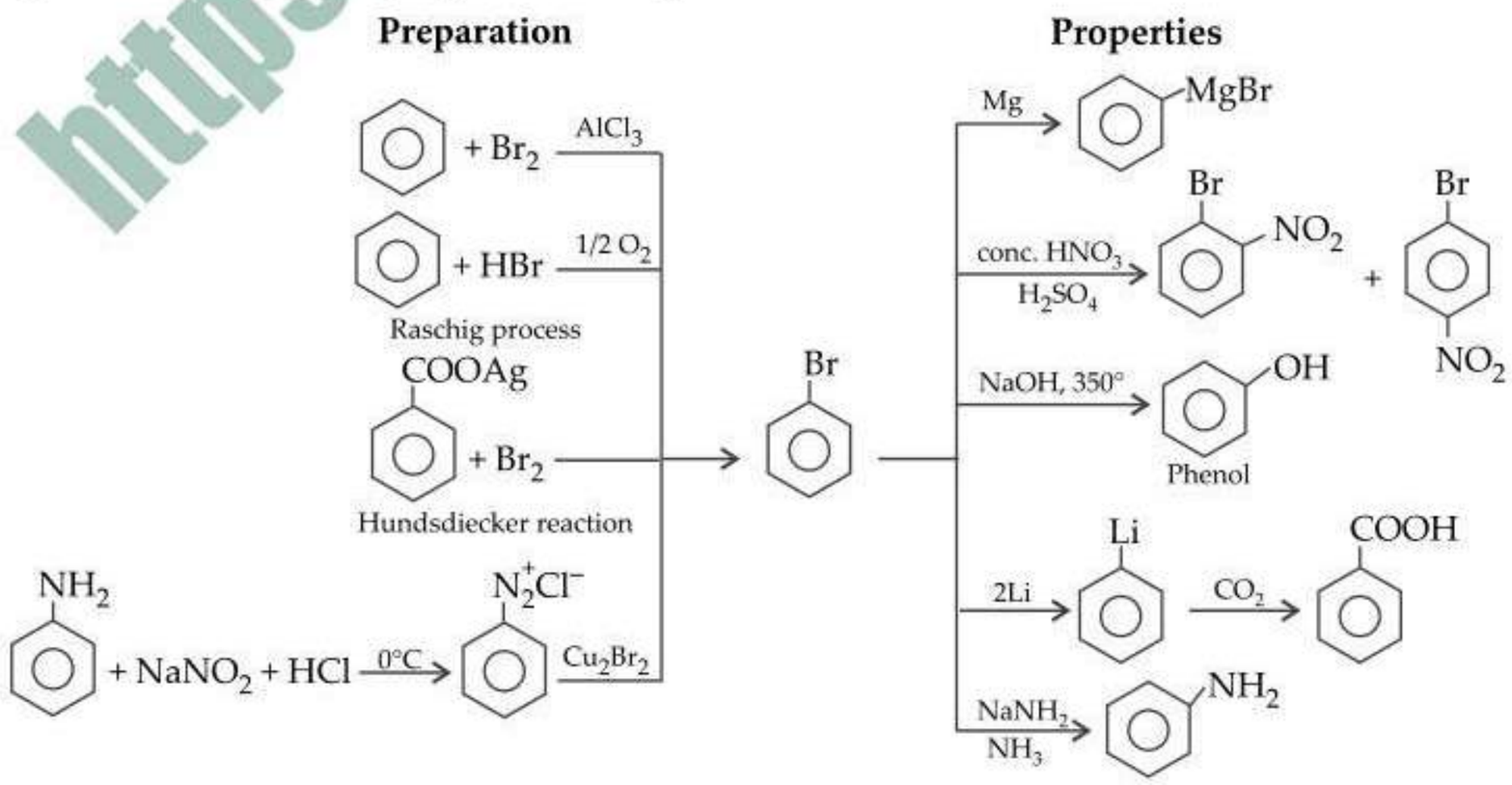




## Optical Rotation

- Optical isomer is known as dextrorotatory isomer (latin : dexter means right) (*d*-form or +ve) if it rotates the plane polarised light to the right (clockwise) and laevorotatory isomer (latin : laevo means left) (*l*-form or –ve) if it rotates the plane polarised light to the left (anticlockwise).
- An equimolar mixture of the *d*- form and *l*-form will be optically inactive and is called racemic mixture (or dl-form or (±)-mixture).
- The process of conversion of an enantiomer into racemic mixture is known as racemisation.
- **Chirality :** The compound is said to have chirality if the central carbon atom is attached to four different groups and this centre is called chiral (asymmetric) centre or stereogenic centre or stereocentre.
- **Achirality :** The compound is said to have achirality if the central carbon atom have atleast two identical groups and this centre is called achiral (symmetric).
- If molecule has a plane of symmetry it is achiral (not chiral) and if molecule has no plane of symmetry it is chiral.
- **Enantiomers / *d* and *l* isomers :** They are the optical isomers which are non-superimposable mirror images (or dissymmetric).
- **Diastereomers :** They are the optical isomers which are not mirror images of each other. They have different physical properties and magnitude of specific rotation.
- **Meso compounds** are those compounds which have two or more even number of chiral carbon atoms and have an internal plane of symmetry. They are optically inactive due to internal compensation.

## Aromatic Halogen Derivatives (Aryl Halides)



## Polyhalogen Compounds

- **Chloroform ($CHCl_3$) :**
  - **Preparation :** By the action of moist bleaching powder on ethanol or acetone.

$$CH_3CH_2OH \xrightarrow{\text{Oxidation}} CH_3CHO \xrightarrow{Cl_2} CCl_3{\cdot}CHO \xrightarrow[Ca(OH)_2]{\text{Hydrolysis}} CHCl_3$$

Chloral — Chloroform

  - **Properties :**

$$CCl_3{\cdot}NO_2 \xleftarrow[\text{Nitration}]{\text{conc. } HNO_3} CHCl_3 \xrightarrow[\text{Air and light}]{\text{Oxidation}} COCl_2$$

Chloropicrin — Phosgene

$$CHCl_3 \xrightarrow[\text{Carbylamine reaction}]{RNH_2 + \text{alc.KOH}} RNC$$

  - **Uses :** In the past it was extensively used as anaesthetic for surgery but now it is rarely used as it causes liver damage.

