(iv)

$$CH_3CH_2-ONa + CH_3-Br \longrightarrow CH_3CH_2-O-CH_3 + NaBr$$

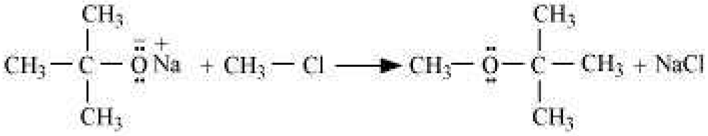
Sodium ethoxide Bromomethane 1-Methoxyethane

Question 11.25:

Illustrate with examples the limitations of Williamson synthesis for the preparation of certain types of ethers.

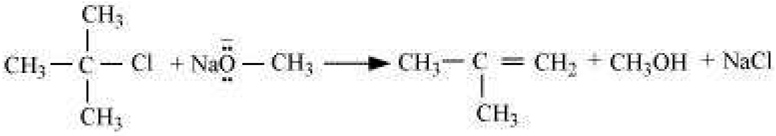
Answer

The reaction of Williamson synthesis involves S_N2 attack of an alkoxide ion on a primary alkyl halide.



$$(CH_3)_3C-\ddot{\underset{..}{O}}^{-}\overset{+}{Na} + CH_3-Cl \longrightarrow CH_3-\ddot{\underset{..}{O}}-C(CH_3)_3 + NaCl$$

But if secondary or tertiary alkyl halides are taken in place of primary alkyl halides, then elimination would compete over substitution. As a result, alkenes would be produced. This is because alkoxides are nucleophiles as well as strong bases. Hence, they react with alkyl halides, which results in an elimination reaction.



$$(CH_3)_3C-Cl + Na\ddot{\underset{..}{O}}-CH_3 \longrightarrow CH_3-\underset{CH_3}{C}=CH_2 + CH_3OH + NaCl$$

Tertiary alkyl halide Alkene

Question 11.26:

How is 1-propoxypropane synthesised from propan-1-ol? Write mechanism of this reaction.

Answer

1-propoxypropane can be synthesized from propan-1-ol by dehydration.

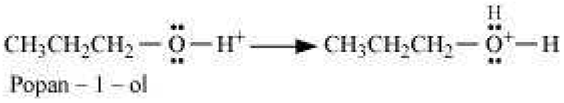
Propan-1-ol undergoes dehydration in the presence of protic acids (such as H_2SO_4, H_3PO_4) to give 1-propoxypropane.

$$2CH_3CH_2CH_2-OH \xrightarrow{H^+} CH_3CH_2CH_2-O-CH_2CH_2CH_3$$

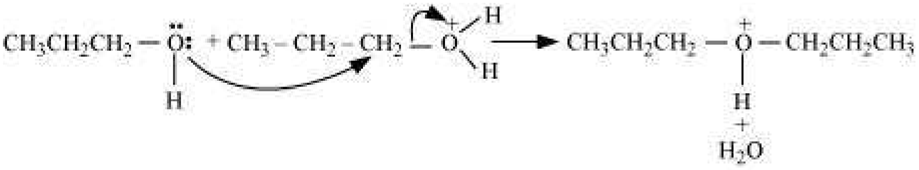
Propane-1-ol 1-Propoxypropane

The mechanism of this reaction involves the following three steps:

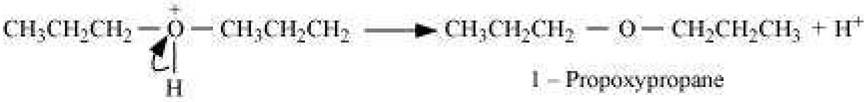
Step 1: Protonation



Step 2: Nucleophilic attack



Step 3: Deprotonation



Question 11.27:

Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

Answer

The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed.

Question 11.28:

Write the equation of the reaction of hydrogen iodide with:

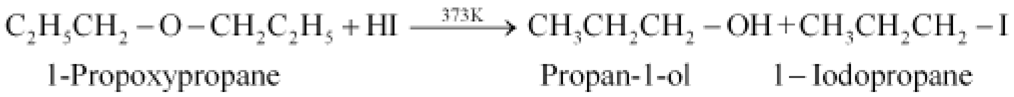
(i) 1-propoxypropane

(ii) Methoxybenzene and

(iii) Benzyl ethyl ether

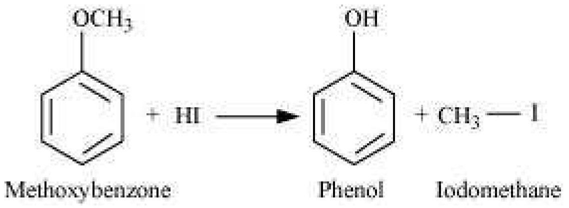
Answer

(i)

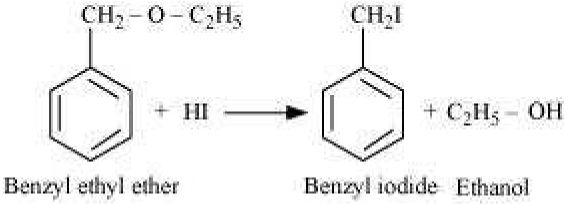


$$\underset{\text{1-Propoxypropane}}{C_2H_5CH_2-O-CH_2C_2H_5} + HI \xrightarrow{373K} \underset{\text{Propan-1-ol}}{CH_3CH_2CH_2-OH} + \underset{\text{1-Iodopropane}}{CH_3CH_2CH_2-I}$$

(ii)



(iii)



Question 11.29:

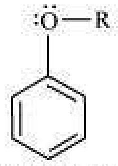
Explain the fact that in aryl alkyl ethers

(i) The alkoxy group activates the benzene ring towards electrophilic substitution and

(ii) It directs the incoming substituents to ortho and para positions in benzene ring.

