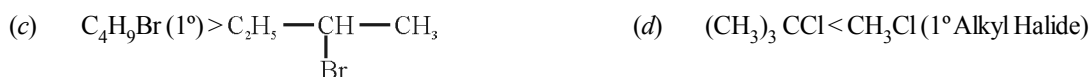
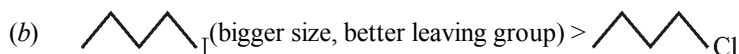
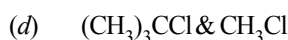
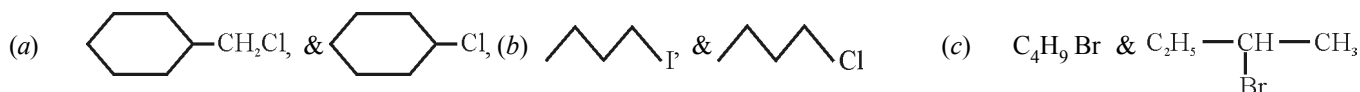


This particular chapter is divided in the following parts with the exam pont of view.

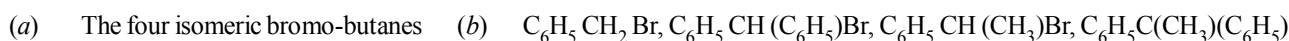
1. Reasoning 2. IUPAC Naming 3. Mechanisms 4. Name Reactions 5. Conversions

REASONINGS

Q1. In the following pairs of halogen compound which is faster under going S_N^2 Rx.



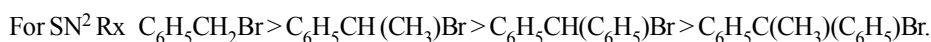
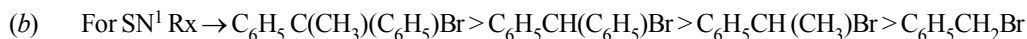
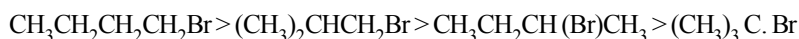
Q2. Predict the order of reactivity of the following compounds in S_N^1 and S_N^2 Rx.



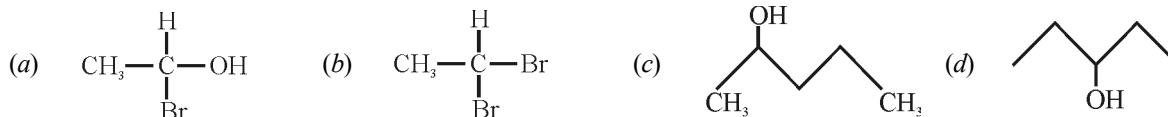
Ans. (a) For S_N^1 Rx. (Reactivity depends on stability of carbo cation $\rightarrow 3^\circ > 2^\circ > 1^\circ$)



For S_N^2 Rx (less steric hindrance more reactive)



Q3. Identify chiral and achiral molecules in each of the following pair :-



Ans. (a) & (c) With four different alkyl group.

Q4. Although chlorine is an EWG yet it is ortho-para directing in electrophilic aromatic substitution Rx.

Ans. Chlorine shows $-I$ effect causing the intermediate carbocation will destabilize but $+R$ effect of Cl stabilizes the intermediate carbocation. The reactivity is controlled by the stronger $-I$ effect while orientation is controlled by weaker resonance effect.

Q5. Haloalkanes react with KCN to form RCN but with AgCN form RNC?

Ans. CN is an ambident group (can be attached from both the ends). In KCN, it is ionic bond, the reaction occurs through C since C-C bonds are more stronger while in AgCN (covalent bonding), only N electron pair is available for bond formation.

Q6. RCl is hydrolysed to ROH slowly but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture.

Ans. I^- is stronger nucleophile so it replaces Cl to form RI then RI is more hydrolysed to yield ROH due to I^- ion is a better leaving group than Cl^- .

Q7. Haloalkanes give nucleophilic substitution while Haloarenes give Electrophilic substitution reactions.

Ans. Haloalkanes are more polar than Haloarenes. so their C has more +ve character so they give nucleophilic substitution while haloarenes has a benzene ring which shows resonance. haloarenes give electrophilic reaction due to -I effect and +R effect.

Q8. Why is sulphuric acid not used during the reaction of Alcohols with KI.

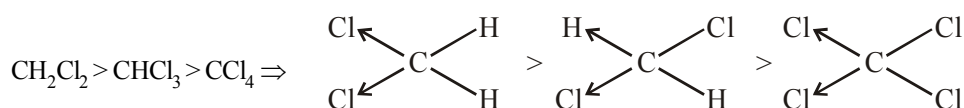
Ans. Sulphuric acid oxidises KI to I₂.