    It is used in preparation of chloretone (drug) and chloropicrin (insecticide).

    It is used to preserve anatomical species.
  - **Environmental effects :** Chloroform when exposed to air and sunlight forms a poisonous compound phosgene, hence it is stored in dark, amber coloured, well stoppered bottles.

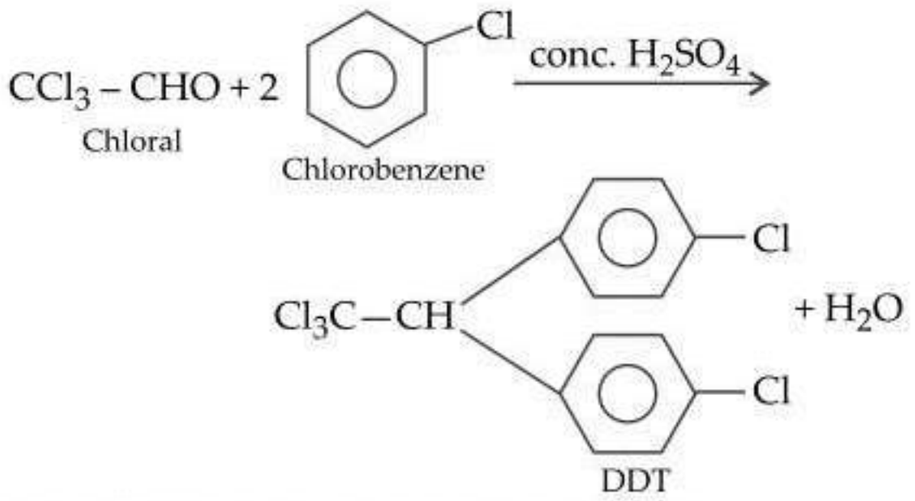
    If mixed with air it is hazardous and causes headache and fatigue and if inhaled for long time affects central nervous system.
- **Iodoform ($CHI_3$) :**
  - **Preparation :** By the action of $I_2$ and alkali on ethanol.

$$CH_3CH_2OH \xrightarrow{\text{Oxidation}} CH_3CHO \xrightarrow{I_2} CI_3 \cdot CHO \xrightarrow[NaOH]{\text{Hydrolysis}} CHI_3$$

Iodination — Iodal — Iodoform

  - **Properties :** $CHI_3$ $\xrightarrow{\text{Red P + HI}}$ $CH_2I_2$; $CHI_3$ $\xrightarrow[\Delta]{\text{Ag Powder}}$ $CH{\equiv}CH$
  - **Uses :** As an antiseptic in dressing of wounds due to liberation of iodine.

    As methylating agent in organic synthesis.
  - **Environmental effects :** It has strong smell.
- **Freons :**
  - Chlorofluoro carbons are known as freons.
  - Freons are phased out due to their part in ozone depletion.
  - This anthropogenic compound is a greenhouse gas and effect greenhouse more than $CO_2$.
  - **Uses :** As refrigerents, blowing agents, propellants in medical applications and degreasing solvent.
  - **Environmental effects :** As a refrigerant causes ozone depletion. Most of the freons have low toxicity and low biological activity. Freons from propane group are more toxic in nature.
- **DDT (Dichlorodiphenyltrichloroethane) :**
  - **Preparation :**




  - **Uses :** In 1940, it was used as pesticides.

    It is a persistent organic pollutant, strongly absorbed by soil.

    It is lipophilic so has a high potential to bioaccumulate.

    It may be directly genotoxic but may also induce enzymes to produce other genotoxic intermediates and DNA adducts.
  - **Environmental effects:** It is not readily metabolized and not destroyed by environmental destructive forces. It is deposited and stored in fatty tissues. If it exists for a long time in soil, plants and animals as well, it produces unforeseen ecological effects. It is replaced by better and safer insecticides due to its ecological problems.
- **Dichloromethane ($CH_2Cl_2$) :**
  - **Uses :** It is used as a degreaser and paint remover.

    It is used to decaffeinate tea and coffee.

    It is used as aerosol spray propellant as it is volatile.

    It is used as a fumigant pesticide for grains and strawberries.
  - **Environmental effects :** When mixed in air in high amount, as it is highly volatile causes nausea, numbness in fingers and toes, dizziness and if in less amount causes impaired vision and hearing. It is highly dangerous if it comes in contact with eyes by damaging cornea.
- **Tetrachloromethane or carbon tetrachloride ($CCl_4$) :**
  - **Uses :** It is used as a dry cleaning agent and as a pesticide to kill insects in stored grains.

    It is also used as a solvent, in the production of refrigerants.
  - **Environmental effects :** On contact it causes eye irritation, damages nerve cells, vomiting sensation, dizziness, unconsciousness or death, thus it has severe adverse health effects.

    When mixed with air it causes ozone depletion, which affects human skin leading to cancer.

# EXAM DRILL

**1.** What is true about DDT among the following?
(a) Biodegradable pollutant
(b) Greenhouse gas
(c) Fertilizer
(d) Non-biodegradable pollutant

**2.** The strong nucleophile and the best leaving group in the following reaction are respectively

$CH_3X + Nu^- \longrightarrow CH_3 - Nu + X^-$

(a) $PhO^-, Cl^-$ (b) $OH^-, Br^-$
(c) $AcO^-, F^-$ (d) $CH_3O^-, I^-$

**3.** The halogen which is most reactive in the halogenation of alkanes under sunlight is
(a) F (b) Cl (c) Br (d) I

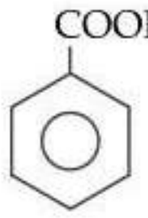
**4.** Which of the following will have a meso isomer?
(a) 2-Chlorobutane
(b) 2-Hydroxypropanoic acid
(c) 2,3-Dichloropentane
(d) 2,3-Dichlorobutane

**5.** $\underset{(X)}{C_6H_4Cl_2} + Cl_2 \xrightarrow{Fe} \underset{(Y)}{C_6H_3Cl_3}$

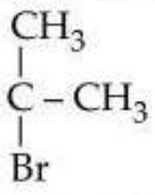
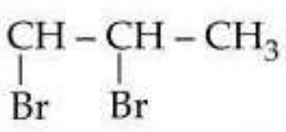
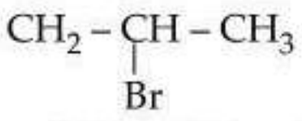
(dichlorobenzene) (trichlorobenzene)

Only one structural isomer of $Y$ is formed. Hence, $X$ is
(a) *o*-isomer (b) *p*-isomer
(c) *m*-isomer (d) none of these.

