Chapter 10- Halo Alkanes and Halo arenes

LEVEL-1 QUESTIONS

1. **Out of PCl5 and SOCl2 which one is better reagent for conversion of alcohol to alkylchloride. Why?**

Answer: $SOCl_2$ .Because all the biproducts are in gaseous state except alkyl halide

$ROH + SOCl_2 \rightarrow R\text{-}Cl + SO_2 \uparrow HCl\uparrow$

2. **Why Con HI is not preferred in the preparation of alkyl iodide from alcohol?**

Answer: Con HI is strong reducing agent a part of alkyl iodide formed is reduced to alkaline hence it is not prepared in the preparation of alkyl halides

$R\text{-}OH + \text{Con } HI \rightarrow RI + H_2O$

$RI + HI \rightarrow RH + I_2$

3. **Haloalkanes undergo nucleuphilic substitution. Why?**

Answer: The C-X bond in the haloalkane is polar in nature due to the high electronegativity of the halogen atom and partial positive charge on carbon the nucleouphilic can attack on the electron deficient carbon

4. **Haloarenes are less reactive than haloalkane towards Nucleophilic substitution reaction. Why?**

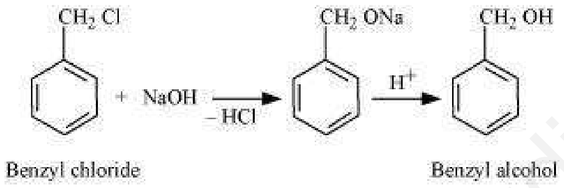
Answer: Haloarenes are less reactive than haloalkane towards nuclophilic substitution because

i. Double bond character of C-X bond in haloarenes due to resonance

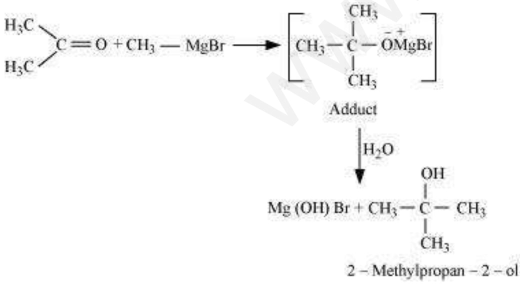
ii. Due to sp2 hybridisation

5. **How will you convert**

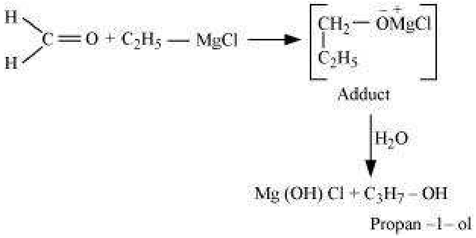
i. Benzyl chloride to benzyl alcohol



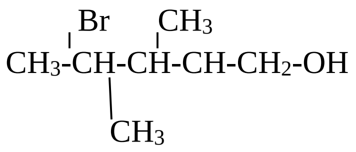
ii**. Methyl magnesium bromide to 2-methylpropan-2-ol**



6. **How will you convert ethylmagnesium chloride to propan-1-ol**



7. Write the structure of 4-bromo-2, 3-dimethylpentan-1-ol?



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}H-\overset{\overset{CH_3}{|}}{C}H-CH-CH_2-OH$$

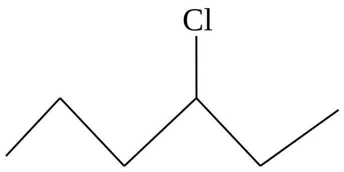
8. Complete the reaction

CH_3-CH_2-CH=CH_2 + HBr in presence ofH^+→ CH_3CH2CH(Br)=CH_2

9.**Explain why alkyl halides, though polar, are immiscible with water?**

Ans.: because they are unable to form H-bonds with H_2O molecules.

1.