Q9. Arrange on the basis of increasing Boiling Point. (a) bromomethane, bromoform, Chloromethane, dichloromethane (b) 1-chloropropane, isopropyl chloride, 1-chlorobutane.

Ans. (a) Bromoform > dibromomethane > bromomethane > Chloromethane (BP \propto molecular wt.)

(b) Isopropyl chloride (side chain) < 1 chloropropane < 1 Chlorobutane (more branching, more surface area less B.P.)

Q10. Which of the following has highest dipole moment CH₃Cl, CH₂Cl₂, CCl₄



Q11. The dipole moment of chloro benzene lower than cyclohexylchloride.

Ans. Cyclohexylchloride has cyclohexyl as a EDG group. It increase electron density at Cl atom makes it polar while in case chlorobenzene which has benzene ring as EWG and resonating ring it dipole moment is lower.

Q12. Alkyl halide though polar not soluble in water.

Ans. Alkyl halide cannot form H-bond with water molecules.

Q13. RMgX should be prepared under anhydrous conditions

Ans. RMgX is very reactive, they react with moisture present in apparatus or the starting material.

Q14. Out of C₆H₅CH₂Cl and C₆H₅CHClC₆H₅ which is Easily hydrolysed by KOH (aq.)

Ans. C₆H₅CHClC₆H₅ is 2° alkyl halide which is more reactive under SN¹ reaction but under SN² reaction 1° alkyl halide (C₆H₅CH₂Cl) is more hydrolysed.

Q15. p-dichlorobenzene has high M.P and low solubility than O-dichlorobenzene.

Ans. p-dichlorobenzene has symmetrical structure so its MP is high and solubility low.

Q16. Why SOCl₂ is used for preparation of Alkyl Halide from ROH.

Ans. On reaction between SOCl₂ and ROH. we get RCl, HCl(g) and SO₂(g) as escapible gases.

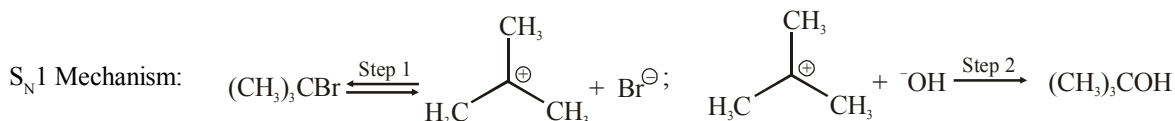
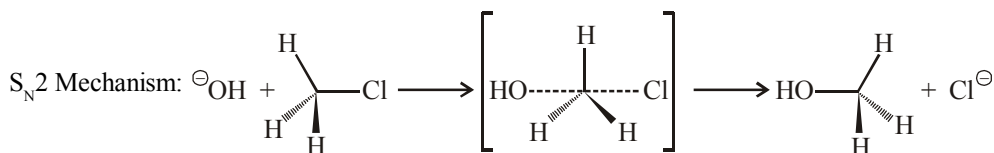
Q17. Arrange the following in order of increasing ease towards nucleophile.Rx.

4-Nitrochlorobenzene, chlorobenzene, 2, 4, 6-trinitrochlorobenzene, 2, 4-dinitrochlorobenzene

Ans. 2, 4, 6 trinitrochlorobenzene > 2, 4-dinitrochlorobenzene > 4-nitrochlorobenzene > Chlorobenzene. Among the aromatic compounds have molecular formula C₇H₇Cl how many isomers are possible. Write structures and name. Identify all the possible monochloro structural isomers that would be expected to form on free radical chlorination of (CH₃)₂CH CH₂CH₃. Differentiate between (a) chiral and achiral, (b) retention and inversion.

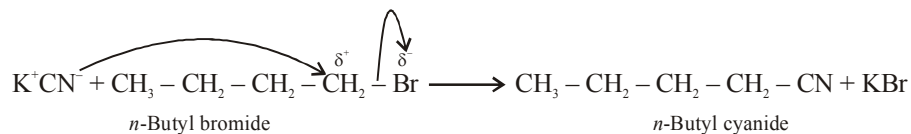
- Q18.** What is enantiomers and racemic mixture.
- Q19.** Allyl chloride is hydrolysed more readily than n-propyl chloride. Vinyl chloride is hydrolysed more slowly than ethyl chloride
- Q20.** Explain. reaction between Alkyl halide and KOH(aq) yield Alcohol but with KOH(aq) yield alkenes.
- Q21.** Which one is better nucleophile Br^- and I^-
- Q22.** Among the isomeric alkanes of molecular formula C_5H_{12} Identify the one than on photochemical chlorination yields (i) A single monochloride, (ii) three isomeric monochlorides, (iii) Four isomeric monochloride. Uses of freon 12, DDT, Carbontetrachloride and Iodoform.

