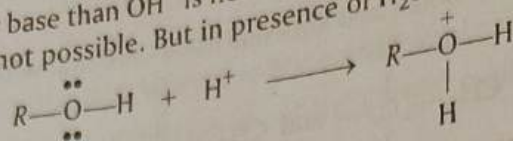
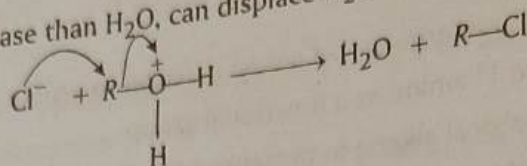


6. Alcohol (ROH) does not react with NaCl but forms RCl in presence of H_2SO_4 .

Ans. Cl^- ion being weaker base than OH^- is not able to displace OH^- ion from ROH. Hence the reaction between Cl^- (from NaCl) and $\text{R}-\text{OH}$ is not possible. But in presence of H_2SO_4 , ROH forms protonated alcohol.



Now, Cl^- ion being stronger base than H_2O , can displace H_2O from protonated alcohol to form RCl.

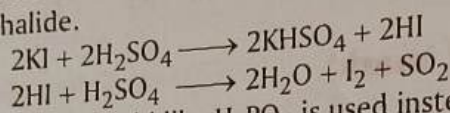


7. Alkyl halides though polar are immiscible with water.

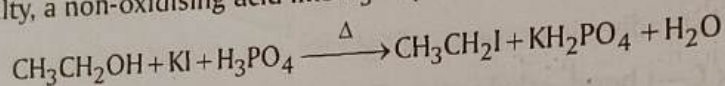
Ans. Alkyl halides being polar molecules are held together by dipole-dipole attraction. The molecules of H_2O are held together by H—bonds. Since the new forces of attraction between water and alkyl halide molecules are weaker than the force of attraction already existing between alkyl halide-alkyl halide molecules and water-water molecules. Therefore, alkyl halides are not soluble in water.

8. Sulphuric acid is not used during the reaction of alcohols with KI.

Ans. H_2SO_4 is an oxidising agent which oxidises HI produced during the reaction to I_2 thus prevents the reaction between an alcohol and HI to form an alkyl halide.

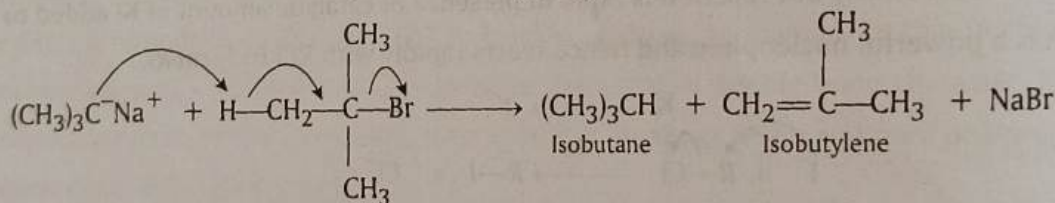
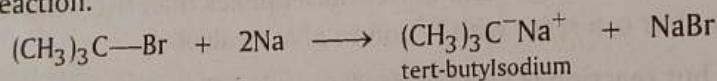


To overcome this difficulty, a non-oxidising acid like H_3PO_4 is used instead of H_2SO_4 .



9. Wurtz reaction fails in case of tertiary alkyl halides.

Ans. Tertiary alkyl halides prefer to undergo dehydrohalogenation in presence of a strong base such as Na metal instead of undergoing Wurtz reaction.



Thus, only 1° and 2° alkyl halide undergo Wurtz reaction while 3° alkyl halides prefer to undergo dehydrohalogenation to form alkenes.

10. Displacement of cyanide and amide ion is never observed in nucleophilic substitution reactions.

Ans. Displacement of cyanide and amide ion is never observed in nucleophilic substitution reactions because both are ambident nucleophiles. Again both are strong nucleophiles.

11. Aryl halides cannot be prepared by the reaction of phenol with HCl in presence of ZnCl_2 .

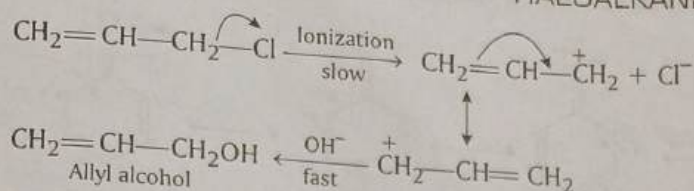
Ans. The C—O bond in phenol acquires double bond character due to resonance effect and it is difficult to break this bond. Hence aryl halides cannot be prepared by the reaction of phenol with HCl.

12. A small amount of ethanol is added to chloroform bottle.

Ans. Because alcohol converts phosgene to harmless ethyl carbonate.

13. Allyl chloride is hydrolysed more readily than *n*-propyl chloride.

Ans. Allyl chloride readily undergoes ionisation to produce resonance stabilized allyl carbocation. Since carbocations are reactive, therefore they readily react with OH^- ions to form allyl alcohol.



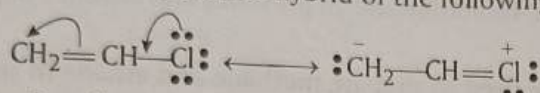
But, *n*-propyl chloride does not undergo ionization to produce *n*-propyl carbocation.

Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product.

Ans. KCN being an ionic compound gives CN^- ion which can act as an ambident nucleophile and can attack the carbon attached to halogen either through C or N. Thus, it can yield cyanides as well as isocyanides. However, C—C bond is relatively stronger than C—N bond. Therefore, the attack mainly takes place through the carbon end of the cyanide ion forming alkyl cyanide as the major product. On the other hand, AgCN being covalent, only N atom is free to act as the donor atom due to presence of a lone pair of electrons on nitrogen atom. Therefore, attack occurs through N-atom of cyanide group forming alkyl isocyanides.

Vinyl chloride is hydrolysed more slowly than ethyl chloride.

Ans. Vinyl chloride is represented as a resonance hybrid of the following two structures :



Due to which, carbon-chlorine bond acquires double bond character. This is not observed in ethyl chloride. Therefore, vinyl chloride undergoes hydrolysis more slowly than ethyl chloride.

Organic chlorides are used in industry as solvents rather than bromides and iodides.

Ans. Because organic chlorides are more volatile than bromides and iodides.

Iodoform shows antiseptic property.

Ans. Due to liberation of free iodine by iodoform.

The C—Cl bond length in chlorobenzene is shorter than that in $\text{CH}_3\text{—Cl}$.

Ans. Due to partial double bond character of C—Cl bond (due to resonance in $\text{C}_6\text{H}_5\text{—Cl}$), bond length of C—Cl in chlorobenzene is shorter than that in $\text{CH}_3\text{—Cl}$.

Haloarenes are less reactive than haloalkanes towards nucleophilic substitution reactions.

Ans. In haloalkanes, carbon is bonded to more electronegative halogen atom so that the high polarity of this molecule makes it more reactive but carbon atom of haloarenes is sp^2 hybridised so that the electron pair of the C—X bond is more tightly held than sp^3 hybridised carbon in haloalkane.

The dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

Ans. In chlorobenzene, the carbon atom of C—Cl bond is sp^2 hybridised and it has more s-character and more electronegative than sp^3 hybridised carbon of cyclohexyl chloride. Again in chlorobenzene, due to resonance, C—Cl bond acquires some bond character and magnitude of negative charge is less on chlorine atom but in cyclohexyl chloride, there is pure single bond and higher magnitude of negative charge on chlorine atom. Since, dipole moment is a product of charge and distance, the dipole moment of cyclohexyl chloride is higher than chlorobenzene.

Ethyl iodide undergoes $\text{S}_\text{N}2$ reaction faster than ethyl bromide.

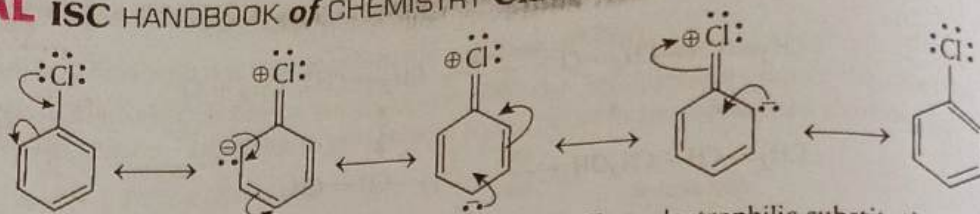
Ans. Iodide is a better leaving group due to large size than bromide. Hence it undergoes $\text{S}_\text{N}2$ reaction faster than ethyl bromide.

p-chlorobenzene has higher melting point than those of *o*- and *m*-isomers.

Ans. Because *p*-isomer has symmetrical structure due to which molecules can easily pack closely in crystal lattice increasing intermolecular forces of attraction.

Although chlorine is an electron withdrawing group but it is ortho and para directing in electrophilic substitution in arenes.

Ans. Chlorobenzene is the resonance hybrid of the following structures.



Since, electron density is maximum at *o*- and *p*-position due to +R effect, electrophilic substitution reactions take place at these positions.

24. Neopentyl chloride $(\text{CH}_3)_3\text{C}-\text{CH}_2\text{Cl}$ does not follow $\text{S}_\text{N}2$ mechanism.

Ans. There is steric hindrance in neo-pentyl chloride, it does not follow $\text{S}_\text{N}2$ mechanism.

25. (i) Chloroform is stored in closed dark brown bottles.

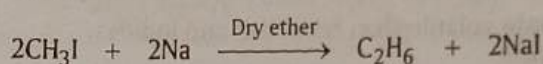
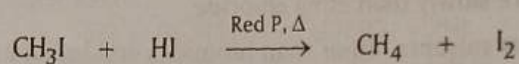
Ans. In presence of sunlight and air, chloroform is oxidised to form poisonous phosgene (COCl_2) gas. In order to prevent this, it is stored in dark brown bottles filled up to the brim.

- (ii) Out of but-1-ene and but-2-ene, which gives same product on reaction with HBr in presence and absence of peroxides?