**6.** Silver benzoate reacts with bromine to form

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

**7.** An unknown alkyl halide ($A$) reacts with alcoholic KOH to produce $C_4H_8$ which on ozonolysis gives one mole of propanone and one mole of formaldehyde. The structure of $A$ is

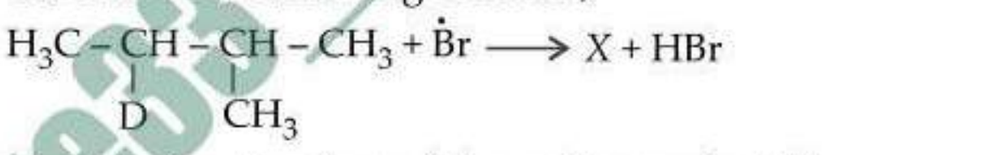
(a) 
(b) 
(c) 
(d) $BrCH_2 - CH_2 - CH_2 - CH_2Br$

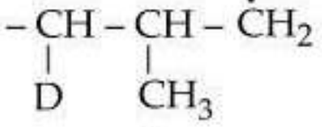
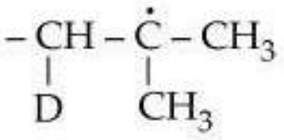
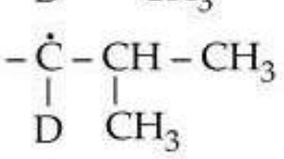
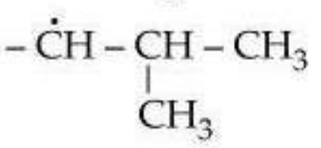
**8.** Chloroform on reaction with conc. $HNO_3$ gives an insecticide and war gas known as
(a) chloropicrin (b) nitromethane
(c) picric acid (d) acetylene.

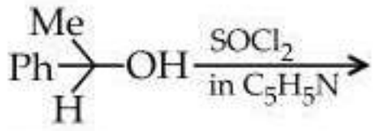
**9.** Vicinal and geminal dihalides can be distinguished by
(a) KOH (aq.) (b) KOH (alc.)
(c) Zn dust (d) none of these

**10.** The reactivities of methyl chloride ($A$), propyl chloride ($B$) and chlorobenzene ($C$) are in the order
(a) $A > B > C$ (b) $C > B > A$
(c) $A > C > B$ (d) $B > A > C$

**11.** Consider the following reaction,



Identify the structure of the major product $X$.
(a) 
(b) 
(c) 
(d) 

**12.** 

Which statement is true for the above reaction?
(a) Retention of configuration
(b) Inversion of configuration
(c) Inversion and retention both
(d) None of the above.

**13.** Product-I $\xleftarrow{\text{aq. KOH}}$ $C_2H_5Br$ $\xrightarrow{\text{alc. KOH}}$ Product-II

The correct statement is
(a) product-I is obtained by the elimination reaction
(b) product-II is obtained by the substitution reaction
(c) the molecular formula of product-I is $C_2H_4$, while the molecular formula of product-II is $C_2H_6O$
(d) product-I is the isomer of dimethyl ether, while product-II is the dehydrated compound of product-I.

**14.** The reactivity of 2-bromo-2-methylbutane(I), 1-bromopentane(II) and 2-bromopentane(III) towards $S_N2$ displacement is such that
(a) I > II > III (b) I > III > II
(c) II > III > I (d) II > I > III

**15.** Fluorobenzene ($C_6H_5F$) can be synthesised in the laboratory
(a) by heating phenol with HF and KF
(b) from aniline by diazotisation followed by heating the diazonium salt with $HBF_4$
(c) by direct fluorination of benzene with $F_2$ gas
(d) by reacting bromobenzene with NaF solution.

**16.** The number of structural and configurational isomers of a bromo compound, $C_5H_9Br$, formed by the addition of HBr to 2-pentyne respectively are
(a) 1 and 2 (b) 2 and 4
(c) 4 and 2 (d) 2 and 1

**17.** Identify Z in the following reaction series,

$$CH_3.CH_2CH_2Br \xrightarrow{\text{Aq. NaOH}} (X) \xrightarrow[\text{heat}]{Al_2O_3} (Y) \xrightarrow{HOCl} (Z)$$

(a) mixture of $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$ and $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH}}$

(b) $CH_3-\underset{OH}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

(c) $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH_2}}$

(d) $CH_3-\underset{Cl}{\underset{|}{CH}}-\underset{Cl}{\underset{|}{CH_2}}$

**18.** Alkyl halides react with dialkyl copper reagents to give
(a) alkenes (b) alkyl copper halides
(c) alkanes (d) alkenyl halides.

**19.** A compound *A* of formula $C_3H_6Cl_2$ on reaction with alkali can give *B* of formula $C_3H_6O$ or *C* of formula $C_3H_4$. *B* on oxidation gave a compound of the formula $C_3H_6O_2$. *C* with dilute $H_2SO_4$ containing $Hg^{2+}$ ion gave *D* of formula $C_3H_6O$, which with bromine and NaOH gave the sodium salt of acid of formula $C_2H_4O_2$. Then *A* is
(a) $CH_3CH_2CHCl_2$ (b) $CH_3CCl_2CH_3$
(c) $CH_2ClCH_2CH_2Cl$ (d) $CH_3CHClCH_2Cl$

**20.** Which of the following statements is true?
(a) Allyl chloride is more reactive than vinyl chloride.
(b) Vinyl chloride is as reactive as allyl chloride.
(c) Vinyl chloride is more reactive than allyl chloride.
(d) Both of them are more reactive than chlorobenzene.

