# UNIT 10

# Haloalkanes and Haloarenes

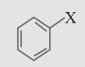
## Points to Remember

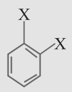
### Classification

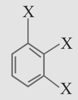
- No. of halogen atoms

$C_2H_5X$
Monohaloakane

$CH_2X\text{-}CH_2X$
Dihaloalkane

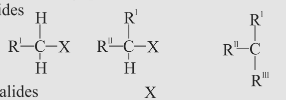

Monohaloarene


Dihaloarene


Trihaoarene

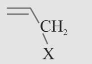
- Compounds containing $sp^3$ C-X bond

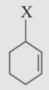
(a) Alkyl halides



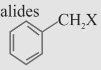
$R^{I}-\overset{H}{\underset{H}{C}}-X \quad R^{II}-\overset{R^{I}}{\underset{H}{C}}-X \quad R^{II}-\overset{R^{I}}{\underset{R^{III}}{C}}-X$

(b) Allylic halides



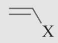


(c) Benzylic halides

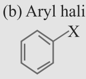


Compounds containing $sp^2$ C-X bond

(a) Vinylic halides



(b) Aryl halides



**Nomenclatute**

**Common name :** Alkyl group followed by halides. Dihalogen derivatves of arenes, prefix o-, p- are used

**IUPAC name :** Numerals are used for position of halogen.

**Nature of C-X bond** :

Carbon-halgoen bond is polarised due to more electronegativity of halogen

**Preperation**

**From alcohol:**

- $R\text{-}OH + HCl \xrightarrow{ZnCl_2} R\text{-}Cl + H_2O$

$3R\text{-}OH + PX_3 \longrightarrow 3R\text{-}X + H_3PO_4$

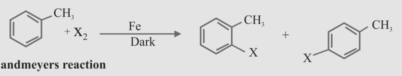
$R\text{-}OH + PCl_3 \longrightarrow R\text{-}Cl + POCl_3 + HCl$

- **From hydrocarbons:**

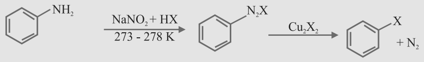
**(a) By free redical halogenation**

$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_2CH_2CH_2Cl + CH_2CH_2CHClCH_3$

**(b) By electrophilic substitution**



**(c) Sandmeyers reaction**



**(d) From alkanes**

$H_2C{=}CH_2 + Br_2 \xrightarrow{CCl_4} H_2\overset{Br}{C}-\underset{Br}{CH_2}$

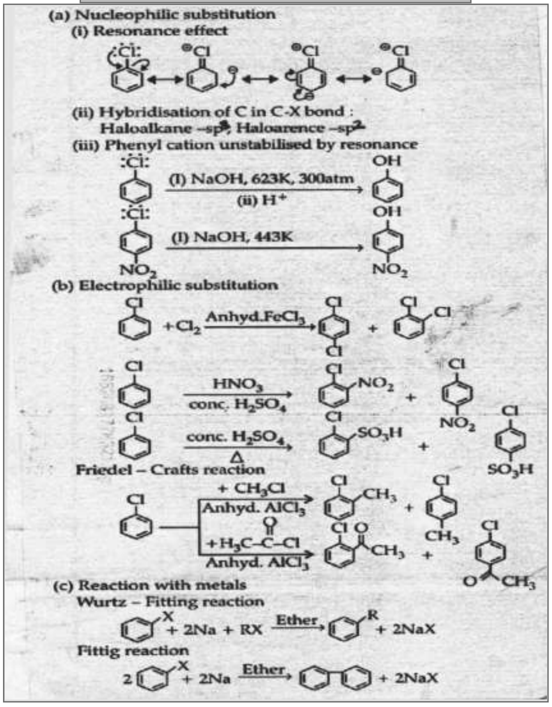
**(e) Halogen exchange**

**R-X + NaI → R-I + NaX**

**R-X + AgF→RF+AgX**

## Properties and Reactions of Haloakanes and Haloarenses

## Reactions



**(a) Nucleophilic substitution**

**(i) Resonance effect**

**(ii) Hybridisation of C in C-X bond :**

**Haloalkane –$sp^3$, Haloarence –$sp^2$**

**(iii) Phenyl cation unstabilised by resonance**

**(b) Electrophilic substitution**

**Friedel – Crafts reaction**

**(c) Reaction with metals**

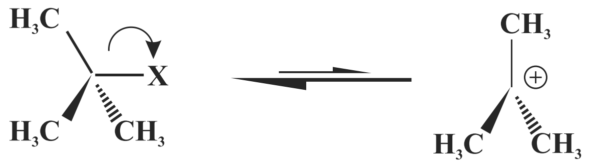
**Wurtz – Fitting reaction**

**Fittig reaction**

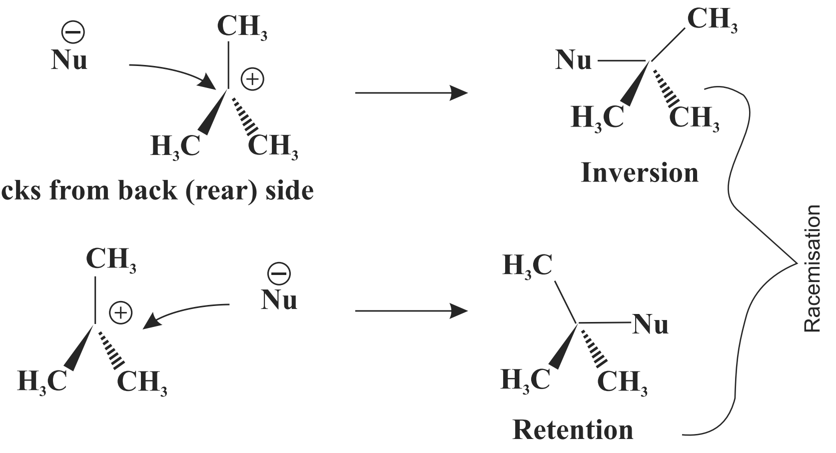
### Mechanisms of $S_N1$ and $S_N2$:

## $S_N1$ Mechanism

**Step - 1**



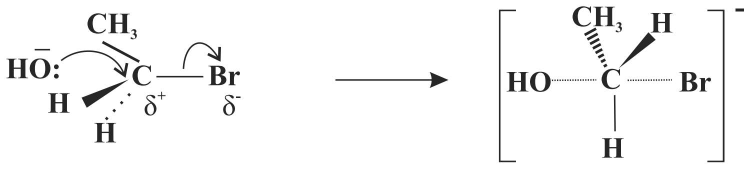
**Step 2**



**$\ominus$ Nu attacks from back (rear) side**

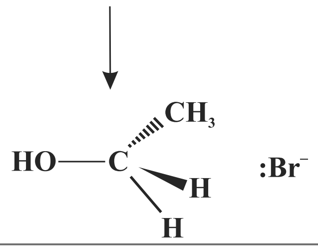
**$\ominus$ Nu attacks from same side as leaving group i.e. $X^{\ominus}$**

## $S_N2$ Mechanism



**Transition state**

Reaction occurs when bromoethane is added to a dilute NaOH solution.



| | **$S_N1$** | **$S_N2$** |
|---|---|---|
| Carbon ($sp^3$) Electrophile | Favored by $3^0$ alkyl halides or benzylic or allylic can also react by an $S_N1$ mechanism<br>**( More stable carbocation)** | Favored by $-CH_3$ and $1^0$ alkyl halides<br>**(less sterically hindered)** |
| Nucleophile | Nature of the nucleophile has no affect on rate. In general, $S_N1$ use neutral, weak nucleophiles | Favored by more reactive nucleophiles<br>$RS^- > NC^- > RO^- > HO^- > Cl^-$ |
| Solvent Effect | Favored by polar, protic solvents. | Favored by polar, aprotic solvents. |

**IMPORTANT POINTS**

- In haloarenes electrophilic substitution reaction occurs at *o*-& *p*-position.
- Haloarenes exhibit nucleophilic substitution reaction at extremely slow rate due to :

  (i) Partial double bond character of C-X bond.