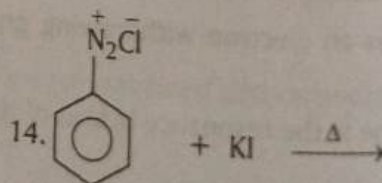
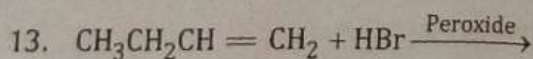
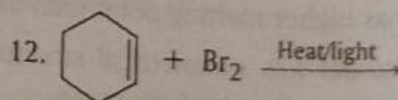
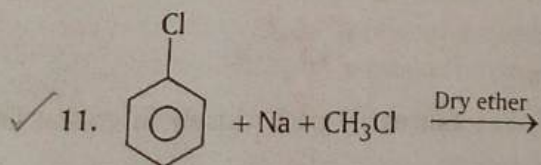
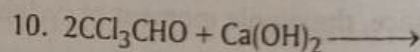
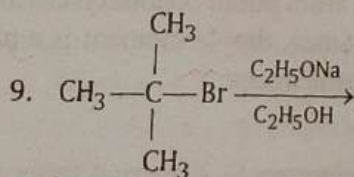
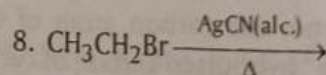
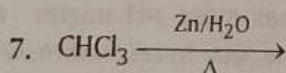
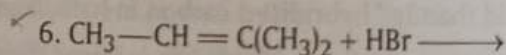
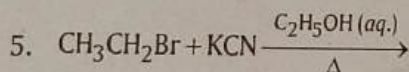
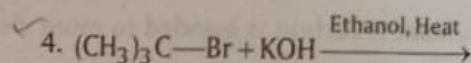
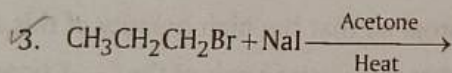
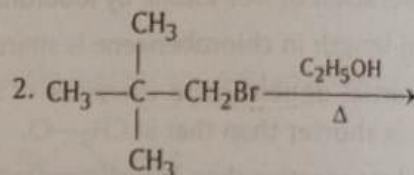
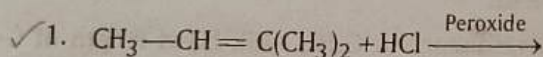
Ans. But-2-ene gives the same product (2-bromobutane) in presence and absence of peroxides because of the symmetrical nature of but-2-ene.

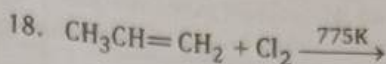
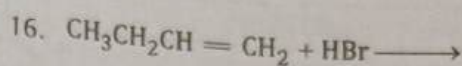
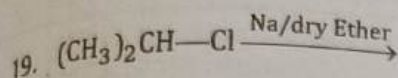
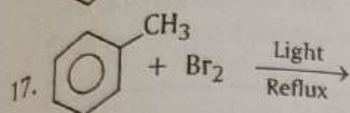
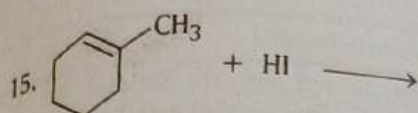
- (iii) Name the alkyl halide which can be used to prepare methane and ethane in single step.

Ans. Methyl iodide (CH_3I).

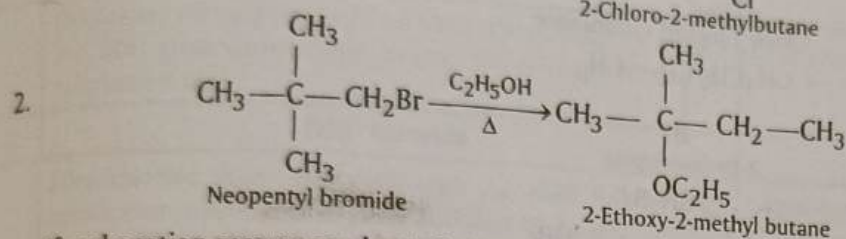
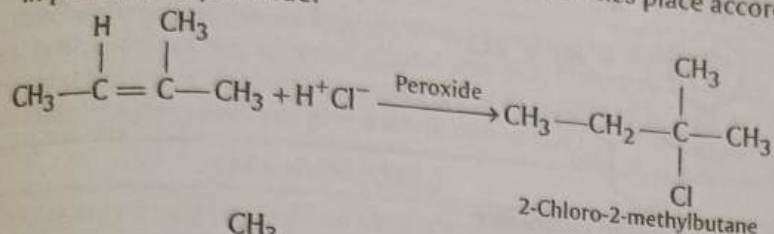


- (iv) Write the products in the following reactions :

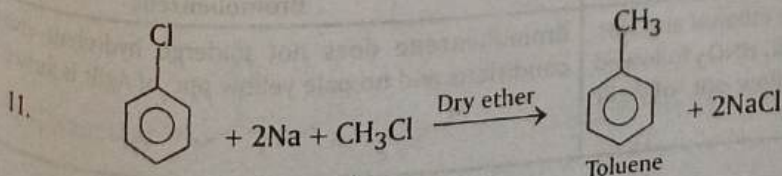
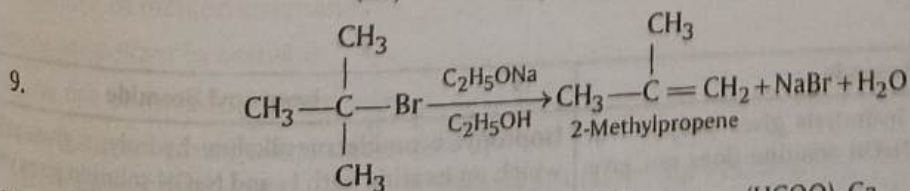
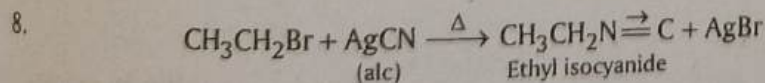
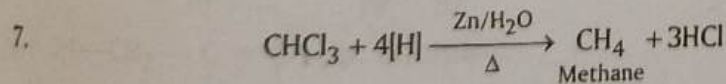
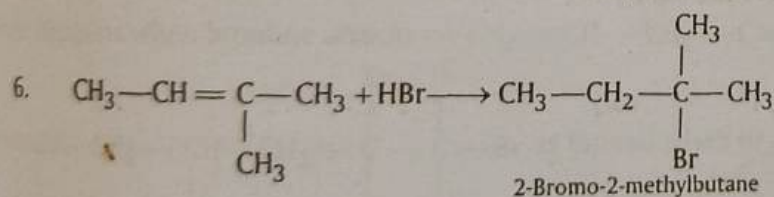
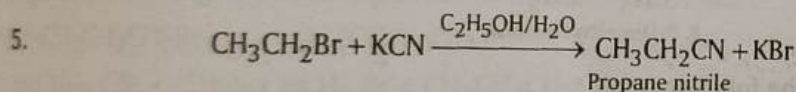
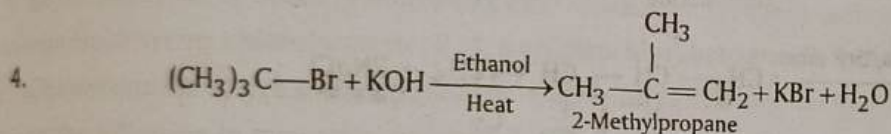
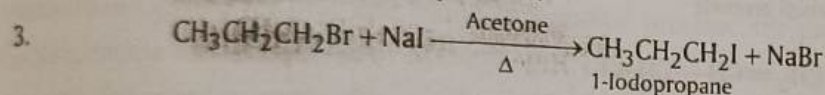


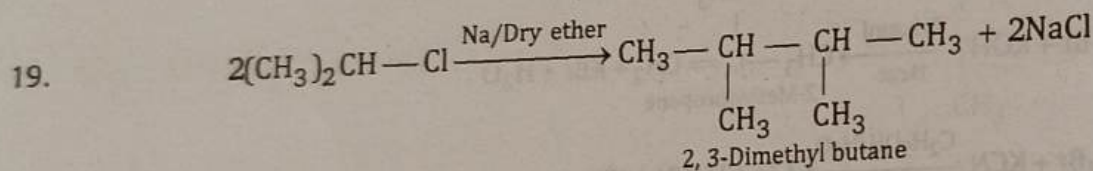
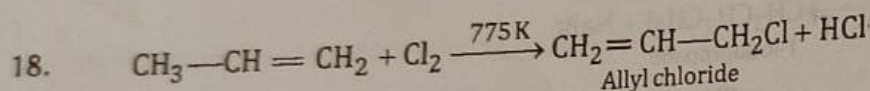
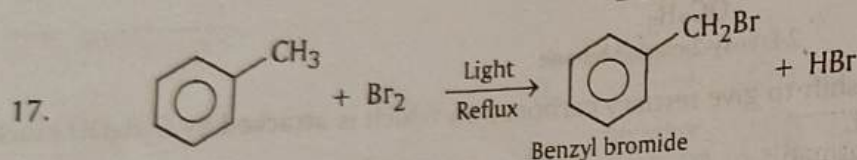
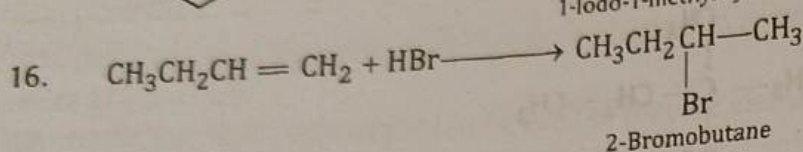
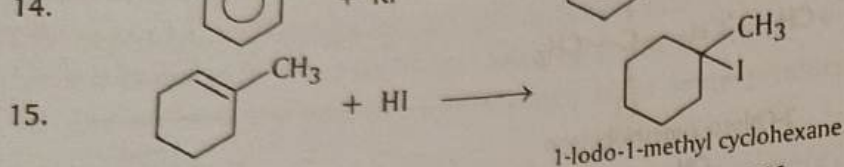
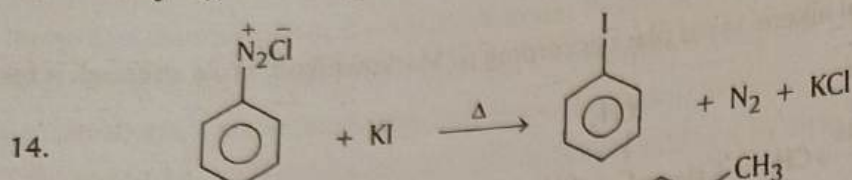
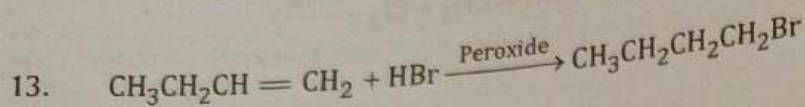
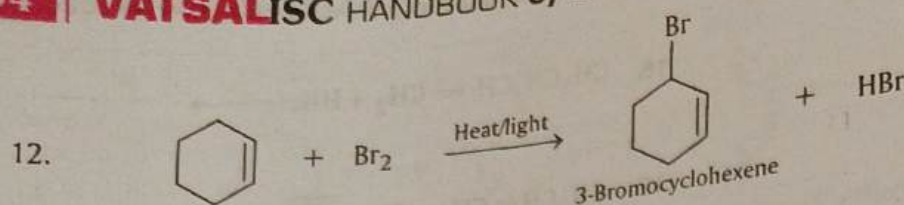