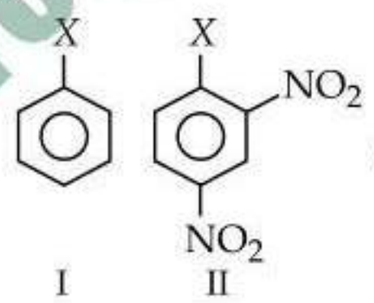
**21.** In elimination reactions, *i.e.*, in the formation of alkenes, the reactivity of halogens in alkyl halides follow the order:
(a) I > Br > Cl (b) Cl > Br > I
(c) Br > Cl > I (d) none of these

**22.** Ethylene on treatment with chlorine gives
(a) ethylene dichloride
(b) ethylene chlorohydrin
(c) $CH_4$
(d) $C_2H_6$

**23.** The C—Mg bond in $CH_3CH_2MgBr$ is
(a) ionic
(b) non-polar covalent
(c) polar covalent
(d) hydrogen.

**24.** $S_N1$ reaction is favoured by
(a) non-polar solvents
(b) more no. of alkyl group on the carbon atom attached to the halogen atom
(c) small groups on the carbon attached to the halogen atom.
(d) none of the above.

**25.** The correct order of increasing reactivity of C—X bond towards nucleophile in the following compounds is




I II

$(CH_3)_3C-X$ III $(CH_3)_2CH-X$ IV

(a) I < II < IV < III (b) II < III < I < IV
(c) IV < III < I < II (d) III < II < I < IV

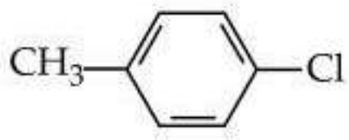
**26.** In the following reaction

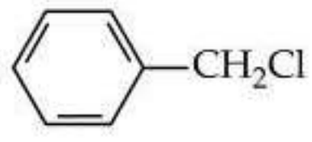
$$C_6H_5CH_2Br \xrightarrow[2.\ H_3O^+]{1.\ Mg,\ Ether} X,$$ the product 'X' is
(a) $C_6H_5CH_2OCH_2C_6H_5$ (b) $C_6H_5CH_2OH$
(c) $C_6H_5CH_3$ (d) $C_6H_5CH_2CH_2C_6H_5$

**27.** It is not possible to detect the presence of chlorine, unless sodium extract is prepared in

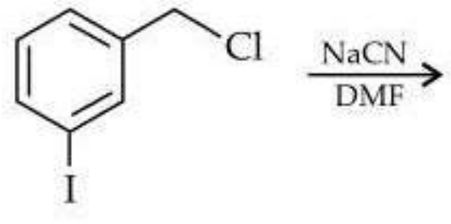
(a) $CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-Cl$

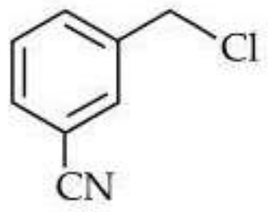
(b) $CH_2=CH-CH_2Cl$

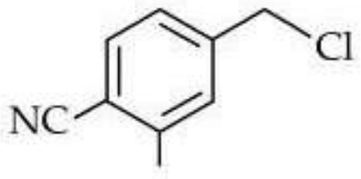
(c) 

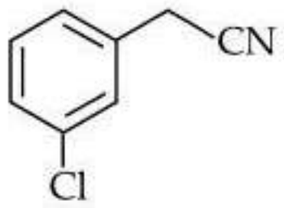

(d) 

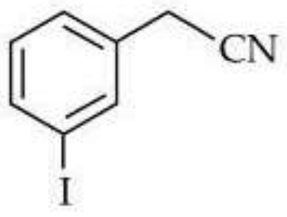

**28.** The structure of the major product formed in the following reaction is



(a) 

(b) 

(c) 

(d) 

**29.** The best method to prepare neopentyl chloride is

(a) $(CH_3)_3CCH_2OH \xrightarrow{PCl_5,\ \Delta}$

(b) $(CH_3)_3CCH_2OH \xrightarrow{HCl,\ \Delta}$

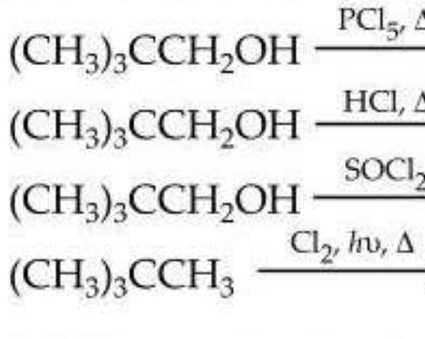
(c) $(CH_3)_3CCH_2OH \xrightarrow{SOCl_2,\ pyridine}$

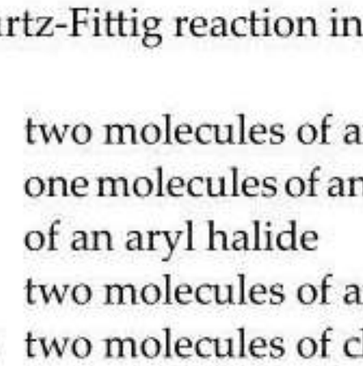
(d) $(CH_3)_3CCH_3 \xrightarrow{Cl_2,\ h\upsilon,\ \Delta}$

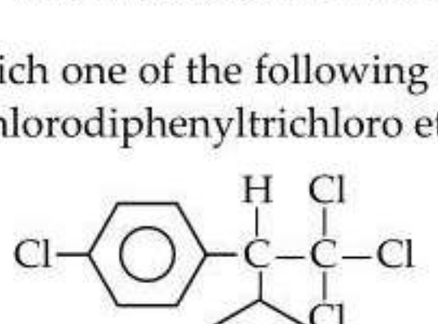
**30.** Wurtz-Fittig reaction involves action of sodium metal on

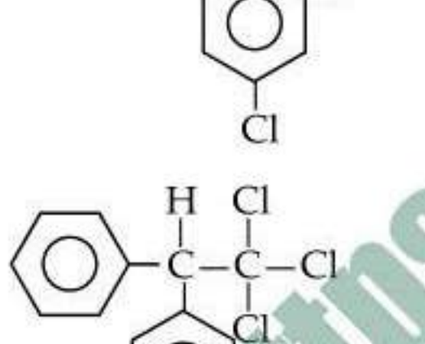
(a) two molecules of an alkyl halide
(b) one molecules of an alkyl halide and one molecule of an aryl halide
(c) two molecules of an aryl halide
(d) two molecules of chloroform.