  (ii) Benzene ring is electron rich.

  (iii) Phenyl carbocation is not stable.

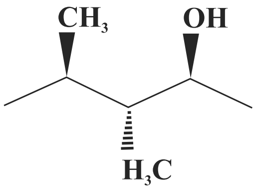
  (iv) More electronegativity of $sp^2$ hybridised carbon in haloarene as compared to $sp^3$ hybridisation in haloalkane

  (v) Steric hindrance due to benzene ring.

## OBJECTIVE TYPE QUESTIONS

### I. MULTIPLE CHOICE QUESTIONS

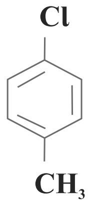
1. The Number of chiral carbons in given molecule is/are-

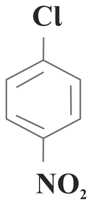


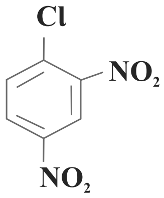
(a) 1 (b) 2

(c) 3 (d) 4

2. The correct increasing order for rate of reaction towards nucleophilic substitution for following is:


**a**


**b**


**c**

(a) a<b<c (b) a<c<b

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

3. Which of the following molecule is chiral?

(a) 2-Bromobutane (b) 1-Bromobutane

(c) 2-Bromopropane (d) 2-Bromopropan-2-ol

4. Reaction of $C_6H_5CH_2Br$ with aqueous sodium hydroxide follows..................

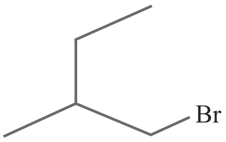
(a) $S_N1$ mechanism

(b) $S_N2$ mechanism

(c) Either $S_N1$ or $S_N2$ mechanism depending on temperature

(d) $E_1$ mechanism

5. The correct IUPAC name for following molecule is-



(a) 1-Bromo-2-ethylpropane

(b) 1-Bromo-2-ethy1-2-methylethane

(c) 1 -Bromo-2-methylbutane

(d) 2-Methyl-1-bromobutane

6. The correct increasing order of boiling points of the following compounds is-

(a) Bromobenzene $<$ 1-Bromobutane $<$ 1-Bromopropane $<$ 1-Bromoethane

(b) Bromobenzene $<$ 1 -Bromoethane $<$ 1 -Bromopropane $<$ 1 -Bromobutane

(c) 1 -Bromopropane $<$ 1 -Bromobutane $<$ 1 -Bromoethane $<$ Bromobenzene

(d) 1-Bromoethane $<$ 1-Bromopropane $<$ 1-Bromobutane $<$ Bromobenzene

7. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of ________________or______________.

(a) $CaF_2$, $CaF_2$ (b) $CoF_2$, $Hg_2F_2$

(c) $Hg_2F_2$, $CaF_2$ (d) NaF, $CaF_2$

8. Which of the following haloalkanes reacts with aqueous KOH most easily?

(a) 1-Bromobutane (b) 2-Bromobutane

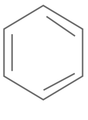
(c) 2-Bromo-2-methylpropane (d) 2-Chlorobutane

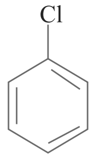
9. Toluene reacts with halogen in the presence of $FeCl_3$ giving *ortho* and *para* compounds. The reaction is :

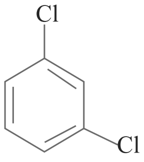
(a) electrophilic elimination (b) electrophilic substitution

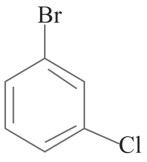
(c) free radical addition (d) nucleophilic substitution

10. Arrange the following compounds in the increasing order of their densities.

(A)


(B)


(C)


(D)


(a) (A) $<$ (B) $<$ (C) $<$ (D) (b) (A) $<$ (C) $<$ (D) $<$ (B)

(c) (D) $<$ (C) $<$ (B) $<$ (A) (d) (B) $<$ (D) $<$ (C) $<$ (A)

11. Chlorobezene is formed by reaction of chlorine with benzene in presence of $AlCl_3$. Which of the following species attacks the benzene ring in this reaction ?
(a) $Cl^-$ (b) $Cl^+$
(c) $AlCl_3$ (d) $AlCl_4^-$

12. Which of the following statement is correct ?
(a) Benzyl halides are more reactive than vinyl and aryl halides.
(b) Vinyl halides are more reactive than alkyl halides.
(c) Aryl halides are more reactive than alkyl halides.
(d) Aryl halides are more reactive than benzyl halides

13. A new carbon-carbon bond is possible in the following reaction:
(a) $C_6H_6 + CH_3Cl$ (anhyd. $AlCl_3$) →
(b) $CH_3CH_2Br + CH_3CH_3NH_2$→
(c) $CH_3$-$Br + CH_3CH_2$-$ONa$→
(d) $CH_3CH_2$-$Br + KOH$ (alc.) →

14. Alcoholic $AgNO_3$ does not give precipitate with-
(a) $C_6H_5CH_2Cl$ (b) $CH_3CH_2Cl$
(c) $C_6H_5Cl$ (d) $CH_3$-$CHCl$-$CH_3$

15. Reaction intermediate of $E_1$ reaction is-
(a) Benzyne (b) Carbocation
(c) Carbanion (d) Free radical

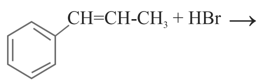
16. Best reagent for preparation of a chloroalkane from alcohol is -
(a) $SOCl_2$ (b) $HCl/ZnCl_2$
(c) $PCl_3$ (d) $Cl_2/CCl_4$

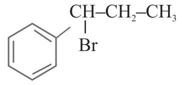
17. Highest nucleophilicity is shown by:-
(a) $F^-$ (b) $OH^-$
(c) $CH_3^-$ (d) $NH_2^-$

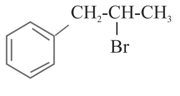
18. Cholroform on reaction with oxygen form poisonous gas
(a) $CO_2$ (b) $COCl_2$
(c) $Cl_2$ (d) $HCl$

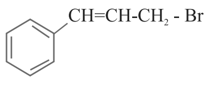
19. The order of reactivity of alkyl halides for $S_N2$ reactions is-
(a) RF >RCl>RBr> RI (b) RF >RBr >RCl> RI
(c) RCl>RBr >RF> RI (d) RI >RBr >RCl> RF

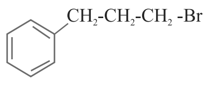
20. An $S_N2$ reaction at an asymmetric carbon gives-
(a) enantiomer of substrate (b) product with opposite optical rotation
(c) mixture of diastereomers (d) single stereoisomer

21. The product in the following reaction is -


(a) 

(b) 

(c) 

(d) 

## II FILL IN THE BLANKS

1. Chlorobenzene may be converted into diphenyl by......................reaction.
2. The mixture containing two enantiomers in equal amount, having zero optical rotation is called......................
3. Reaction of haloalkanes with magnesium metal in dry ether forms the category of compounds called......................
4. The major product of Friedel-Crafts acetylation of chlorobenzene is...................
5. Polyhalogen compound having antiseptic property is........................
6. Alkyl halides are................... in water but...................in organic solvents.
7. Bimolecular nucleophilic substitution of optically active haloalkanes leads to the ...................of the configuration.
8. The molecules which rotates the plane-polarized light in clockwise direction are called...................
9. Halogens...................the aromatic ring towards electrophilic substitution due to -I effect of halogens.