Ans. 1. The addition of HCl to unsymmetrical alkene takes place according to Markownikoff's rule although it takes place in presence of peroxide.



1° carbocation rearranges by 1, 2-alkyl shift to give tertiary carbocation which is attacked by C₂H₅OH (nucleophile) and by losing proton forms the product.





v) Which would undergo S_N1 reaction faster in the following pair?

$\text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ and $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$

Ans $\text{CH}_3\text{CH}(\text{Br})\text{CH}_3$.

i) Give one chemical test to distinguish between :

1. *n*-propyl bromide and isopropyl bromide
2. Ethyl bromide and bromobenzene
3. Chlorobenzene and benzyl chloride
4. Chloroform and iodoform
5. Chlorobenzene and *n*-hexyl chloride
6. Chloroform and carbontetrachloride
7. Ethyl chloride and chlorobenzene

Ans.

1.	<i>n</i> -propyl Bromide	Isopropyl Bromide
	<i>n</i> -propyl bromide on alkaline hydrolysis gives propan-1-ol which on heating with I ₂ and NaOH solution does not give yellow ppt. of iodoform.	Isopropyl bromide on alkaline hydrolysis gives propan-2-ol which on heating with I ₂ and NaOH solution gives yellow ppt. of iodoform.
2.	Ethyl Bromide	Bromobenzene
	Ethyl bromide on heating with aq KOH gives ethanol and KBr. The reaction mixture on acidification with dil. HNO ₃ followed by treatment with AgNO ₃ solution gives yellow ppt. of AgBr which is soluble in conc. ammonia solution.	Bromobenzene does not undergo hydrolysis under these conditions and no pale yellow ppt. of AgBr is formed.

3.	Chlorobenzene (C_6H_5Cl) It does not undergo hydrolysis. Therefore, acidification of the reaction mixture with dil. HNO_3 followed by addition of $AgNO_3$ solution does not produce white ppt. of $AgCl$.	Benzyl Chloride ($C_6H_5CH_2Cl$) It undergoes hydrolysis upon heating with aq. KOH and forms benzyl alcohol and KCl . The reaction mixture on acidification with dil. HNO_3 followed by treatment with $AgNO_3$ solution gives white ppt. of $AgCl$.
4.	Chloroform When chloroform is heated with alcoholic $AgNO_3$, white ppt. of $AgCl$ is not obtained.	Iodoform When iodoform is heated with alcoholic $AgNO_3$, a yellow coloured ppt. of silver iodide is produced.
5.	Chlorobenzene (C_6H_5Cl) Chlorobenzene does not undergo hydrolysis on heating with aq. KOH and does not produce phenol and KCl . Therefore, treatment of the reaction mixture with dil. HNO_3 followed by addition of $AgNO_3$ does not give a white ppt. of $AgCl$.	n-hexyl Chloride ($C_6H_{13}Cl$) n-hexyl chloride on heating with aq. KOH gives n-hexyl alcohol and KCl . The reaction mixture on acidification with dil. HNO_3 followed by treatment with $AgNO_3$ solution gives a white ppt. of $AgCl$.
6.	Chloroform ($CHCl_3$) Chloroform on warming with an alcoholic solution of aniline and KOH gives carbylamine having offensive smell due to carbylamine test.	Carbontetrachloride (CCl_4) Carbontetrachloride does not give carbyl amine test.
7.	Ethyl chloride Ethyl chloride upon hydrolysis with aq. KOH followed by acidification with dil. HNO_3 and addition of $AgNO_3$ solution gives white ppt. of $AgCl$.	Chlorobenzene Chlorobenzene does not respond to this test.

(vii) A hydrocarbon C_5H_{12} gives only one monochlorination product. Identify the hydrocarbon.

Ans Neopentane has all equivalent hydrogens. Therefore it gives only one monochlorination product.

(viii) Arrange the following in order of increasing ease towards nucleophilic substitution.

4-chloronitrobenzene; chlorobenzene; 2, 4, 6-trinitrochlorobenzene; 2, 4-dinitrochlorobenzene

Ans Chlorobenzene < 4-chloronitrobenzene < 2, 4-dinitrochlorobenzene < 2, 4, 6-trinitrochlorobenzene

(ix) Arrange the following in increasing order of their boiling points :

(a) $CH_3CH_2CH_2CH_2Br$ (b) $(CH_3)_3CBr$ (c) $(CH_3)_2CHCH_2Br$

Ans $(CH_3)_3CBr < (CH_3)_2CHCH_2Br < CH_3CH_2CH_2CH_2Br$

(x) What happens when bromine attacks on $CH_2=CH-CH_2-C\equiv CH$?

Ans $Br-CH_2-\underset{\substack{| \\ Br}}{CH}-CH_2-\underset{\substack{| \\ Br}}{C}-\underset{\substack{| \\ Br}}{C}-Br$ is formed when Br_2 is in excess. When only one mole of Br_2 is used, then

$CH_2=CH-CH_2-\underset{\substack{| \\ Br}}{C}=\underset{\substack{| \\ H}}{C}-Br$ is formed.

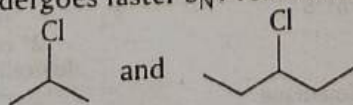
(xi) Give one use of dichloromethane.

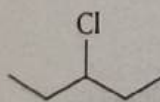
Ans As propellant in aerosols.

(xii) Give one use of tetrachloromethane.

Ans As a solvent for oils, fats and waxes.

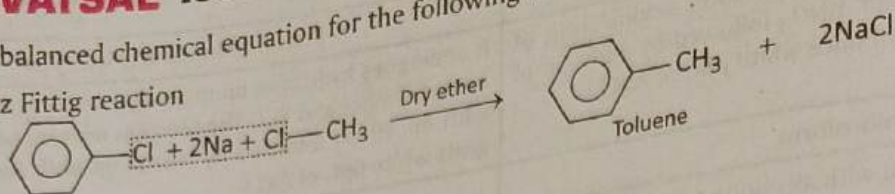
(iii) Which compound in the following pair undergoes faster S_N1 reaction?



Ans Compound  undergoes S_N1 reaction fast as it forms more stable carbocation (3°).

(xiv)

Ans.



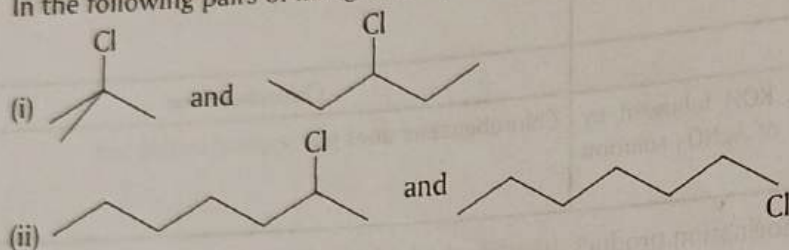
E. Short Answer Questions (2 marks)

- Short Answer Questions (2 marks)**
1. When the alkyl bromides (listed here) were subjected to hydrolysis in a mixture of ethanol and water (80% ethanol, 20% water) at 55°C, the rates of reaction showed the following order :
- $$(CH_3)_3CBr > CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr$$
- fastest The other three halides

Give an explanation for this order of reactivity.

Ans. $(\text{CH}_3)_3\text{CBr}$ reacts by $\text{S}_{\text{N}}1$ mechanism and this reaction takes place faster. The other three halides react by $\text{S}_{\text{N}}2$ mechanism and their reactions are slower because the nucleophile (H_2O) is weak. The reaction rates are affected by steric hindrance.

- ✓2. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reactions?



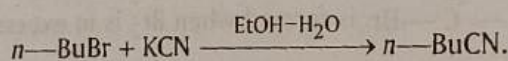
Ans. (i) First compound is 3° alkyl halide and second compound is 2° alkyl halide. S_N1 reaction proceeds through formation of carbocation. 3° alkyl halide reacts faster due to formation of more stable carbocation.

(ii) First compound is 2° alkyl halide whereas second compound is 1° alkyl halide. First compound reacts faster in reaction due to formation of more stable 2° carbocation.

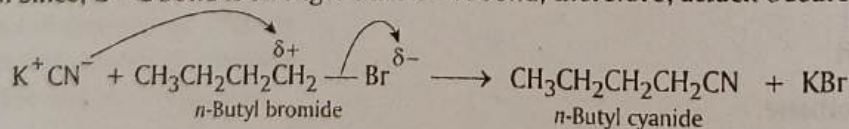
3. Which compound in each of the following pairs will react faster in S_N2 reactions with OH^- ?