**31.** Which one of the following is the correct formula for dichlorodiphenyltrichloro ethane?

(a) 

(b) 

(c) 

(d) 

**32.** Chlorobenzene on heating with aqueous $NH_3$ under pressure in the presence of cuprous oxide gives

(a) benzamide
(b) nitrobenzene
(c) aniline
(d) chloroaminobenzene.

**33.** Chlorobenzene on treatment with sodium in dry ether gives diphenyl. The name of the reaction is

(a) Fittig reaction
(b) Wurtz -Fittig reaction
(c) Sandmeyer reaction
(d) Gatterman reaction

**34.** The compound that does not undergo hydrolysis by $S_N1$ mechanism is

(a) $CH_2{=}CHCH_2Cl$
(b) $C_6H_5Cl$
(c) $C_6H_5CH_2Cl$
(d) $C_6H_5CH(CH_3)Cl$

**35.** Benzene reacts with $I_2$ in presence of which of the following to give iodobenzene?

(a) $HNO_3$ (b) HI
(c) $SO_2$ (d) $H_2O$

**36.** Which of the following does not form Grignard reagent?

(a) $CH_3F$ (b) $CH_3Cl$
(c) $CH_3Br$ (d) $CH_3I$

**37.** Which is *gem*-dihalide?

(a) $CH_3CHBr_2$ (b) $CH_2BrCH_2Br$
(c) $CH_3CHBrCH_2Br$ (d) None of these.

**38.** The order of reactivity of the following alcohols with halogen acids is

(I) $CH_3CH_2{-}CH_2{-}OH$

(II) $CH_3CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}OH$

(III) $CH_3CH_2{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{-}OH$

(a) (I) > (II) > (III) (b) (III) > (II) > (I)
(c) (II) > (I) > (III) (d) (I) > (III) > (II)

**39.** The reaction described below is

$$CH_3(CH_2)_5 \quad (CH_2)_5CH_3$$
$$H_3C \diagdown \quad / \quad CH_3 \xrightarrow{OH^-} HO-C$$
$$H \quad Br \quad H$$

(a) $S_E1$ (b) $S_N2$
(c) $S_N1$ (d) $S_E2$

**40.** Which set of reagents will produce $CCl_2F_2$?

(a) $C + F_2 + Cl_2 \longrightarrow$

(b) $CH_3Cl + F_2 \longrightarrow$

(c) $CCl_4 + SbF_3 \xrightarrow{SbCl_5}$

(d) $CCl_4 + F_2 \longrightarrow$

**41.** What should be the correct IUPAC name for diethylbromomethane?
(a) 1-Bromo-1, 1-diethylmethane
(b) 3-Bromopentane
(c) 1-Bromo-1-ethylpropane
(d) 1-Bromopentane

**42.** Which reagent will be used for the following reaction?
$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$
(a) $Cl_2$/UV light
(b) $NaCl + H_2SO_4$
(c) $Cl_2$ gas in dark
(d) $Cl_2$ gas in the presence of iron in dark.

**43.** The given reaction is an example of
$C_2H_5Br + KCN_{(aq)} \longrightarrow C_2H_5CN + KBr$
(a) elimination
(b) nucleophilic substitution
(c) electrophilic substitution
(d) redox change.

**44.** Tertiary alkyl halides are practically inert to substitution by $S_N2$ mechanism because of
(a) insolubility
(b) instability
(c) inductive effect
(d) steric hindrance.

**45.** The compound added to prevent chloroform to form phosgene gas is
(a) $CH_3COOH$ (b) $CH_3OH$
(c) $CH_3COCH_3$ (d) $C_2H_5OH$



## DAY 24 OMR SHEET

Time : 45 min

### INSTRUCTIONS

- Use HB pencil only and darken each circle completely.
- If you wish to change your answer, erase the already darkened circle completely and then darken the appropriate circle.
- Mark only one choice for each question as indicated.

**Correct marking** ● ⓑ ⓒ ⓓ
**Wrong marking** ⊗ ✓ ◑ ⊙

| | | | | |
|---|---|---|---|---|
| 1. ⓐ ⓑ ⓒ ⓓ | 10. ⓐ ⓑ ⓒ ⓓ | 19. ⓐ ⓑ ⓒ ⓓ | 28. ⓐ ⓑ ⓒ ⓓ | 37. ⓐ ⓑ ⓒ ⓓ |
| 2. ⓐ ⓑ ⓒ ⓓ | 11. ⓐ ⓑ ⓒ ⓓ | 20. ⓐ ⓑ ⓒ ⓓ | 29. ⓐ ⓑ ⓒ ⓓ | 38. ⓐ ⓑ ⓒ ⓓ |
| 3. ⓐ ⓑ ⓒ ⓓ | 12. ⓐ ⓑ ⓒ ⓓ | 21. ⓐ ⓑ ⓒ ⓓ | 30. ⓐ ⓑ ⓒ ⓓ | 39. ⓐ ⓑ ⓒ ⓓ |
| 4. ⓐ ⓑ ⓒ ⓓ | 13. ⓐ ⓑ ⓒ ⓓ | 22. ⓐ ⓑ ⓒ ⓓ | 31. ⓐ ⓑ ⓒ ⓓ | 40. ⓐ ⓑ ⓒ ⓓ |
| 5. ⓐ ⓑ ⓒ ⓓ | 14. ⓐ ⓑ ⓒ ⓓ | 23. ⓐ ⓑ ⓒ ⓓ | 32. ⓐ ⓑ ⓒ ⓓ | 41. ⓐ ⓑ ⓒ ⓓ |
| 6. ⓐ ⓑ ⓒ ⓓ | 15. ⓐ ⓑ ⓒ ⓓ | 24. ⓐ ⓑ ⓒ ⓓ | 33. ⓐ ⓑ ⓒ ⓓ | 42. ⓐ ⓑ ⓒ ⓓ |
| 7. ⓐ ⓑ ⓒ ⓓ | 16. ⓐ ⓑ ⓒ ⓓ | 25. ⓐ ⓑ ⓒ ⓓ | 34. ⓐ ⓑ ⓒ ⓓ | 43. ⓐ ⓑ ⓒ ⓓ |
| 8. ⓐ ⓑ ⓒ ⓓ | 17. ⓐ ⓑ ⓒ ⓓ | 26. ⓐ ⓑ ⓒ ⓓ | 35. ⓐ ⓑ ⓒ ⓓ | 44. ⓐ ⓑ ⓒ ⓓ |
| 9. ⓐ ⓑ ⓒ ⓓ | 18. ⓐ ⓑ ⓒ ⓓ | 27. ⓐ ⓑ ⓒ ⓓ | 36. ⓐ ⓑ ⓒ ⓓ | 45. ⓐ ⓑ ⓒ ⓓ |