## III ASSERTION REASON TYPE QUESTIONS

In these questions, a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices:

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.
(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.
(c) Assertion is correct statement but reason is wrong statement.
(d) Assertion is wrong statement but reason is correct statement.

1. **ASSERTION :** $S_N2$ reaction is accompanied by the inversion of configuration.
   **REASON:** $S_N2$ reaction occurs in two step.
2. **ASSERTION :** Treatment of chloroethane with saturated solution of AgCN give ethylisocyanide as major product.
   **REASON :** Cyanide ion ($CN^-$) is an ambidentate nucleophile.
3. **ASSERTION :** The boiling points of alkyl halides decreases in the order :
   $RI > RBr > RCl > RF$
   **REASON :** The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.
4. **ASSERTION :** tert-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.
   **REASON :** In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.
5. **ASSERTION :** Presence of a nitro group at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution.
   **REASON :** Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.
6. **ASSERTION :** In monohaloarenes, further electrophilic substitution occurs at *ortho* and *para* positions.
   **REASON :** Halogens are deactivating towards electrophilic substitution reactions.

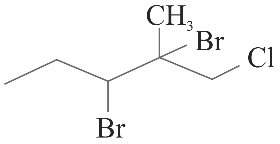
7. **ASSERTION :** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.
   **REASON :** Oxidising agent oxidises HI into $I_2$.
8. **ASSERTION:** The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.
   **REASON:** Vinyl group is electron donating group.
9. **ASSERTION:** Silver nitrite gives nitro alkane when it reacts with an alkyl halide.
   **REASON:** Silver nitrite is an ionic compound.
10. **ASSERTION:** Chloroform is generally stored in completely filled bottles in dark.
    **REASON :** $CHCl_3$ get oxidised to phosgene in atmosphere.
11. **ASSERTION:** Neopentyl chloride undergoes $S_N2$ reaction easily.
    **REASON:** Neopentyl chloride is a tertiary halide.
12. **ASSERTION :** It is difficult to substitute chlorine by -OH in chlorobenzene in comparison to that in chloroethane.
    **REASON :** Chlorine-carbon (C-Cl) bond in chlorobenzene has a partial double bond character due to resonance.
13. **ASSERTION:** 2-Bromobutane reacts with aqueous KOH forming racemic mixture.
    **REASON:** 2-Bromobutane forms secondary carbocation which leads to bimolecular substitution reaction.

## IV ONE WORD ANSWER TYPE QUESTIONS

1. Name the category of nucleophiles to which $CN^-$, $NO_2^-$ belongs, which may attack through two different sites.
2. Name the reaction which converts aniline into chlorobenzene.
3. Which isomer of dichlorobenzene has highest boiling point?
4. If elimination takes place according to Zaitsev (Saytzeff) rule then from which carbon removal of -H takes place?
5. Which mechanism $Ph_3C$-Cl follows when it reacts with aqueous NaOH?
6. Name the instrument used to measure optical rotation.
7. Name the category of the molecules related by non-superimposable mirror images of each other.
8. Which gas is formed by the reaction of chloroform with oxygen in presence of light?
9. Name the first chlorinated organic insecticide used against mosquito during world war II?
10. Write name of major product formed by reaction of ethyl magnesium bromide with water.
11. What will be major product when 2-Bromopentane reacts with alcoholic KOH ?
12. What will be the sign of optical rotation for a laevorotatory molecule?

## VERY SHORT ANSWER TYPE QUESTIONS (1 Mark)

1. Give IUPAC name of:



Ans : 1-Chloro-2,3-dibromo-2-methylpentane

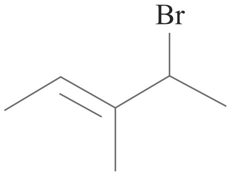
2. Identify A and B in each of the following process :

$CH_3CH_2Cl \xrightarrow{NaCN} A \xrightarrow{H_2/Ni} B$

Ans : A: $CH_3$-$CH_2$-CN; B: $CH_3CH_2CH_2NH_2$

3. Draw the structure of 4-bromo-3-methylpent-2-ene.

Ans:



4. Why Grignard reagent should be prepared under anhydrous condition?

Ans: It reacts with water and converts into corresponding hydrocarbon. ($RMgX+H_2O \rightarrow RH+MgX(OH)$)

5. Chloroform is stored in dark coloured and sealed bottles. Why ?

Ans: It is slowly oxidised by air in presence of light to form $COCl_2$(Phosgene) which is a poisonous gas. ($CHCl_3+\frac{1}{2}O_2 \rightarrow COCl_2+2HCl$)

6. An alkyl halide having molecular formula $C_4H_9Cl$ is optically active. Write its structure.

Ans: $\begin{array}{l}CH_3\text{-}\underset{\displaystyle|\atop\displaystyle Cl}{CH}\text{-}CH_2\text{-}CH_3\end{array}$

7. An organic compound 'A' on treatment with KCN gave 'B' which on hydrolysis with dil. HCl gave acetic acid. Identify A.

Ans: $CH_3Cl$

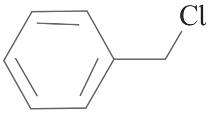
8. Arrange the following in order of their increasing reactivity in nucleophilic substitution reaction : $CH_3F$, $CH_3I$, $CH_3Br$, $CH_3Cl$

Ans: $CH_3F$, $CH_3Cl$, $CH_3Br$, $CH_3I$

9. Allyl chloride is more reactive than n-propyl chloride toward nucleophilic substitution reaction. Why?

Ans: Due to more stability of allyl carbocation than n-propyl carbocation.

10. Complete the reaction:



$+Na \xrightarrow[\text{ether}]{\text{dry}}$

Ans: $PhCH_2CH_2Ph$ (Wurtz reaction)

11. Give one chemical test to distinguish between chlorobenzene and benzyl chloride?

Ans: $AgNO_3$ test: benzyl chloride gives white precipitate.

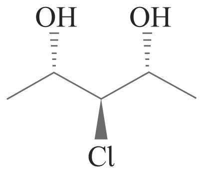
12. The presence of nitro group ($-NO_2$) at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution. Explain.

Ans: Nitro group withdraws electrons by -R, -I effect resulting in lesser election density on benzene ring.