MECHANISMS



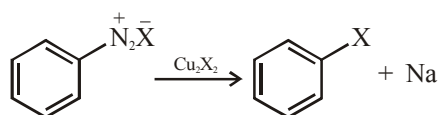
Sr. No.	Factors	$\text{S}_\text{N}2$ Reactions	$\text{S}_\text{N}1$ Reactions
1	Number or Steps	One: $\text{R} : \text{L} + \text{Nu}^- \rightarrow \text{R} : \text{Nu} + \text{L}$	Two: 1. $\text{R} : \text{L} \xrightarrow{\text{Slow}} \text{R}^+ + \text{L}$ 2. $\text{R}^+ + \text{Nu}^- \xrightarrow{\text{Fast}} \text{R} : \text{Nu}$
2	Reaction rate and order	Second order: $\text{Rate} \propto [\text{Substrate}] [\text{Nucleophile}]$ or $\text{Rate} = k_2[\text{RL}][\text{Nu}]$	First order: $\text{Rate} \propto [\text{Substrate}]$ or $\text{Rate} = k_1[\text{RL}]$
3	Molecularity	Bimolecular	Unimolecular
4	TS of slow step	$\text{Nu}^- \cdots \text{C} \cdots \text{L}$	$\text{Nu}^- \cdots \text{C}^+ \cdots \text{L} \cdots \text{Nu}^-$
5	Reacting nucleophile	The carbon of the substrate is attacked by the nucleophile, exclusively from the back side.	The nucleophile can attack the carbon of the substrate from both sides. However, the attack from the back side predominates.
6	Stereochemistry	Complete inversion of configuration takes place	Inversion and retention takes place
7	Reactivity order of alkyl halides	Methyl $\text{I} > 1^\circ > 2^\circ > 3^\circ$ halides. ($\text{I} > \text{Br} > \text{Cl} > \text{F}$)	$3^\circ > 2^\circ > 1^\circ > \text{methyl}$ halides. ($\text{I} > \text{Br} > \text{Cl} > \text{F}$)
8	Rearrangement	No rearranged product is formed (except for allylic)	Rearranged products can be formed.
9	Nature of nucleophiles	Favoured by strong and high concentration of nucleophiles.	Favoured by mild and low concentration of nucleophiles
10	Polarity	Favoured by solvents of low polarity	Favoured by solvents of high polarity.
11	Reaction rate determining factor	By steric hindrance	By electronic factor (stability of R)
12	Catalysis	Not catalysed by any catalyst (phase transfer)	Catalysed by Lewis and Bronsted acids, e.g., Aq. AlCl_3 , ZnCl_2 and strong HA.

Write the mechanism of the following reaction: $n\text{BuBr} + \text{KCN} \xrightarrow{\text{EtOH-H}_2\text{O}} n\text{BuCN}$



NAME REACTIONS

1. Sandmeyer's Reaction:

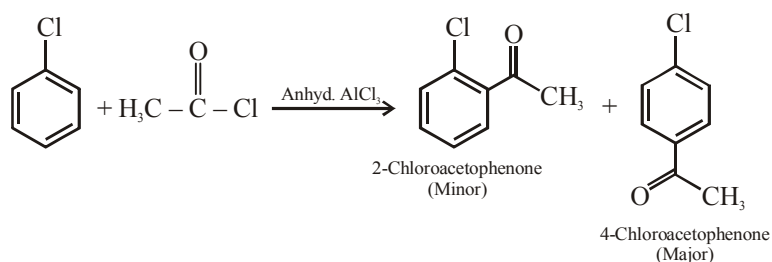
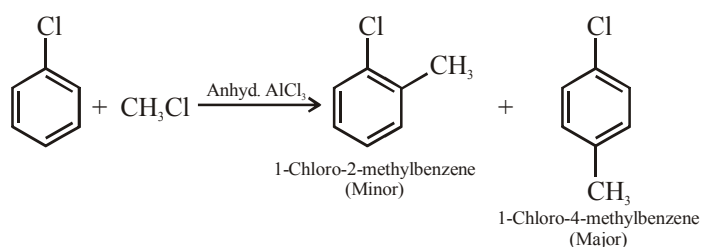