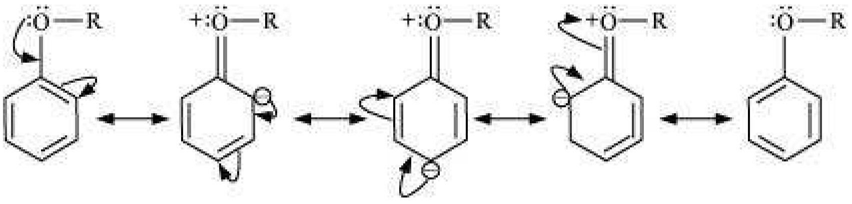
Answer

(i)



Aryl alkyl ether

In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.



Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene ring.

Question 11.30:

Write the mechanism of the reaction of HI with methoxymethane.

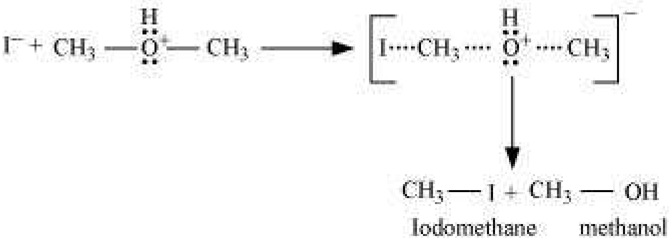
Answer

The mechanism of the reaction of HI with methoxymethane involves the following steps:

Step1: Protonation of methoxymethane:

$$CH_3-\ddot{O}-CH_3 + H-I \rightleftharpoons CH_3-\overset{H}{O^+}-CH_3 + I^-$$

Step2: Nucleophilic attack of I^-:



$$I^- + CH_3-\overset{H}{O^+}-CH_3 \longrightarrow \left[I\cdots CH_3\cdots \overset{H}{O^+}\cdots CH_3\right]^- \longrightarrow \underset{\text{Iodomethane}}{CH_3-I} + \underset{\text{methanol}}{CH_3-OH}$$

Step3:

When HI is in excess and the reaction is carried out at a high temperature, the methanol formed in the second step reacts with another HI molecule and gets converted to methyl iodide

$$CH_3-\ddot{O}-H + H-I \rightleftharpoons CH_3-\overset{H}{O^+}H + I^-$$

$$I^- + CH_3-\overset{+}{O}H_2 \longrightarrow CH_3-I + H_2O$$

Question 11.31:

Write equations of the following reactions:

(i) Friedel-Crafts reaction−alkylation of anisole.

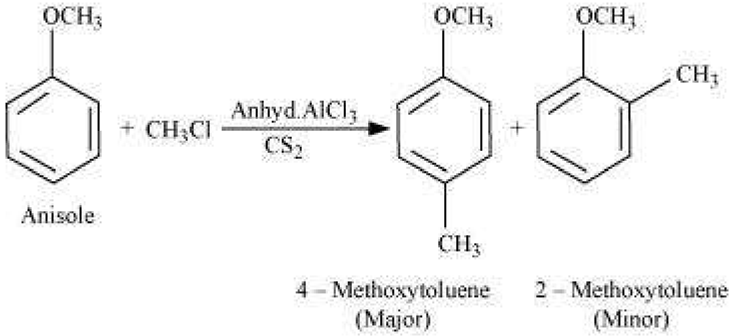
(ii) Nitration of anisole.

(iii) Bromination of anisole in ethanoic acid medium.

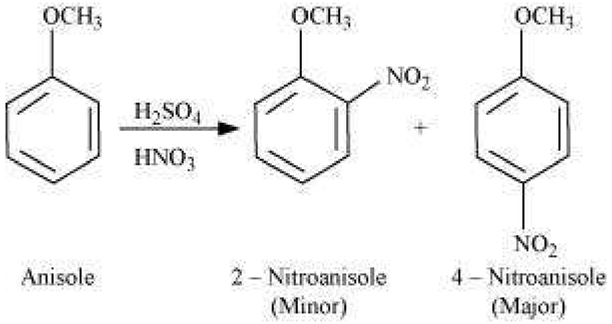
(iv) Friedel-Craft’s acetylation of anisole.

Answer

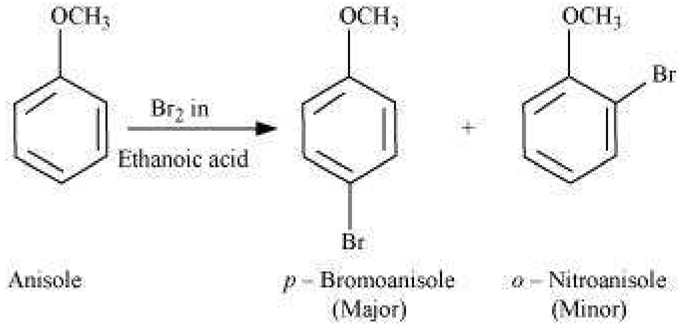
(i)


OCH_3
Anisole
+ CH_3Cl
Anhyd.$AlCl_3$
CS_2
OCH_3
CH_3
4 – Methoxytoluene
(Major)
+
OCH_3
CH_3
2 – Methoxytoluene
(Minor)