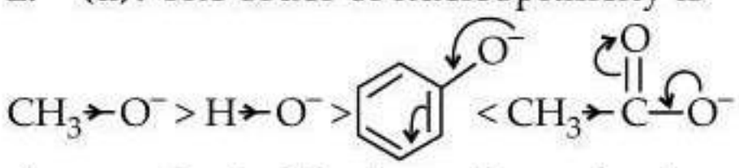
(1) Number of questions attempted : _____ (3) Marks scored : _____
(2) Number of questions correct : _____

For every correct answer award yourself 4 marks. For every incorrect answer deduct 1 mark.

# HINTS & SOLUTIONS

**1. (d):** DDT is not completely biodegradable.

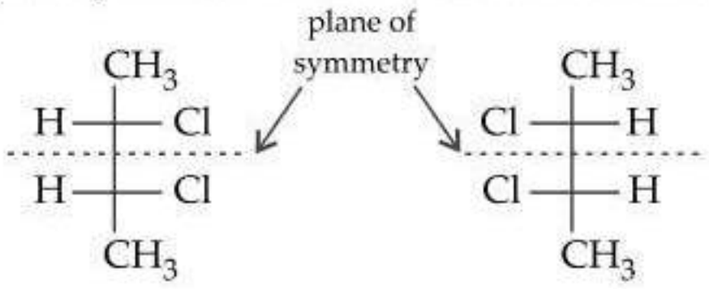
**2. (d):** The order of nucleophilicity is



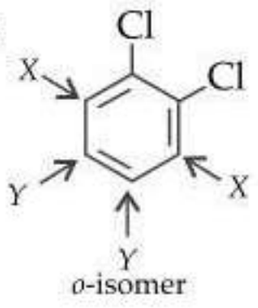
Among the halide ions, the order in which the leaving groups depart is $I^- > Br^- > Cl^- > F^-$

**3. (b)**

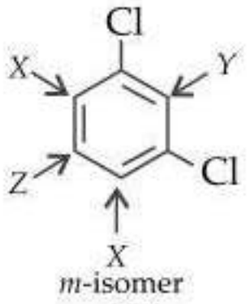
**4. (d):** 2,3-Dichlorobutane contains a plane of symmetry *i.e.*, the upper half of the molecule is the mirror image of the lower half. The rotation of one half of the molecule will therefore exactly counter balance the rotation of other half, causing the molecule to be optically inactive. Such an internally compensated molecule is said to be a *meso* form.




**5. (b):**



Two isomers possible

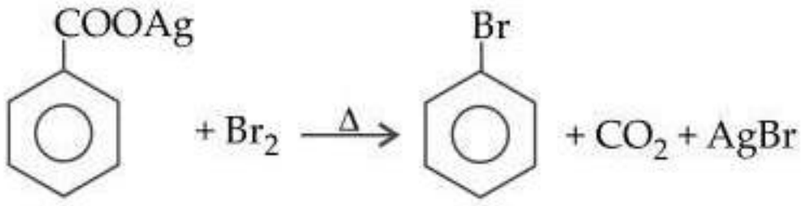


Three isomers possible

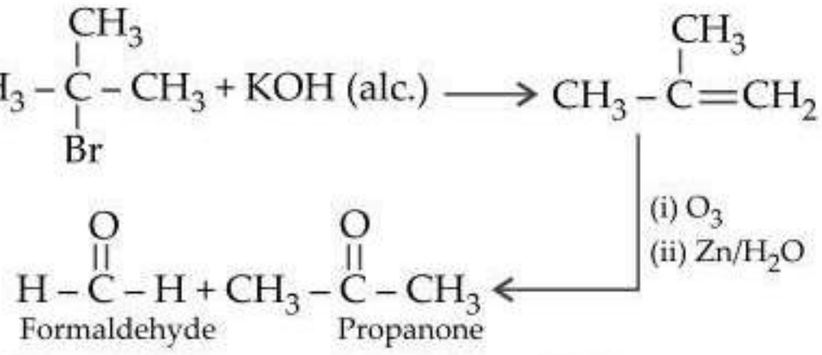
All equivalent
So only one isomer possible

*p*-isomer

**6. (b):** Hunsdiecker reaction



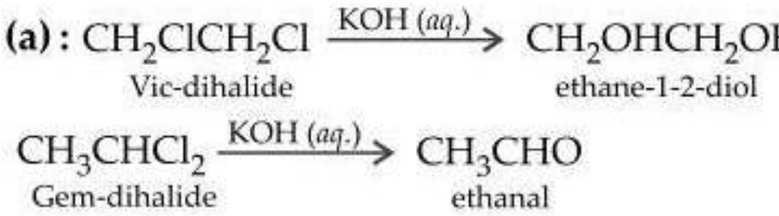
**7. (a):**




**8. (a):** $CHCl_3 + HNO_3 \longrightarrow CCl_3{\cdot}NO_2 + H_2O$

$CCl_3{\cdot}NO_2$ is called chloropicrin.