2. Finkelstein Reaction: $\text{RX} + \text{NaI} \rightarrow \text{RI} + \text{NaX}$ (solvent - Acetone)

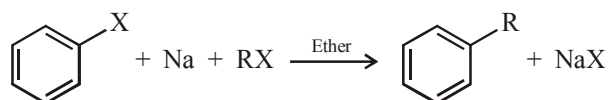
3. Swarts Reaction: $\text{CH}_3\text{Br} + \text{AgF} \rightarrow \text{CH}_3\text{F} + \text{AgBr}$

4. Wurtz Reaction: $\text{RX} + 2\text{Na} + \text{RX} \rightarrow \text{R-R} + 2\text{NaX}$

5. Friedel Crafts Reaction:



6. Wurtz Fitting Reaction:

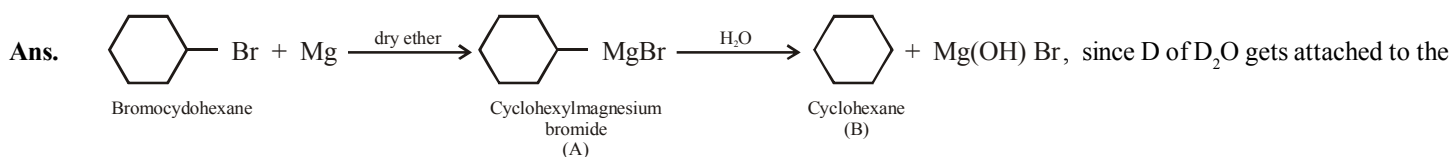
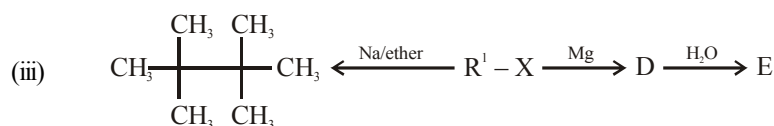
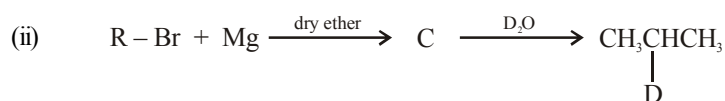
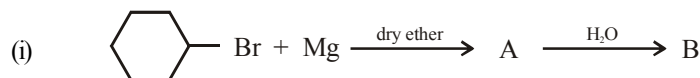


7. Fitting Reaction:



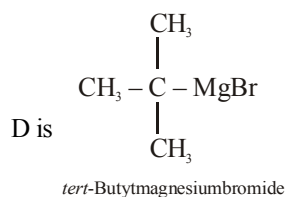
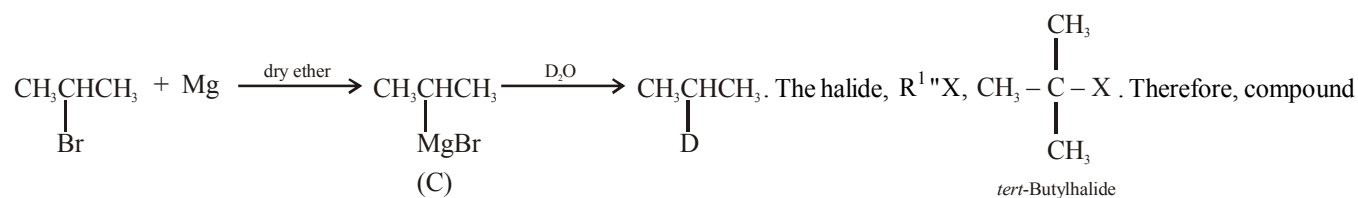
CONVERSIONS

Q1. Identify A, B, C, D, E, R and R' in the following:



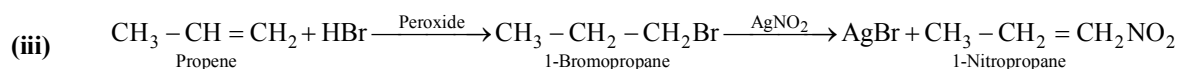
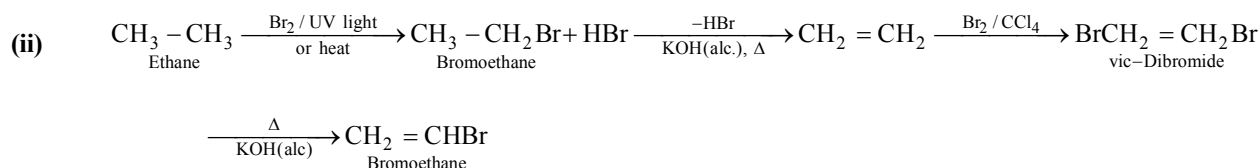
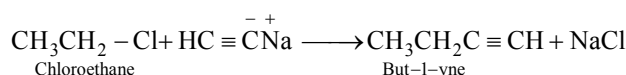
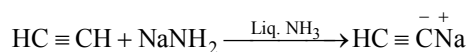
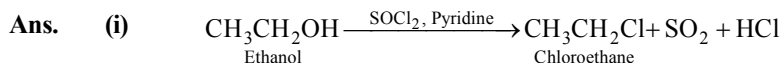
carbon atom to which MgBr is attached, C is $\text{CH}_3\underset{\text{MgBr}}{\text{CH}}\text{CH}_3$. Therefore, the compound R-Br is $\text{CH}_3\underset{\text{Br}}{\text{CH}}\text{CH}_3$

Isopropylmagnesium bromide
2-Bromopropane

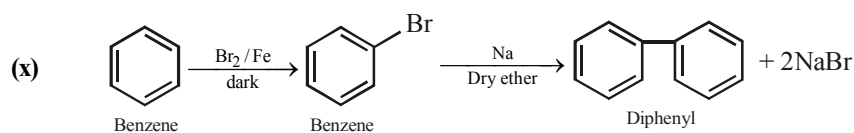
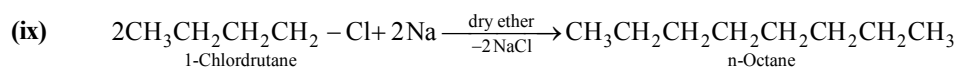
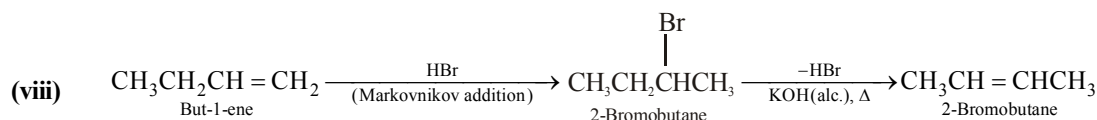
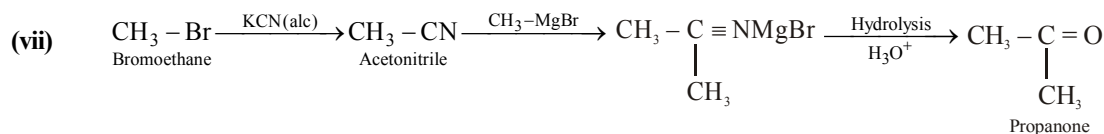
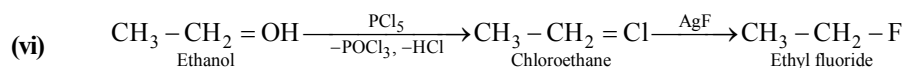
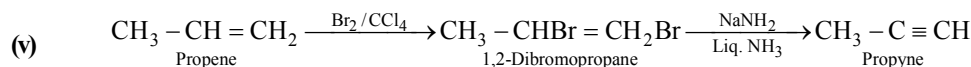


Q2. How will you bring about the following conversions?

- | | |
|---------------------------------|--------------------------------|
| (i) Ethanol to but-1-yne | (ii) Ethane to bromoethene |
| (iii) Propene to 1-nitropropane | (iv) Toluene to benzyl alcohol |
| (v) Propene to propyne | (vi) Ethanol to ethyl fluoride |
| (vii) Bromomethane to propanone | (viii) But-1-ene to but-2-ene |
| (ix) 1-Chlorobutane to n-octane | (x) Benzene to biphenyl. |