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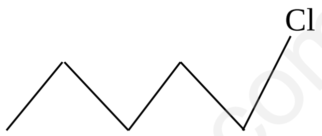
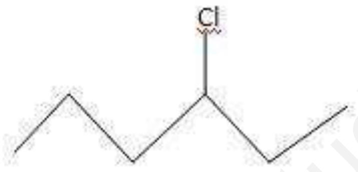


10. Which one of the above undergo S_N1 substitution reaction faster and why?

Ans.:

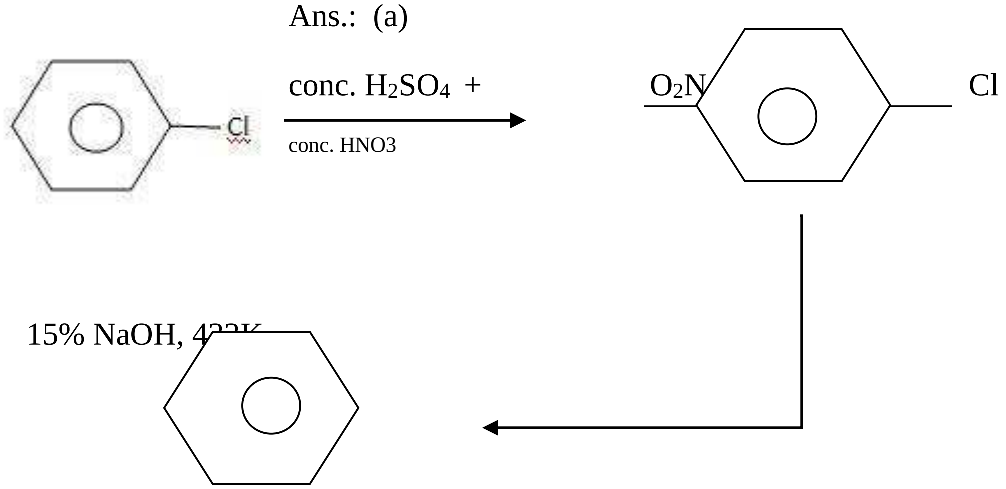


2^o halide reacts faster than 1^0 halide because of the greater stability of secondary carbocation than primary.

11. Convert

(a) Chlorobenzene to *p*-nitrophenol
(b) Aniline to phenylisocyannide

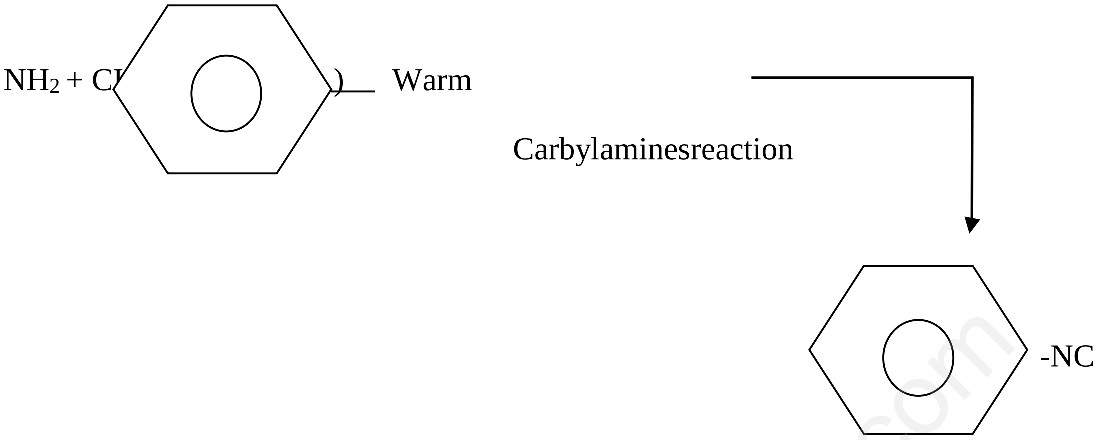
Ans.: (a)



O_2N —— OH ——

Dil. HCl

(b)



12. Write the name reaction

(a) Finkelstein reaction
(b) Dow's process

Ans.: (a) $R - X + NaI \xrightarrow{\text{Dry acetone}} R - I + NaX$ [X = Cl, Br]

(b) In the Dow process the chlorobenzene reacts with the sodium hydroxide at high temperature

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + 2NaOH \xrightarrow[\text{High Pressure}]{300^oC} C_6H_5ONa + NaCl + H_2O$$

sodium phenoxide on treatment with mineral acid yields phenol.

$$2C_6H_5ONa + H_2SO_4 \longrightarrow 2C_6H_5OH + Na_2SO_4$$

13.Distinguish between Chloro cyclo hexane & Chloro benzene

Ans.: chloro cyclo hexane will give white ppt. with $AgNO_3$. Whereas chloro benzene does not give white ppt. with $AgNO_3$.