13. For the preparation of alkyl chloride from alcohols, thionyl chloride ($SOCl_2$) is preferred. Give reason.

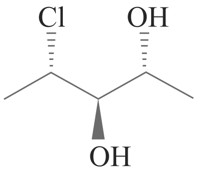
Ans: The by-products are gaseous $SO_2$ and HCl which can be easily removed to give pure haloalkane.

14. Which of the following molecule is optically active?



a

or



b

Ans: b is optically active

15. The dipole moment of chlorobenzene is lower than cyclohexyl chloride. Why?

Ans: Due to $sp^2$ hybridised carbon in chlorobenzene which is more electronegative and reduces polarity of C-Cl bond.

16. Name the compound which will be formed by reaction of (–)-1-chlorobutane with KOH?

Ans: (+)-Butan-1-ol

17. What happens when methylchloride is treated with KCN?

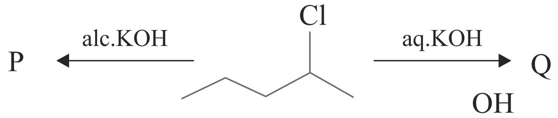
Ans: $CH_3$-CN will be formed

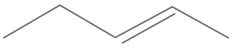
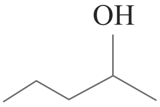
18. Identify X and Y :

$R\text{-}Br + Mg \xrightarrow{\text{Dry Ether}} X \xrightarrow{D_2O} Y$

Ans. X: R-MgBr Y: R-D

19. Complete by writing structures of P and Q:

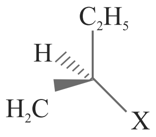


Ans. P:  Q: 

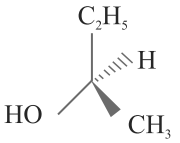
20. Name the product formed when 2,4,6- trinitrochlorobenzene reacts with warm water.

Ans. Picric acid(2,4,6-trinitrophenol)

21. Write structure of product formed when following undergoes $S_N2$ reaction taking $OH^-$ as nucleophile:



Ans.



22. Optical rotation of an enantiomer is +12.5°. Write optical rotation of :

(i) Its mirror image

(ii) mixture of enantiomer & mirror image (1:1)

Ans. (i)-12.5° (ii) Zero

23. Out of pentan-2-ol and pentan-3-ol, which is chiral molecule?

Ans. Pentan-2-ol

## SHORT ANSWER TYPE QUESTIONS (2 or 3 Marks)

1. Why is sulphuric acid not used during the reaction of alcohols with KI?

Ans: $H_2SO_4$ cannot be used along with KI in the conversion of an alcohol to an alkyl iodide as it converts KI to corresponding acid, HI which is then oxidised by it to $I_2$.

2. Which compound in each of the following pairs will react faster in $S_N2$ reaction with $OH^-$?

(i) $CH_3Br$ or $CH_3I$ (ii) $(CH_3)_3CCl$ or $CH_3Cl$

Ans: (i) $CH_3I$ will react faster than $CH_3Br$, as iodide is a better leaving group.

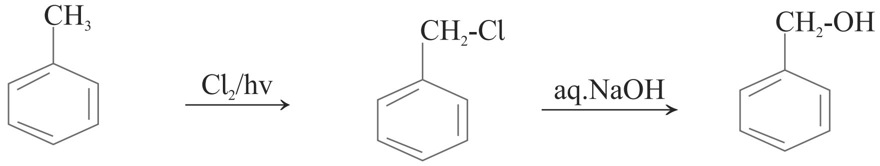
(ii) $CH_3Cl$ as it is primary haloalkanes with less steric hindrance.

3. Carry out the following conversions in not more than two steps :

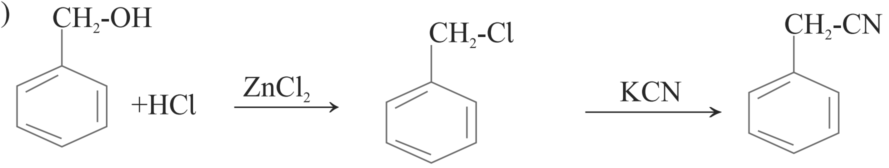
(i) Toluene to Benzyl alcohol

(ii) Benzyl alcohol to phenylethanenitrile

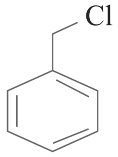
Ans: (i)



(ii)

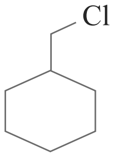


4. Which of the following compounds would undergo $S_N1$ Reaction faster and why ?



**a**

or



**b**

Ans: **a** will be more reactive due to higher stability of benzyl carbocation.

6. Complete the following reaction :

(i) $C_6H_5N_2^+Cl^- + KI \rightarrow$

(ii) $CH_2{=}CH_2 + Br_2 \rightarrow$

(iii) $CH_3CH_2OH + SOCl_2 \rightarrow$

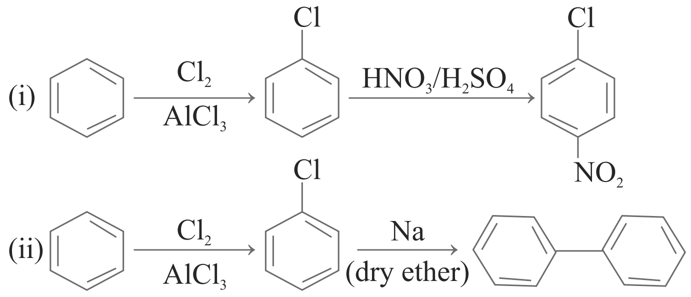
Ans: (i) $C_6H_5I$, (ii) $CH_2Br\text{-}CH_2Br$, (iii) $CH_3CH_2Cl$

7. Convert :

(i) Benzene to *p*- nitrochlorobenzene

(ii) Benzene to diphenyl

Ans:



8. What happens when :

(i) Propene is treated with HBr in presence of peroxide.

(ii) Benzene is treated with methyl chloride in presence of $AlCl_3$.

Ans: (i) l-Bromopropane is formed (Anti-Markonikov addition)

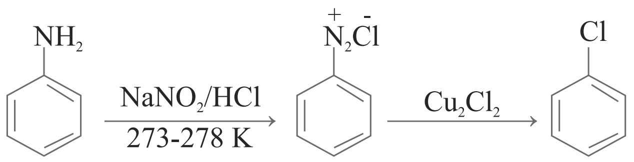
(ii) Toluene is formed (Friedel-Crafts Alkylation)

9. Write short note on :

(i) Sandmeyer reaction (ii) Finkelstein reaction

Ans:

(i)



(ii)

10. Name the reagent used to convert:

(i) 2-Chloropropane to 2- nitropropane

(ii) Chloroethane to butane

Ans: (i) $AgNO_2$ (ii) Na / dry ether

11. Give reasons :

(i) Boiling point of alkyl bromide is higher than alkyl chloride.

(ii) Alkyl halides are better solvents than aryl halides.

Ans: (i) High magnitude of van der Waals forces in alkyl bromides.

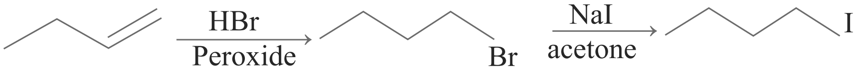
(ii) C - X is more polar in alkyl halides.