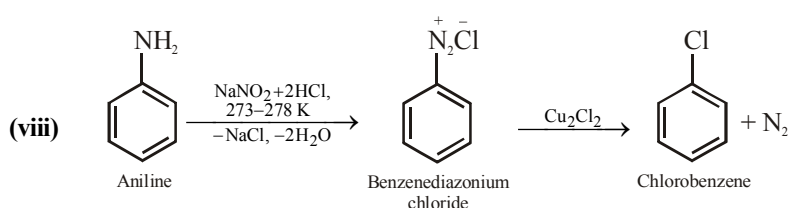
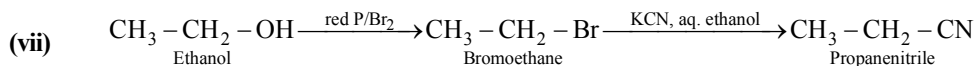
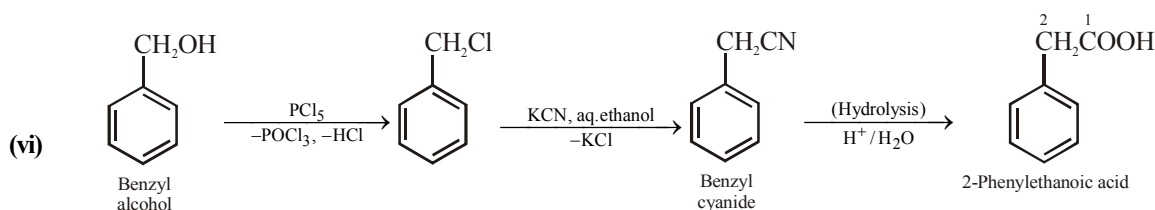
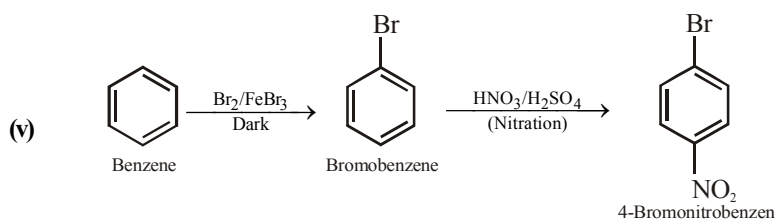
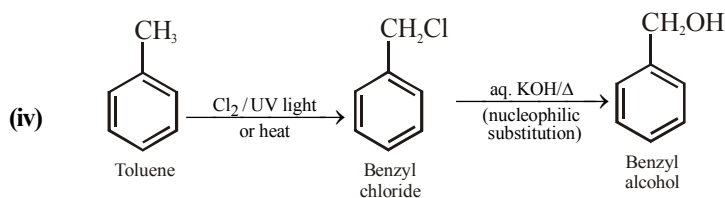
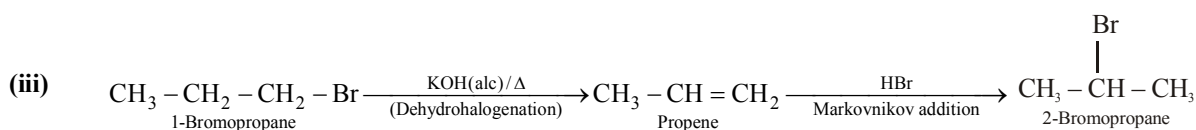
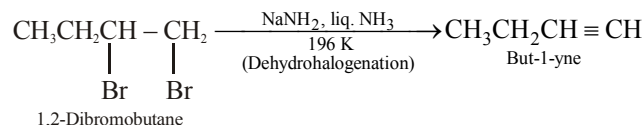
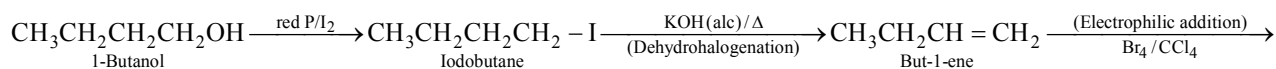
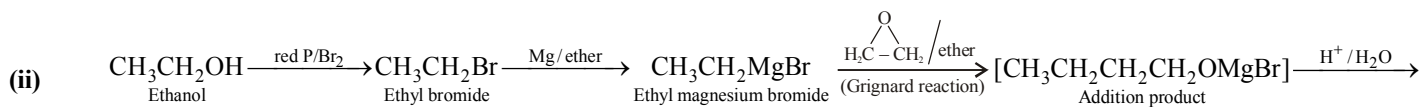
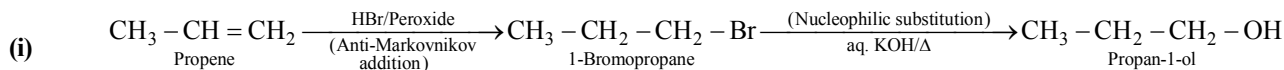
(iv) Do yourself.