Ans. (i) Since, I^- ion is a better leaving group than Br^- ion, therefore, CH_3I reacts faster than CH_3Br in S_N2 reaction.
 OH^- ion and $C-I$ bond is weaker than $C-Br$.
 (ii) Due to less steric hindrance 1° alkyl halides are more reactive than *tert*-alkyl halides in S_N2 reactions. Therefore, CH_3Cl will react at a faster rate than $(CH_3)_3CCl$ in a S_N2 reaction with OH^- ion.

4. Explain the following reaction :

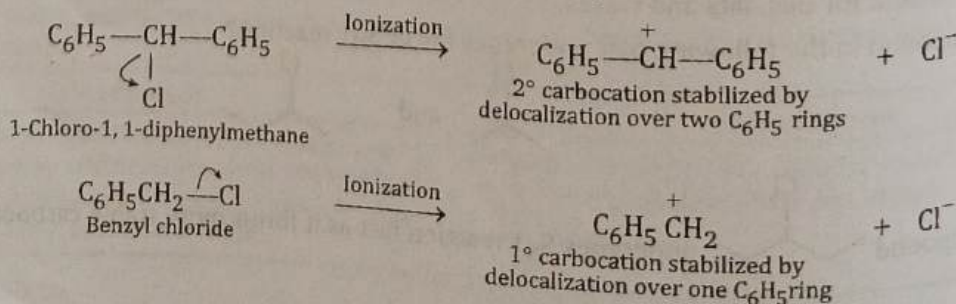


Ans. CN^- ion is an ambident nucleophile. Therefore, it can attack the carbon atom of $\text{C}-\text{Br}$ bond in $n\text{-BuBr}$ through C or N. Since, $\text{C}-\text{C}$ bond is stronger than $\text{C}-\text{N}$ bond, therefore, attack occurs through C to form $n\text{-butyl cyanide}$.



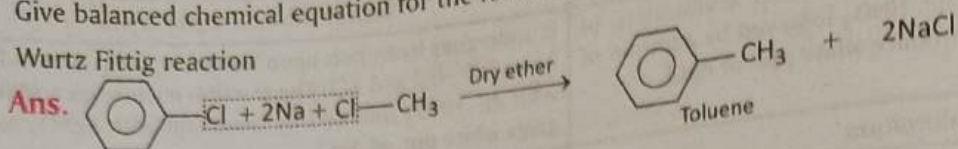
5. Out of $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ and $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ which is more easily hydrolysed by aqueous KOH?

Ans. $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ is a 1° aralkyl halide while $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$ is a 2° aralkyl halide.



(xiv)

Ans.



E. Short Answer Questions (2 marks)

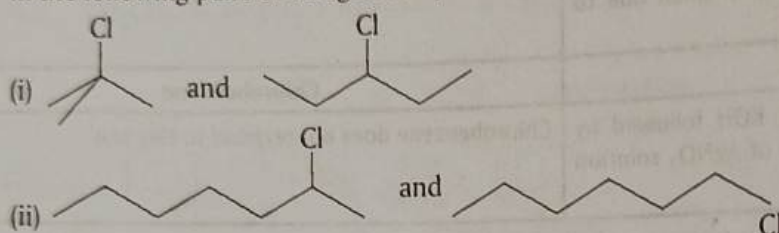
1. When the alkyl bromides (listed here) were subjected to hydrolysis in a mixture of ethanol and water (80% ethanol, 20% water) at 55°C, the rates of reaction showed the following order :

$$(CH_3)_3CBr > CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr$$

1. When the alkyl bromides (listed here) were subjected to hydrolysis (in 20% water) at 55°C, the rates of reaction showed the following order :
 $(\text{CH}_3)_3\text{CBr} > \text{CH}_3\text{Br} > \text{CH}_3\text{CH}_2\text{Br} > (\text{CH}_3)_2\text{CHBr}$

Ans. $(\text{CH}_3)_3\text{CBr}$ reacts by $\text{S}_\text{N}1$ mechanism and this reaction takes place faster. The other three halides react by $\text{S}_\text{N}2$ mechanism and their reactions are slower because the nucleophile (H_2O) is weak. The reaction rates are affected by hindrance.

2. In the following pairs of halogen compounds, which compound undergoes faster S_N1 reactions?

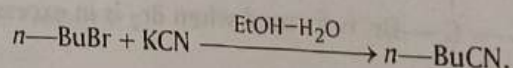


3. Which compound in each of the following pairs will react faster in S_N2 reactions with OH^- ?

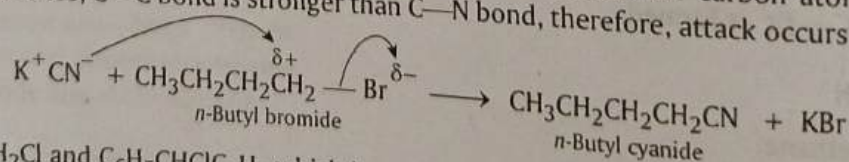
- (i) CH_3Br or CH_3I (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl .

- Ans.** (i) Since, I^- ion is a better leaving group than Br^- ion, therefore, CH_3I reacts faster than CH_3Br in S_N2 reaction. OH^- ion and $C-I$ bond is weaker than $C-Br$.
- (ii) Due to less steric hindrance 1° alkyl halides are more reactive than *tert*-alkyl halides in S_N2 reactions. Therefore, CH_3Cl will react at a faster rate than $(CH_3)_3CCl$ in a S_N2 reaction with OH^- ion.

4. Explain the following reaction :

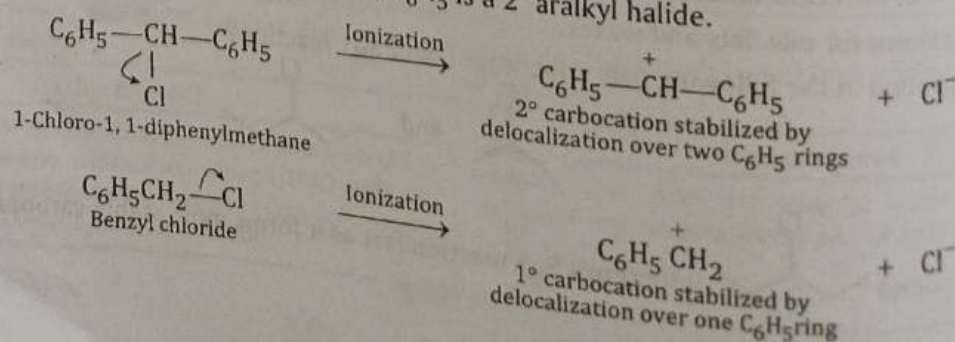


- Ans.** CN^- ion is an ambident nucleophile. Therefore, it can attack the carbon atom of $\text{C}-\text{Br}$ bond in $n\text{-BuBr}$ through C or N. Since, $\text{C}-\text{C}$ bond is stronger than $\text{C}-\text{N}$ bond, therefore, attack occurs through C to form $n\text{-butyl cyanide}$.



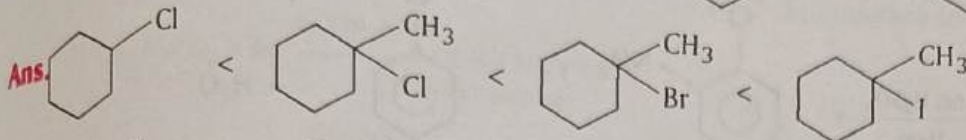
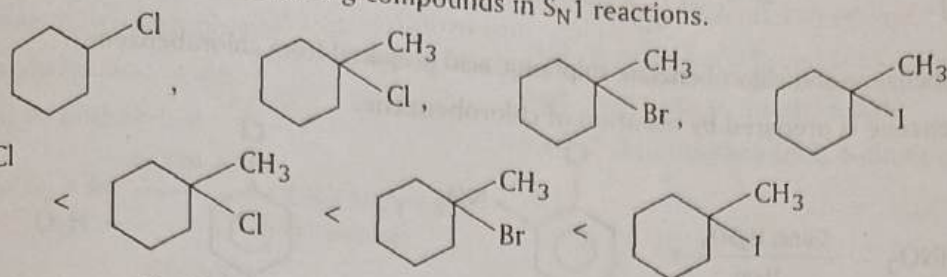
5. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$ which is more easily hydrolysed by aqueous KOH?
Ans. $C_6H_5CH_2Cl$ is a 1° aralkyl halide while $C_6H_5CH(Cl)C_6H_5$ is a 2° aralkyl halide.

- Ans.** $C_6H_5CH_2Cl$ is a 1° aralkyl halide while $C_6H_5CH(Cl)C_6H_5$ is a 2° aralkyl halide.



In S_N1 reactions, reactivity depends upon the stability of carbocations. Since, the carbocation $C_6H_5CH^+C_6H_5$ (where the +ve charge is delocalised over two C_6H_5 rings) is more stable than the carbocation, $C_6H_5CH_2^+$ (where +ve charge is delocalized over one C_6H_5 ring), therefore, $C_6H_5CHClC_6H_5$ gets hydrolysed more easily than $C_6H_5CH_2Cl$ under S_N1 conditions. However, under S_N2 conditions, the reactivity depends on steric hindrance, therefore, under S_N2 conditions, $C_6H_5CH_2Cl$ gets hydrolysed more easily than $C_6H_5CHClC_6H_5$.

6. Predict the order of reactivity of the following compounds in S_N1 reactions.



Because first compound is 2° alkyl halide while all others are 3° alkyl halides. Since, 3° alkyl halides are more reactive than 2° in S_N1 as well as reactivity increases in the order chloride $<$ bromide $<$ iodide.

7. Which one of the following pairs of reaction would you expect to proceed faster? Give reason.

- The S_N2 displacement of 2-bromopropane by $C_2H_5O^-$ ion or CN^- ion.
- Nucleophilic substitution reaction on bromobenzene or benzyl bromide.

Ans. (i) Since, CN^- ion, is stronger nucleophile (–ve charge on less electronegative carbon atom) than $C_2H_5O^-$ ion, the reaction proceeds faster with CN^- ion than $C_2H_5O^-$ ion.