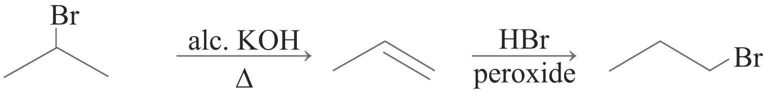
12. Carry out the following conversion :

(i) But-l-ene to n-Butyl iodide

(ii) 2-Bromopropane to 1-Bromopropane

Ans:

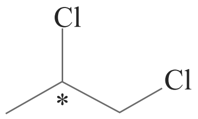
(i) 

(ii) 

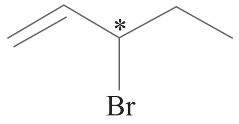
13. Identify and indicate the presence of center of chirality (if any) in the following molecules. How many stereoisomers are possible for those containing chiral center?

(i) 1,2- Dichloropropane (ii) 3- Bromopent-1-ene

Ans:



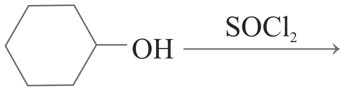
1,2-Dichloropropane

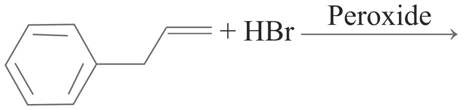


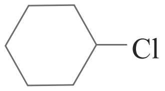
3-Bromopent-1-ene

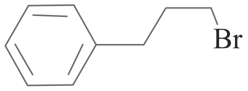
[*marked carbon are chiral centres]

14. Complete the reactions:

(a) 

(b) 

Ans : (a) 

(b) 

15. Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN form isocyanide as the chief product. Explain

Ans : KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C-C bond is more stable than C-N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

16. An organic compound **A** react with $PCl_5$ to give compound **B**, compound **B** react with Na /ether to give n-butane . What are compounds **A** and **B** ?

Ans : **A** = $C_2H_5OH$, **B** = $C_2H_5Cl$

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

Ans: In aqueous medium i.e. water, KOH will produce strong nucleophile $OH^-$ which will bring about the substitution of alkyl halides to form alcohols. At the same time, the $OH^-$ ions will be highly hydrated also. They will not be able to abstract a proton ($H^+$) from the β-carbon atom to form alkenes.

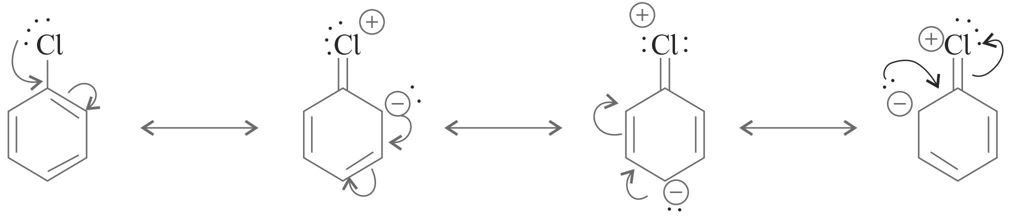
In alcoholic KOH, the solution will also contain ethoxide ions ($C_2H_5O^-$) in addition to $OH^-$ ions. They being a stronger base than $OH^-$ ions, will abstract a $H^+$ ion from the β-carbon atom giving alkene as the product as a result of dehydrohalogenation.

## LONG ANSWER TYPE QUESTIONS (5 Marks)

1. Haloarenes are extremely less reactive towards nucleophilic substitution reactions. Explain.

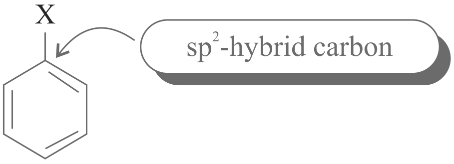
Ans: Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

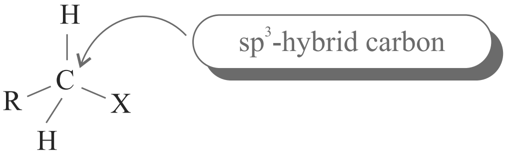
(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



C-Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) Difference in hybridisation of carbon atom in C-X bond: In haloalkane, the carbon atom attached to halogen is $sp^3$ hybridised while in case of haloarene, the carbon atom attached to halogen is $sp^2$-hybridised.





The $sp^2$ hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than $sp^3$-hybridised carbon in haloalkane with less s-character. Since it is difficult to break a shorter bond than a longer bond therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

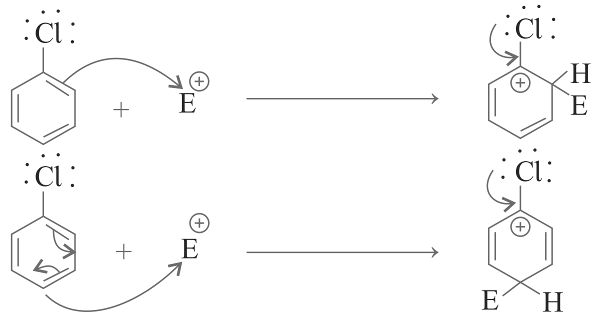
(iii) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, $S_N1$ mechanism is ruled out.

(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

2. Although chlorine is an electron withdrawing group, yet it is *ortho*- and *para*-directing in electrophilic aromatic substitution reaction. Explain.

Ans: Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.

Inductive effect destabilises the
intermediate carbocation



Resonance effect stabilises the
intermediate carbocation

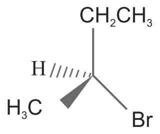
Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at *ortho*- and *para*- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect tends to oppose the inductive effect for the attack at *ortho*- and *para*-positions and hence makes the deactivation less for *ortho*- and *para*-attack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect.

3. A primary alkyl halide (**A**), $C_4H_9Br$ reacted with hot alcoholic KOH to give compound (**B**). Compound (**B**) reacted with HBr to give (**C**), which is an isomer of (A). When (**A**) was reacted with sodium metal, it gave a compound (**D**), $C_8H_{18}$ which was different than the compound when n-butyl bromide was reacted with sodium. Give the structural formula of (**A**) and write equations of all the reactions.

Ans: (A) 1 -Bromo-2-methylpropane
(B) 2-Methylprop-1-ene
(C) 2-Bromo-2-methylpropane
(D) 2,5-Dimethylhexane

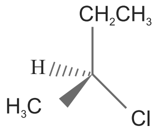
3. Write wedge and dash representation of 2-Bromobutane then write structures of molecules when:

Ans: (i) It undergoes retention on reaction with HCl
(ii) It undergoes inversion on reaction with $OH^-$
(iii) It undergoes $S_N1$ reaction with $H_2O$

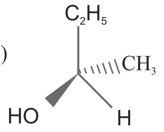


2-Bromobutane

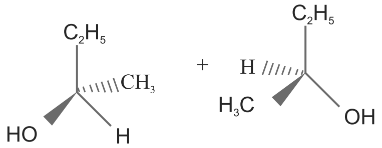
(i)



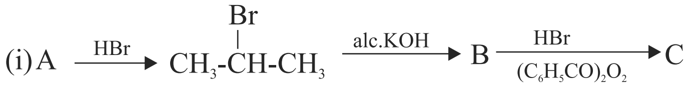
(ii)



(iii)



5. Predict A to E in following sequence of reactions:



$$\text{(i) A} \xrightarrow{\text{HBr}} CH_3\text{-}\overset{\overset{\text{Br}}{|}}{C}H\text{-}CH_3 \xrightarrow{\text{alc.KOH}} \text{B} \xrightarrow[(C_6H_5CO)_2O_2]{\text{HBr}} \text{C}$$

$$\text{(ii) } CH_3Br \xrightarrow{\text{KCN}} \text{D} \xrightarrow{H_3O^+} \text{E}$$

Ans. A: $CH_3–CH=CH_2$ B: $CH_3\text{-}CH=CH_2$ C: $CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$

D: $CH_3\text{-}CN$ E: $CH_3\text{-}COOH$

6. Give reasons:

(i) ( $\underline{+}$ )- Butan-2-ol is optically inactive

(ii) Iodoethane is more reactive than chloroethane in $S_N2$ reaction

(iii) *p*-dichlorobenzene has higher metting point than *o*-& *m*-isomers.