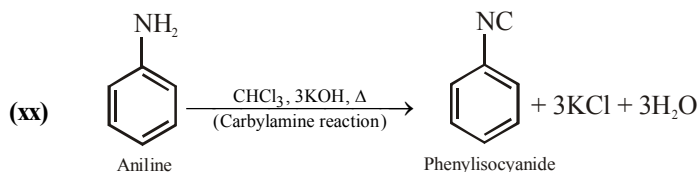
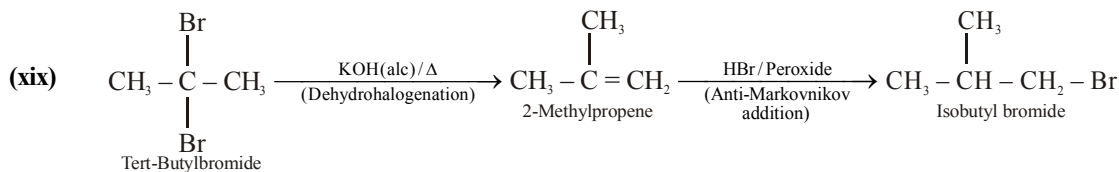


1.
$$\underset{\text{1-Chloropropane}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}} + \text{NaI} \xrightarrow[\text{(Finkelstein reaction)}]{\text{acetone, heat}} \underset{\text{1-Iodopropane}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{I}} + \text{NaCl}$$
2.
$$\underset{\text{2-Bromo-2-methylpropane}}{(\text{CH}_3)_3\text{CBr}} + \text{KOH} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{ethanol, heat}} \underset{\text{2-Methylpropene}}{\text{CH}_3 - \underset{\text{CH}_3}{\underset{|}{\text{C}}} = \text{CH}_2} + \text{KBr} + \text{H}_2\text{O}$$
3.
$$\underset{\text{2-Bromobutane}}{\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3} + \text{NaOH} \xrightarrow{\text{water}} \underset{\text{Butan-2-ol}}{\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_3} + \text{NaBr}$$
4.
$$\underset{\text{Bromobutane}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}} + \text{KCN} \xrightarrow[\text{(Nucleophilic substitution)}]{\text{aq. ethanol}} \underset{\text{Cyanoethane}}{\text{CH}_3\text{CH}_2\text{CN}} + \text{KBr}$$
5.
$$\underset{\text{Sodium phenoxide}}{\text{C}_6\text{H}_5\text{ONa}} + \underset{\text{Chloroethane}}{\text{C}_2\text{H}_5\text{Cl}} \xrightarrow{\text{(Williamson synthesis)}} \underset{\text{Phenetole}}{\text{C}_6\text{H}_5 - \text{O} - \text{C}_2\text{H}_5} + \text{NaCl}$$
6.
$$\underset{\text{1-Propanol}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}} + \text{SOCl}_2 \longrightarrow \underset{\text{1-Chloropropane}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}} + \text{SO}_2 + \text{HCl}$$
7.
$$\underset{\text{But-1-ene}}{\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2} + \text{HBr} \xrightarrow[\text{(Anti-Markovnikov's addition)}]{\text{Peroxide}} \underset{\text{1-Bromobutane}}{\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 - \text{Br}}$$
8.
$$\underset{\text{2-Methylbut-2-ene}}{\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2} + \text{HBr} \xrightarrow[\text{(Markovnikov addition)}]{} \underset{\text{2-Bromo-2-methylbutane}}{\text{CH}_3 - \text{CH}_2 - \underset{\text{CH}_3}{\underset{|}{\text{C}}} - \text{CH}_3}$$

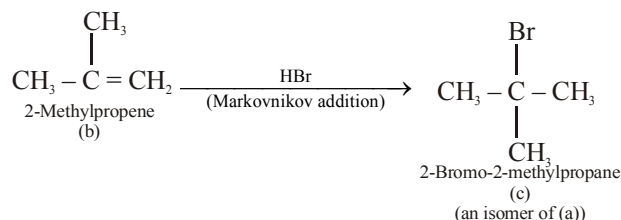
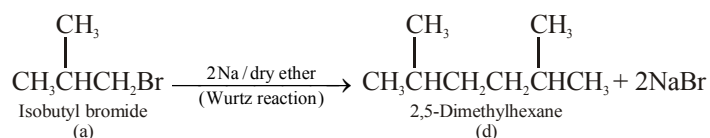
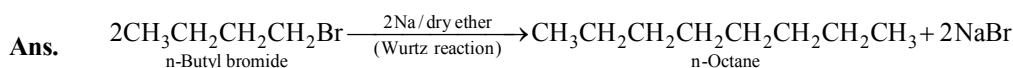
Q3. How the following conversions can be carried out?