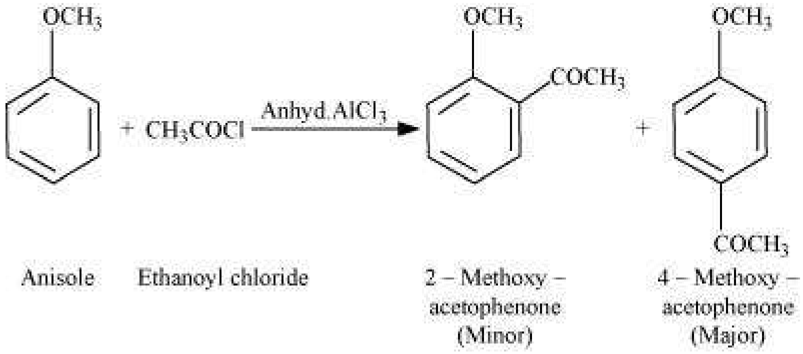
(ii)


OCH_3
Anisole
H_2SO_4
HNO_3
OCH_3
NO_2
2 – Nitroanisole
(Minor)
+
OCH_3
NO_2
4 – Nitroanisole
(Major)

(iii)


OCH_3
Anisole
Br_2 in
Ethanoic acid
OCH_3
Br
p – Bromoanisole
(Major)
+
OCH_3
Br
o – Nitroanisole
(Minor)

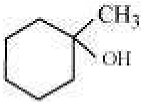
(iv)


OCH_3
Anisole
+ CH_3COCl
Ethanoyl chloride
Anhyd.$AlCl_3$
OCH_3
$COCH_3$
2 – Methoxy – acetophenone
(Minor)
+
OCH_3
$COCH_3$
4 – Methoxy – acetophenone
(Major)

Question 11.32:

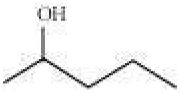
Show how would you synthesise the following alcohols from appropriate alkenes?

(i)

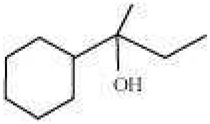


(ii)

(iii)



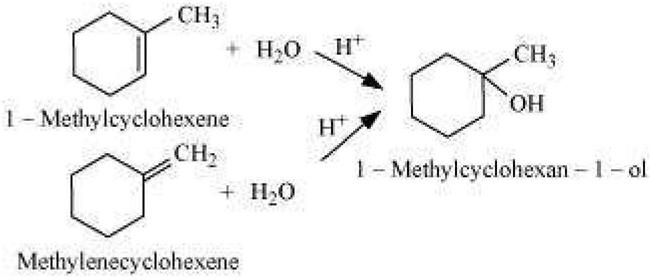
(iv)



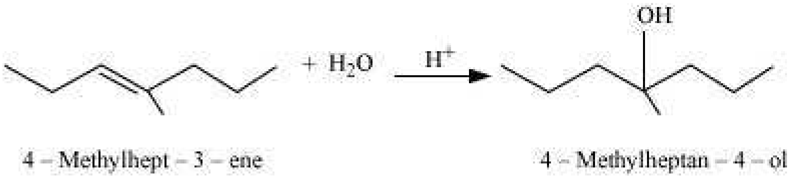
Answer

The given alcohols can be synthesized by applying Markovnikov's rule of acid-catalyzed hydration of appropriate alkenes.

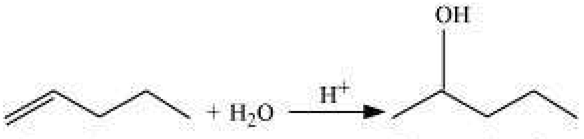
(i)



(ii)

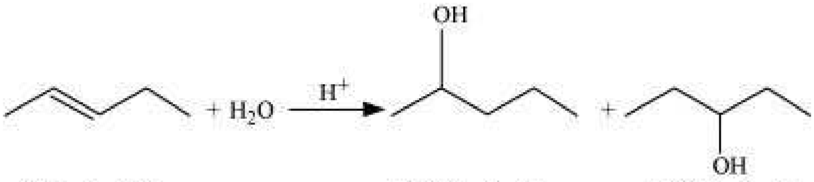


(iii)



Pent – 1 – ene Pentan – 2 – ol

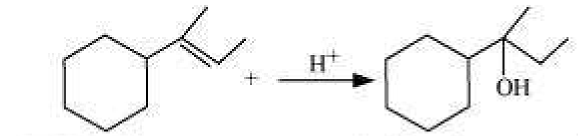
Acid-catalyzed hydration of pent-2-ene also produces pentan-2-ol but along with pentan-3-ol.



Pent – 2 – ene Pentan – 2 – ol Pentan – 3 – ol

Thus, the first reaction is preferred over the second one to get pentan-2-ol.

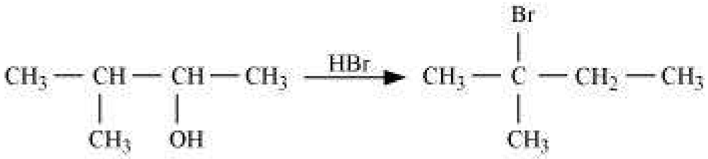
(iv)



2 – Cyclohexylbut – 2 – ene 2 – Cyclohexylbutan – 2 – ol

Question 11.33:

When 3-methylbutan-2-ol is treated with HBr, the following reaction takes place:



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

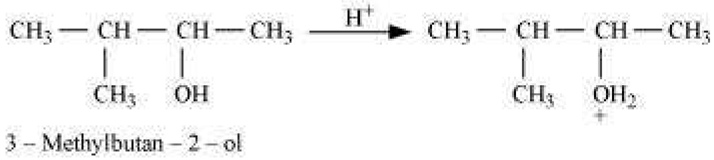
Give a mechanism for this reaction.