(iv) Haloalkanes easily dissolves in organic solvents.

(v) Grignard's reagent is stored in moistue proof cotainers.

Ans. (i) Rotation due to one enantiomer cancelled out by another in racemic mixure.

(ii) Because I is better leaving group than Cl

(iii) Due to symmetry of *p*-isomer, it fits in lattice better

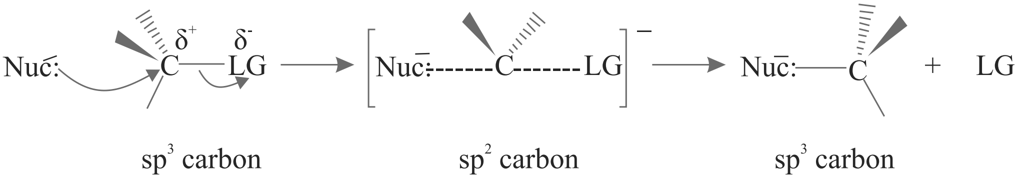
(iv) New intermolecular attractions between haloalkanes and solvent have much same strength as the ones being broken.

(v) Grignard's reagent reacts with water forming corresponding alkane.

## CASE STUDY BASED QUESTIONS

1. **Read the passage and answer the following questions:**

The bimolecular nucleophilic substitution ($S_N2$) reactions are among the fundamental and most important organic reactions. Traditionally, the mechanism of the $S_N2$ reactions is studied using qualitative transition state theory. The functionalized $sp^3$ hybridized carbon in a substrate molecule functions as an electrophilic center. This electrophilicity is considered due to a partial positive charge created on carbon by the electronegative functional group. A nuelcophile (Nuc-) attacks the $sp^3$ hybridized carbon from the opposite side of the leaving group (-LG). This nucleophilic attack results in a transition state in which the carbon atom becomes $sp^2$ hybridized with the C-LG bond partially broken and the Nuc-C bond partially formed. Finally, the C-LG bond is broken completely coincident with formation of the Nuc-C bond, giving the nucleophilic substitution product.



**Reference :** Xiaoping Sun, **Mechanistic Studies of Nucleophilic Substitution and β-Elimination Reactions**, *Symmetry* **2010**, 2(1), 201-212;https://doi.org/10.3390/sym2010201

(A) Which of the following undergoes $S_N2$ reaction at fastest rate?

(a) Chloropropane (b) Bromopropane

(c) Iodopropane (d) Chlorobenzene

(B) $S_N2$ reaction accompanied by................of the configuration.

(a) Retention (b) Inversion

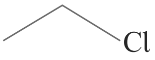
(c) Racemisation (d) Tautomerism

(C) Reaction of $(CH_3)_3$ C-Cl with aq. NaOH gives:

(a) $(CH_3)_3$ CH-OH (b) $(CH_3)_2$ CH-OH

(c) (a) and (b) (d) But-2-ene

(D) The correct order of rate of reaction in $S_N2$ for following molecules are: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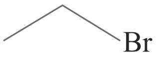
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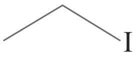

3

(a) $1 > 2 > 3$ (b) $2 > 1 > 3$
(c) $1 > 3 > 2$ (d) $3 > 2 > 1$

2. **Read the passage and answer the following questions:**

Halogenation of alcohols is a useful reaction as alcohol-starting materials are cheap and large varieties are commercially available. Many procedures are known that convert alcohols to halides however, they can involve harsh conditions and hazardous chemicals. For example, the chlorination of alcohols is traditionally performed using HCl gas or thionyl chloride, both of which are hazardous to human health and often produce many side reactions. Although improvements have been made upon these halogenation reactions, further green methodology is desired. On a laboratory scale, ammonium halide salts ($NH_4X$) are solid reagents, which means they are easy to handle and measure.

Discovering a mild, neutral, highly selective and environmentally friendly system for catalytic dehydroxyhalogenation is desirable but it is not a trivial task. Compromises in the journey towards an ideal sustainable process have to be made. This is exhibited by some of the trends found in the literature regarding chlorination of alcohols. Some reports involve the use of tripbenylphosphine ($PPh_3$) as a superstoichiometric additive in dehydroxychlorination reactions.

**Reference :** Petten, C.F., Kalviri, H.A. & Kelton, F.M. **Halodehydroxylation of alcohols to yield benzylic and alkyl halides in ionic liquids**. *Sustain Chem Process* 3, 16 (2015). https://doi.org/ 1 0.1186/s40508-015-0043-4

(A) Which of the following reaction may be used for the formation of 2-Fluorobutane?

(a) Finkelstein Reaction (b) Swarts Reaction
(c) Sandmeyer Reaction (d) $S_N2$ Reaction

(B) For the reaction, $R\text{-}OH + HX \rightarrow R\text{-}X + H_2O$ the rate of reaction will be highest with the-

(a) Ethanol (b) Propan-1-ol
(c) Propan-2-ol (d) 2-Methylbutan-2-ol

(C) When primary, secondary and tertiary alcohols reacts with Lucas' reagent ($HCl + \text{Anhy. } ZnCl_2$), the incorrect observation is-

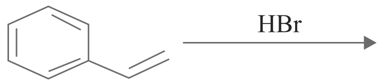
(a) Primary alcohol gives turbidity immediately.

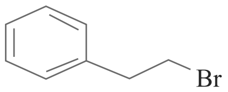
(b) Secondary alcohols gives turbidity in 5-10 minutes.

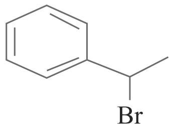
(c) Tertiary alcohols are most reactive.

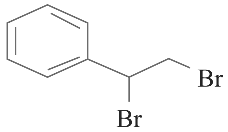
(d) Reaction follows $S_N1$ pathway.