(ii) Due to resonance, $C-Br$ bond in bromobenzene has some double bond character while in benzyl bromide $C-Br$ bond has only single bond character. Therefore, bromobenzene is less reactive than benzyl bromide.

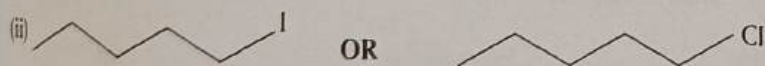
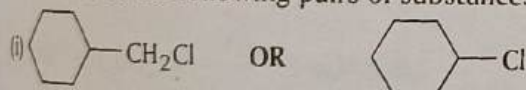
8. Which compound in each of the following pairs will react faster in S_N2 reaction with OH^- ? Why?

- CH_3Br or CH_3I
- $(CH_3)_3CCl$ or CH_3Cl

Ans. (i) CH_3I will react faster as compared to CH_3Br because CH_3I has lower bond dissociation energy and I^- ion is better leaving group. In presence of nucleophile, it will be released at a faster rate.

(ii) CH_3Cl will react faster as compared to $(CH_3)_3CCl$ because 1° halides undergo S_N2 mechanism faster than 3° halides.

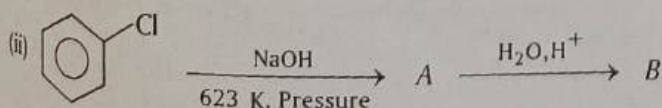
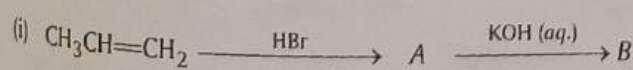
9. Which one in the following pairs of substances undergoes S_N2 reaction faster and why?

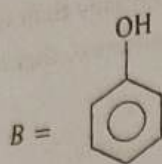
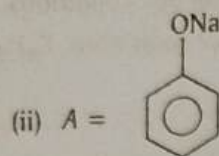
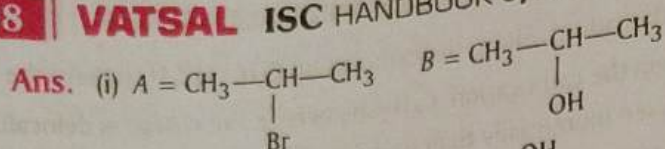


Ans. (i) CH_2Cl , it is primary halide and undergoes S_N2 reaction faster.

(ii) I , as iodide ion is better leaving group because of larger size and undergoes S_N2 reaction faster.

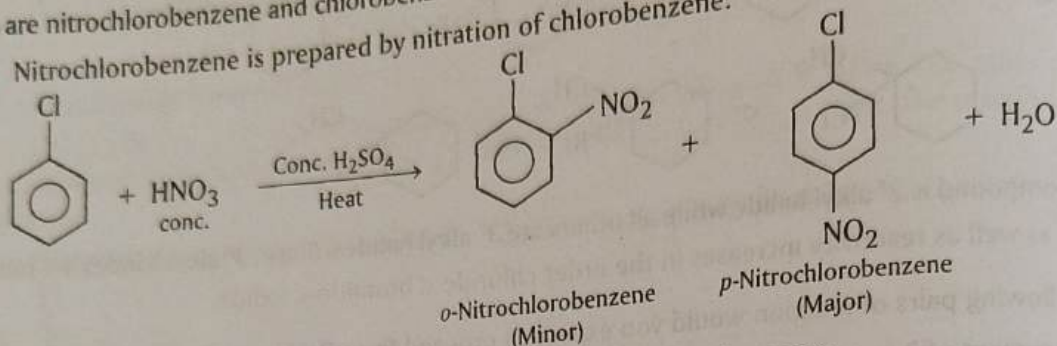
10. Identify A and B :



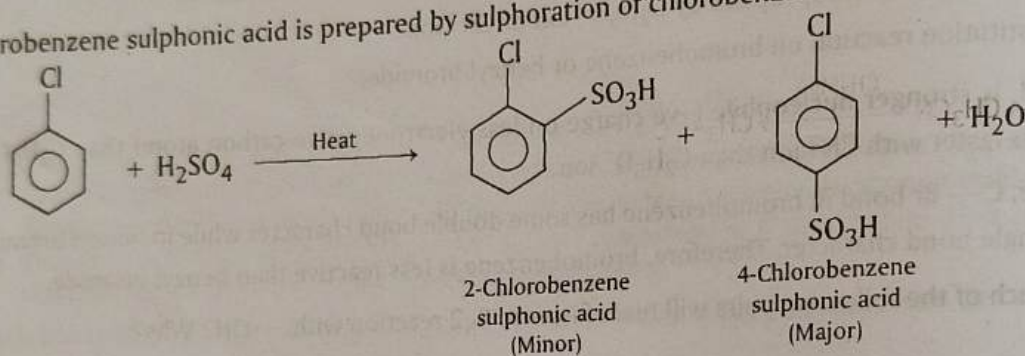


11. How are nitrochlorobenzene and chlorobenzene sulphonic acid prepared from chlorobenzene?

Ans. Nitrochlorobenzene is prepared by nitration of chlorobenzene.

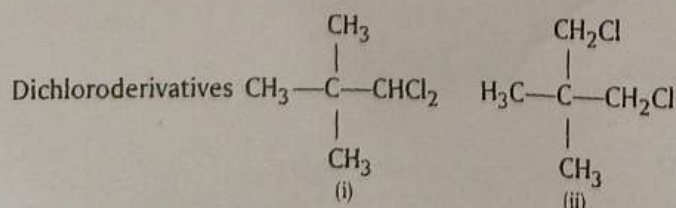
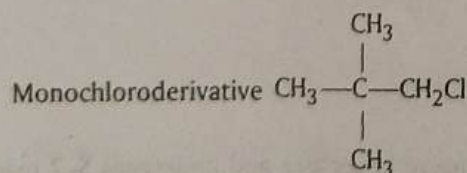
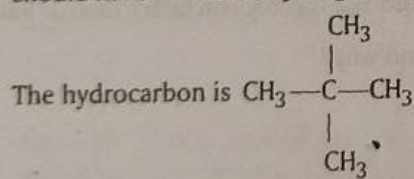


Chlorobenzene sulphonic acid is prepared by sulphuration of chlorobenzene.



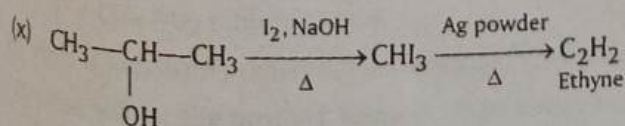
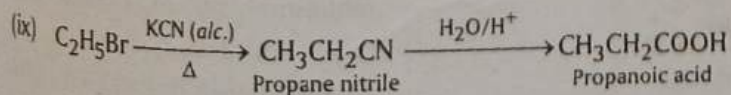
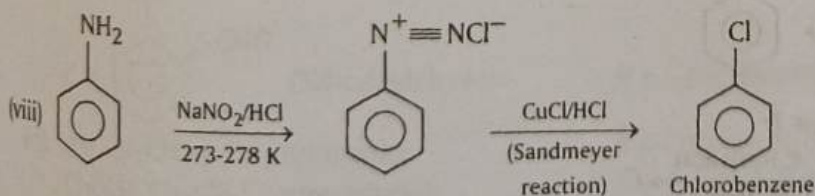
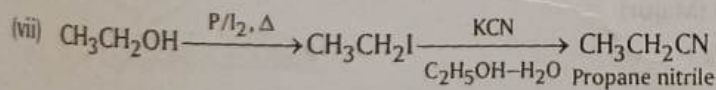
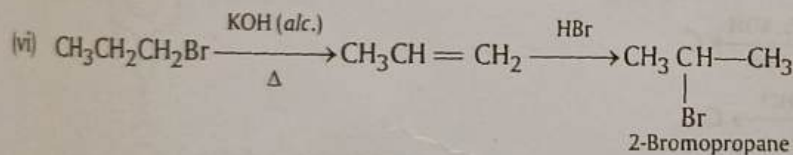
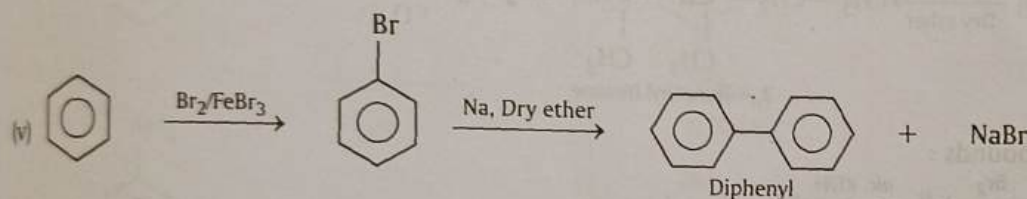
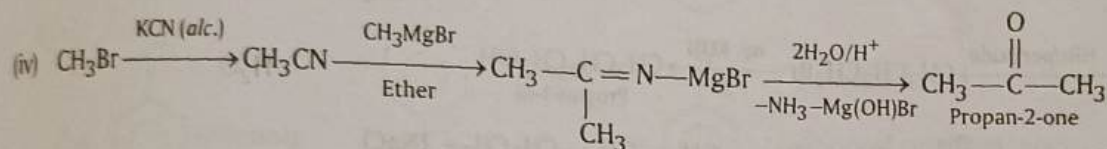
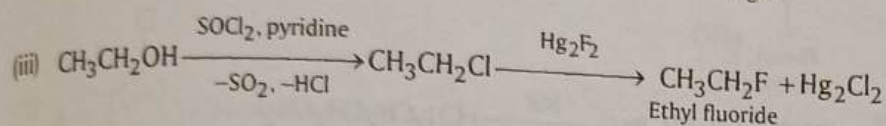
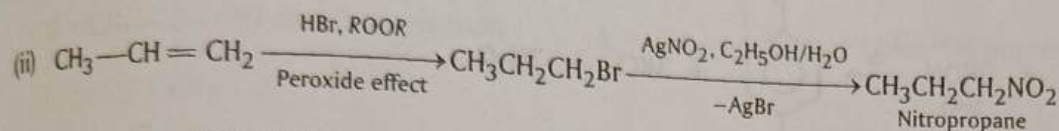
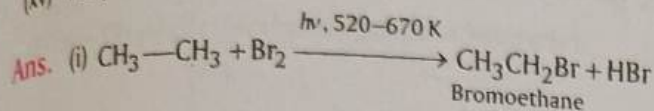
12. A hydrocarbon of molecular mass 72 g mol^{-1} gives a single monochloroderivative and two dichloroderivatives on photochlorination. Give the structure of the hydrocarbon.