(Hint : The secondary carbocation formed in step II rearranges to a more stable tertiary carbocation by a hydride ion shift from 3rd carbon atom.

Answer

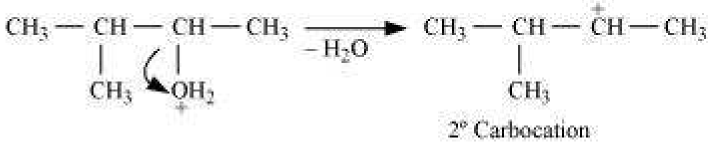
The mechanism of the given reaction involves the following steps:

Step 1: Protonation



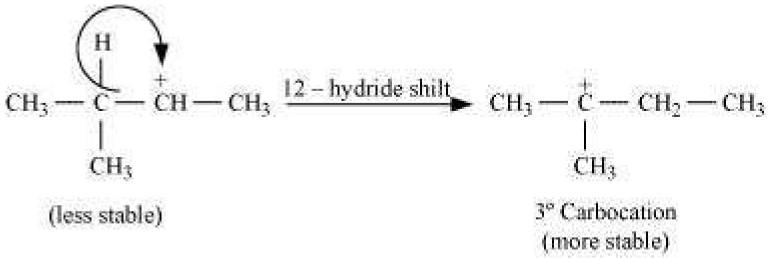
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{OH}{\underset{|}{CH}}-CH_3 \xrightarrow{H^+} CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{\underset{+}{OH_2}}{\underset{|}{CH}}-CH_3$$

Step 2: Formation of 2° carbocation by the elimination of a water molecule



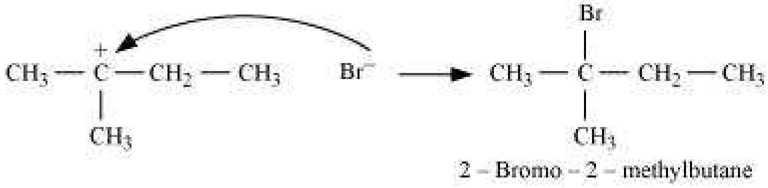
$$CH_3-\underset{CH_3}{\underset{|}{CH}}-\underset{\underset{+}{OH_2}}{\underset{|}{CH}}-CH_3 \xrightarrow[-H_2O]{} CH_3-\underset{CH_3}{\underset{|}{CH}}-\overset{+}{CH}-CH_3$$

Step 3: Re-arrangement by the hydride-ion shift



$$CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{H}{|}}{C}}}-\overset{+}{CH}-CH_3 \xrightarrow{12 - \text{hydride shilt}} CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_2-CH_3$$

Step 4: Nucleophilic attack



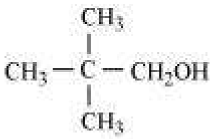
$$CH_3-\underset{CH_3}{\underset{|}{\overset{+}{C}}}-CH_2-CH_3 \quad Br^- \longrightarrow CH_3-\underset{CH_3}{\underset{|}{\overset{\overset{Br}{|}}{C}}}-CH_2-CH_3$$

Text solution

Question 11.1:

Classify the following as primary, secondary and tertiary alcohols:

(i)

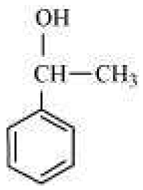


$CH_3-C(CH_3)_2-CH_2OH$

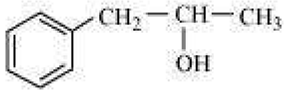
(ii) $H_2C=CH-CH_2OH$

(iii) $CH_3-CH_2-CH_2-OH$

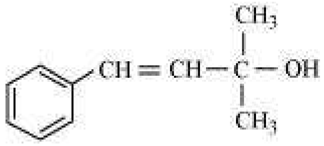
(iv)



(v)



(vi)



Answer

Primary alcohol → (i), (ii), (iii)

Secondary alcohol → (iv), (v)

Tertiary alcohol → (vi)

Question 11.2:

Identify allylic alcohols in the above examples.

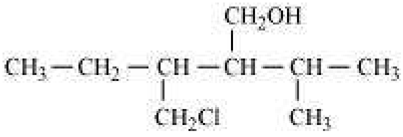
Answer

The alcohols given in (ii) and (vi) are allylic alcohols.

Question 11.3:

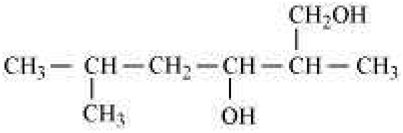
Name the following compounds according to IUPAC system.

(i)



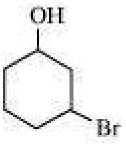
$$CH_3-CH_2-\underset{\substack{|\\CH_2Cl}}{CH}-\overset{\substack{CH_2OH\\|}}{CH}-\underset{\substack{|\\CH_3}}{CH}-CH_3$$

(ii)

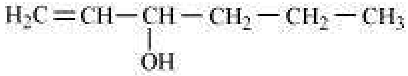


$$CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2-\underset{\substack{|\\OH}}{CH}-\overset{\substack{CH_2OH\\|}}{CH}-CH_3$$

(iii)

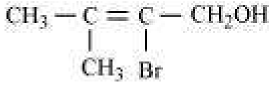


(iv)



$H_2C{=}CH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}CH_2{-}CH_3$

(v)



$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}}{=}\underset{\displaystyle Br}{\underset{|}{C}}{-}CH_2OH$

Answer

(i) 3-Chloromethyl-2-isopropylpentan-1-ol

(ii) 2, 5-Dimethylhexane-1, 3-diol

(iii) 3-Bromocyclohexanol

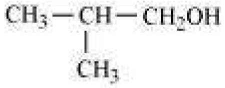
(iv) Hex-1-en-3-ol

(v) 2-Bromo-3-methylbut-2-en-1-ol

Question 11.4:

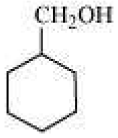
Show how are the following alcohols prepared by the reaction of a suitable Grignard reagent on methanal?