14.Arrange each in set of compounds in the order of increasing boiling points.
(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.
(ii) 1 – chloropropane, Isopropyl chloride, 1- chlorobutane.
Ans.: (i) Boiling point increases with increase in molecular mass.

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii) Isopropyl chloride < 1 – chloropropane < 1- chlorobutane.

Isopropyl chloride being branched has lower B. P. than 1 – chloropropane.

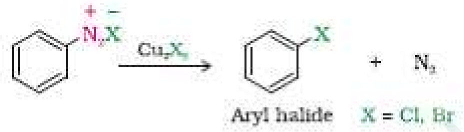
15.i) Why are haloarenes less reactive than haloalkanes towards nucleophilic substitution reactions .
ii)Halo alkane react with KCN form alkyl cyanides as amain product while AgCN forms isocyanides as the chief product. Explain.

Answer(i) haloarenes less reactive than haloalkanes towards nucleophilic substitution reactions because haloalkane shows different resonating structures and it has SP2 hybridised carbon.
(ii) 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.

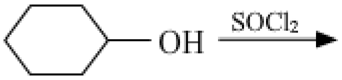
16.Explain the following name reactions.
i)Swarts reaction
ii)Wurtz reaction
iii)Sandmayers reaction

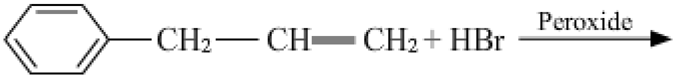
Answer(i) $H_3C{-}Br + AgF \longrightarrow H_3C{-}F + AgBr$

(ii) 

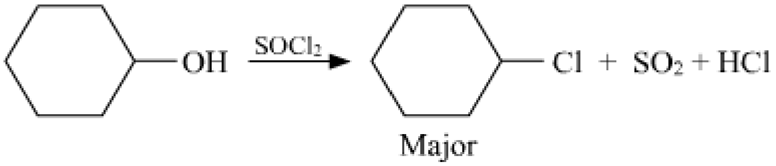
(iii) 

17.Draw the structure of major monohalo product in each of the following reactions :

(i) 

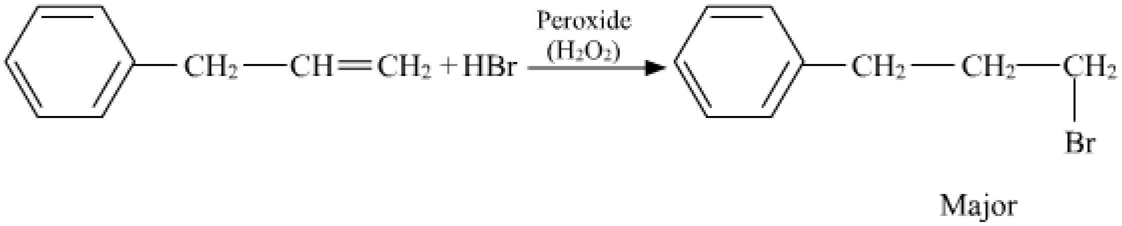
(ii) 

Solution:



(i)

(ii) Addition in presence of peroxide yields product according to anti-Markovnikov rule of addition.



18. (a)Write the formula of main product formed in the following chemical reactions.

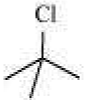
(i) $(CH_3)_2CH\text{-}Cl + Na \xrightarrow{\text{Dry ether}}$

(ii) $CH_3Br + AgF \xrightarrow{\Delta}$

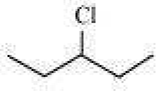
(iii) $CH_3CH_2Br + NaI \xrightarrow{\text{Dry acetone}}$

(b)In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)



and



(ii)

and

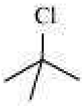
Answer:

(a)(i) $(CH_3)_2CH\text{-}Cl + Na \xrightarrow{\text{Dry ether}} (CH_3)_2CH\text{-}CH(CH_3)_2 + NaCl$