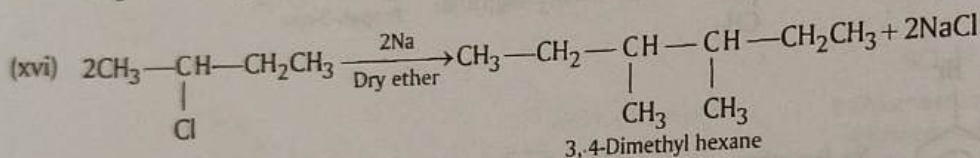
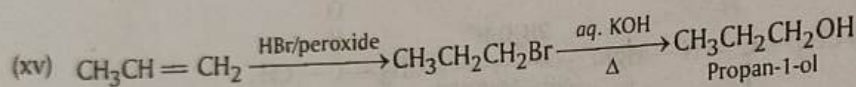
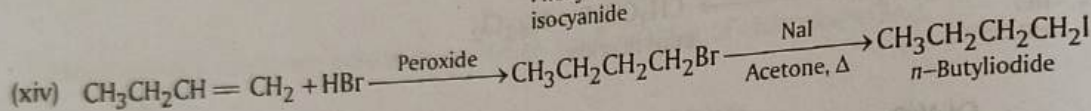
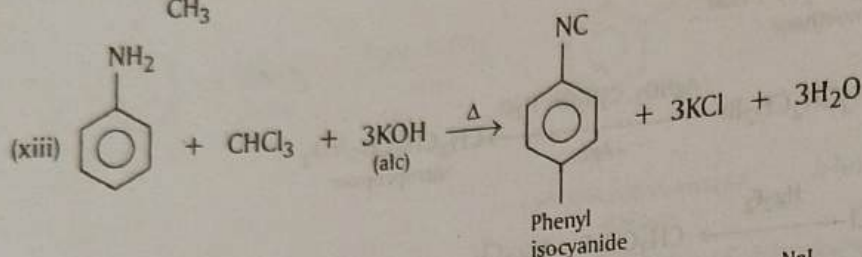
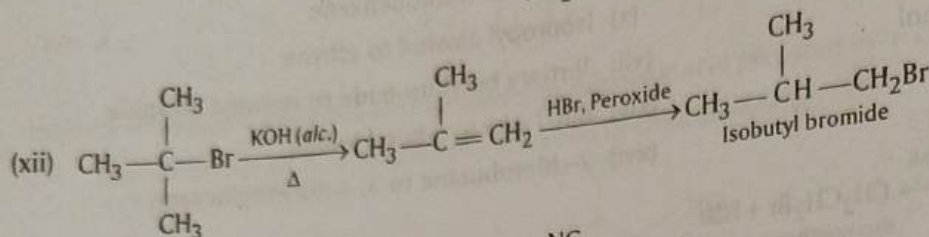
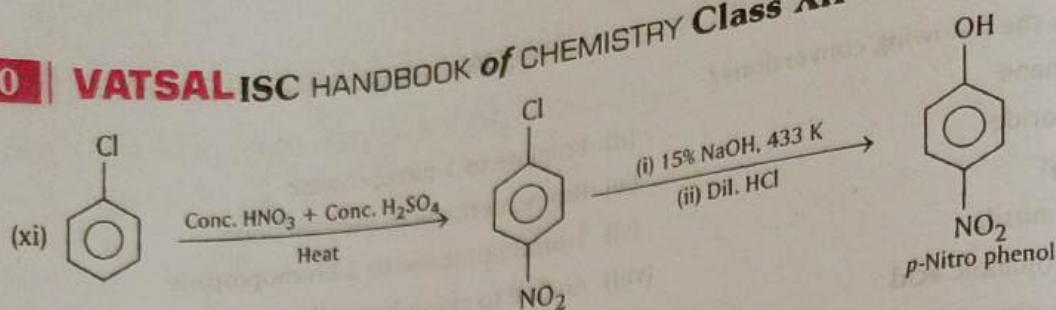
Ans. C_5H_{12} , pentane has molecular mass 72 g mol^{-1} i.e., the isomer of pentane which yields single monochloroderivative should have all the 12 hydrogen equivalent.



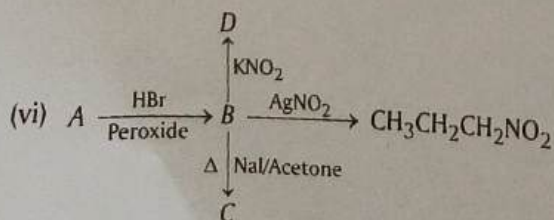
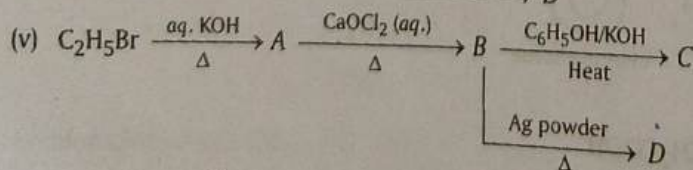
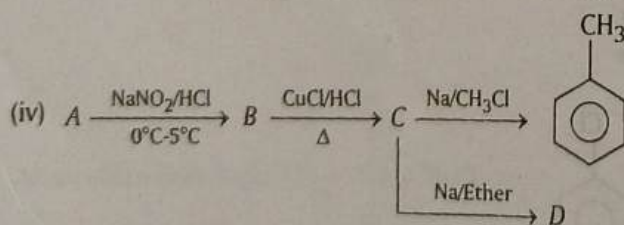
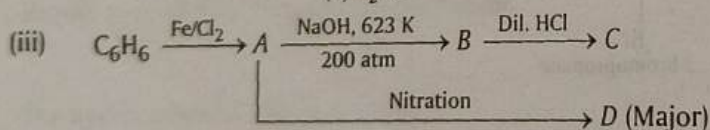
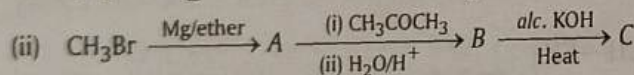
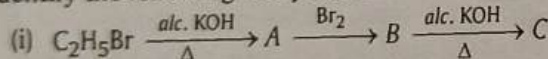
13. How will you bring about the following conversions?

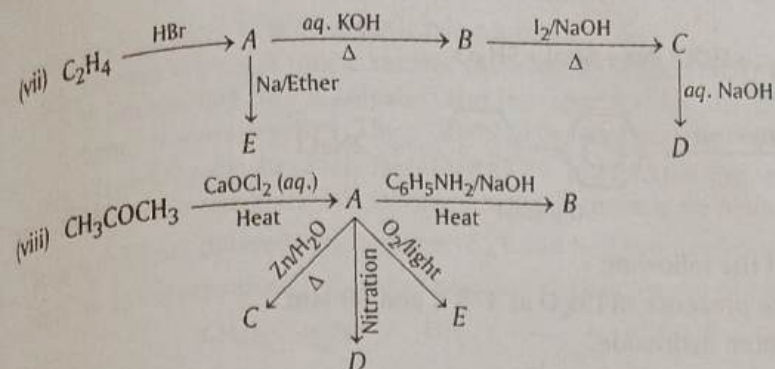
- (i) Ethane to bromoethane
 (ii) Ethanol to ethyl fluoride
 (iii) Benzene to diphenyl
 (iv) Ethanol to propane nitrile
 (v) Ethyl bromide to propanoic acid
 (vi) Chlorobenzene to *p*-nitrophenol
 (vii) Aniline to phenyl isocyanide
 (viii) Prop-1-ene to propan-1-ol
 (ix) Propene to 1-nitropropane
 (x) Bromomethane to propan-2-one
 (xi) 1-bromopropane to 2-bromopropane
 (xii) Aniline to chlorobenzene
 (xiii) Isopropyl alcohol to ethyne
 (xiv) Tertiary butyl bromide to isobutyl bromide
 (xv) But-1-ene to *n*-butyl iodide
 (xvi) 2-chlorobutane to 3, 4-dimethylhexane





✓ 14. Identify the following compounds :



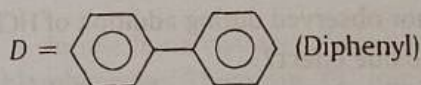
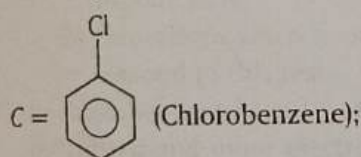
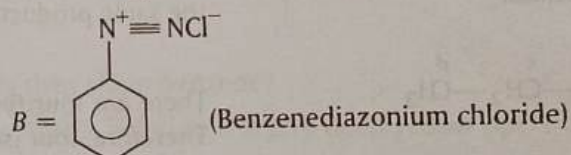
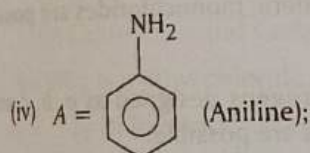
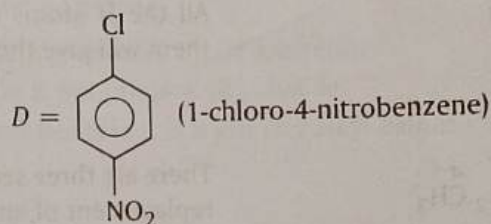
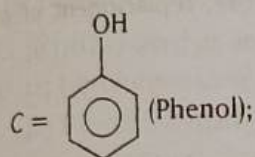
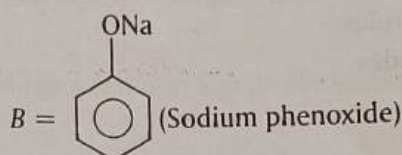
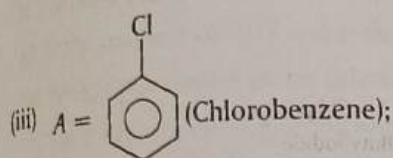
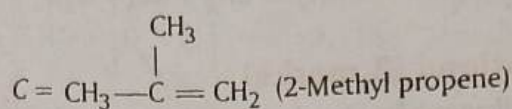
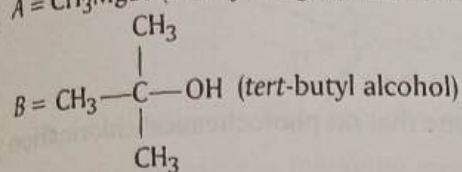