(i)



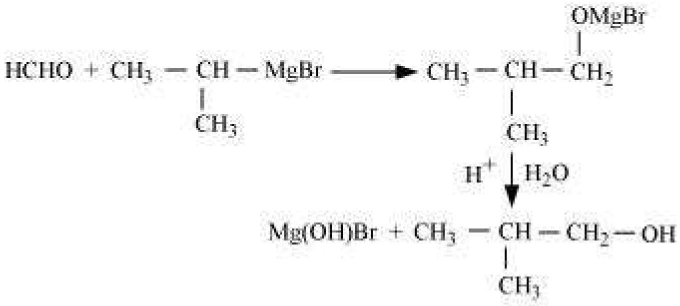
$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2OH$

(ii)



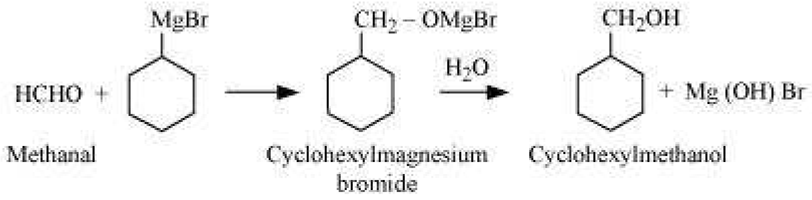
Answer

(i)



$$HCHO + CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-MgBr \longrightarrow CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\overset{\displaystyle OMgBr}{\overset{|}{CH_2}} \xrightarrow{H^+,\ H_2O} Mg(OH)Br + CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-OH$$

(ii)



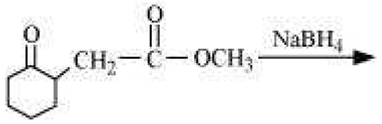
Question 11.5:

Write structures of the products of the following reactions:

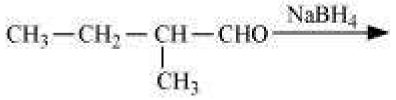
(i)

$CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$

(ii)



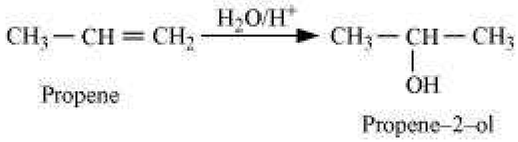
(iii)



$CH_3-CH_2-\underset{\substack{|\\CH_3}}{CH}-CHO \xrightarrow{NaBH_4}$

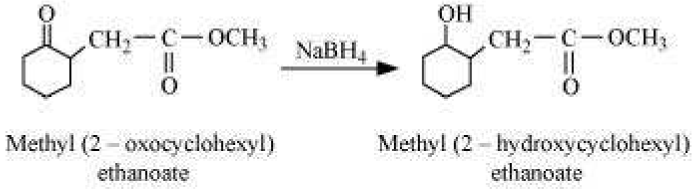
Answer

(i)

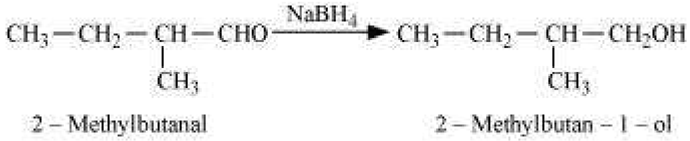


$CH_3-CH=CH_2 \xrightarrow{H_2O/H^+} CH_3-\underset{\substack{|\\OH}}{CH}-CH_3$

(ii)



(iii)



$CH_3-CH_2-\underset{\substack{|\\CH_3}}{CH}-CHO \xrightarrow{NaBH_4} CH_3-CH_2-\underset{\substack{|\\CH_3}}{CH}-CH_2OH$

Question 11.6:

Give structures of the products you would expect when each of the following alcohol reacts with (a) HCl-ZnCl$_2$ (b) HBr and (c) SOCl$_2$.

(i) Butan-1-ol

(ii) 2-Methylbutan-2-ol

Answer

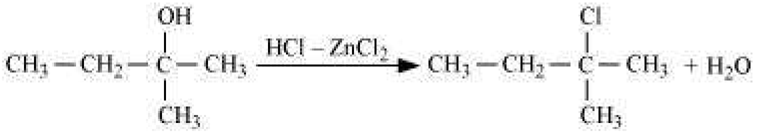
(a)

(i)

$$\underset{\text{Butan}-1-\text{ol}}{CH_3-CH_2-CH_2-CH_2-OH} \xrightarrow{HCl-ZnCl_2} \text{No reaction}$$

Primary alcohols do not react appreciably with Lucas' reagent (HCl-ZnCl$_2$) at room temperature.

(ii)



$$CH_3-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3 \xrightarrow{HCl-ZnCl_2} CH_3-CH_2-\overset{Cl}{\underset{CH_3}{C}}-CH_3 + H_2O$$

2 – Methylbutan – 2 – ol (3°)

2 – Chloro – 2 – Methylbutane
(White turbidity)

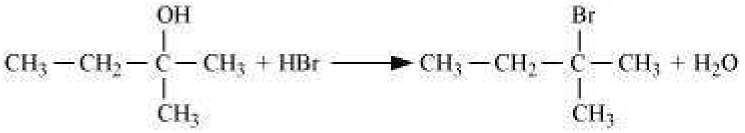
Tertiary alcohols react immediately with Lucas' reagent.