- | | |
|--|--|
| (i) Propene to propan-1-ol | (ii) Ethanol to but-1-yne |
| (iii) 1-Bromopropane to 2-bromopropane | (iv) Toluene to benzyl alcohol |
| (v) Benzene to 4-bromonitrobenzene | (vi) Benzyl alcohol to 2-phenylethanoic acid |
| (vii) Ethanol to propanenitrile | (viii) Aniline to chlorobenzene |
| (ix) 2-Chlorobutane to 3, 4-dimethylhexane | (x) 2-Methyl-1-propene to 2-chloro-2-methylpropane |
| (xi) Ethyl chloride to propanoic acid | (xii) But-1-ene to n-butyliodide |
| (xiii) 2-Chloropropane to 1-propanol | (xiv) Isopropyl alcohol to iodoform |
| (xv) Chlorobenzene to <i>p</i> -nitrophenol | (xvi) 2-Bromopropane to 1-bromopropane |
| (xvii) Chloroethane to butane | (xviii) Benzene to diphenyl |
| (xix) <i>tert</i> -Butyl bromide to isobutyl bromide | (xx) Aniline to phenylisocyanide |







Q4. Primary alkyl halide $\text{C}_4\text{H}_9\text{Br}$ (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.



PREVIOUS YEARS CBSE QUESTIONS

2012

- Explain the mechanism of acid catalysed hydration of an alkene to form corresponding alcohol.
- Answer the following questions:
 - What is meant by chirality of a compound? Give an Example.
 - Which of the following compound is more easily hydrolysed by KOH and why? $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$
 - Which one undergoes $\text{S}_\text{N}2$ substitution reaction faster and why?  and 

2011

- Write the IUPAC name of the following compound : $(\text{CH}_3)_3\text{CCH}_2\text{Br}$
- Answer the following :
 - Haloalkanes easily dissolve in organic solvents, why ?
 - What is known as a racemic mixture? Give an example.
 - Of the two bromoderivatives, $\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)\text{Br}$ and $\text{C}_6\text{H}_5\text{CH}(\text{C}_6\text{H}_5)\text{Br}$, which one is more reactive in $\text{S}_\text{N}1$ substitution reaction and why?

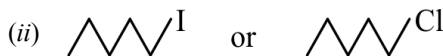
2010

- A solution of KOH hydrolyses $\text{CH}_3\text{CHClCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$. Which one of these is more easily hydrolysed?

2. How are the following conversions carried out?
 (i) Benzyl chloride to benzyl alcohol, (ii) Methyl magnesium bromide to 2-methylpropan-2-ol
3. State one use each of DDT and iodoform.

2009

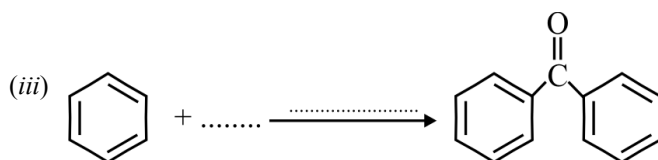
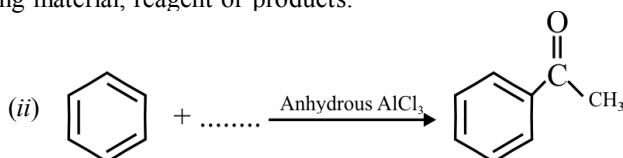
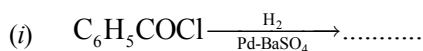
1. Which ones in the following pairs of substances undergoes S_N2 substitution reaction faster and why?



2. (a) How are the following obtained?

(i) Benzoic acid and ethyl benzene. (ii) benzaldehyde from toluene

(b) Complete each synthesis by giving the missing material, reagent or products:



2008

1. Explain as to why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.
 (2 marks)

Hint:

Aryl halides contain a benzene ring. Typical reactions in this case are electrophilic substitution reactions.

Factors responsible for diminished reactivity of haloarenes towards nucleophilic reactions are:

- (a) Resonance effect (b) Difference in hybridisation of carbon atom in the C-X bond
 (c) Instability of phenyl cation (d) Electronic repulsions

On the other hand, carbon carrying the halogen in haloalkanes is more electron deficient than in haloarenes. As a result haloalkanes undergo nucleophilic substitutions more readily than haloarenes.

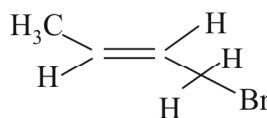
2. Which compound in each of the following pairs will react faster in S_N2 reaction with $-OH^-$? Why? (2 marks)

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

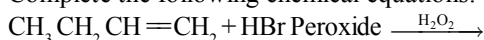
Answer:

(i) CH_3I (ii) CH_3Cl

3. (a) State the IUPAC name of the following compound:



(b) Complete the following chemical equations:



Answer:

(a) 1-Bromobut-2-ene (b) $CH_3CH_2CH_2-CH_2Br$