**9. (a):**



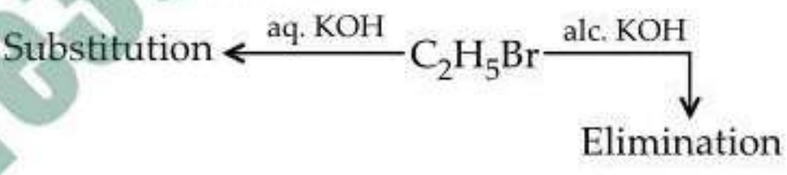

**10. (a):** Among the primary halides reactivity order is $CH_3X > C_3H_7X > C_6H_5X$, also chlorobenzene is less reactive due to resonance.

**11. (b):** $Br_2$ is less reactive and more selective, thus, formation of 3° free radical will be the major product.

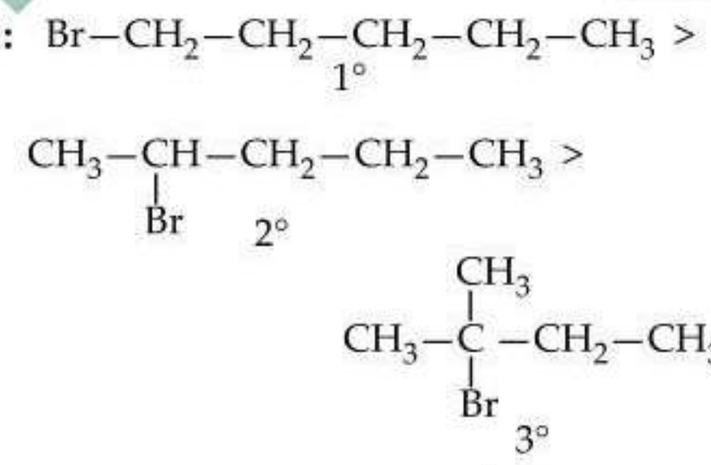
**12. (b):**

Stronger nucleophilic $Cl^-$ attacks from back and causes inversion of configuration.

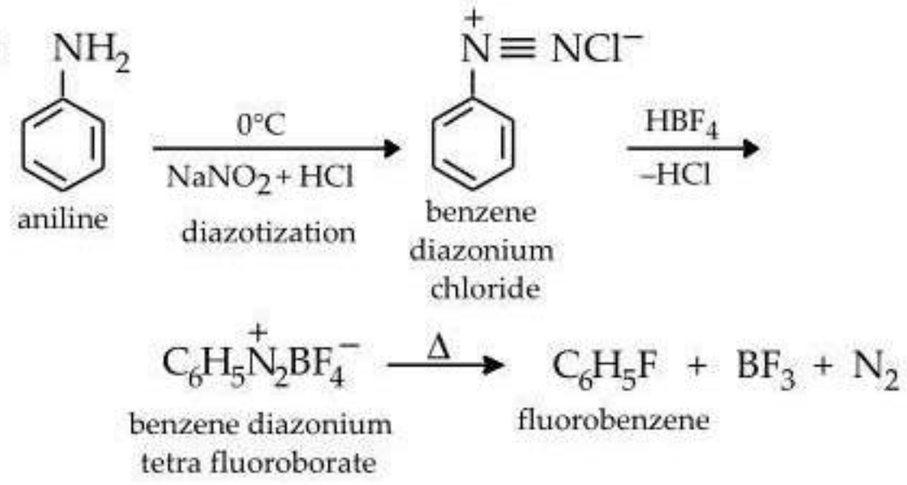
**13. (d):**



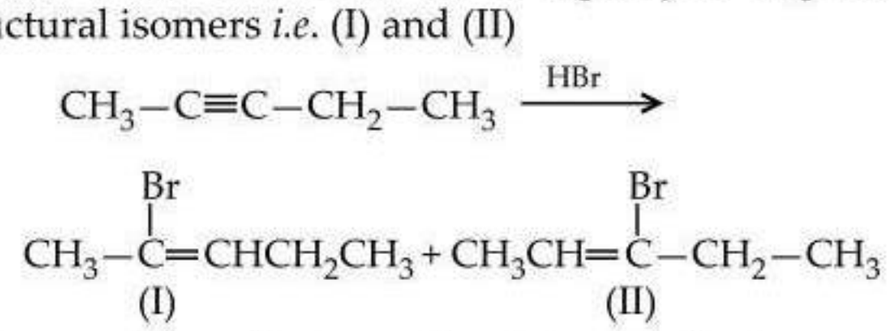

**14. (c):**




**15. (b):**

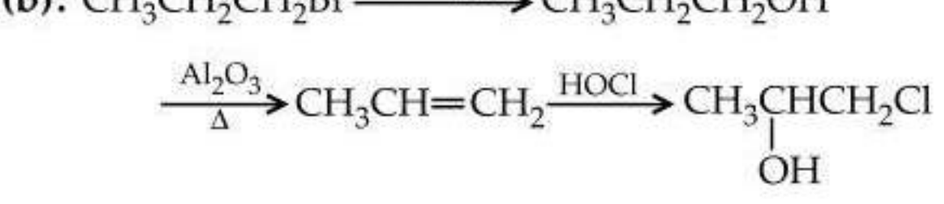



**16. (b):** When HBr adds on to 2-pentyne it gives two structural isomers *i.e.* (I) and (II)




Each one of these (*i.e.* I and II) exists as a pair of geometrical isomers (*cis*-and *trans*-). Thus we have two structural and four configurational isomers.

**17. (b):**



**18. (c) :** In Corey House synthesis of alkane, alkyl halide reacts with lithium dialkyl cuprate.

$R_2CuLi + R'X \rightarrow RR' + RCu + LiX$

**19. (a) :** $C_3H_6Cl_2$ (*A*) $\xrightarrow{KOH}$ $C_3H_6O$ (*B*); $C_3H_6Cl_2$ (*A*) $\xrightarrow{KOH(alc.)}$ $C_3H_4$ (*C*)

$$CH_3C{\equiv}CH \xrightarrow[H^+, Hg^{2+}]{H_2O} CH_3COCH_3 \text{ (D)} \xrightarrow[+NaOH]{Br_2} CHBr_3 + CH_3COONa$$

Since, *B* and *D* are different thus, *B* is $CH_3CH_2CHO$ and so *A* is $CH_3CH_2CHCl_2$.