(b)

(i)

$$\underset{\text{Butan}-1-\text{ol}}{CH_3CH_2CH_2CH_2OH} + HBr \xrightarrow[-H_2O]{} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$$

(ii)



$$CH_3-CH_2-\overset{OH}{\underset{CH_3}{C}}-CH_3 + HBr \longrightarrow CH_3-CH_2-\overset{Br}{\underset{CH_3}{C}}-CH_3 + H_2O$$

2 – Methylbutan – 2 – ol (3°)

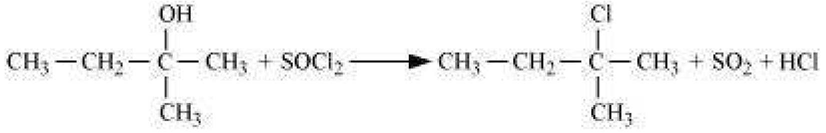
2 – Bromo – 2 – Methylbutane

(c)

(i)

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} + SOCl_2 \longrightarrow \underset{\text{1-chlorobutane}}{CH_3CH_2CH_2CH_2Cl} + SO_2 + HCl$$

(ii)



$$CH_3-CH_2-\underset{CH_3}{\overset{OH}{\underset{|}{\overset{|}{C}}}}-CH_3 + SOCl_2 \longrightarrow CH_3-CH_2-\underset{CH_3}{\overset{Cl}{\underset{|}{\overset{|}{C}}}}-CH_3 + SO_2 + HCl$$

2 – Methylbutan – 2 – ol 2 – Chloro – 2 – Methylbutane

Question 11.7:

Predict the major product of acid catalysed dehydration of

(i) 1-methylcyclohexanol and

(ii) butan-1-ol

Answer

i.

1 – Methylcyclohexanol 1 – Methylcyclohexene (Major product)

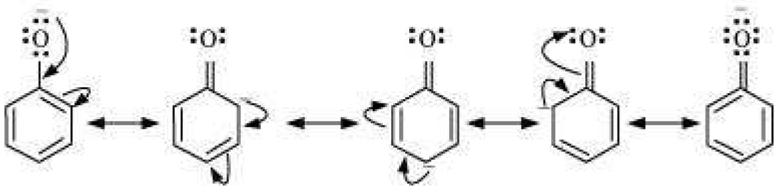
(ii)

$$\underset{\text{Butan-1-ol}}{CH_3CH_2CH_2CH_2OH} \xrightarrow[H^+]{\text{Dehydration}} \underset{\substack{\text{But-2-ene}\\ \text{(Major product)}}}{CH_3CH=CHCH_3} + H_2O$$

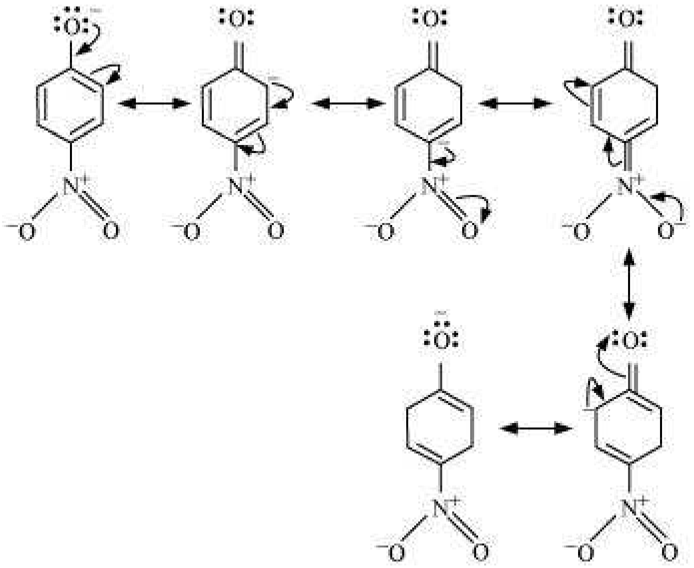
Question 11.8:

Ortho and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

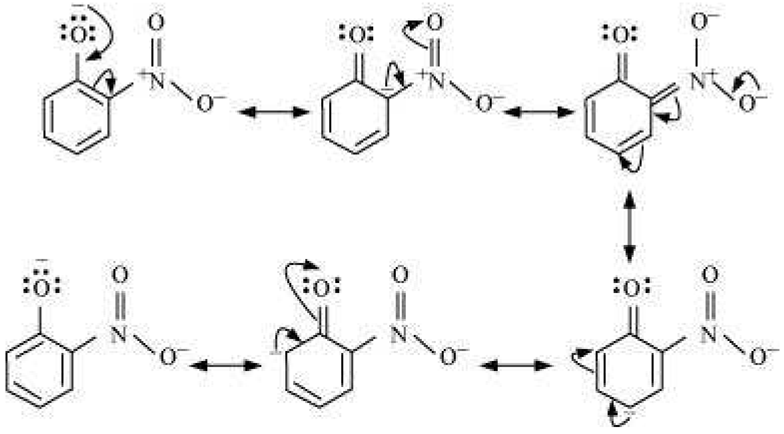
Answer



Resonance structure of the phenoxide ion



Resonance structures of *p*-nitrophenoxide ion



Resonance structures of *m*-nitrophenoxide ion

It can be observed that the presence of nitro groups increases the stability of phenoxide ion.