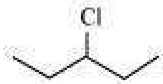
(ii) $CH_3Br + AgF \xrightarrow{\Delta} CH_3F + AgBr$

(iii) $CH_3CH_2Br + NaI \xrightarrow{\text{Dry acetone}} CH_3CH_2I + NaBr$

(b) (i)



2 – Chloro – 2 – methylpropane (3°)
(I)



3 – chloropentane (2°)
(II)

S_N1 reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2°. Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of S_N1 reaction. Since 3° carbocation is more stable than 2° carbocation. (I), i.e. 2−chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

(ii)


2 – chloroheptane (2°)
(I)


1 – chlorohexane (1°)
(II)

The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2−chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

LEVEL-2 QUESTIONS

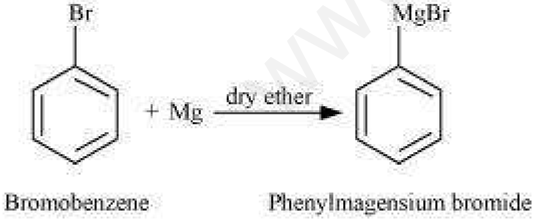
1. What happens when
(i) n-butyl chloride is treated with alcoholic KOH,
(ii) bromobenzene is treated with Mg in the presence of dry ether,
(iii) chlorobenzene is subjected to hydrolysis,
(iv) ethyl chloride is treated with aqueous KOH,
(v) methyl bromide is treated with sodium in the presence of dry ether,

Answer :

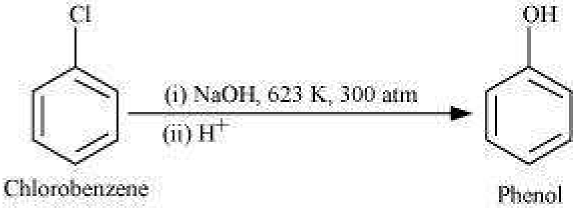
(i) When n−butyl chloride is treated with alcoholic KOH, the formation of but−l−ene takes place. This reaction is a dehydrohalogenation reaction.

$$\underset{n-\text{Butyl chloride}}{CH_3-CH_2-CH_2-CH_2-Cl} \xrightarrow[\text{(Dehydrohalogenation)}]{\text{KOH(alc)}/\Delta} \underset{\text{But-l-ene}}{CH_3-CH_2-CH=CH_2} + KCl + H_2O$$

(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.



(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.

$$CH_3-CH_2-Cl \xrightarrow[\text{(Hydrolysis)}]{KOH_{(aq)}} CH_3-CH_2-OH + KCl$$

Ethyl chloride Ethanol

(v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.

$$2\,CH_3-Br + 2\,Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} CH_3-CH_3 + 2NaBr$$

Methyl bromide Ethane

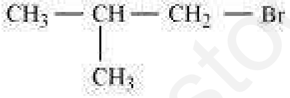
2. Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b).Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

Answer :

There are two primary alkyl halides having the formula, C_4H_9Br. They are *n* − bulyl bromide and isobutyl bromide.

$CH_3-CH_2-CH_2-CH_2-Br$

n – Butyl bromide



$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2-Br$

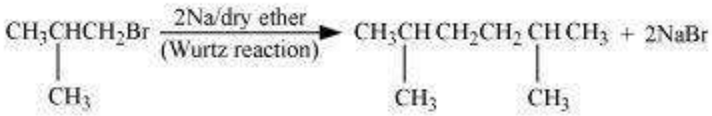
Isobutyl bromide

Therefore, compound (a) is either *n*−butyl bromide or isobutyl bromide.

Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, C_8H_{18}, which is different from the compound formed when *n*−butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

$$2CH_3CH_2CH_2CH_2Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3 + 2NaBr$$

n – Butyl bromide *n* – Octane



$$CH_3\underset{\underset{CH_3}{|}}{C}HCH_2Br \xrightarrow[\text{(Wurtz reaction)}]{\text{2Na/dry ether}} CH_3\underset{\underset{CH_3}{|}}{C}H\,CH_2CH_2\,\underset{\underset{CH_3}{|}}{C}H\,CH_3 + 2NaBr$$