Ans. (i) $A = C_2H_4$ (Ethene);

(ii) $A = CH_3MgBr$ (Methyl magnesium bromide);

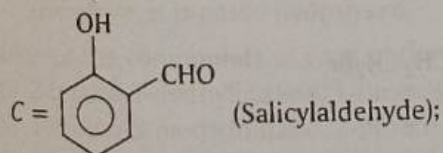
$B = C_2H_4Br_2$ (1, 2-Dibromoethane);

$C = C_2H_2$ (Ethyne)



(v) $A = C_2H_5OH$ (Ethanol);

$B = CHCl_3$ (Chloroform);



$D = C_2H_2$ (Ethyne)

(vi) $A = CH_3CH=CH_2$ (Propene);

$B = CH_3CH_2CH_2Br$ (Bromopropane)

$C = CH_3CH_2CH_2I$ (Iodopropane);

$D = CH_3CH_2CH_2ONO$ (Propyl nitrite)

(vii) $A = C_2H_5Br$ (Ethyl bromide);

$C = CHI_3$ (Iodoform);

$B = C_2H_5OH$ (Ethanol)

$D = HCOONa$ (Sodium formate);

$E = C_4H_{10}$ (Butane)

(viii) $A = CHCl_3$ (Chloroform);

$B = C_6H_5NC$ (Phenyl isocyanide);

$C = CH_4$ (Methane);

$D = CCl_3NO_2$ (Chloropicrin);

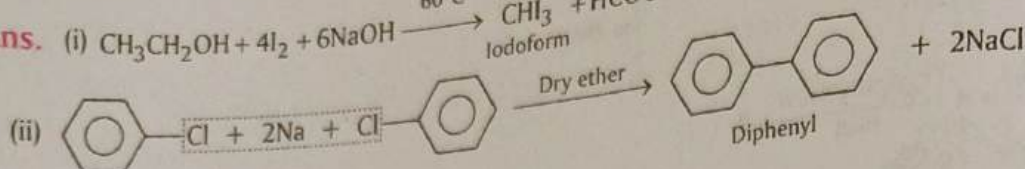
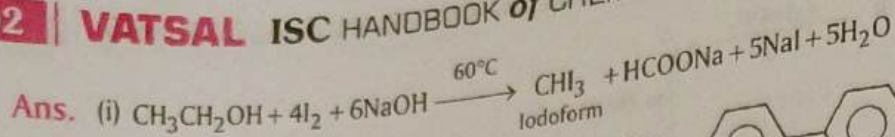
$E = COCl_2$ (Phosgene)

15. (i) How is iodoform prepared from ethanol? Give balanced equation.

(2015)

(ii) What will be the product formed when chlorobenzene is heated with sodium metal in the presence of dry ether?

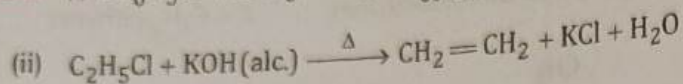
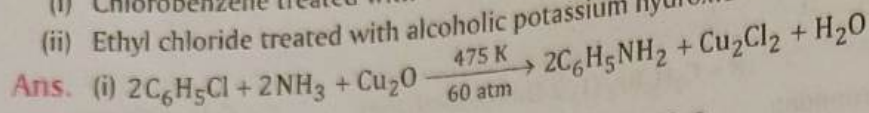
(2015)



16. Write the balanced chemical equation for each of the following :

(i) Chlorobenzene treated with ammonia in the presence of Cu_2O at 475 K and 60 atm.

(ii) Ethyl chloride treated with alcoholic potassium hydroxide.



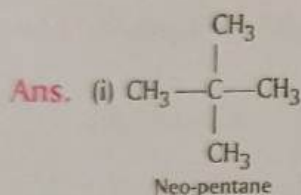
Short Answer Questions (3 marks)

1. Among the isomeric alkanes of molecular formula C_5H_{12} , identify the one that on photochemical chlorination yields

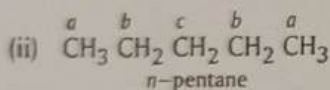
(i) a single monochloride.

(ii) three isomeric monochlorides.

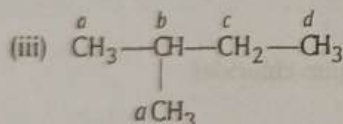
(iii) four isomeric monochlorides.



All the H atoms are equivalent. Therefore, replacement of any one of them will give the same product.



There are three sets of equivalent hydrogens designated as a, b and c. The replacement of any one of the equivalent hydrogens of each set will give the same product. Therefore, three isomeric monochlorides are possible.



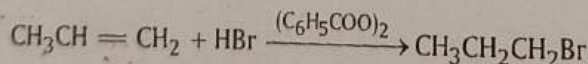
There are four types of equivalent hydrogens designated as a, b, c and d. Therefore, four isomeric monochlorides are possible.

2. (i) What is peroxide effect? Illustrate with an example.

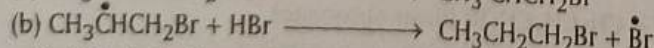
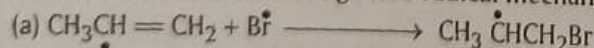
(ii) Why is peroxide effect not observed during addition of HCl to alkenes?

(iii) Will but-2-ene show peroxide effect?

Ans. (i) In presence of peroxide, the negative end of HBr to unsymmetrical alkenes takes place at that carbon which has greater number of hydrogen atoms. For example,



(ii) Peroxide effect occurs through free radical mechanism i.e.,



with HBr, both these steps are exothermic therefore it is observed with HBr but with HCl, step (a) is exothermic but step (b) is endothermic. Therefore, peroxide effect is not observed with HCl or HI.

(iii) Since, But-2-ene is symmetrical and peroxide effect is observed in unsymmetrical alkene. Therefore, peroxide effect is not observed with But-2-ene.

3. Which reagent in each pair will react faster with hydroxide ion?

(i) CH_3Br or CH_3I

(ii) $\text{CH}_3\text{CH}_2\text{I}$ in ethanol or $(\text{CH}_3)_2\text{S}=\text{O}$ (DMSO)

(iii) $\text{H}_2\text{C}=\text{CHBr}$ or $\text{H}_2\text{C}=\text{CHCH}_2\text{Br}$

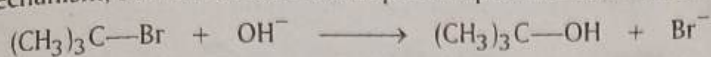
Ans. (i) CH_3I , since I^- is a better leaving group.

(ii) Ethanol is a polar protic solvent (hydroxylic) while DMSO is a polar aprotic (i.e., non-hydroxylic) solvent, therefore in ethanol OH^- ion is solvated and less reactive. On the other hand, OH^- ion is a naked nucleophile in DMSO and hence is more reactive. Thus, $\text{CH}_3\text{CH}_2\text{I}$ reacts faster in DMSO than in $\text{CH}_3\text{CH}_2\text{OH}$.

(iii) $\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$ reacts faster with OH^- ion and undergoes substitution reaction because allyl carbocation is more resonance stabilised but in vinyl bromide, there is no resonance and is less reactive.

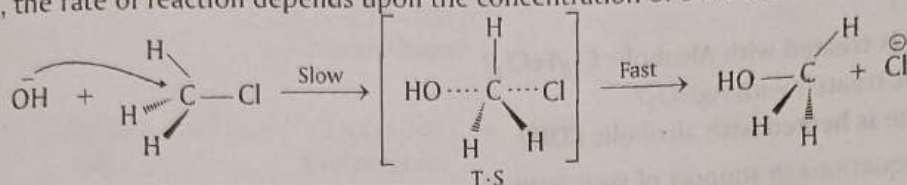
How would you differentiate between $\text{S}_\text{N}1$ and $\text{S}_\text{N}2$ mechanism of substitution reaction? Give one example of each.

Ans. In $\text{S}_\text{N}1$ mechanism, the rate of reaction depends upon the concentration of only one reactant i.e., *tert*-butyl bromide.



It involves the formation of more stable carbocation intermediate inversion as well as retention of configuration.

In $\text{S}_\text{N}2$ mechanism, the rate of reaction depends upon the concentration of both the reactants.



It involves the formation of transition state and inversion of configuration.

(i) State one use of DDT and iodoform.

(ii) Which compound in the following couples will react faster in $\text{S}_\text{N}2$ displacement and why?

(a) 1-Bromopentane or 2-Bromopentane.

(b) 1-Bromo-2-methyl butane or 2-Bromo-2-methyl butane.

Ans. (i) DDT is used as an insecticide and iodoform is used as a mild antiseptic.

(ii) (a) 1-Bromopentane will react faster because it is a primary alkyl halide.

(b) 1-Bromo-2-methyl butane will react faster because it is a primary alkyl halide.

6. (i) Write a chemical test to distinguish between :

(a) Chlorobenzene and iodoform.

(b) Chloroform and Carbon tetrachloride.

(ii) Why is methyl chloride hydrolysed more easily than chlorobenzene?