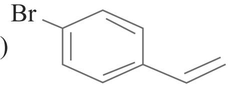
(D) The correct product of following reaction is-



(a)


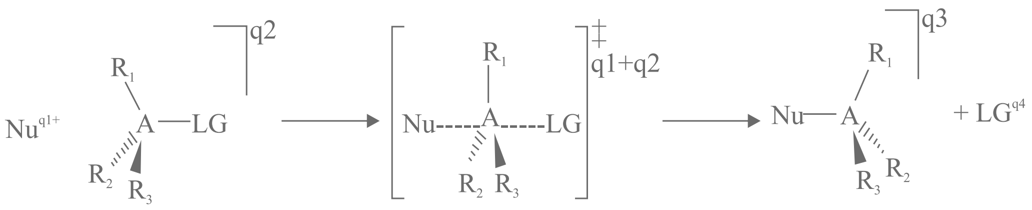
(b)


(c)


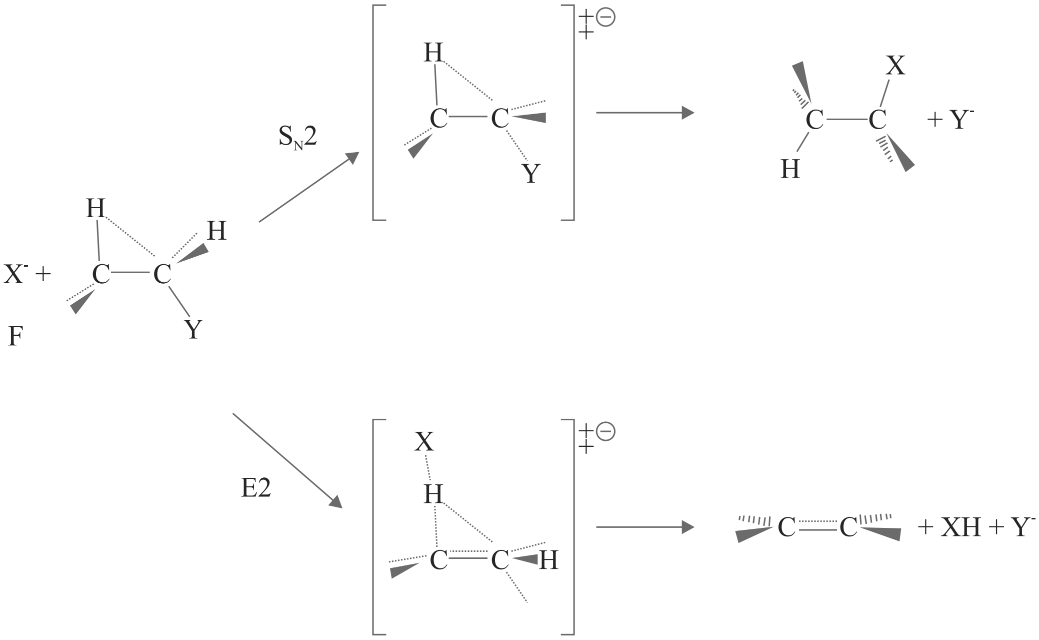
(d)


3. **Read the passage and answer the following questions:**

Bimolecular nucleophilic substitution ($S_N2$) reactions constitute one of the most widely-used organic chemistry reactions, both in chemistry and biology. The general reaction scheme is summarized in Scheme I, where a nucleophile $Nu^q$ attacks the central atom A and simultaneously a leaving group LG is displaced. The reaction can proceed for either anionic species (typically $q1=q4<0$), neutral (radical) species (typically $q1=q2=q3+q4=0$), or cationic species (typically $q2=q3>0$), together with a wide range of nucleophiles, leaving groups and central atoms. The number and nature of the substituents around the central atom play a major role in determining reactivity.



$S_N2$ substitution is, in principle, always in competition with base induced elimination (E2), and the two pathways may occur as unwanted side reactions of each other.



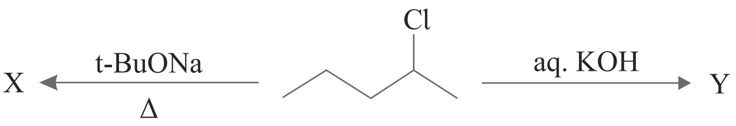
**Reference :** T.A. Hamlin, M. Swart, F. M. Bickelhaupt, **Nucleophilic Substitution ($S_N2$): Dependence on Nucleophile, Leaving Group, Central Atom, Substituents, and Solvent** *ChemPhysChem* **2018**, 19, 1315.

(A) Which of the following molecule leads to fastest reaction according to $S_N2$ mechanism?

(a) 2-Chloropropane (b) 1-Chloropropane

(c) Chlorophenylmethane (d) 2-Chlorotoluene

(B) In given reactions, X and Y are respectively-



(a) Pent-l-ene, Pent-2-ene

(b) Pent-2-ene, Pentan-2-ol

(c) Pentan-2-ol, Pent-2-ene

(d) Pent- 1 -ene, Pentan-2-ol

(C) Which of the following haloalkane reacts with nucleophile forming racemic mixture?

(a) 1 -Chloropropane (b) Chlorobenzene

(c) 2-Chlorobutane (d) 1 -Chlorobutane

(D) Which of the following statement is incorrect about $S_N2$ reaction?

(a) It takes place in single step.

(b) It is accompanied by the inversion of configuration.

(c) Stability of carbocation determines the rate of reaction.

(d) Iodopropane undergoes $S_N2$ faster than Chloropropanc.

4. **Read the passage and answers the following questions:**

Nucleophilic substitution reaction of haloalkane can be conducted according to both $S_N1$ and $S_N2$ mechanisms. However, which mechanism it is based on is related to such factors as the structure of haloalkane, and properties of leaving group, ucleophilic reagent and solvent.

**Influences of halogen : No** matter which mechanism the nucleophilic substitution reaction is based on, the leaving group always leave the central carbon atom with electron pair. This is just the opposite of the situation that nucleophilic reagent attacks the central carbon atom with electron pair. Therefore, the weaker the alkalinity of leaving group is , the more stable the anion formed is and it will be more easier for the leaving group to leave the central carbon atom; that is to say, the reactant is more easier to be substituted. The alkalinity order of halogen ion is F < Br < CI < F and the order of their leaving tendency should be $I^-$ > Br-> $Cl^-$ > F . Therefore, in four halides with the same alkyl and different halogens, the order of substitution reaction rate is RI> RBr > RCI > RF. In addition, if the leaving group is very easy to leave, many carbocation intermediates are generated in the reaction and the reaction is based on $S_N1$ mechanism. If the leaving group is not easy to leave, the reaction is based on $S_N2$ mechanism.

**Influences of solvent polarity:** In $S_N1$ reaction, the polarity of the system increases from the reactant to the transition state, because polar solvent has a greater stabilizing effect on the transition state than the reactant, thereby reduce activation energy and accelerate the reaction. In $S_N2$ reaction, the polarity, of the system generally does not change from the reactant to the transition state and only charge dispersion occurs. At this time, polar solvent has a great stabilizing effect on Nu than the transition state, thereby increasing activation energy and low down the reaction rate. For example, the decomposition rate ( $S_N1$) of tertiary chlorobutane in 25°C water (dielectric constant 79) is 300000 times faster than in ethanol (dielectric constant 24). The reaction rate ($S_N2$) of 2-bromopropane and NaOH in ethanol containing 40% water is twice slower than in absolute ethanol. In a word, the level of solvent polarity has influence on both $S_N1$ and $S_N2$reactions, but with different results. Generally speaking, weak polar solvent is favorable for $S_N2$ reaction, while strong polar solvent is favorable for $S_N1$ reaction, because only under the action of polar solvent can halogenated hydrocarbon dissociate into carbocation and halogen ion and solvents with a strong polarity is favorable for solvation of carbocation, increasing its stability. Generally speaking, the substitution reaction of tertiary haloalkane is based on $S_N1$ mechanism in solvents with a strong polarity (for example, ethanol containing water).