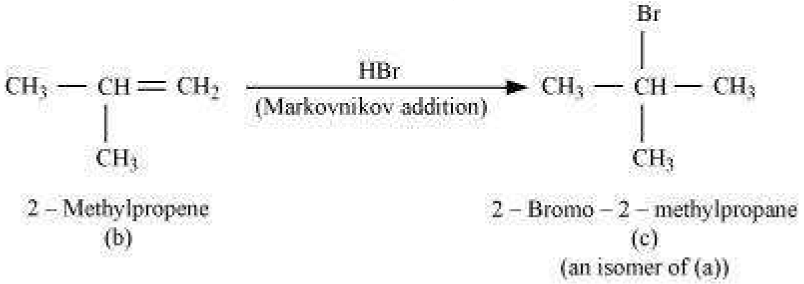
Isobutyl bromide
(a)

2, 5 – Dimethylhexane
(d)

Thus, compound (d) is 2, 5−dimethylhexane.

It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2−methylpropene.

Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2−bromo−2−methylpropane.



3. (a) How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) 1-Bromopropane to 2-bromopropane

(b) Explain why

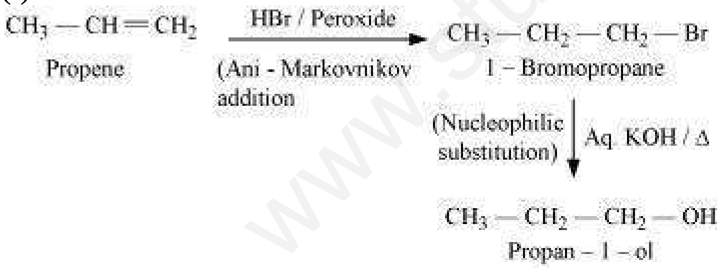
(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

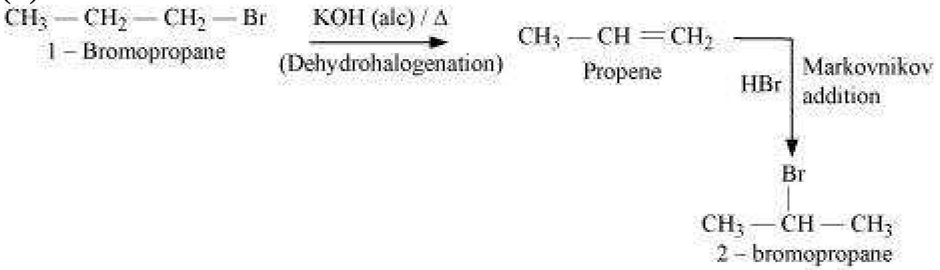
(iii) Grignard reagents should be prepared under anhydrous conditions?

Answer :

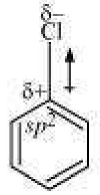
(i)



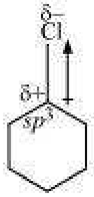
(ii)



(b) (i)



Chlorobenzene



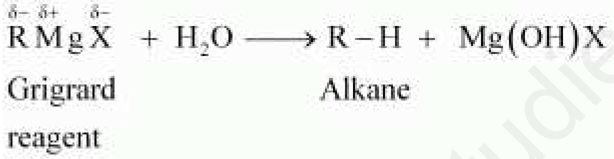
Cyclohexyl chloride

In chlorobenzene, the Cl-atom is linked to a sp^2 hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a sp^3 hybridized carbon atom. Now, sp^2 hybridized carbon has more s-character than sp^3 hybridized carbon atom. Therefore, the former is more electronegative than the latter. Therefore, the density of electrons of C−Cl bond near the Cl-atom is less in chlorobenzene than in cydohexyl chloride.

Moreover, the −R effect of the benzene ring of chlorobenzene decreases the electron density of the C−Cl bond near the Cl-atom. As a result, the polarity of the C−Cl bond in chlorobenzene decreases. Hence, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(ii) To be miscible with water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water.

(iii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes.

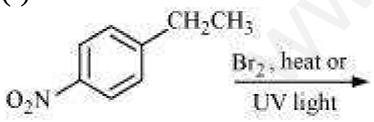


$$\underset{\text{Grigrard reagent}}{\overset{\delta-}{R}\overset{\delta+}{Mg}\overset{\delta-}{X}} + H_2O \longrightarrow \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

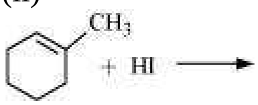
Therefore, Grignard reagents should be prepared under anhydrous conditions.