Ans. (i) (a) Iodoform when heated with alcoholic AgNO_3 solution will give deep yellow ppt. but chlorobenzene will not respond to it.

(b) Chloroform when heated with 1° amine and KOH gives offensive smelling isocyanide while CCl_4 does not respond to this test.

(ii) In chlorobenzene, due to $+R$ effect, there is double bond character between C and Cl. Again carbon atom is sp^2 hybridised and more electronegative in chlorobenzene. Therefore, Cl^- ion is not easily replaced. But in methyl chloride there is no resonance and carbon atom is sp^3 hybridised and there is single bond between C and Cl atom. Therefore, it is easily hydrolysed.

7. Rearrange the compounds of each of the following sets in order of reactivity towards $\text{S}_\text{N}2$ displacement :

(i) 2-bromo-2-methylbutane, 1-bromopentane, 2-bromopentane.

(ii) 1-bromo-3-methylbutane, 2-bromo-2-methylbutane, 3-bromo-2-methylbutane.

(iii) 1-bromobutane, 1-bromo-2-methylpropane, 1-bromo-2-methylbutane, 1-bromo-3-methylbutane.

Ans. (i) $\text{S}_\text{N}2$ reactions depend upon steric hindrance. More is steric hindrance, slower the rate of reaction, so order of reactivity is $1^\circ > 2^\circ > 3^\circ$.

\therefore 1-bromopentane > 2-bromopentane > 2-bromo-2-methyl butane.

(ii) 1-bromo-3-methylbutane > 3-bromo-2-methylbutane > 2-bromo-2-methylbutane.

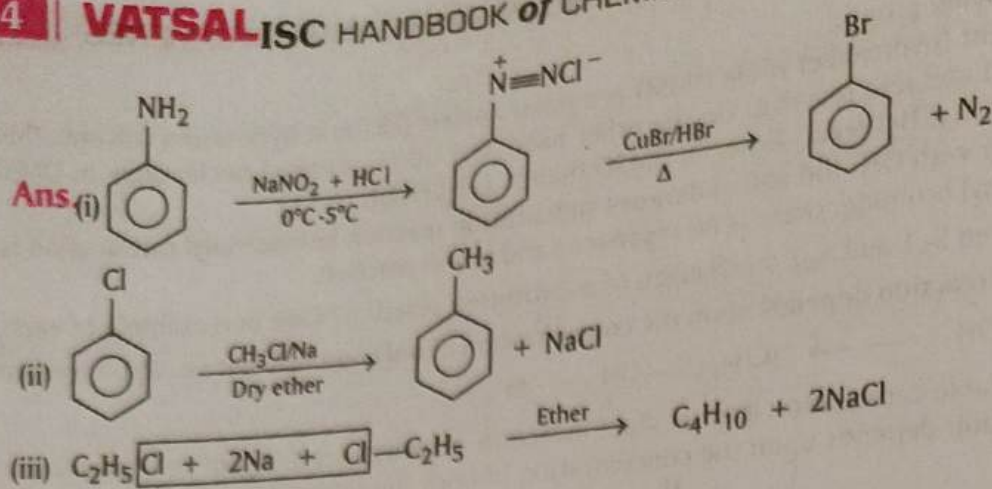
(iii) 1-bromobutane > 1-bromo-3-methylbutane > 1-bromo-2-methylbutane > 1-bromo-2-methylpropane.

8. How can the following conversions be carried out :

(i) Aniline to bromobenzene.

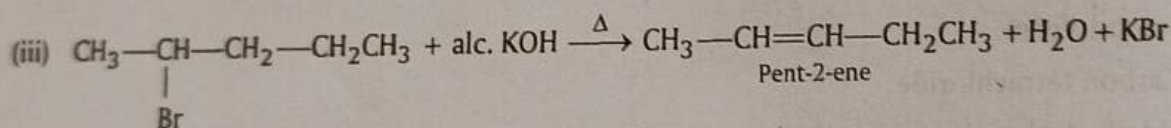
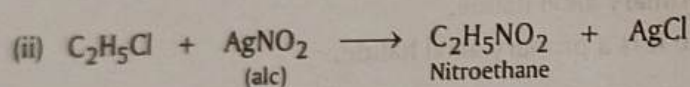
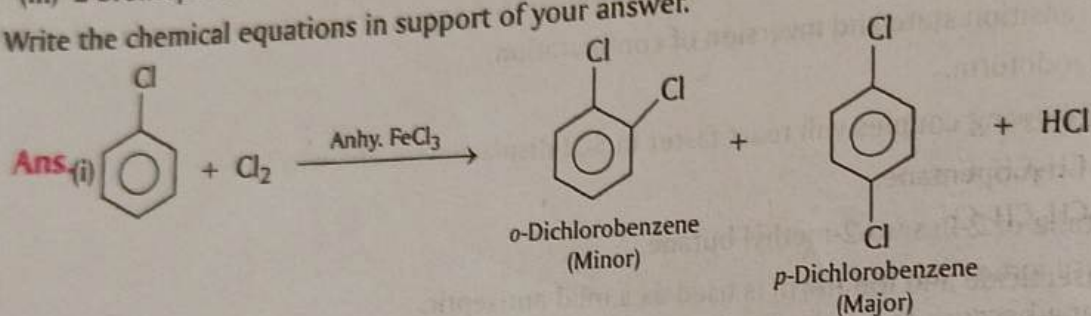
(ii) Chlorobenzene to toluene

(iii) Chloroethane to butane.



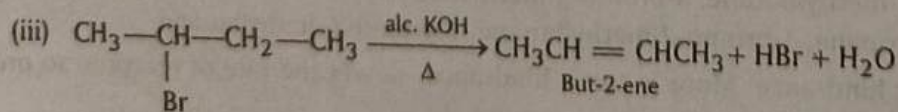
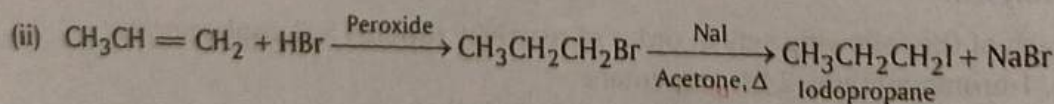
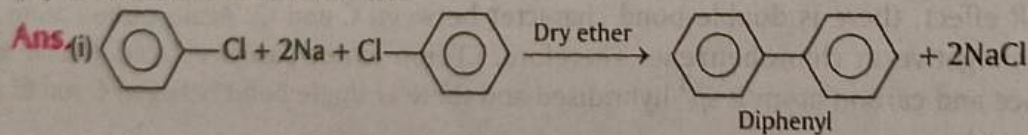
9. What happens when :
- chlorobenzene is treated with Alcoholic Cl2/FeCl3?
 - ethyl chloride is treated with AgNO2?
 - 2-bromopentane is heated with alcoholic KOH?

Write the chemical equations in support of your answer.

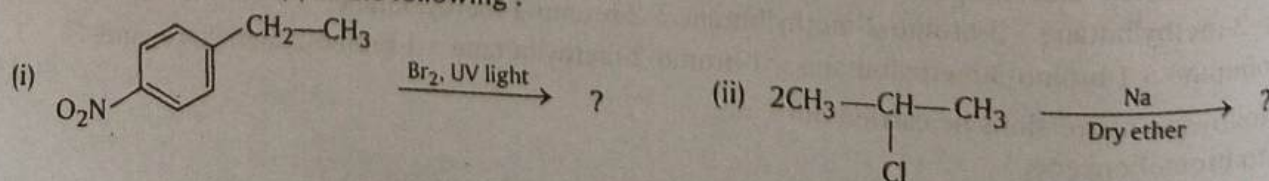


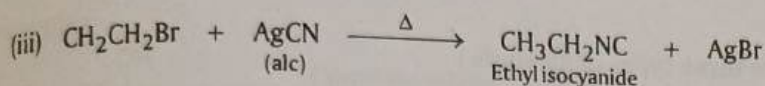
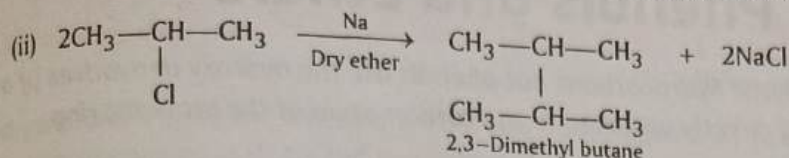
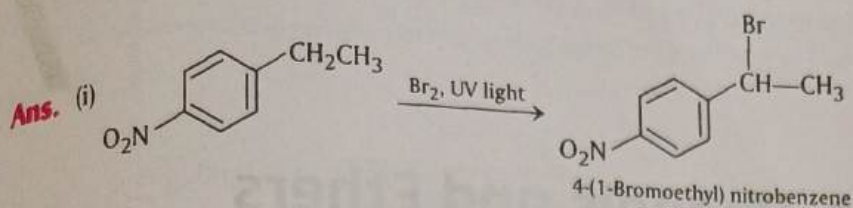
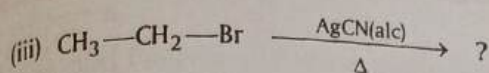
10. How do you convert?

- Chlorobenzene to diphenyl
- Propene to 1-iodopropane
- 2-Bromobutane to But-2-ene



11. Write the major product(s) in the following :





12. Which alkyl halides would you expect to react more rapidly by an $\text{S}_\text{N}2$ mechanism?

Explain your answer.

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$
- (ii) $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{Cl}$ or $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$
- (iii) $\text{C}_6\text{H}_5\text{Br}$ or $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$

Ans. (i) 1-Iodobutane because iodide ion is a better leaving group than chloride ion.

(ii) 1-chloro-3-methyl butane because the carbon bearing the leaving group is less hindered than in 1-chloro-2-methyl butane.

(iii) 1-chlorohexane because it is a primary halide, phenyl halides are unreactive in $\text{S}_\text{N}2$ reactions.

13. How will you convert the following :

- (i) Chlorobenzene to diphenyl
- (ii) Propene to 1-bromopropane
- (iii) Chlorobenzene to aniline.

(2020)