**Reference** A Brief Discussion on Nucleophilic Substitution Reaction on **Saturated Carbon Atom**. In *Applied Mechanics and Materials* (Vol. 312, pp. 433-437). Trans. Tech Publications Ltd.) (Ding, Y. (2013).

(A) Solvent in which $S_N1$ mechanism is favoured is:
(a) benzene
(b) carbon tetrachloride
(c) acetic acid
(d) carbon disulphide

(B) Nucleophilic substitution will be fastest in case of:
(a) 1-Chloro-2,2-dimethyl propane
(b) 1-Iodo-2,2-dimethyl propane
(c) 1-Bromo-2,2-dimethyl propane
(d) 1-Fluoro-2,2-dimethyl propane

(C) $S_N1$ reaction will be fastest in which of the following solvents?
(a) Acetone (dielectric constant 21)
(b) Ethanol (dielectric constant 24)
(c) Methanol (dielectric constant 32)
(d) Chloroform (dielectric constant 5)

(D) Polar solvents make the reaction faster as they:
(a) destabilize transition state and decrease the activation energy
(b) destabilize transition state and increase the activation energy
(c) stabilize transition state and increase the activation energy
(d) stabilize transition state and decrease the activation energy

(E) $S_N1$ reaction will be fastest in case of:
(a) l-Chloro-2-methylpropane
(b) 1-Iodo-2-methylpropane
(c) 1-Chlorobutane
(d) 1-Iodobutane

## ANSWERS

### I MULTIPLE CHOICE QUESTIONS

1. b 2. a 3. a 4. b 5. c 6. d 7. b 8. a 9. b
10. a 11. b 12. a 13. a 14. c 15. b 16. a 17. c 18. b
19. d 20. d 21. a

### II FILL IN THE BLANKS

1. Fittig
2. Racemic mixture.
3. Grignard reagent.
4. *p*-chloroacetophenone.
5. Iodoform.
6. Insoluble, soluble.
7. Inversion.
8. Dextrorotatory.
9. Deactivates

### III ASSERTION REASON TYPE QUESTIONS

1. c
2. b
3. b
4. d
5. a
6. b
7. d
8. c
9. c
10. a
11. d
12. a
13. c

### IV ONE WORD TYPE QUESTIONS

1. Ambident nucleophile.
2. Sandmeyer reaction.
3. para-dichlorobenzene.
4. β-carbon.
5. $S_N1$.
6. Polarimeter.
7. Enantiomers.
8. Phosgene
9. DDT
10. Ethane
11. Pent-2-ene
12. Negative

## CASE STUDY BASED QUESTIONS

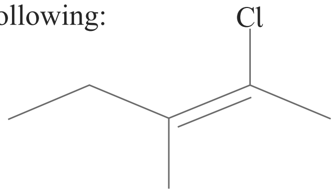
1. (A) - (c) (B) - (b) (C) - (a) (D) - (d)
2. (A) - (b) (B) - (d) (C) - (a) (D) - (b)
3. (A) - (b) (B) - (b) (C) - (c) (D) - (c)
4. (A)-(c) (B)-(b) (C)-(c) (D)-(c) (E)-(b)

## UNIT TEST-1

## HALOALKANES AND HALOARENES

**Maximum Marks : 20** **Time Allowed : 1 Hr**

1. Write IUPAC name of following: 1



2. The correct ascending order of nucleophilic substitution reactions for following molecules is- 1

(I) Chlorobenzene (II) 4-Nitrochlorobenzene

(III) 4-Chlorotoluene

(a) I, II, III (b) I, III, II

(c) III, I, II d) III, II, I

3. How will you convert aniline into iodobenzene? 1

4. Chlorobenzene on reaction with chloromethane in presence of zinc chloride forms- 1

(a) *o*-dichlorobenzene

(b) *o*-chlorotoluene

(c) *p*-chlorotoluene

(d) *o*-chlorotoluene and *p*-chlorotoluene

5. A solution of a molecule (X) rotates plane polarised light 32° clockwise. Which of the following is incorrect? 1

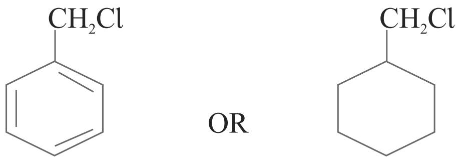
(a) X is optically active

(b) X is dextrorotatory

(c) X has all achiral carbons

(d) X forms non-superimposable

6. Which of the following undergoes $S_N2$ reaction faster and Why? 2



7. How will you synthesize following from aniline? Write chemical equations. 2
   (i) Chlorobenzene (ii) Iodobenzene

8. Explain following giving examples: 2
   (i) racemic mixture (ii) enantiomers

9. What happens when: 3
   (i) Bromoethane reacts with sodium ethoxide
   (ii) Chloroethanc reacts with AgCN.
   (iii) 2-Bromo-2-methylbutane is heated with ethanolic KOH.

10. Explain following: 3
    (i) Aryl chlorides and bromides can be easily prepared by electrophilic substitution of aromatic hydrocarbons with chlorine and bromine respectively in the presence of Lewis acid catalysts but for preparation of aryl iodides presence of an oxidising agent is required.
    (ii) Grignard reagent is kept under anhydrous conditions.
    (iii) Reactions through $S_N2$ mechanisms are accompanied by inversion of configuration.

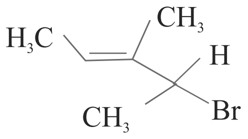
11. Convert the following: 3
    (i) Ethanol to iodoethane
    (ii) Toluene to benzyl alcohol
    (iii) Benzene to diphenyl.

## UNIT TEST-2

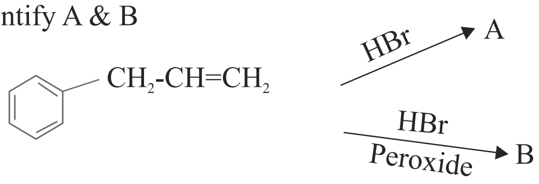
## HALOALKANES AND HALOARENES

**Maximum Marks : 20** **Time Allowed : 1 Hr**

1. Write the IUPAC name of 1



2. Identify A & B

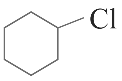


3. Define ambident nucleophile with suitable examples. 1
4. How will you convert chloroethane into butane? 1
5. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHCl$ $C_6H_5$, which is more easily hydrolysed by queous KOH ? 1
6. (i) Chloroform is kept in completely filled bottles in dark. Explain the reason.
   (ii) Mention one application of Iodoform 2
7. How Grignard's reagent is prepared using alkyl halides ? Why it is kept under anhydrous conditions ? 2
8. Explain following terms giving exmpales: 2
   (i) Chirality
   (ii) Inversion of configuration
9. Discuss mechanisms of $S_N1$ and $S_N2$ taking appropriate examples of optically active alkyl halides. 3
10. Which of the following undergoes $S_N2$ faster and why? 3

(a)

Or

(b)



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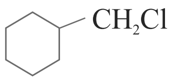
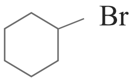


(c)



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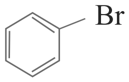

11. Convert following: 3
    (i) Aniline to phenylisocyanide
    (ii) Benzene to 4-Bromonitrobenzene
    (iii) Propene to Propan-1-ol