Question 11.9:

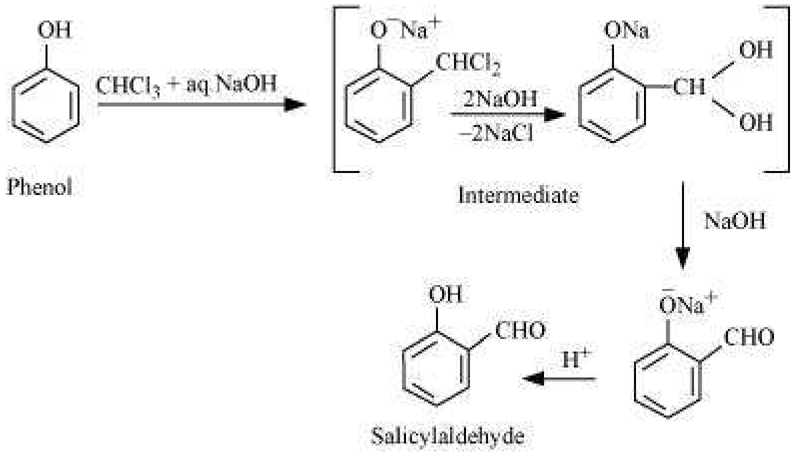
Write the equations involved in the following reactions:

(i) Reimer-Tiemann reaction

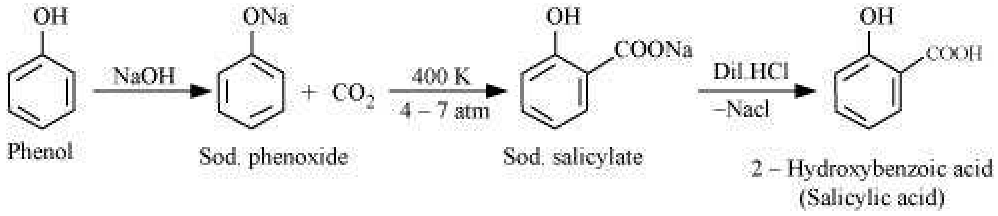
(ii) Kolbe’s reaction

Answer

i. **Reimer-Tiemann reaction**



ii. **Kolbe's reaction**



Question 11.10:

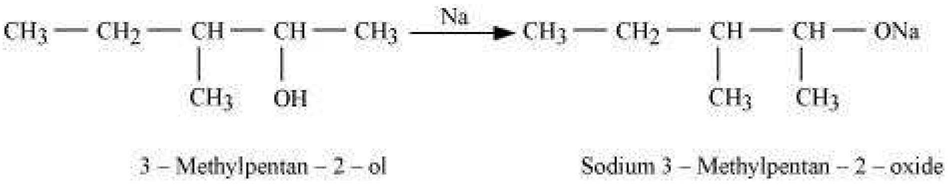
Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

Answer

In Williamson synthesis, an alkyl halide reacts with an alkoxide ion. Also, it is an S_N2 reaction. In the reaction, alkyl halides should be primary having the least steric hindrance. Hence, an alkyl halide is obtained from ethanol and alkoxide ion from 3-methylpentan-2-ol.

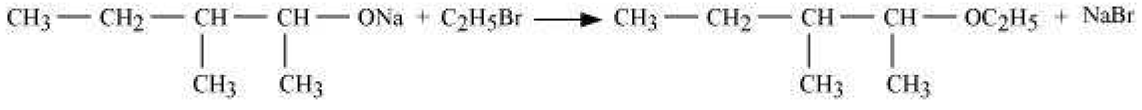
$$C_2H_5OH \xrightarrow{HBr} C_2H_5Br$$

Ethanol Bromoethane



$$CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 \xrightarrow{Na} CH_3-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-\underset{\displaystyle CH_3}{\underset{|}{CH}}-ONa$$

3 – Methylpentan – 2 – ol Sodium 3 – Methylpentan – 2 – oxide



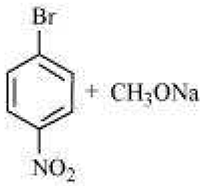
$$CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-ONa + C_2H_5Br \longrightarrow CH_3-CH_2-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{CH_3}{|}}{CH}-OC_2H_5 + NaBr$$

2 – Ethoxy – 3 – methylpentane

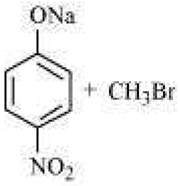
Question 11.11:

Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?

(i)

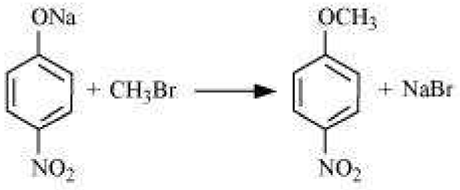


(ii)



Answer

Set (ii) is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene.



1 – Methoxy – 4 – nitrobenzene

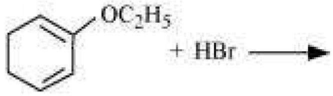
In set (i), sodium methoxide (CH_3ONa) is a strong nucleophile as well as a strong base. Hence, an elimination reaction predominates over a substitution reaction.