**20. (a) :** Allyl carbonium shows resonance and thus, allyl chloride is more reactive. Vinyl chloride does not show resonance and thus is less reactive.

**21. (a) :** Larger the bond length, easy to break the bond and so, greater is the reactivity.

**22. (a) :** $CH_2{=}CH_2 + Cl_2 \longrightarrow CH_2ClCH_2Cl$

**23. (c) :** C—Mg bond is covalent but polar.

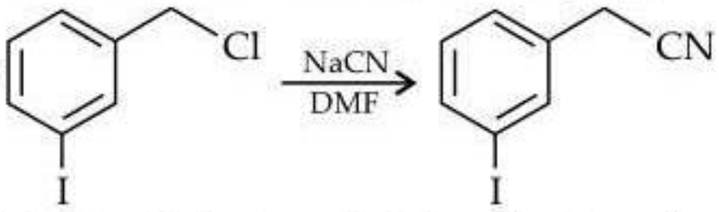
**24. (b):** Follow inductive effect.

**25. (a) :** I < II < IV < III

The order of reactivity is dependent on the stability of the intermediate carbocation formed by cleavage of C—*X* bond. The 3° carbocation (formed from III) will be more stable than its 2° counter part (formed from IV) which in turn will be more stable than the arenium ion (formed from I). Also, the aryl halide has a double bond character in the C—*X* bond which makes the cleavage more difficult. However, inspite of all the stated factors, II will be more reactive than I due to the presence of the electron withdrawing $-NO_2$ group. C—*X* bond becomes weak and undergoes nucleophilic substitution reaction.

**26. (c) :** $C_6H_5CH_2Br \xrightarrow{Mg, \text{ether}} C_6H_5CH_2MgBr \xrightarrow{H_3O^+} C_6H_5CH_3 + Mg(Br)(OH)$

**27. (c) :** All other compounds can easily undergo nucleophilic substitution reaction, except (c).

**28. (d):** 

Chloride is 1° aliphatic which is substituted easily in as compared to iodide which is arylic and more stable due to delocalisation hence, difficult to substitute.

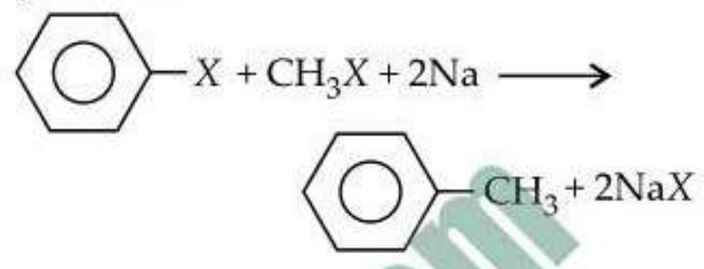
**29. (d):** $CH_3-C(CH_3)_2-CH_2OH \xrightarrow[\text{or } SOCl_2, \text{ pyridine}]{PCl_5, \Delta \text{ or } HCl, \Delta}$

$$\left[CH_3-C(CH_3)_2-CH_2^+ \rightarrow CH_3-C^+(CH_3)-CH_2CH_3 \xrightarrow{Cl^-}\right] CH_3-C(Cl)(CH_3)-CH_2CH_3$$

Free radicals, on the other hand, do not undergo rearrangement and hence the best method of preparation is through Free radical chlorination.

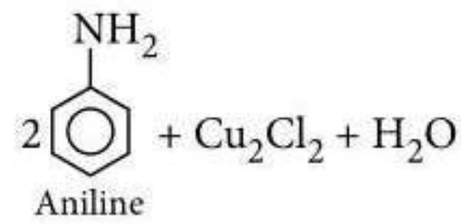
$$CH_3-C(CH_3)_2-CH_3 \xrightarrow{Cl_2, h\upsilon} CH_3-C(CH_3)_2-CH_2Cl$$

**30. (b):** One molecule of alkyl halide and one molecule of an aryl halide.

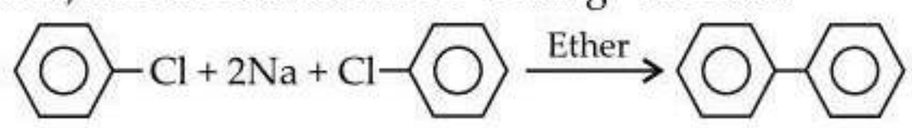


**31. (a) :** Follow IUPAC rules.

**32. (c) :** 



**33. (a) :** If only aryl halide reacts with sodium in presence of ether, the reaction is called "Fitting" reaction.



**34. (b):** Aryl halides (*e.g.* $C_6H_5Cl$) do not hydrolysed by $S_N1$ mechanism under ordinary conditions.

**35. (a)**

**36. (a) :** The C—F bond energy is maximum in $CH_3F$. Thus, methyl fluoride is less reactive and does not form Grignard reagent with Mg.

**37. (a) :** A *gem*-dihalide possesses two halogens on the same carbon atom.

**38. (b):** The reactivity of alcohols towards halogen acids decreases in the order : 3° > 2° > 1° *i.e.*, (III) > (II) > (I).

**39. (b):** In case of optically active alkyl halides, the product formed as a result of $S_N2$ mechanism has the inverted configuration as compared to the reactant.

**40. (c) :** $3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} \underset{\text{Freon-12}}{3CCl_2F_2} + 2SbCl_3$

**41. (b):** $\overset{5}{C}H_3\overset{4}{C}H_2-\overset{3}{C}HBr-\overset{2}{C}H_2\overset{1}{C}H_3$ (3-Bromopentane)

**42. (a)**

**43. (b) :** Br is replaced by a nucleophile $CN^-$.

**44. (d)**

**45. (d):** $COCl_2 + 2C_2H_5OH \longrightarrow \underset{\text{Diethyl carbonate (non-toxic)}}{O{=}C(OC_2H_5)_2} + 2HCl$