4. (a)Draw the structures of major monohalo products in each of the following reactions:

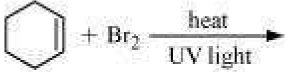
(i)



(ii)



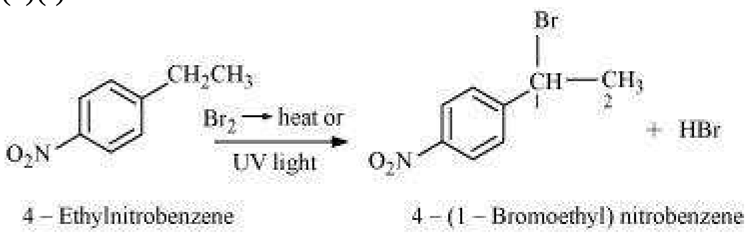
(iii)



(b)Predict the order of reactivity of the four isomeric bromobutanes in S_N1 and S_N2 reactions.

Answer :

(a)(i)



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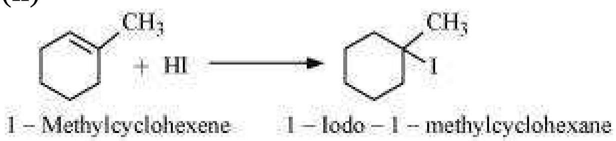
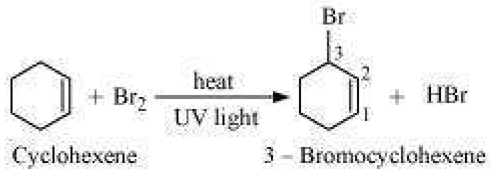


(iii)



(b) $CH_3CH_2CH_2CH_2Br < (CH_3)_2CHCH_2Br < CH_3CH_2CH(Br)CH_3 < (CH_3)_3CBr(S_N1)$
$CH_3CH_2CH_2CH_2Br > (CH_3)_2CHCH_2Br > CH_3CH_2CH(Br)CH_3 > (CH_3)_3CBr(S_N2)$

Of the two primary bromides, the carbocation intermediate derived from$(CH_3)_2CHCH_2Br$ is more stable than derived from $CH_3CH_2CH_2CH_2B$ because of greater electron donating inductive effect of $(CH_3)_2CH$- group. Therefore, $(CH_3)_2CHCH_2Br$ is more reactive than $CH_3CH_2CH_2CH_2Br$ in S_N1 reactions.
$CH_3CH_2CH(Br)CH_3$ is a secondary bromide and $(CH_3)_3CBr$ is a tertiary bromide. Hence the above order is followed in S_N1. The reactivity in S_N2 reactions follows the reverse order as the steric hinderance around the electrophilic carbon increases in that order.

LEVEL- 3 QUESTIONS

Q1. How many dichloro-substitution products are possible for isobutene? Give their structures and IUPAC names.

Q2. Although benzene is highly unsaturated, it does not undergo addition reaction. Explain

Q3. Explain why the central carbon-carbon bond in 1,3-butadienne is shorter than than that in butane.

Q4. Identify the compound ‘A’ from the following information:

(i) Molecular formula of ‘A’ is C_5H_8.
(ii) ‘A’ reacts with only one mole of H2 in the presence of catalyst to form a saturated compound.
(iii) ‘A’ on ozonolysis forms a compound forms a compound,$OHC\text{-}CH_2.CH_2.CH_2\text{-}CHO$.

Q5. Two cyclic dienes A and B have molecular formula C_6H_8. The mixture of the two on reductive ozonolysis gave the following products:
Succinaldehyde, Propane-1,3-dial and glyoxal. Mixture of A and B on hydrogenation produces only cyclohexane. Suggest the structre of A and B.

Q6. Bring out the conversion:

(i) Carbon and hydrogen to toluene
(ii) Calcium carbideto oxalic acid.

7. Primary alkyl halide C_4H_9Br (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.

8. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

9. Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

10. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane

(ii) 2-Chloro-2-methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.