Question 11.12:

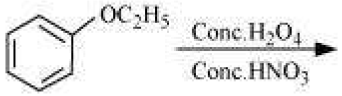
Predict the products of the following reactions:

(i) $CH_3-CH_2-CH_2-O-CH_3 + HBr \rightarrow$

(ii)



(iii)



(iv) $(CH_3)_3C-OC_2H_5 \xrightarrow{HI}$

Answer

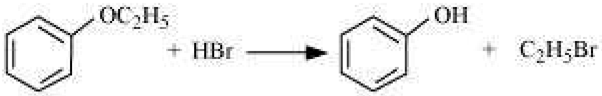
(i)

$$CH_3-CH_2-CH_2-O-CH_3 + HBr \longrightarrow CH_3-CH_2-CH_2-OH + CH_3-Br$$

n-propylmethyl ether

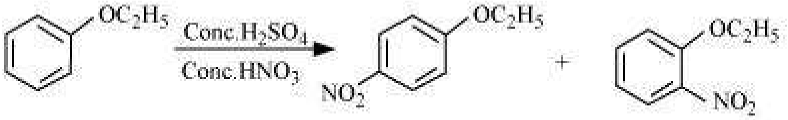
Propanol Bromomethane

(ii)



Ethoxybenzene Phenol Bromoethane

(iii)



Ethoxybenzene 4 – Ethoxynitrobenzene (Major) 2 – Ethoxynitrobenzene (Minor)

(iv)

$$(CH_3)_3C-OC_2H_5 \xrightarrow{HI} (CH_3)_3C-I + C_2H_5OH$$

tert-Butyl ethyl ether *tert*-Butyliodide Ethanol

Question 12.1:

What is meant by the following terms? Give an example of the reaction in each case.

(i) Cyanohydrin **(ii)** Acetal

(iii) Semicarbazone **(iv)** Aldol

(v) Hemiacetal **(vi)** Oxime

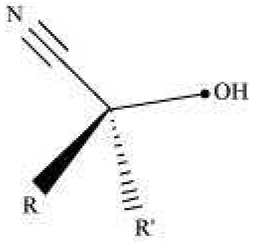
(vii) Ketal **(vii)** Imine

(ix) 2,4-DNP-derivative **(x)** Schiff’s base

Answer

(i) Cyanohydrin:

Cyanohydrins are organic compounds having the formula RR’C(OH)CN, where R and R’ can be alkyl or aryl groups.



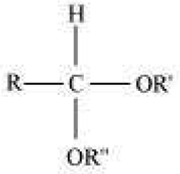
Aldehydes and ketones react with hydrogen cyanide (HCN) in the presence of excess sodium cyanide (NaCN) as a catalyst to field cyanohydrin. These reactions are known as cyanohydrin reactions.

$$\underset{\text{Ketone}}{RR'C=O} + HCN \xrightarrow{NaCN} \underset{\text{Cyanohydrin}}{RR'C(OH)CN}$$

Cyanohydrins are useful synthetic intermediates.

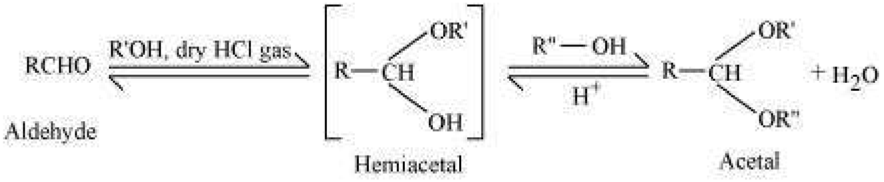
(ii) Acetal:

Acetals are gem−dialkoxy alkanes in which two alkoxy groups are present on the terminal carbon atom. One bond is connected to an alkyl group while the other is connected to a hydrogen atom.



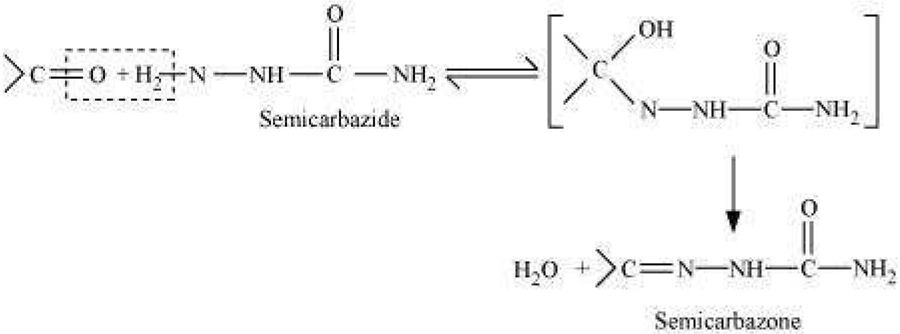
General structure of an acetal

When aldehydes are treated with two equivalents of a monohydric alcohol in the presence of dry HCl gas, hemiacetals are produced that further react with one more molecule of alcohol to yield acetal.



(iii) Semicarbarbazone:

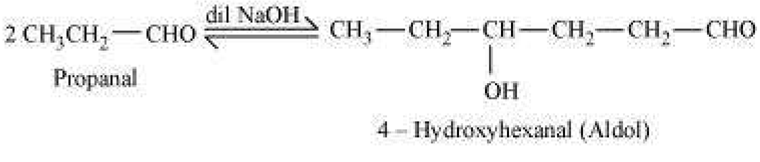
Semicarbazones are derivatives of aldehydes and ketones produced by the condensation reaction between a ketone or aldehyde and semicarbazide.



Semicarbazones are useful for identification and characterization of aldehydes and ketones.

(iv) Aldol:

A β-hydroxy aldehyde or ketone is known as an aldol. It is produced by the condensation reaction of two molecules of the same or one molecule each of two different aldehydes or ketones in the presence of a base.



(v) Hemiacetal:

Hemiacetals are $\alpha-$alkoxyalcohols